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First Quarter Progress Report for
the Advanced Battery Materials
Research (BMR) Program

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Approved by

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TABLE OF CONTENTS

A Message from the Advanced Battery Materials Research Manager	1
Task 1 – Advanced Electrode Architectures	3
Task 1.1 – Vincent Battaglia (Lawrence Berkeley National Laboratory)	4
Task 1.2 – Karim Zaghib (HydroQuebec).....	6
Task 1.3 – Yet-Ming Chiang, Massachusetts Institute of Technology.....	8
Task 1.4 – Gao Liu (Lawrence Berkeley National Laboratory)	10
Task 1.5 – Vincent Battaglia (Lawrence Berkeley National Laboratory)	12
Task 2 – Silicon Anode Research.....	14
Task 2.1 – Ji-Guang (Jason) Zhang, Jun Liu (Pacific Northwest National Laboratory).....	15
Task 2.2 – Yi Cui (Stanford University)	17
Task 3 – High Energy Density Cathodes for Advanced Lithium-ion	19
Task 3.1– Jagjit Nanda (Oak Ridge National Laboratory).....	20
Task 3.2 – Stanley Whittingham (SUNY Binghamton).....	23
Task 3.3 – Ji-Guang Zhang and Jie Xiao (Pacific Northwest National Laboratory).....	25
Task 3.4 – Patrick Looney, Feng Wang (Brookhaven National Laboratory).....	27
Task 3.5 – Michael M. Thackeray and Jason R. Croy (Argonne National Laboratory)	30
Task 3.6 – Arumugam Manthiram (University of Texas, Austin)	33
Task 3.7 – Jim Kiggans and Andrew Kercher (Oak Ridge National Laboratory)	36
Task 3.8 – Marca Doeff (Lawrence Berkeley National Laboratory)	39
Task 3.9 – John B. Goodenough (UT Austin).....	41
Task 4 – Electrolytes for High Voltage High Energy Lithium-ion Batteries	43
Task 4.1 – Zhengcheng Zhang (Argonne National Laboratory).....	44
Task 4.2 – Ron Hendershot (Daikin America)	46
Task 4.3 – Dee Strand (Wildcat Discovery Technologies)	48

Task 5 – Diagnostics	51
Task 5.1 – Guoying Chen (Lawrence Berkeley National Laboratory).....	52
Task 5.2 – Robert Kostecki (Lawrence Berkeley National Laboratory)	55
Task 5.3 – Xiao-Qing Yang and Xiqian Yu (Brookhaven National Laboratory)	58
Task 5.4 – Clare Grey (Cambridge University)	61
Task 5.5 – Shirley Meng (UC San Diego)	63
Task 5.6 – Gabor Somorjai (UC Berkeley), Phil Ross (Lawrence Berkeley National Laboratory)	66
Task 5.7 – Chongmin Wang (Pacific Northwest National Laboratory).....	68
Task 5.8 – Michael M. Thackeray and Jason R. Croy (Argonne National Laboratory)	71
Task 6 – Modeling Advanced Electrode Materials	74
Task 6.1 – Venkat Srinivasan (Lawrence Berkeley National Laboratory).....	75
Task 6.2 – Kristin Persson (Lawrence Berkeley National Laboratory)	77
Task 6.3 – Gerbrand Ceder (MIT).....	79
Task 6.4 – Perla Balbuena (Texas A&M University)	81
Task 6.5 – Xingcheng Xiao (General Motors), Yue Qi (Michigan State University).....	83
Task 6.6 – Dean Wheeler and Brian Mazzeo (Brigham Young University)	85
Task 7 – Metallic Lithium and Solid Electrolytes	87
Task 7.1 – Nancy Dudney (ORNL), Erik Herbert (UTK), Jeff Sakamoto (UM)	88
Task 7.2 – Jeff Sakamoto (Univ. of Michigan)	91
Task 7.3 – Nancy Dudney and Sergiy Kalnaus (Oak Ridge National Laboratory)	93
Task 7.4 – Eric Wachsman, Liangbing Hu, Yifei Mo (University of Maryland, College Park).....	96
Task 7.5 – Yi Cui (Stanford University)	99
Task 8 – Li – S Batteries	101
Task 8.1 – Prashant N. Kumta (University of Pittsburgh).....	102
Task 8.2 – Nitash Balsara (Lawrence Berkeley National Laboratory)	105

Task 8.3 – Khalil Amine (Argonne National Laboratory)el Chemistry: LithiumSelenium	108
Task 8.4 – Hong Gan (Brookhaven National Laboratory); Co-PI: Esther Takeuchi (Brookhaven National Laboratory and Stony Brook University).....	111
Task 8.5: Jie Xiao and Jun Liu (Pacific Northwest National Laboratory)	113
Task 8.6 – Yi Cui (Stanford University)	115
Task 8.7 – Perla Balbuena (Texas A&M University)	117
Task 9 – Li-Air Batteries.....	120
Task 9.1 – Ji-Guang Zhang and Wu Xu (Pacific Northwest National Laboratory)	121
Taks 9.2 – Vincent Giordani (Liox).....	124
Task 9.3 – Khalil Amine (Argonne National Laboratory).....	127
Task 9.4 – Deyang Qu (UMASS Boston) and Xiao-Qing Yang (Brookhaven National Laboratory).....	130
Task 10 – Na-ion Batteries	132
Task 10.1 – Xiao-Qing Yang and Xiqian Yu (Brookhaven National Laboratory)	133

LIST OF FIGURES

Figure 1: Capacity Fade Curves for LCO, High Voltage LCO, and NCM	5
Figure 2: (a) Design of anode-to-cathode balance showing 40% utilization of Si capacity and (b) initial charge-discharge profiles of 20Ah large format cells based on a nano-Si anode and a high-voltage LMNO cathode.....	7
Figure 3: (a) Design of anode-to-cathode balance showing 90% utilization of Si capacity and (b) initial charge-discharge profiles of 60Ah large format cells based on nano-Si anode and high energy NCM cathode.....	7
Figure 4: Cross sections of graphite anodes formulated with CMC binder and freeze-cast at the cooling rates indicated. Electrodes were lyophilized to retain structure. Total porosity is 58-60 vol%.	9
Figure 5: Galvanostatic discharge voltage vs. capacity for 800 μm thick electrode sectioned from sample directionally freeze-cast at 7.5°C/min. Left: Multiple cycles at C/5 rate. Right: Comparison of result at C/10, C/5 and 1C discharge rate.	9
Figure 6: (a) Schematics of the utilization of SLMP for the SiO electrode. SLMP particles are loaded on to the SiO anode. Rolling compression was used to crush the Li_2CO_3 shell of SLMP to release lithium metal and laminate it on the surface of SiO electrode. This process is called SLMP activation. (b) SLMP particles loaded on the SiO electrode before activation. The inset shows	

the SEM image of a single SLMP particle. (c) The SiO electrode surface after electrolytes are added onto the SiO electrode with activated SLMP after 12 hours. This shows the disappearance of SLMP and indicates the successful prelithiation of the SiO electrode. (d) SiO/NMC full cell performance with or without the SLMP capacity-enhancement additive, two cycles at C/20, two cycles at C/10, and then C/3. The first cycle voltage curves of the two cells.....	11
Figure 7: Capacity Fade Curves for LCO, High Voltage LCO, and NCM	13
Figure 8: Three types of self-healing polymers investigated as binders for Si anodes.....	16
Figure 9: Three types of self-healing polymers used as binders for Si anodes.....	16
Figure 10: The comparison of discharge capacitances as a function of temperature for Li-ion capacitors filled with commercial and PNNL electrolytes.	16
Figure 11: (a) Schematic diagrams showing Si NPs react with melted Li to form Li_xSi NPs. A dense passivation layer is formed on the Li_xSi NPs after exposure to trace amounts of oxygen, preventing the Li_xSi alloy from further oxidation in dry air. (b) STEM image of $\text{Li}_x\text{Si-Li}_2\text{O}$ core-shell NPs. (c) Voltage profiles of $\text{Li}_x\text{Si-Li}_2\text{O}$ NPs.	18
Figure 12: (a) First cycle voltage profiles of Si NPs/ $\text{Li}_x\text{Si-Li}_2\text{O}$ composite and Si NPs control cell. (b) First cycle voltage profiles of MCMB/ $\text{Li}_x\text{Si-Li}_2\text{O}$ composite (81:9 by weight) and MCMB control cell. The table shows that the 1st CE is tuned by the amount of $\text{Li}_x\text{Si-Li}_2\text{O}$ additives. (c) The capacity retention of $\text{Li}_x\text{Si-Li}_2\text{O}$ NPs exposed to dry air with varying durations. The inset shows the trend of capacity decay. (d) The capacity retention of $\text{Li}_x\text{Si-Li}_2\text{O}$ NPs exposed to air at different humidity levels.	18
Figure 13: (Left) Analysis of EIS spectrum of LMR-NMC cathode at 4 V. (Right) Activation energy as a function of temperature for various EIS contributions.	21
Figure 14: Parallel capacitance (left) and resistance (right) as function of voltage for LMR-NMC cathode at RT.....	22
Figure 15: (left) x-ray diffraction patterns and (right) discharge of CuF_2 and $\text{Cu}_{0.8}\text{Fe}_{0.2}\text{F}_2$	24
Figure 16: Cycling capacity using LiPF_6 and FSI based electrolytes of (left) baseline carbon anode, and (right) advanced Sn-Fe-C anode.....	24
Figure 17: Crystal structure of material after initial charge/discharge process. (a) High resolution STEM image. (b) STEM image enlarged from the region labelled by green rectangle in (a). (c) Intensity plot along the red line (TM layer) shown in (b). (d) Intensity plot along the yellow line (Li layer) shown in (b). (e) Atomic model of the [100] zone projection of R-3m phase, where the lithium sites at surface region are occupied by the TM ions to form defect spinel structure in [011] projection.	26
Figure 18: <i>In-situ</i> studies of ion exchange in $\text{Li}(\text{Na})\text{VPO}_5\text{F}_x$. (a) Time-resolved XRD patterns, (b) the integrated Bragg peak intensity of (311) of the Na-phase (phase I) and Li-phase (phase II) at fixed temperatures, 72 oC and 120 oC, (c) illustration of the configuration of Na^+ ions (golden) and Li^+ ions (green) in the <i>ab</i> plane determined by structure refinement.	28
Figure 19: (a) Synchrotron HR-XRD patterns and (b) initial voltage profiles of $\text{Li/LT-LiCo}_{1-x}\text{Ni}_x\text{O}_2$ ($x = 0$ and 0.1) cells cycled between 2.5 and 3.9 V at the rate of 15 mA/g. The selected 2θ ranges in (a), highlighted in separate panes, show the non-uniform distribution of lattice parameters in	

LT-LiCoO ₂ . Inset in (b) compares the cycling stability of LT-LiCoO ₂ and LT-LiCo _{0.9} Ni _{0.1} O ₂	31
Figure 20: SEM images of the (a) PMMA colloidal crystal, (b) 3-DOM carbon, (c) α-LiVOPO ₄ , and (d) α-LiVOPO ₄ /PEDOT composite. The scale bars in (a, b) and (c, d) are 1 μm and 500 nm, respectively.	34
Figure 21: XRD patterns of the as-prepared α-LiVOPO ₄ , chemically delithiated α-LiVOPO ₄ , and α-LiVOPO ₄ /PEDOT composite. Asterisks indicate β-LiVOPO ₄	34
Figure 22: Electrochemical data at C/20 rate of the various α-LiVOPO ₄ electrodes.	34
Figure 23: Microscopy showed that a discharged nickel-based glass cathode showed no gross cracking (a: TEM image) and had nickel uniformly distributed inside glass particles (b: EDXS).	37
Figure 24: Short 10 cycle tests of an iron-based MP glass cathode material (400 μm particle size) at a wide range of specific currents	37
Figure 25: (a) Discharge capacity comparison of NMC materials prepared by spray pyrolysis and co-precipitation; (b) Surface reconstruction comparison of NMC materials prepared by spray pyrolysis and co-precipitation after 20 cycles, represented by Mn oxidation states.	40
Figure 26: Crosslinked polymer membranes with polyethylene oxide, double vinyl sulfones, double vinyl ester, and perfluorohexane units (from the left).	42
Figure 27: (a) Electrochemical floating test of electrolyte voltage stability with different FEC/DMC ratios with 0.5 M LiPF ₆ (leakage current recorded at the end of 10h-hold at potentials of 4.9 to 5.2 V; (b) electrolyte wetting of Celgard 2325 separator (1) FEC/F-EMC=1/1, (2) FEC/F-MiPC/F-EMC=2/1/1, (3) FEC/HF-DEC=1/1, (4) FEC/TF-DEC = 1/1; (c) LNMO/A12 cell cycling performance with electrolyte (2) 1.0 M LiPF ₆ in FEC/F-MiPC/F-EMC=2/1/1 with Celgard 2325 separator and glass fiber separator.	45
Figure 28: (left) LNMO/A12 cell performance with 1.0 M LiPF ₆ in FEC/TF-DEC 1/1 with glass fiber separator; (right) Electrolyte discoloration after storage for a month: 1.0 M LiPF ₆ in (1) FEC/F-EMC=1/1, (2) FEC/F-MiPC/F-EMC=2/1/1, (3) FEC/HF-DEC=1/1, (4) FEC/TF-DEC = 1/1 and (5) EC/F-EMC = 1/1.	45
Figure 29: OCV vs. Gas generation data.....	47
Figure 30: 4.2V 72h 60°C storage data	47
Figure 31: Conventional hydrocarbon electrolyte data	47
Figure 32: dQ/dV vs. V data.	47
Figure 33: Several promising HD/LV combinations show performance comparable to the carbonate control electrolyte	49
Figure 34: Significant cycle life improvement at 200 cycles for the noncarbonate formulation over an EC/EMC control	49
Figure 35: Noncarbonate formulation performance (colors = different salts; open/close = without/with SEI additive	49
Figure 36: a) dQ/dV profiles, b) and c) percentage of the phases present during in situ discharge of x=0.5 and x=0.3, and d) rate capability of the crystal samples	53
Figure 37: a) Raman and b) FTIR of Li _x MNO.....	53
Figure 38: Possible formation pathway of the metal complexes upon EC oxidation at the Li _x Ni _{0.5} Mn _{1.5} O ₄ surface by an electron transfer, propagation, proton transfer and a proton coupled electron transfer (PCET) mechanism.	56

Figure 39: <i>In situ</i> XRD-MS data of electrochemically delithiated LMO and NCM mixture with weight ratio of 3:1.	59
Figure 40: ^7Li MAS NMR spectra of $\text{Li}_{1.08}\text{Mn}_{1.92}\text{O}_4$ electrodes at different state of charge (SOC). The spectra were acquired at 4.7 T with MAS frequency of 40 kHz. The impurity Li_2MnO_3 (marked on the spectra) is electrochemically inactive upon charging. The isotropic shift regions are marked with a red dashed square; the other spectral regions are dominated by the spinning sidebands.	62
Figure 41: ^7Li NMR T2' measurements of $\text{Li}_{1.08}\text{Mn}_{1.92}\text{O}_4$ measured during battery cycling over two cycles (1st cycle 0 – 1; 2nd cycle 1- 2). The measurements were performed at 13, 25, 40, 60 and 70 °C.	62
Figure 42: (a) Specific capacity versus cycling for galvanostatic cycling of a-Si thin films at C/2 rate and (b) Coulombic efficiency comparison of cells cycled with traditional electrolyte, 1:1 EC:DEC (squares), and FEC-containing electrolyte, 45:45:10 EC:DEC:FEC (circles).	64
Figure 43: A relative composition of the 10nm outer SEI after: first lithiation; first delithiation; and 100 cycles. The layer resulted from and was in fluid communication with electrolyte comprising (a) 1:1 EC:DEC and (b) 45:45:10 EC:DEC:FEC.	64
Figure 44: FTIR spectra of surface film formed by reacting metallic Li with VC, VC/LiPF ₆ , FEC, FEC/LiPF ₆ and EC/LiPF ₆ solvents in comparison with pure VC, FEC, and poly-VC.	67
Figure 45: (a-c) [010] zone STEM-HAADF images to show a 10-cycles Li_2MnO_3 particle and its outer surface lattice structure. (d) and (e) highlight the lattice difference between Mn_3O_4 -spinel and I41 structure. Purple and green indicate Mn and Li, respectively. (f) [100] zone STEM-HAADF image of the surface layer after 10 cycles. STEM-HAADF images to show inner bulk lattice structure of pristine sample (g) and 10-cycles sample (h). The intensity profile along the blue lines in (g) and (h) are shown in each figure.	69
Figure 46: (a) Ga K-edge EXAFS and (b) corresponding fits of cycled $\text{Li}/\text{LiCo}_{0.95}\text{Ga}_{0.05}\text{O}_2$ cells. (c) A comparison of delithiation behavior on cycle 2 for $\text{Li}/\text{LiCo}_{1-x}\text{Ga}_x\text{O}_2$ cells ($x=0, 0.05, \text{ and } 0.075$) cycled to 20 mAh/g at 0.2 mA/g.	72
Figure 47: Updated model (Updated) and Dilute model (Dilute) predictions of Li_2S deposition at 3.5 C discharge current throughout cathode at the end of discharge.	76
Figure 48: A schematic of a migrated TM impacting Li migration in the Li layer.	78
Figure 49: Density of states (DOS) of LiCoO_2 as predicted by various electronic structure methods in comparison to experimental spectroscopic measurement.	80
Figure 50: Computed voltage profiles of $\text{Li}_{1-x}\text{CoO}_2$ ($0 \leq x \leq 1$), as predicted by GGA, GGA+U, and HSE with different mixing parameters in comparison to the experimental reference.	80
Figure 51: Investigation of large-volume changes on SEI stability.	84
Figure 52: Lithiation of oxide shell.	84
Figure 53: Photo of apparatus with μ4LP (contact pads on the bottom), with a piece of clear acrylic covering the sampling window and keeping electrolyte from evaporating.	86
Figure 54: XRD of the LLZO pellet after hot pressing. There is no evidence of impurities.	89
Figure 55: Scanning electron microscopy of a typical hot pressed LLZO pellet: (a) 500 X, and b) 2000 X. 89	

Figure 56: Cumulative hardness for selected maps. Areas 7 and 8 had visible dark areas; areas 9 and 13 were still white.	89
Figure 57: Cumulative hardness for selected maps. Areas 7 and 8 had visible dark areas; areas 9 and 13 were still white.	94
Figure 58: XRD of synthesized garnet	97
Figure 59: XRD pattern of $\text{Li}_2\text{FeMn}_3\text{O}_8$	97
Figure 60: First principles calculated Li grand canonical phase diagram of a Li-La-Zr-O system.....	97
Figure 61: Stable lithium metal cycling enabled by interconnected carbon hollow spheres. (a) Fabrication process (b) SEM images. (c) Cycling performance of lithium metal with (solid) and without (open) hollow carbon coating at different current densities	100
Figure 62: h-BN as interfacial layer for lithium metal. Morphologies of lithium metal surface without (a and c) and with (b and d) h-BN coating at first cycle (a and b) and tenth cycle (c and d). (e) and (f) Coulombic efficiency and average voltage hysteresis of lithium metal anode upon cycling, with and without h-BN coating at different current densities and areal capacities	100
Figure 63: Optimization studies into preparation of sulfur nanoparticles (SNPs)	103
Figure 64: Density of states calculation of Li-ion conductor coatings on sulfur	103
Figure 65: Effect of thickness of LIC on gravimetric capacity	103
Figure 66: Schematic of Li-S cell used for XAS experiments	106
Figure 67: Voltage profiles for three Li-S cells	106
Figure 68: XAS for Li-S cells (A), (B), and (C).....	106
Figure 69: Preparation of POP–sulfur composites with micropores as host materials for accommodation of nanosized sulfur particles.	109
Figure 70: Figure 2 Li–S cells with POP–sulfur composite cathodes cycled between 1.5 and 3.0 V at a current density of 200 mA g^{-1} current. Voltage profiles (a), and capacity retention (b) of POP–A–S composite cell; 1st cycle charge discharge profiles of POP–B–S and POP–C–S composite cells (c), and cycling performance of POP–B–S and POPC–S composite cells (d). (Electrolyte: 1 M LiTFSI in 1,3-dioxolane (DOL) and $\text{CHF}_2\text{CF}_2\text{CH}_2\text{OCF}_2\text{CF}_2\text{H}$ in a 1 : 2 volume ratio.).....	109
Figure 71: Li/CuS discharge voltage profile.....	112
Figure 72: Li/CuS cell cycle test under two different voltage windows.....	112
Figure 73: Li/FeS ₂ discharge voltage profile.....	112
Figure 74: Li/FeS ₂ discharge voltage profile	112
Figure 75: (a) Areal specific capacity in dependence of the sulfur loading obtained at 0.1C, (b) electrode thickness as a function of pressure, (c) areal capacity in dependence of pressure applied for calendaring the electrode, and (d) cycling stability of cell cycled at 0.1C (1C=1000 mAh/g)	114
Figure 76: (a) Schematic of the synthesis process, (b) SEM image and (c) TEM image of $\text{Li}_2\text{S}@\text{TiS}_2$ structures.	116
Figure 77: (a) Specific capacity and Coulombic efficiency of $\text{Li}_2\text{S}@\text{TiS}_2$ cathodes upon prolonged 400 charge–discharge cycles at 0.5C (b) Specific capacity and (c) charge–discharge voltage profiles of $\text{Li}_2\text{S}@\text{TiS}_2$ cathodes cycled from 0.2C to 4C. (d) First cycle discharge voltage profile and (e) areal capacity of $\text{Li}_2\text{S}@\text{TiS}_2$ cathodes with high mass loading cycled from 0.1 to 0.6 mA cm^{-2}	116

Figure 78: a) Procedure for synthesizing carbon-sulfur composites, b) SEM of carbon micro-compartment as a substrate for nanosulfur loading, c) SEM of carbon micro-compartment after sonochemical loading of sulfur nanoparticles.	118
Figure 79: a) Precipitation-induced microstructure change, b) Pore size distribution, c) Ionic conductivity, d) Porosity with different precipitation thicknesses.	119
Figure 80: (a) Structural morphology (b) and pore data information of three BAG air electrodes. (c) Voltage profiles of BAG-50 and (d) cycling stability of the three BAG electrodes in Li-O ₂ cells.	122
Figure 81: SEM images of (a) carbon cloth and (b) ZCO-coated carbon cloth, and voltage profiles (c) and cycling stability (d) of the Li-O ₂ cells with the carbon cloth electrodes w and w/o ZCO.	122
Figure 82: (a) DSC of LiNO ₃ :KNO ₃ :CsNO ₃ eutectic (10 °C/min, Ar). (b) Voltage profile of the tenth cycle of a cell with this eutectic 2 mAh discharge at 0.2 mA/cm ² and a PTFE bonded Super P carbon cathode.	125
Figure 83: Raman and XRD data for the activated carbon showing dependence of the LiO ₂ component of current density	128
Figure 85: DFT calculations showing that the origin of the 1505 cm ⁻¹ peak is due to the LiO ₂ -carbon interaction.	128
Figure 84: Illustration of the disproportionation mechanism for formation of Li ₂ O ₂ from LiO ₂	128
Figure 86: Cyclic voltammetry for O ₂ reduction on different carbon electrodes in alkaline electrolyte (D.Qu Carbon 45(2007)1296-1301) and in Acetonitrile.	131
Figure 87: Re-oxidation of B-O ₂₂ - complex in acetonitrile electrolyte.	131
Figure 88: (a) Cr K-edge XANES spectra of pristine (x = 0), half charged (x = 0.25), fully charged (x = 0.5) Na _{1-x} CrO ₂ and CrO _x references (Cr ₂ O ₃ , CrO ₂ and CrO ₃); (b) Least-square fits of calculated FT-EXAFS phase and amplitude functions (solid red lines) to the experimental EXAFS spectra (solid and open circles) for pristine (x = 0), half charged (x = 0.25) and fully charged (x = 0.5) Na _{1-x} CrO ₂ . Phase shift was not corrected in the FT magnitude of EXAFS spectra.	134

February 18, 2015

A MESSAGE FROM THE ADVANCED BATTERY MATERIALS RESEARCH MANAGER

1st Quarterly Report for FY2015

After a long and productive history, the Batteries for Advanced Transportation Technologies (BATT) program has ended. Its promising research topics have transitioned into the newly devised Advanced Battery Materials Research (BMR) Program at the Vehicle Technologies Office (VTO) of the DOE Office of Energy Efficiency and Renewable Energy. The new name better reflects its materials focus and further differentiates it from other VTO battery programs. BMR will continue to address the fundamental issues of materials and electrochemical interactions associated with lithium ion and beyond-lithium battery technologies. Quarterly reports and the Annual Merit Review Meeting will remain the major avenues for disseminating information to the battery and automotive community.

The BMR program is divided into ten topic areas, namely cell analysis, silicon anodes, advanced cathodes, liquid electrolytes, diagnostics, electrode modeling, metallic lithium and solid electrolytes, lithium sulfur batteries, lithium air batteries, and sodium ion batteries. Advancements made in any of the BMR topic areas will follow an analogous path to the vehicle market. Once promising materials are identified, the corresponding technology will be nurtured and evaluated at the cell level under the Applied Battery Research Program. If successful, it will then be handed over to our Advanced Battery Development Program for evaluation as prototype cells and modules to ensure that it meets the industry's targeted energy density, cost and cycle life goals (listed in the adjacent table).

I would like to take this opportunity to welcome the following principal investigators who recently joined the program.

- Professor Perla Balbuena, Texas A&M University
- Professor Prashant Kumta, University of Pittsburgh
- Professor Jeff Sakamoto, University of Michigan
- Professor Eric Wachsman, University of Maryland
- Professor Stanley Whittingham, Binghamton University
- Dr. Nancy Dudney, Oakridge National Laboratory
- Dr. Hong Gan, Brookhaven National Laboratory
- Dr. Vincent Giordani, Liox

Energy Storage Performance Requirements	Cell Level Targets
Specific Energy	400 Wh/kg
Energy Density	600 Wh/L
Calendar Life	10 Year
Cycle Life @ 80% DOD	1000 Cycles
Recharge Rate	1.4 kW
Regeneration Pulse Power	300 W/kg
Discharge Pulse Power	700 W/kg
Discharge Pulse Power Density	1500 W/l
Temperature Range	-35 to +52 C

Table 1: Summary of PEV end of life cell level targets

I invite you to learn more about their studies as well as the progress and achievements of other BMR investigators by going through this quarterly report and its future issues.

Finally, this year our Annual Merit Review meeting will take place at the Crystal Gateway Marriott in Crystal City, Virginia on June 9-11, 2015. It will showcase 35 oral presentations belonging to BMR. This is a great venue to learn more about our program and to interact first-hand with our principal investigators. Information regarding the meeting may be found at <http://www.annualmeritreview.energy.gov/> in the near future. Please register to attend this meeting.

Sincerely,

Tien Q. Duong

Manager, Advanced Battery Materials Research (BMR) Program
Energy Storage R&D
Office of Vehicle Technologies
Energy Efficiency and Renewable Energy
U.S. Department of Energy

TASK 1 – ADVANCED ELECTRODE ARCHITECTURES

Summary

Energy density is a critical characterization parameter for batteries for electric vehicles as there is only so much room for the battery and the vehicle needs to travel over 200 miles. The DOE targets are 500 Wh/L on a system basis and 750 Wh/L on a cell basis. Not only do the batteries have to have high energy density, they need to do so and still deliver 1000 Wh/L for 30 seconds on the system level. To meet these requirements not only entails finding new, high energy density electrochemical couples, but also highly efficient electrode structures that minimize inactive material content, allow for expansion and contraction from one to several thousands of cycles, and allow for full access to the active materials by the electrolyte. In that vein, the DOE OVT supports five projects in the ABMR Program under Electrode Architectures: 1) Electrode Fabrication and Materials Benchmarking, 2) Assembly of Battery Materials and Electrodes, 3) Design and Scalable Assembly of High-density, Low-tortuosity Electrodes, 4) Hierarchical Assembly of Inorganic/Organic Hybrid Si Negative Electrodes, and 5) Electrode Failure Analysis.

One of the more promising active materials for higher energy-density Li-ion batteries is the use of Si as the anode. It has a specific capacity of over 3500 mAh/g and an average voltage during delithiation of 0.4 V vs. the Li/Li⁺ electrode. This material suffers from two major problems both associated with the 300% volume change the material experiences as it goes from a fully delithiated state to a fully lithiated one: 1) the volume change results in a change in exposed surface area to electrolyte during cycling that consumes electrolyte and results in a lithium imbalance between the two electrodes, and 2) the volume change causes the particles to become electrically disconnected (which is further enhanced if particle fracturing also occurs) during cycling. Some of the projects in this task are focused specifically on Si to make it a more robust electrode by finding better binders.

Another approach to higher energy density is to make the electrodes thicker. The problem with thicker electrodes is that the salt in the electrolyte has to travel a farther distance to meet the current needs of the entire electrode throughout the discharge. If the salt cannot reach the back of the electrode at the discharge rates required of batteries for automobiles, the battery is said to be running at its limiting current. If the diffusional path through the electrode is tortuous or the volume for electrolyte is too low, the limiting current is reduced. The other problem with thicker electrodes is that they tend to not cycle as well as thinner electrodes and thus reach the end-of-life condition sooner, delivering fewer cycles. Two of the projects in this task are focused on increasing the limiting current of thick electrodes while maintaining cycleability through the fabrication of less tortuous electrodes or of electrodes with less binder and more room for electrolyte.

If these projects are successful, they would result in a 25% increase in energy density as a result of replacing graphite with Si, and another 20% increase in energy density by moving from 2 mAh/cm² electrodes to 4 mAh/cm² electrodes. This would result in a net increase of 50% in energy density of the cell, and so a battery that once allowed a vehicle to travel only 200 miles could now travel 300 miles.

Highlights

Task 1. Exercised three baseline cell chemistries beyond 50 cycles at 4.3 V.

Task 2. Large cells (20 Ah and 60 Ah) constructed and cycled with nano-Si anodes.

Task 3. Fabricated highly oriented, low tortuosity electrodes capable of greater than 10 mA/cm² at C/5.

Task 4. Demonstrated the successful pre-lithiation of SiO in a SiO/NCM full cell.

Task 5. Demonstrated baseline cycleability of three cell chemistries at 4.1 V.

Task 1.1 – Vincent Battaglia (Lawrence Berkeley National Laboratory)

Physical, Chemical, and Electrochemical Failure Analysis of Electrodes and Cells

PROJECT OBJECTIVE: This project investigates failure modes of targeted chemistries as defined by the BATT Program and its Focus Groups. The emphasis of this effort for 2015 will be on the High-Voltage and Si Anode Focus Groups. The objectives are to identify and quantify the chemical and physical aspects of cell cycling and aging that lead to reduced electrochemical performance. Specifically, research will focus on the effects on material stability as a result of increasing the cell voltage of Graphite/NCM cells from 4.2 V to 4.7 V. In addition, differences in performance between Graphite/NCM and Si/NCM will be investigated. Specifically, investigations into the differences in cell performance as a result of coulombic inefficiencies and the effects of increased electrode loadings on cycleability will be carried out.

PROJECT IMPACT: Success with understanding and improving the stability of NCM in the presence of electrolyte at voltages greater than 4.3 V vs. Li/Li⁺ will translate to an increase in capacity and voltage and hence a compounding improvement in energy density by as much as 45%. Improvement in the loading of anodes and cathodes from 2 to 5 mAh/cm² could result in larger fractions of active materials in cells and a projected increase in energy density by an additional 20 %.

OUT-YEAR GOALS: Provide a prescription of the physical and structural properties required to increase the accessible capacity of layered oxide materials. Demonstrate high loading cells with an increased energy density of 20% with no change in chemistry or operating parameters.

COLLABORATIONS: Many ABMR PIs

Milestones

1. Measure and report the difference in capacity fade in mAh/h between LCO and HV-LCO at 4.3 V in mAh/h. (12/31/14) **Complete**
2. Identify and report the electrochemical phenomena that is responsible for the capacity fade of the LCO and HV-LCO cells at 4.3 V. (3/31/15) **Ongoing**
3. Measure and report the phenomena responsible for the capacity fade of a 3 mAh/cm² cell in mAh/h (6/30/15) **Ongoing**
4. Measure and report the self-discharge rate of the baseline Li/S cell in mA/(g of S) and decide if this is an appropriate baseline design. (9/30/15) **Ongoing**

Progress Report

Milestone 1. Measure and report the difference in capacity fade in mAh/h between LCO and HV-LCO at 4.3 V in mAh/h.

After establishing baseline performance at a cutoff voltage of 4.1 V for the LCO, high voltage LCO (HV LCO), and NCM, (see the other quarterly report for this year), cells were made and cycled between 2.8 and 4.3 V against Li metal counter electrodes.

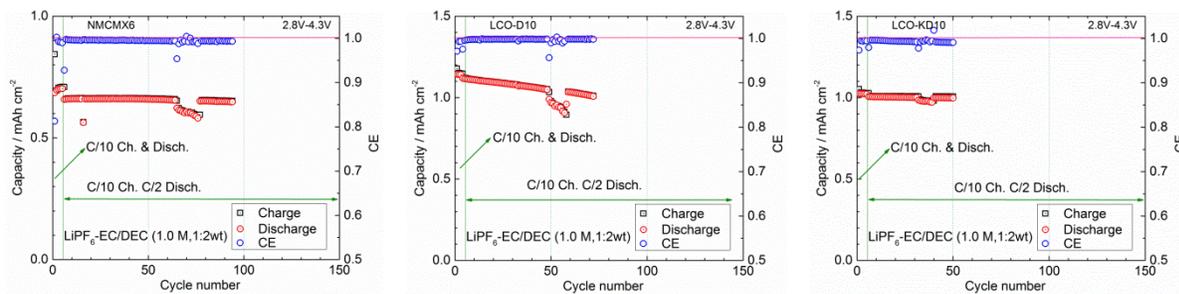


Figure 1: Capacity Fade Curves for LCO, High Voltage LCO, and NCM

One can see that of the three cells, the LCO is showing the most capacity fade. For all of the cells, there was a series of lower capacity cycles for around 10 cycles. These cycles occurred over the holiday break. We were told that the cyclers and environmental chambers in which the cells were housed would remain on back-up power during a retrofit of the power to the building. After a week of preparation for this event, the facility managers decided to not put the environmental chambers on backup power without telling us. The cells cycled but at lower temperatures than the 30°C that is typical. Fortunately, the cells recovered their full cycling capacity once full power was restored to the building. Sources for the differences in the cycleability between cells and between 4.1 and 4.3 V will be investigated in the next quarter.

Milestone 2. Identify and report the electrochemical phenomena that is responsible for the capacity fade of the LCO and HV-LCO cells at 4.3 V.

Cells are presently being cycled; see Milestone 1. An indepth investigation of the differences in capacity fade will take place in quarter 2.

Milestone 3. Measure and report the phenomena responsible for the capacity fade of a 3 mAh/cm² cell in mAh/h. Not started.

Milestone 4. Measure and report the self-discharge rate of the baseline Li/S cell in mA/(g of S) and decide if this is an appropriate baseline design. See reports under Milestones 1 and 2.

Task 1.2 – Karim Zaghib (HydroQuebec)

Assembly of Battery Materials and Electrodes

PROJECT OBJECTIVE: To develop high-capacity, low-cost electrodes with good cycle stability and rate capability to replace graphite in Li-ion batteries. In our recent study on the Si-based electrodes, the effort was directed on the architecture to design electrodes by using low-cost materials. The study of the electrode formulations showed that the mixing process, carbon/Si ratio and the binder type are factors influencing the electrode structure. The *in-situ* analyses revealed that Si-nano particles mitigate the volume changes, and thus protect the electrode from cracks and delamination. Furthermore, if the threshold of the stress is controlled by optimizing the cycling protocols, the particles and the electrode experience low stress.

PROJECT IMPACT: The aim of this project is to overcome the electrochemical capacity limitations (both gravimetric and volumetric) of conventional carbon anodes. This is achieved by developing a low-cost electrode that utilizes a high-capacity material such as silicon. Controlling the composition (i.e., loading of the active material, ratio of binder and carbon additive) of the electrode yielded a more tolerant anode with acceptable volume change and acceptable cycle life with low capacity fade. A high-energy Li-ion cell will be produced using the optimized Si-based and LMNO electrodes.

OUT-YEAR GOALS: Complete the optimization of the electrode composition by varying the carbon additive ratio and the carbon type. In addition to *In-Situ* SEM analyses, *In-Situ* impedance spectroscopy will be introduced to enhance the understanding of capacity fade of the Si-material. These analyses will clarify the mechanism leading to the electrode failure mode and to guide further improvements and design of the electrode architecture. Complete the optimization of the synthesis method of Si-nano powder developed at HQ. As a final goal, the optimized Si-anode and LiMnNiO cathode will be coated in the pilot line and then used to assemble laminate 20 Ah Li-ion cells using the new pilot stacking machine at HQ.

COLLABORATIONS: LBNL (Gao Liu, Vince Battaglia, and Venkat Srinivasan), University of Texas at Austin (John Goodenough) and BNL (Xiao-Qing Yang).

Milestones

1. Complete the optimization of the nano-Si-anode formulation. (12/31/14) **Complete**
2. Complete the optimization of the synthesis of the nano-size Si method developed at HQ.
Go/No-Go decision: Terminate the Si synthesis effort if the capacity is less than 1200 mAh/g (3/31/15)
3. Produce and supply laminate films of Si-anode and LMNO-cathode (10 m) to BATT PIs. (6/30/15)
4. Produce and supply large format 20 Ah high-energy stacking cells (4) to BATT PIs. (9/30/15)

Progress Report

Milestone 1. Complete the optimization of the nano-Si anode formulation. Based on the previous result that the Si nanopowder showed good cycle life when SOC is controlled to <40% with a combination of aqueous binder system, the formulation of nano-Si anode has been scaled up in the pilot-line to verify the performance in a large-format cell. Figure 2(a) indicates the active zone of Si anode when it is coupled with a high voltage LMNO spinel cathode. The cell showed a designed capacity of 20Ah, but exposed two problems to be addressed; first, the energy density of the cell did not surpass that of conventional batteries, and, second, severe gas evolution continued with cycling, which can not be observed in coin-cell testing. The mechanism behind the gas generation is under investigation.

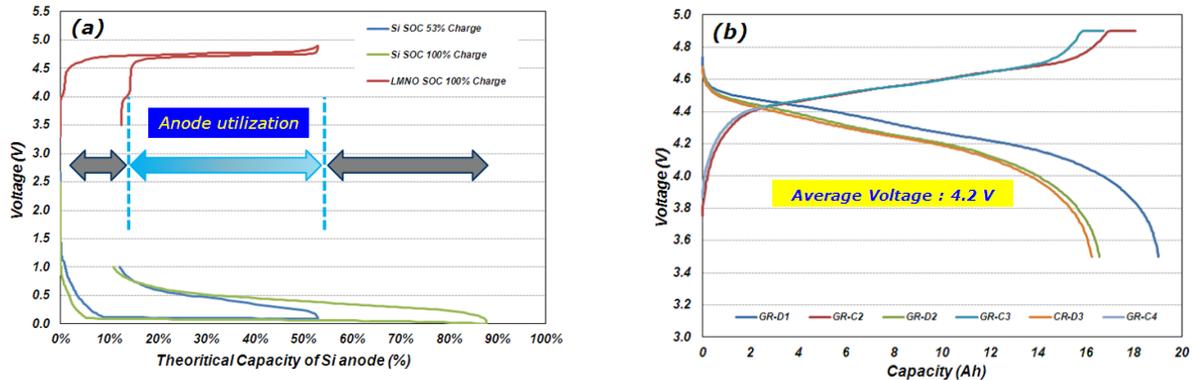


Figure 2: (a) Design of anode-to-cathode balance showing 40% utilization of Si capacity and (b) initial charge-discharge profiles of 20Ah large format cells based on a nano-Si anode and a high-voltage LMNO cathode.

The formulation of the anode electrode was modified to mitigate the volume expansion of Si particles and retard the deformation of the electrode. Figure 3 demonstrates the enhanced utilization of the Si anode by implementing a mixture of granular and fibrous graphite. The cells assembled using the developed electrode showed a capacity of 60 Ah and an energy density of 250 Wh/g. The formulation of the anode electrode will be further optimized based on the post-mortem analysis, which will occur with the completion of the cycle life testing.

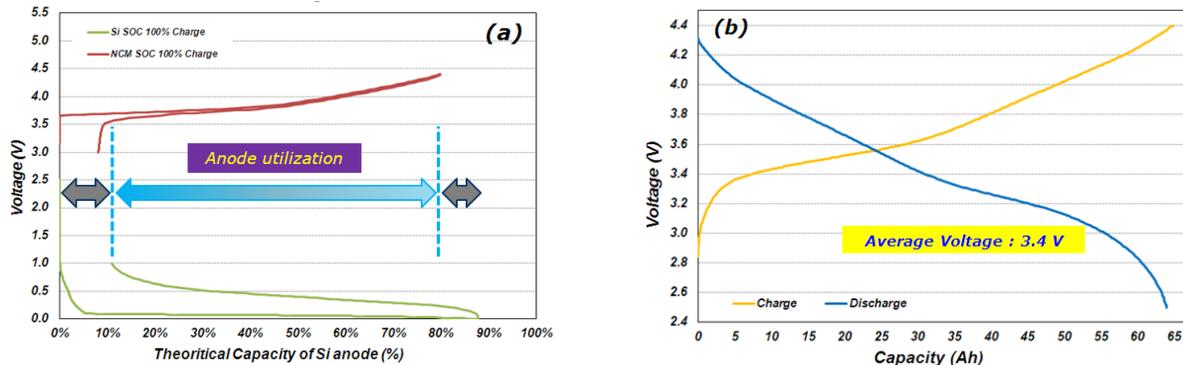


Figure 3: (a) Design of anode-to-cathode balance showing 90% utilization of Si capacity and (b) initial charge-discharge profiles of 60Ah large format cells based on nano-Si anode and high energy NCM cathode.

Task 1.3 – Yet-Ming Chiang, Massachusetts Institute of Technology

Design and Scalable Assembly of High-Density, Low-Tortuosity Electrodes

PROJECT OBJECTIVE: To develop a scalable high density binder-free low-tortuosity electrode design and fabrication process to enable increased cell-level energy density compared to conventional Li-ion technology. Characterize and optimize the electronic and ionic transport properties of controlled porosity and tortuosity electrodes as well as densely-sintered reference materials in $\text{Li}(\text{Ni}, \text{Co}, \text{Al})\text{O}_2$ (NCA), high capacity Li_2MnO_3 - LiMO_2 and high voltage $\text{LiM}_x\text{Mn}_{2-x}\text{O}_4$ and $\text{LiM}_x\text{Mn}_{2-x}\text{O}_{4-y}\text{F}_y$ spinels in order to elucidate rate limiting steps. Success is measured by the area capacity (mAh/cm^2) that is realized at defined C-rates or current densities. Develop corresponding anodes and demonstrate full cells.

PROJECT IMPACT: The high cost ($\$/\text{kWh}$) and low energy density of current automotive lithium-ion technology is in part due to the need for thin electrodes and associated high inactive materials content. If successful this project will enable use of electrodes based on known families of cathode and anode actives but with at least 3 times the areal capacity (mAh/cm^2) of current technology while satisfying the duty cycles of vehicle applications. This will be accomplished via new electrode architectures fabricated by scalable methods with higher active materials density and reduced inactive content, and will in turn enable higher energy density and lower-cost EV cells and packs.

OUT-YEAR GOALS: Identify anodes and fabrication approaches that enable full cells in which both electrodes have high area capacity under EV operating conditions. Anode approach will include identifying compounds amenable to same fabrication approach as cathode, or use of very high capacity anodes such as stabilized lithium or Si-alloys that in conventional form can capacity-match the cathodes. Use data from best performing electrochemical couple in techno-economic modeling of EV cell and pack performance parameters.

Milestones

1. Fabricate and test at least one anode compound in an electrode structure having at least $10 \text{ mAh}/\text{cm}^2$ theoretical capacity. (12/31/14) **Complete**
2. Demonstrate at least $5 \text{ mAh}/\text{cm}^2$ capacity per unit area at 1C continuous cycling rate for at least one candidate anode. (3/31/15) **Complete**
3. Downselect at least one anode composition for follow-on work. *Go/No-Go milestone:* Downselect based on demonstrated area capacity of at least $7.5 \text{ mAh}/\text{cm}^2$ at 1C continuous rate. (6/30/15) **Ongoing**
4. Demonstrate an anode with at least $10 \text{ mAh}/\text{cm}^2$ capacity per unit area for a 2C 30 sec pulse. (9/30/15) **Ongoing**

Progress Report

Milestone 1. Fabricate and test at least one anode compound in an electrode structure having at least 10 mAh/cm² theoretical capacity. (12/31/14)

Aqueous suspensions were prepared using battery-grade graphite and CMC binder (5 wt% relative to the graphite) and containing no conductive carbon additive. The formulations prepared are similar to suspensions for an aqueous electrode coating process for Li-ion. Directional freezing experiments were conducted in a similar manner to past experiments for cathodes except that electrodes were not sintered after lyophilization. As shown in Figure 4, highly-oriented, low-tortuosity pore-channels were obtained at cooling rates of 5°C/min and 7.5°C/min. The final porosity of the electrodes was 58 to 60 vol%. When sectioned to 800 μm thickness, the anodes have theoretical area capacity of about 25 mAh/cm². When tested at a C/5 rate, stable cycling was observed over 10 cycles, as shown in Fig. 2 (left) with area capacity of 15 mAh/cm². At a C/10 rate, approximately 18 mAh/cm² is reached, Figure 5 (right).

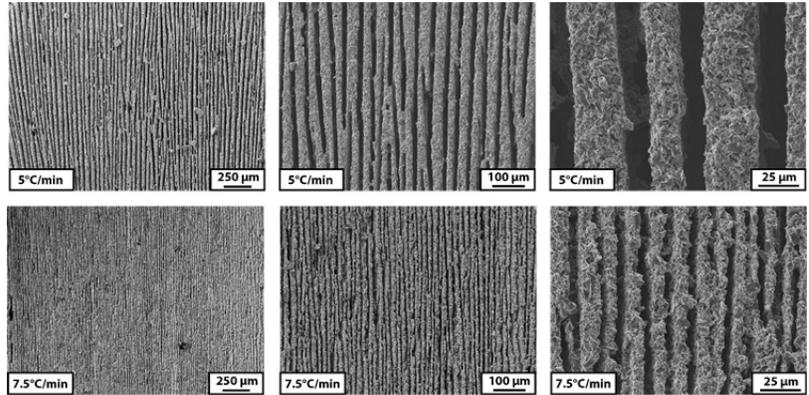


Figure 4: Cross sections of graphite anodes formulated with CMC binder and freeze-cast at the cooling rates indicated. Electrodes were lyophilized to retain structure. Total porosity is 58-60 vol%.

obtained at cooling rates of 5°C/min and 7.5°C/min. The final porosity of the electrodes was 58 to 60 vol%. When sectioned to 800 μm thickness, the anodes have theoretical area capacity of about 25 mAh/cm². When tested at a C/5 rate, stable cycling was observed over 10 cycles, as shown in Fig. 2 (left) with area capacity of 15 mAh/cm². At a C/10 rate, approximately 18 mAh/cm² is reached, Figure 5 (right).

Milestone 2. Demonstrate at least 5 mAh/cm² capacity per unit area at 1C continuous cycling rate for at least one candidate anode. (3/31/15).

The directionally-freeze cast graphite electrodes in Figure 4 were tested at C/10, C/5, and 1C rates at room temperature in Li half-cells of Swagelok type. Results are shown in Figure 5 (right). At a 1C rate, the area capacity is 6 mAh/cm², meeting Milestone 2.

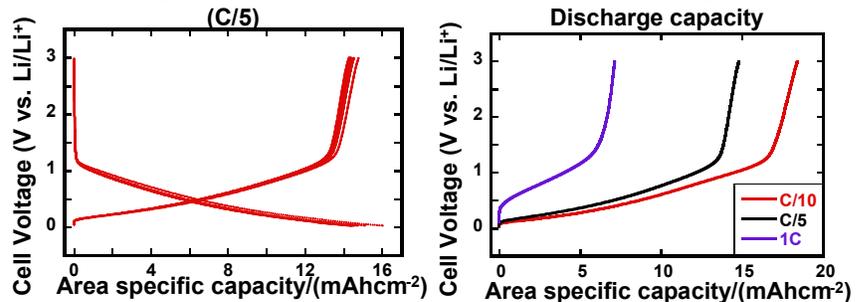


Figure 5: Galvanostatic discharge voltage vs. capacity for 800 μm thick electrode sectioned from sample directionally freeze-cast at 7.5°C/min. Left: Multiple cycles at C/5 rate. Right: Comparison of result at C/10, C/5 and 1C discharge rate.

Task 1.4 – Gao Liu (Lawrence Berkeley National Laboratory)

Hierarchical Assembly of Inorganic/Organic Hybrid Si Negative Electrodes

PROJECT OBJECTIVE: This proposed work aims to enable Si as a high capacity and long cycle-life material for negative electrode to address two of the barriers of lithium-ion chemistry for EV/PHEV application, insufficient energy density and poor cycle life performance. The proposed work will combine material synthesis and composite particle formation with electrode design and engineering to develop high capacity, long life and low cost hierarchical Si based electrode. State of the art Li-ion negative electrodes employ graphitic active materials with theoretical capacities of 372 mAh/g. Si, a naturally abundant material, possesses the highest capacity of all Li-ion anode materials. It has a theoretical capacity of 4200 mAh/g for full lithiation to the $\text{Li}_{22}\text{Si}_5$ phase. However, Si volume change disrupts the integrity of electrode and induces excessive side reactions, leading to fast capacity fade.

PROJECT IMPACT: This work addresses the adverse effects of Si volume change and minimizes the side reactions to significantly improve capacity and lifetime to develop negative electrode with Li-ion storage capacity over 2000 mAh/g (electrode level capacity) and significantly improve the coulombic efficiency. The research and development activity will provide an in-depth understanding of the challenges associated with assembling large volume change materials into electrodes, and will develop a practical hierarchical assembly approach to enable Si materials as negative electrodes in Li-ion batteries.

OUT-YEAR GOALS: There are three aspects of this proposed work – bulk assembly, surface stabilization and lithium enrichment, which are formulated into 10 tasks in a four-year period. 1) Develop hierarchical electrode structure to maintain electrode mechanical stability and electrical conductivity. (Bulk assembly) 2) Form in situ compliant coating on Si and electrode surface to minimize Si surface reaction. (Surface stabilization) 3) Use prelithiation to compensate first cycle loss of the Si electrode. (Li enrichment) In the end of the 4th year, the goal is to achieve a Si based electrode at higher mass loading of Si, and can be extensively cycled cycles with minimum capacity loss at high coulombic efficiency to qualified for vehicle application.

COLLABORATIONS: Vince Battaglia and Venkat Srinivasan (LBNL), Xingcheng Xiao (GM), Jason Zhang (PNNL), Tong Wei, Wanli Yang, Chongming Wang (PNNL), and the Si-Anode Focus Group.

Milestones

- 1) Design and synthesis at least two functional conductive polymers for Si based electrode. (Dec. 31) **Complete**
- 2) Develop methodologies to improve the Si electrode first cycle efficiency to 90%. (Mar. 31) **Complete**
- 3) Design and synthesize new surface stabilizing additive, and test it with Si based electrode. (Jun. 30) **Ongoing**
- 4) Go/No-Go Apply hierarchical electrode design to achieve a 3 mAh/cm² loading. (Sep. 31) **Ongoing**

Progress Report

Silicon monoxide (SiO) is considered a promising alternative anode material for lithium-ion batteries (LIBs), with a specific capacity of 1000 to 1500 mAh/g, to the standard graphite anode (372 mAh/g). One caveat for the application of SiO is its low 1st cycle efficiency. During the 1st cycle lithiation process, besides the reversible reaction with the Si phase, lithium reacts with silicon dioxide to form silicate. Only 65% of the lithium can reversibly delithiate: this is a detriment to full cell applications. Thus, an appropriate prelithiation step is critical.

Stabilized lithium metal powder (SLMP[®]) is used to prelithiate the SiO anode in the SiO/NMC full cell. SLMP is a micron-size lithium metal powder with *ca.* a 2 wt% lithium carbonate surface coating. The amount of SLMP added to a cell was calculated to theoretically eliminate all the irreversible capacity in the first cycle. A calendar machine was used in a glove box to pressure-activate the SLMP particles (Figure 6a). This operation breaks the lithium carbonate (Li_2CO_3) shell and allows lithium to be in direct electrical contact with the SiO materials in the anode.

A 96-hour rest period was used to allow the crushed SLMP to fully prelithiate the SiO anode before current-driven charging of the cells. As a control, a second SiO/NMC full cell without SLMP was allowed to rest for 96 hours before cycling. Both cells were put through a formation process consisting of two cycles at C/20 and two cycles at C/10 prior to C/3 cycling. Apparent improvement was shown for the SLMP-loaded full cells. The first cycle CE increased from 48% to *ca.* 90% with the SLMP (shown in the inset of Figure 6d). SLMP enabled the NMC/SiO full cell to maintain a reversible capacity of *ca.* 110 mAh/g after more than 100 cycles at C/3.

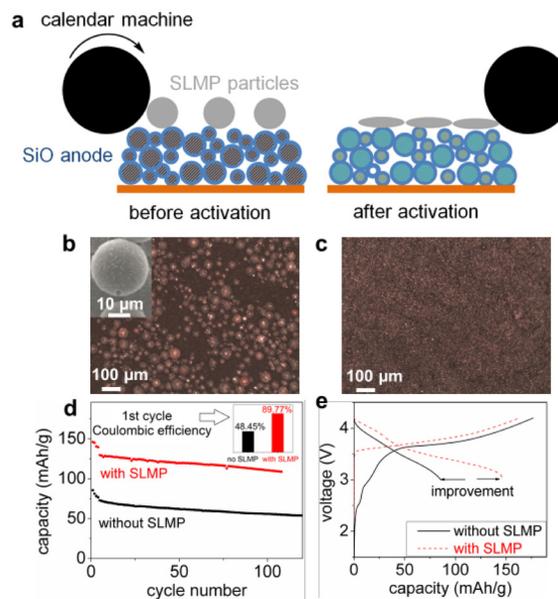


Figure 6: (a) Schematics of the utilization of SLMP for the SiO electrode. SLMP particles are loaded on to the SiO anode. Rolling compression was used to crush the Li_2CO_3 shell of SLMP to release lithium metal and laminate it on the surface of SiO electrode. This process is called SLMP activation. (b) SLMP particles loaded on the SiO electrode before activation. The inset shows the SEM image of a single SLMP particle. (c) The SiO electrode surface after electrolytes are added onto the SiO electrode with activated SLMP after 12 hours. This shows the disappearance of SLMP and indicates the successful prelithiation of the SiO electrode. (d) SiO/NMC full cell performance with or without the SLMP capacity-enhancement additive, two cycles at C/20, two cycles at C/10, and then C/3. The first cycle voltage curves of the two cells.

Task 1.5 – Vincent Battaglia (Lawrence Berkeley National Laboratory)

Studies in Advanced Electrode Fabrication

PROJECT OBJECTIVE: This project supports ABMR PIs through the supply of electrode materials, laminates, and cells as defined by the ABMR Focus Groups. The emphasis of the 2015 effort will be on the High-Voltage Focus Group, the Si-Anode Focus Group, and a nascent Li/S effort. The objectives are to screen sources of materials, define baseline chemistries, and benchmark performance of materials targeted to specific Focus Group topics. This provides a common chemistry and performance metrics that other ABMR institutions can use as a benchmark for their own efforts on the subject. In addition, test configurations will be designed and built to identify and isolate problems associated with poor performance. Also, Li/S cells will be designed and tested.

PROJECT IMPACT: Identification of baseline chemistries and availability of baseline laminates will allow a group of ABMR PIs to work as a team. Such team work is considered crucial in the acceleration of the advancement of today's Li-ion and Li/S systems. Since all of the focus groups are dedicated on some aspect of increased energy density, all of this work will have an impact on this area.

OUT-YEAR GOALS: This framework of a common chemistry will accelerate advancements in energy density and should lead to baseline systems with an increased energy density of at least 40%. It should also provide a recipe for making electrodes of experimental materials that are of high enough performance to allow for critical down select – an important part of the process in advancing any technology.

COLLABORATIONS: Many ABMR PIs

Milestones

1. Identify and report the source of additional impedance of a symmetric cell. (12/31/14) **Complete**
2. Measure and report the gas composition of a symmetric cathode/cathode cell and an anode/anode cell. (3/31/15) **Ongoing**
3. Identify the first iteration of the baseline Li/S cell. (6/30/15) **Ongoing**
4. Measure and report gas volume *versus* rate of side reaction at several upper voltage cut-off points. (9/30/15) **Ongoing**

Progress Report

Milestone 1. Identify and report the source of additional impedance of a symmetric cell. This quarter was spent developing baseline electrodes for the high voltage study. Electrodes were made of LCO, High-Voltage LCO (HV LCO), and NCM, all from the same commercial supplier. The electrodes were cycled against Li to test their cycleability. The approach is to start with conditions demonstrating excellent cycleability and then to push the voltage up until the cycleability begins to suffer. To demonstrate excellent cycleability, electrodes of modest loadings were formulated and cycled against Li metal under mild conditions of 30°C and between 2.8 and 4.1 V. (See Figure 7.)

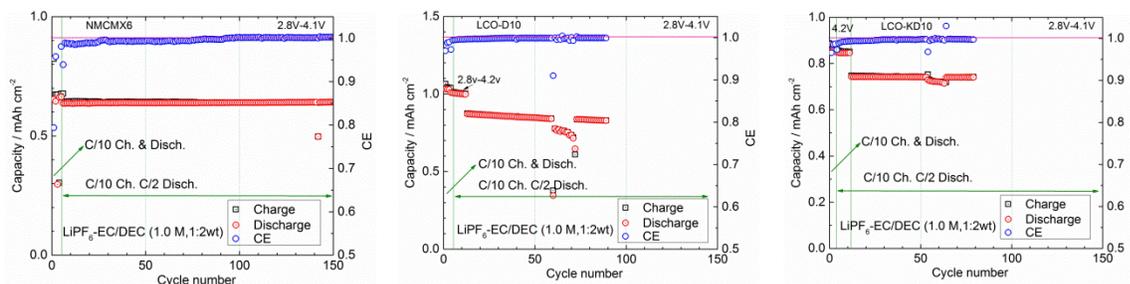


Figure 7: Capacity Fade Curves for LCO, High Voltage LCO, and NCM

Unfortunately, the two LCO-based cells were initially cycled between 2.8 and 4.2 V for a few cycles before it was noticed and then changed to 4.1 V. The cell with LCO shows a slight degree of capacity fade at 4.1 V after cycling at 4.2 for 10 cycles so this experiment is being repeated. The cells with NCM and HV LCO show almost no capacity fade for the first 150 and 80 cycles, respectively. With the benchmarking nearly completed, the next step will be to start pushing up the voltage and investigating modes of capacity fade. A three electrode cell will be involved in those investigations and the symmetric cells of cathodes will be prepared and evaluated in the next quarter.

Milestone 2. Measure and report the gas composition of a symmetric cathode/cathode cell and an anode/anode cell: A pouch cell was developed that consists of two valves. One valve will allow a sweeping gas in and the other to allow the gas to leave.

Milestone 3. Identify the first iteration of the baseline Li/S cell: Cell hardware for testing Li/S cells was identified and purchased. The cell is due to arrive early January. There are a handful of investigators at LBNL developing technologies for this chemistry including Elton Cairns, Gao Liu, Venkat Srinivasan, and Nitash Balsara. We intend to work closely with those investigators and incorporate their technologies into the selected cell hardware.

Milestone 4. Measure and report gas volume *versus* rate of side reaction at several upper voltage cut-off points: Ongoing

See reports under Milestones 1 and 2.

TASK 2 – SILICON ANODE RESEARCH

Most Li-ion batteries used in the state of the art electric vehicles (EVs) contain graphite as their anode material. Limited capacity of graphite (LiC_6 , 372 mAh/g) is one of the barriers that prevent long range operation of EVs required by the EV Everywhere Grand Challenge proposed by DOE/EERE. In this regards, Silicon (Si) is one of the most promising candidate as an alternative anode for Li-ion battery applications. Si is environmentally benign and ubiquitous. The theoretical specific capacity of silicon is 4212 mAh/g ($\text{Li}_{21}\text{Si}_5$), which is 10 times greater than the specific capacity of graphite. However, the high specific capacity of silicon is associated with large volume changes (more than 300 percent) when alloyed with lithium. These extreme volume changes can cause severe cracking and disintegration of the electrode and lead to significant capacity loss.

Significant scientific research has been conducted to circumvent the deterioration of silicon-based anode materials during cycling. Various strategies, such as reduction of particle size, generation of active/inactive composites, fabrication of silicon-based thin films, use of alternative binders, and the synthesis of one-dimensional silicon nanostructures have been implemented by a number of research groups. Fundamental mechanistic research also has been performed to better understand the electrochemical lithiation and delithiation processes during cycling in terms of crystal structure, phase transitions, morphological changes, and reaction kinetics. Although significant progresses have been made on the development of the silicon-based anodes, there are still many obstacles that prevent their practical application. Long-term cycling stability remains the foremost challenge for Si based anode, especially for high loading electrode ($> 3\text{mAh/cm}^2$) required for many practical applications. The cyclability of full cells using silicon-based anodes is also complicated by multiple factors, such as diffusion-induced stress and fracture, loss of electrical contact among silicon particles and between silicon and current collector, and the breakdown of SEI layers during volume expansion/contraction processes. The design and engineering of a full cell with a silicon-based anode still needs to be optimized. Critical research remaining in this area includes, but is not limited to, the following:

- Low cost manufacturing processes have to be found to produce nano-structured silicon with the desired properties.
- The effects of SEI formation and stability on the cyclability of silicon-based anodes need to be further investigated. Electrolytes and additives that can produce a stable SEI layer need to be developed.
- The properties of binder and conductive matrix need to be developed. They should provide flexible but stable electrical contacts among silicon particles and between particles and the current collector under repeated volume changes during charge/ discharge processes.
- The performances of full cells using silicon-based anode need to be investigated and optimized.

The main goal of this project is to have a fundamental understanding on the failure mechanism on Si based anode and improve its long term stability, especially for thick electrode operated at full cell conditions. Success of this project will enable Li-ion batteries with a specific energy of $>350\text{ Wh/kg}$ (in cell level), 1000 deep-discharge cycles, 15-year calendar life, and less than 20% capacity fade over a 10-year to meet the goal of *EV everywhere*.

Task 2.1 – Ji-Guang (Jason) Zhang, Jun Liu (Pacific Northwest National Laboratory)

Development of Silicon-Based High Capacity Anodes

PROJECT OBJECTIVE: The objective of this project is to develop high-capacity and low-cost Si-based anodes with good cycle stability and rate capability to replace graphite in Li-ion batteries. The porous structured Si and the rigid-skeleton supported Si/C composite anode (B4C/Si/C) will be further optimized to improve the performance and to lower the cost. Nanocomposites of silicon and Li-ion conducting lithium oxide will be prepared by novel in situ chemical reduction methods to solve the problems associated with large first cycle irreversible capacity loss, while achieving acceptable coulombic efficiencies. Large irreversible capacity loss in the first cycle will also be minimized by pre-doping Li into the anode using stabilized lithium metal powder or additional sacrificial Li electrode. The optimized materials will be used as the baseline for both thick electrode fabrication and studies to advance our fundamental understanding of the degradation mechanism of Si-based anodes. The electrode structures will be modified to enable high utilization of thick electrode. Mechanical and electrochemical stability of the SEI layer will be investigated by electrochemical method, simulation and in situ microscopic analysis to guide their further improvement.

PROJECT IMPACT: Si-based anodes have much larger specific capacities compared with conventional graphite anodes. However, the cyclability of Si-based anodes is limited because of the large volume expansion that is characteristic of these anodes. This work will develop a low-cost approach to extend the cycle life of high-capacity, Si-based anodes. The success of this work will further increase the energy density of Li-ion batteries and accelerate market acceptance of electrical vehicles (EV), especially for plug-in hybrid electrical vehicles (PHEV) required by the EV Everywhere Grand Challenge proposed by DOE/EERE.

OUT-YEAR-GOALS: The main goal of the proposed work is to enable Li-ion batteries with a specific energy of >200 Wh/kg (in cell level for PHEVs), 5000 deep-discharge cycles, 15-year calendar life, improved abuse tolerance, and less than 20% capacity fade over a 10-year period.

COLLABORATIONS: We will continue to collaborate with following battery groups on anode development:

- Jim Zheng at Florida State University- Pre-lithiated anodes for Li-ion batteries and Li-ion capacitors
- Prof. Michael Sailor at UCSD—Preparation of porous Si.
- Prof. David Ji—Oregon State University- Preparation of porous Si by thermite reactions.

Milestones

- 1) Identify the stability window of SEI formed on Si based anode (12/31/2014) **Completed**
- 2) Optimize the synthesis conditions of the rigid-skeleton supported Si composite (3/31/2015)
- 3) Demonstrate the operation of full cell using Si anode and selected cathode with >80% capacity retention over 100 cycles. (6/30/2015)
- 4) Achieve >80% capacity retention over 200 cycles of thick electrodes (~3 mAh/cm²) through optimization of the Si electrode structure and binder. (9/30/2015)

Progress Report

A stable window for SEI formation was identified from tuning the voltage window. By lowering the charge voltage from 1 V to 0.6V, the capacity retention of Si/B₄C/graphite (SBG) composite anode of similar loading can be improved by 20% with slight loss in capacity. This is an indication that the SEI formed on Si anode is stable between 0 to 0.6V. The effect of binders to the cycling stability of high loading Si electrodes is investigated. Different types of binders such as PAALi, LA133, and several types of self-healing polymers are investigated with the SBG material. However, the cycling stability of the electrode prepared by these binders are inferior as compared with those prepared with CMC binder. The self-healing polymers (Figure 8, Figure 9) are slightly soluble in the electrolyte and hence the capacity fades very fast.

Porous Si from thermite reaction (in collaboration with Oregon State University) shows good cycling stability. The porous Si exhibits a capacity of ~1.73 mAh/cm² with ~76% capacity retention over 200 cycles. The battery was cycled using the standard BATT (BMR) protocol: 0.005 to 1 V; three formation cycles at 0.06 mA/cm²; 0.75 mA/cm² for delithiation and 0.5 mA/cm² for lithiation. To further improve the cycling stability, a new type of multi-layer core-shell structured rigid-skeleton supported Si composite (Figure 10) is under development. By designing spherical graphite/nano-Si coating/ graphene core-shell structure, we expect to get improved cycling stability for high loading Si anodes.

In collaboration with Florida State University, pre-lithiation method has been used to improve the capacity and lifetime of Li-ion capacitors made with activated carbon cathode and hard carbon/stabilized lithium metal powder anode electrodes. After the pouch cell Li-ion capacitors were made, different electrolytes including commercial LP30 (1 M LiPF₆ in EC:DMC at 1:1 ratio) and PNNL homemade electrolytes were filled into two Li-ion capacitors. The Li-ion capacitor could be operated at temperatures as low as -40 °C, and the discharge capacity at -40 °C was about 55% of that at room temperature. Figure 10 shows a comparison of discharge capacitance of two Li-ion capacitors using commercial LP30 and PNNL homemade electrolytes, respectively. It can be seen that the performance at low temperatures for using PNNL electrolyte has been significantly improved. The cycle life of Li-ion capacitor using PNNL electrolyte was tested, it was found that the discharge capacity was still remained over 95% after 10,000 cycles.

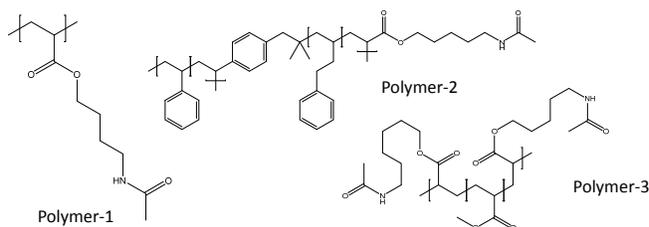


Figure 8: Three types of self-healing polymers investigated as binders for Si anodes.

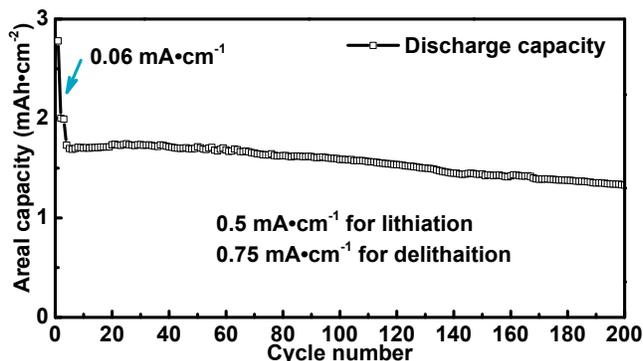


Figure 9: Three types of self-healing polymers used as binders for Si anodes.

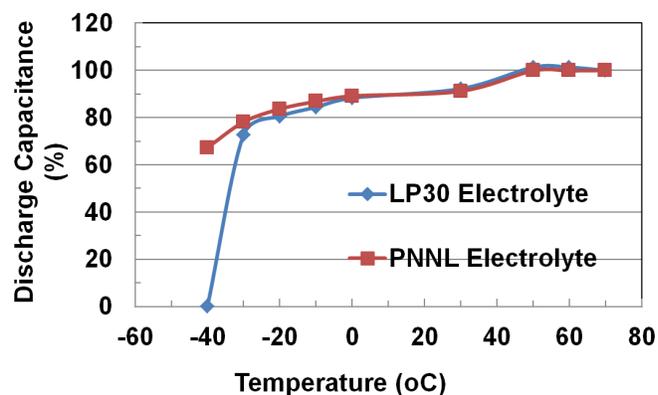


Figure 10: The comparison of discharge capacitances as a function of temperature for Li-ion capacitors filled with commercial and PNNL electrolytes.

Task 2.2 – Yi Cui (Stanford University)

Pre-Lithiation of Silicon Anode for High Energy Li Ion Batteries

PROJECT OBJECTIVE: Prelithiation of high capacity electrode materials such as Si is an important means to enable those materials in high-energy batteries. This study pursues two main directions: 1) developing facile and practical methods to increase first-cycle Coulombic efficiency of Si anodes, and 2) synthesizing fully lithiated Si to pair with high capacity lithium-free cathode materials.

PROJECT IMPACT: The first-cycle Coulombic efficiency of anode materials will be increased dramatically via prelithiation. Prelithiation of high capacity electrode materials will enable those materials in next generation high-energy-density lithium ion batteries. This project's success will make high-energy-density lithium ion batteries for electric vehicles.

OUT-YEAR GOALS: Compounds containing large quantity of Li will be synthesized for pre-storing Li ions inside batteries. First-cycle Coulombic efficiency (1st CE) will be improved and optimized (over 95%) by prelithiating anode materials with the synthesized Li-rich compounds.

COLLABORATIONS:

- BATT program PI's
- SLAC: In-situ X-ray, Dr. Michael Toney.
- Stanford: Prof. Nix, mechanics.

Milestones

- 1) Prelithiate anode materials by direct contact of Li metal foil to anodes (Jan-14) **Completed**
- 2) Synthesize Li_xSi nanoparticles with high capacity ($> 1000 \text{ mAh/g Si}$) (July-14) **Completed**
- 3) Prelithiate anode materials with dry-air stable $\text{Li}_x\text{Si-Li}_2\text{O}$ core-shell nanoparticles (Dec. 2014). On going

Progress Report

$\text{Li}_x\text{Si-Li}_2\text{O}$ core-shell nanoparticles (NPs) have been used as an excellent prelithiation reagent to compensate the first cycle capacity loss of various anode materials. These NPs were produced with a facile and scalable synthesis approach by direct alloying of Si NPs with Li metal foil as shown in Figure 11a. A dense passivation layer was formed on the Li_xSi NPs after exposure to trace amounts of oxygen. STEM image (Figure 11b) shows an obvious core-shell structure. $\text{Li}_x\text{Si-Li}_2\text{O}$ NPs are compatible with conventional slurry process and exhibit high capacity under the dry air conditions with the protection of Li_2O passivation shell. Using 1,3-dioxolane or toluene as the slurry solvent, $\text{Li}_x\text{Si-Li}_2\text{O}$ NPs show a high capacity of 1310 mAh/g, determined by subtracting the first lithiation capacity from the delithiation capacity.

Both Si NPs and graphite anodes are successfully prelithiated with $\text{Li}_x\text{Si-Li}_2\text{O}$ NPs to achieve high 1st cycle Coulombic efficiencies of 94% to > 100% as shown in Figure 12 and Figure 12b. It suppresses the undesired consumption of Li from cathode materials during SEI formation. After exposing to dry air for one day, there is 1175mAh/g capacity, only 9% decay from time zero. The capacity of the $\text{Li}_x\text{Si-Li}_2\text{O}$ NPs decays slowly with exposure time (Figure 12c). The electrochemical performance (Figure 12d) demonstrates that 6 h of exposure to air with dew point of -30°C does not affect the capacity. Even in air with a dew point of -10°C , the $\text{Li}_x\text{Si-Li}_2\text{O}$ NPs still exhibit a capacity of 819 mAh g^{-1} , indicating the NPs are stable enough to undergo the whole battery fabrication process in industry.

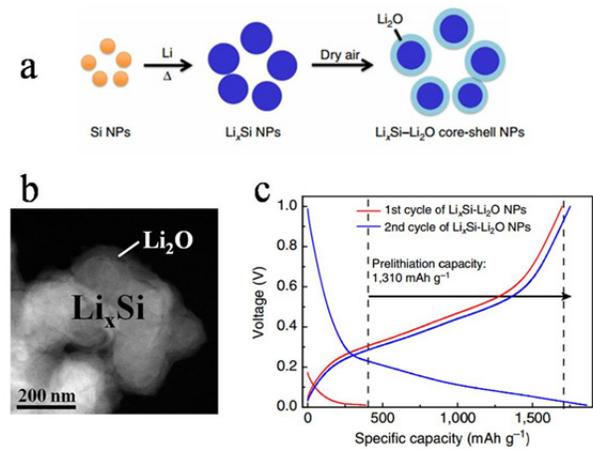


Figure 11: (a) Schematic diagrams showing Si NPs react with melted Li to form Li_xSi NPs. A dense passivation layer is formed on the Li_xSi NPs after exposure to trace amounts of oxygen, preventing the Li_xSi alloy from further oxidation in dry air. (b) STEM image of $\text{Li}_x\text{Si-Li}_2\text{O}$ core-shell NPs. (c) Voltage profiles of $\text{Li}_x\text{Si-Li}_2\text{O}$ NPs.

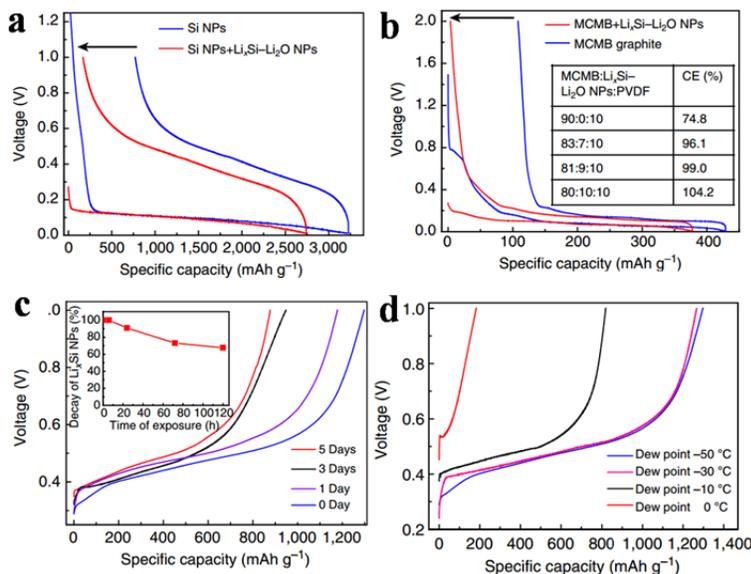


Figure 12: (a) First cycle voltage profiles of Si NPs/ $\text{Li}_x\text{Si-Li}_2\text{O}$ composite and Si NPs control cell. (b) First cycle voltage profiles of MCMB/ $\text{Li}_x\text{Si-Li}_2\text{O}$ composite (81:9 by weight) and MCMB control cell. The table shows that the 1st CE is tuned by the amount of $\text{Li}_x\text{Si-Li}_2\text{O}$ additives. (c) The capacity retention of $\text{Li}_x\text{Si-Li}_2\text{O}$ NPs exposed to dry air with varying durations. The inset shows the trend of capacity decay. (d) The capacity retention of $\text{Li}_x\text{Si-Li}_2\text{O}$ NPs exposed to air at different humidity levels.

TASK 3 – HIGH ENERGY DENSITY CATHODES FOR ADVANCED LITHIUM-ION

Development of high energy density, low cost, thermally stable and environmentally safe electrode materials is one of the key enablers for advanced batteries for transportation. High energy density is synonymous with reducing the cost per unit weight or volume. Currently, one of the major technical barriers towards development of high energy density lithium-ion batteries (LiBs) is the lack of availability of robust high capacity cathodes. To give an example, the most commonly used anode material for LiBs is graphitic carbon, which has a specific capacity of 372 mAh/g, while even the most advanced cathodes like lithium nickel manganese cobalt oxide (NMC) has a maximum capacity of around 180 mAh/g. This calls for an immediate need for developing high capacity (and voltage) intercalation type cathodes that have stable reversible capacity in the range of 250 mAh/g and beyond. Alternative high capacity cathode chemistries such as those based on conversion mechanism, Li-S, or metal air chemistries still have fundamental issues that need to be addressed before integration into cells for automotive use. A number of high voltage cathode chemistries have been developed under the BATT (now BMR) program which includes Li-rich NMC and Ni-Mn spinels. Current efforts are directed towards understanding the various mechanisms which limit capacity and improving stability (both bulk and interfacial) under high voltage cycling. Approaches include aliovalent or isovalent doping or substitution to stabilize cathode structures during delithiation as well as surface coatings to improve the interfacial stability. Efforts are also directed towards developing new high capacity phases having different polyanionic groups such as phosphates, fluorites and vanadates. To be successful in these efforts the research team needs to address the following technical barriers as listed below.

Technical Barriers

- 1) Low gravimetric and volumetric capacity.
- 2) Intrinsically lower electronic and/or ionic conductivity leading to poor rate capability.
- 3) Structural and phase instability during continuous high voltage (> 4.5 V) electrochemistry.
- 4) Transition metal dissolution leading to capacity fades and cell failure.
- 5) Interfacial stability and compatibility with other high capacity anodes such as silicon and other metal alloys.

Successful demonstration of high energy cathodes will enable high energy cells that meet or exceed the DOE cell level target of 400 Wh/kg and 600 Wh/L, respectively with a system level cost target \$125/kWh.

Task 3.1– Jagjit Nanda (Oak Ridge National Laboratory)

Studies on High Energy Density Lithium-ion Electrodes

PROJECT OBJECTIVE: The overall project goal is development of high energy density lithium-ion electrodes for EV and PHEV application that meet and/or exceed the DOE energy density and life cycle targets as from the USDRIVE/USABC roadmap. Specifically, this projects aims to address and mitigate the technical barriers associated with high voltage cathode compositions such as lithium-manganese rich NMC (LMR-NMC) and $\text{Li}_2\text{M}^{\text{I}}\text{M}^{\text{II}}\text{O}_2$, where M^{I} and M^{II} are transition metals that do not include Mn or Co. Major emphasis is placed on developing new materials modifications (including synthetic approaches) for high voltage cathodes that will mitigate issues such as: (i) voltage fade associated with LMR-NMC composition that leads to loss of energy over the cycle life; (ii) transition metal dissolution that leads to capacity and power fade; (iii) thermal and structural stability under the operating SOC range; and (iv) voltage hysteresis associated with multivalent transition metal compositions. Another enabling feature of the project is utilizing (and developing) various advanced characterization and diagnostic methods at the electrode and/or cell level for studying cell and/or electrode degradation under abuse conditions. The techniques include EIS, Micro-Raman, aberration corrected electron microscopy combined with EELS, X-ray photoelectron spectroscopy, ICP-AES, Fluorescence, and X-ray and Neutron diffraction.

PROJECT IMPACT: The project has both short term and long term deliverables directed towards VTO Energy Storage 2015 and 2022 goals. Specifically, we are working on advanced electrode couples that have cell level energy density targets of 400 Wh/kg and 600 Wh/l for 5000 cycles. Increasing the energy density per unit mass or volume ultimately reduces the cost of battery packs consistent with DOE 2022 EV everywhere goal of \$125/kWh.

OUT-YEAR GOALS: The project is directed towards developing high capacity cathodes for advanced lithium-ion batteries. The goal is to develop new cathode materials that have high capacity, are based on low-cost materials and meet the DOE road map in terms of safety and cycle life. Under this project two kinds of high energy cathode materials are studied. Over last few years the PI has worked on improving cycle life and mitigating energy losses in high voltage Li-rich composite cathodes (referred to as LMR-NMC) in collaboration with the voltage fade team at Argonne National Laboratory. Efforts also include surface modification of LMR-NMC cathode materials to improve their electrochemical performance under high voltage cycling ($> 4.5\text{V}$). Tasks also include working in collaboration with researchers at Stanford Synchrotron Research Laboratory (SSRL) and APS (LBNL) for understanding local changes in morphology and microstructure under *in situ* and *ex situ* conditions. In a parallel effort we are developing new high capacity cathode systems that are not Mn rich but based on Cu-Ni phases. New solid state synthesis and structural characterization are underway to stabilize the structure of $\text{Li}_2\text{Cu}_{1-x}\text{Ni}_x\text{O}_2$ upon > 1 Li removal.

COLLABORATIONS:

Y. Liu, Stanford Synchrotron Research Laboratory, SLAC: X-ray Imaging and XANES

Guoying Chen, LBNL, In-situ XAS and XRD

Kang Xu, Army Research Laboratory, High voltage electrolyte additives

Bryant Polzin, Argonne Research Laboratory

Milestones

- 1) Q1: Investigation of the surface reactivity, vacancy disorder and interfacial kinetics of LMR-NMC composite cathodes to mitigate voltage fade and TM dissolution to achieve DOE cell level EV goals of 400 Wh/Kg and 600 Wh/L for 5000 cycles. (ongoing)

- 2) Q2: Stabilize the structure and electrochemical performance of high capacity $\text{Li}_2\text{Cu}_x\text{Ni}_{1-x}\text{O}_2$ cathodes to achieve capacity between 250-300 mAh/g for > 50 charge-discharge cycles at C/3 rate. (March 2015)
- 3) Q3: Undertake *in situ* and *ex-situ* x-ray synchrotron and spectroscopic studies to correlate changes in local structure, surface chemistry and morphology of cycled high energy density electrodes (LMR-NMC and 5V Mn-Ni spinel) and compare the changes with pristine or uncycled electrodes. (50% complete)
- 4) Q4: Investigate and measure interfacial and grain boundary resistance between high voltage cathode-solid electrolyte interfaces between 0.1 to 2 mA/cm² current density and within temperature ranges between 25-60 °C. (July 2015)

Progress Report

This quarter we performed EIS studies on LMR-NMC/Graphitefull cells as a function of state-of-charge and temperature. The goal is to extract the charge transfer resistance and the bulk lithium-ion diffusivity from EIS analysis and study their dependencies as a function of lithium concentration. EIS measurements were carried out using a three electrode reference cell designed by EL-Cell. The electrode HE-5050 (cathode) and A12 graphite (anode) were obtained from Argonne National Laboratory and cells were conditioned as per the standard ABR protocol before the EIS measurement. LMR-NMC material changes its phase/composition gradually as a function of cycling which makes it a difficult chemistry for quantitative analysis using the EIS method. Distortion at high frequencies caused by the reference electrode was evaluated by comparing half cell and full cell data. Standard LiPF_6 salt in carbonate solvents was used as the electrolyte (Selectilyte) with glass fiber separators. EIS response of the LMR-NMC cathode was studied as a function of SOC/voltage and temperature (0, 10, 20, 25, 30, 40 °C). The EIS response shown below at 4 V (Fig.1) can be fit using an equivalent circuit model consisting of a ohmic part (R_1) and possibly a charge transfer resistance (R_2). The charge transfer resistance is in parallel with some capacitance, but the physical origins of the capacitance are unclear at this time. This capacitance may be related to the concentration of lithium in the bulk, but could also arise from double-layer and/or space charge. The low frequency tail looks very much like finite Li-ion diffusion but given

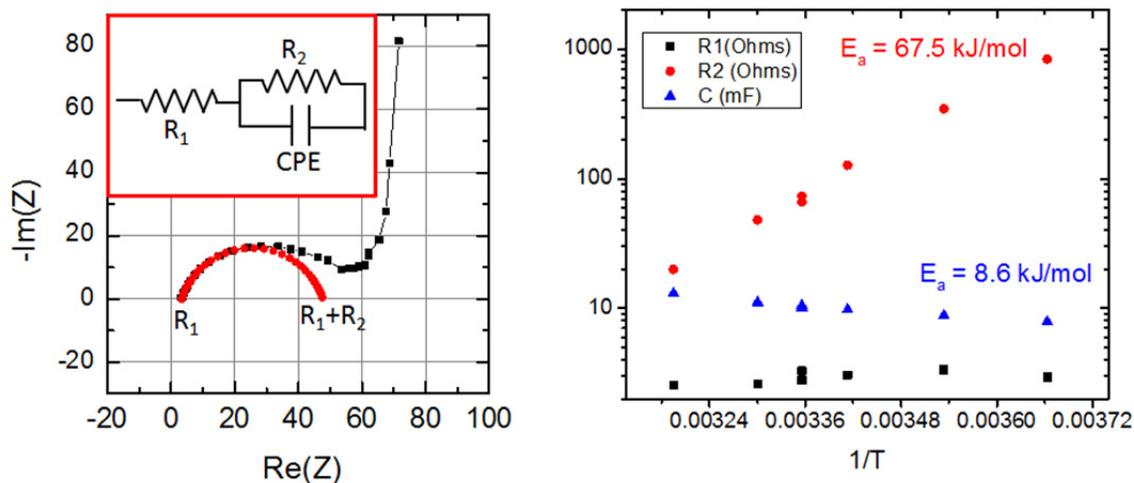


Figure 13: (Left) Analysis of EIS spectrum of LMR-NMC cathode at 4 V. (Right) Activation energy as a function of temperature for various EIS contributions.

the extremely slow time response it is difficult to ascertain. Instead, for our analysis we focus on the high frequency region. Figure 13 right panel shows the extracted resistances and capacitance as function of

temperature. The parallel resistance shows single-activation energy of 67.5 kJ/mol which agrees well with the energy barrier needed to break-up the solvation sheath of molecules closely coordinated to Li^+ in carbonate electrolytes (Kang Xu, JECS, 2007). As the next step we fit the high frequency arc at different voltage/SOC (3.5–4.5V) and show the variation of R_2 and CPE as function of voltage (Figure 14)

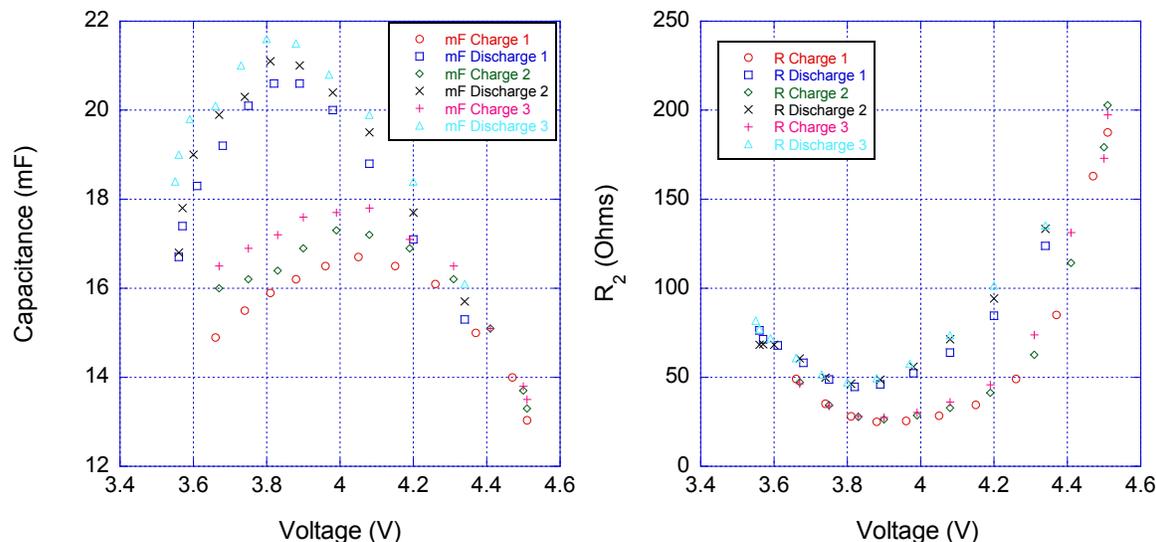


Figure 14: Parallel capacitance (left) and resistance (right) as function of voltage for LMR-NMC cathode at RT

As shown in Figure 14 the capacitance and resistance show strong voltage dependence with large hysteresis between charge and discharge, even after considerable rest period (2h at OCV prior to EIS measurement). Quantitative EIS analysis for LMR-NMC composition is challenging due to dynamic phase or compositional changes associated with this chemistry that shift the EIS spectra over a period of several days (data not shown). Further work is continuing to conclude and complete this piece of work with a go-no go decision.

Patents/Publications/Presentations

Journal Publications (this quarter)

1. Raman Microscopy of Lithium-Manganese-rich Transition Metal Oxide Cathodes, R. E. Ruther, A. F. Callender, H. Zhou, S. K. Martha and J. Nanda, Journal of the Electrochemical Society, 162 (1) A1-A5 (2015).
2. Direct Synthesis and fabrication of C-Si-SiO₂ Monolithic Composite Electrodes Comprised of Lignin-derived Carbon Fibers Embedded with Silicon, O. Rios, S. K. Martha, M. A. McGuire, Wyatt Tenhaeff, K. More, C. Daniel, J. Nanda, Energy Technology 2014, DOI: 10.1002/ente.201402049.

Task 3.2 – Stanley Whittingham (SUNY Binghamton)

High Energy Density Lithium Battery

PROJECT OBJECTIVE: To develop the anode and cathode materials for high-energy density cells for use in plug-in hybrid electric vehicles (PHEVs) and in electric vehicles (EV) that offer substantially enhanced performance over current batteries used in PHEVs and with reduced cost.

Specifically, the primary objectives are to:

- Increase the volumetric capacity of the anode by a factor of 1.5 over today’s carbons
 - Using a SnFeC composite conversion reaction anode
- Increase the capacity of the cathode
 - Using a high capacity conversion reaction cathode, CuF_2 , and/or
 - Using a high capacity 2 Li intercalation reaction cathode, VOPO_4
- Enable cells with an energy density exceeding 1 kWh/liter

PROJECT IMPACT: The volumetric energy density of today’s lithium-ion batteries is limited primarily by the low volumetric capacity of the carbon anode. If the volume of the anode could be cut in half, and the capacity of the cathode to over 200 Ah/kg, then the cell energy density can be increased by over 50% to approach 1 kWh/liter (actual cell). This will increase the driving range of vehicles.

Moreover, smaller cells using lower cost manufacturing will lower the cost of tomorrow’s batteries.

OUT-YEAR GOALS:

The long-term stretch goal of this project is to enable cells with an energy density of 1 kWh/liter. This will be accomplished by replacing both the present carbon used in Li-ion batteries with anodes that approach double the volumetric capacity of carbon, and the present intercalation cathodes with materials that significantly exceed 200 Ah/kg. By the end of this project it is anticipated that cells will be available that can exceed the volumetric energy density of today’s Li-ion batteries by 50%.

COLLABORATIONS:

The Advanced Photon Source (Argonne National Laboratory) and when available the National Synchrotron Light Source II (Brookhaven National Laboratory) will be used to determine the phases formed in both ex-situ and operando electrochemical cells.

Milestones

- 1) Demonstrate synthesis and complete characterization of CuF_2 . (Dec-14) Ongoing
- 2) Determine discharge product of CuF_2 . (Mar-15)
- 3) Begin cyclability testing of CuF_2 (Jun-15)
- 4) Demonstrate more than 100 cycles on Sn_2Fe at 1.5 times the volumetric energy density of carbon. (Sep-15)
- 5) Go/No-Go: Demonstrate cyclability of CuF_2 . Criteria: Capacity of 200 mAh/g over 10 cycles. (Sep-15)

Progress Report

The goal of this project is to synthesize tin-based anodes that have 1.5 times the volumetric capacity of the present carbons, and conversion and intercalation cathodes with capacities over 200 Ah/kg. The major effort in this first quarter was to assemble the permanent research team. Two potential postdoctoral associates have been identified and offers are in place. In the meantime, an interim postdoc has initiated studies on the conversion cathode material. A graduate student has initiated studies on the tin-based anode for this project, and generated base-line data for the carbon anode against which the tin-based anode will be compared.

Milestone (1): Carbon/CuF₂ and carbon Cu_{1-y}Fe_yFe₂ composites have been synthesized by a mechanochemical approach. They appear to be single phase as shown by x-ray diffraction (Figure 15). An initial electrochemical discharge reaction shows a capacity between 400 and 500 mAh/g for both compositions.

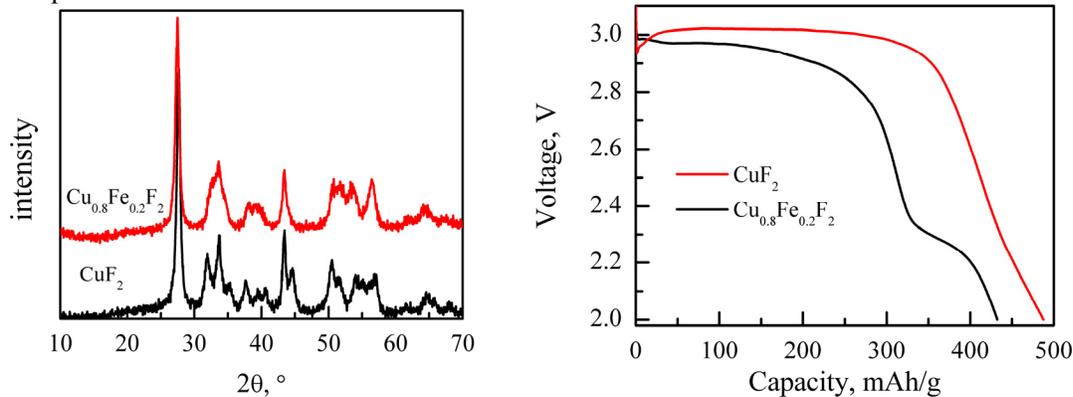


Figure 15: (left) x-ray diffraction patterns and (right) discharge of CuF₂ and Cu_{0.8}Fe_{0.2}F₂.

Milestone (4): Cycling data on the baseline carbon anode as well as on the Sn₂Fe anode have been obtained using both the standard LiPF₆ electrolyte salt and an FSI salt. The latter is reported to be more stable for higher voltage materials. These results are shown in Figure 16, and show no deleterious effect on the anode. A slight improvement in the first cycle capacity loss is observed.

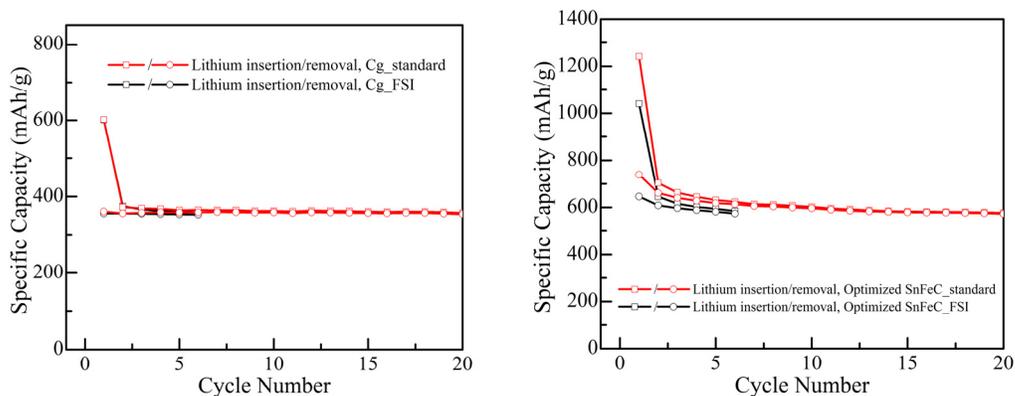


Figure 16: Cycling capacity using LiPF₆ and FSI based electrolytes of (left) baseline carbon anode, and (right) advanced Sn-Fe-C anode.

Q1 Patents/Publications/Presentations

Not Applicable

Task 3.3 – Ji-Guang Zhang and Jie Xiao (Pacific Northwest National Laboratory)

Project Title: Development of High-Energy Cathode Materials

PROJECT OBJECTIVE:

The objective of this project is to develop high-energy, low-cost, cathode materials with long cycle-life. Based on the knowledge gathered in FY14 on the failure mechanism of Li-Mn-rich (LMR) cathode, synthesis modification will be pursued to improve the distribution of different transition metal cations at the atomic level. Leveraging with PNNL's advanced characterization capabilities, the effects from synthesis alteration and the surface treatment will be monitored and correlated to the electrochemical properties of LMR to guide the rational design of LMR. Extension of the cutoff voltage on traditional layered $\text{LiNi}_{1/3}\text{Mn}_{1/3}\text{Co}_{1/3}\text{O}_2$ (NMC) will be also investigated to increase the usable energy density from NMC while still maintaining the structure integrity and long lifespan.

PROJECT IMPACT:

Although state-of-the-art cathode materials such as LMR layered composites have very high energy densities, their voltage fade and long-term cycling stability still need to be further improved. In this work, we will investigate the fundamental fading mechanism of LMR cathodes and develop new approaches to reduce the energy loss of these high-energy cathode materials. The success of this work will increase the energy density of Li-ion batteries and accelerate market acceptant of electrical vehicles (EV), especially for plug-in hybrid electrical vehicles (PHEV) required by the EV Everywhere Grand Challenge proposed by DOE/EERE.

OUT-YEAR-GOALS:

- The long-term goal of the proposed work is to enable Li-ion batteries with a specific energy of 200Wh/kg (for PHEVs), 5000 deep-discharge cycles, 15-year calendar life, improved abuse tolerance, and less than 20% capacity fade over a 10-year period.

COLLABORATIONS:

- Dr. Bryant Polzin (ANL)- LMR electrode supply
- Dr. X.Q. Yang (LBNL) – *in situ* XRD characterization during cycling
- Dr. Karim Zaghib (Hydro-Quebec) – material synthesis
- Dr. Kang Xu (ARL) – new electrolyte.

Milestones

- 1) Investigate the transition metal migration pathway in LMR during cycling. (12/31/14) **Complete**
- 2) Identify appropriate synthesis step to enhance the homogenous cation distribution in the lattice and demonstrate 200 stable cycling with less than 10% energy loss. (3/31/15) **On going**
- 3) Develop the surface treatment approaches to improve the stability of high energy cathode at high voltage conditions. (6/30/2015) **On going**
- 4) Demonstrate high voltage operation of modified NMC with 180 mAh/g capacity and less than 20% capacity fade for 100 cycling. (9/30/2015) **On going**

Progress Report

In FY14, hydrothermal-assisted solid-state synthesis has been explored to improve the homogeneous distribution of transition metal cations within the lattice at the atomic level. The as-prepared lithium-manganese-rich (LMR) cathode material was further used as a platform to investigate the migration pathway of cations during cycling. The Q1 milestone has been completed in this period.

As reported earlier, LMR synthesized from hydrothermal assisted method displayed very uniform cation distribution from particle surface to the bulk of (data not shown here). However, after the initial charge/discharge cycle at C/10 rate, a few atomic layers of TM ions have already been observed in the Li layer at the edge of particles, although this surface reconstruction layer is only about 2 nm (Figure 17a,b). The bulk structure well matched the atomic model of the R-3m phase in the [100] zone projection and the nearest atomic

column distance in the [100] projection was around 0.28 nm (Figure 17c). Intensity plot along the Li layer displayed a low intensity in one octahedral sites followed by a high intensity in the adjacent octahedral sites, indicating that the TM ions migration to Li layer did not successively occupy the lithium vacancies so the repulsion between the neighboring TM ions can be reduced (Figure 17d). Such a cation arrangement was tentatively ascribed to the LT-LiCoO₂ type defect spinel structure viewed along the [011] zone axis (Figure 17e), which has been further confirmed in the surface reconstruction layer after more cycling. The reversible Li

insertion/ removal into/from the disordered rock-salt structure is ascribed to the Li excess environment that permits Li percolation in the disordered rock-salt structure despite the increased kinetic barrier. Clarification of the phase transformation pathway, cation redistribution, oxygen vacancy and Mn valence change provides unique understanding of the voltage fade and capacity degradation mechanisms in the LMR cathode.

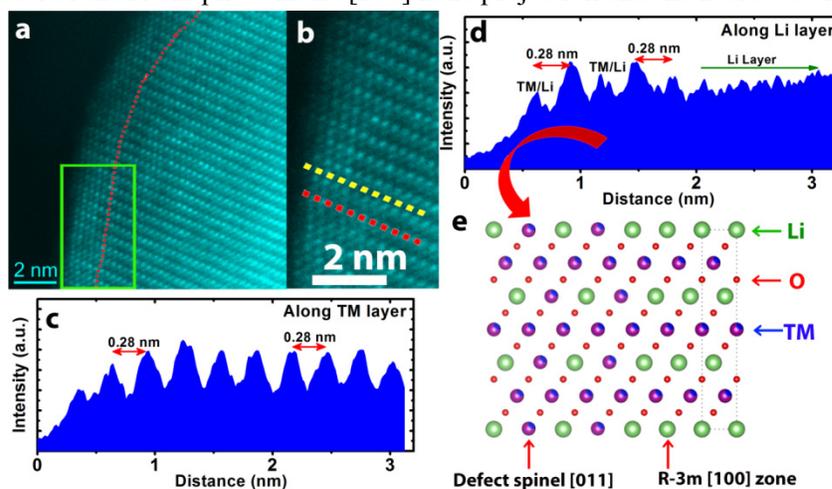


Figure 17: Crystal structure of material after initial charge/discharge process. (a) High resolution STEM image. (b) STEM image enlarged from the region labelled by green rectangle in (a). (c) Intensity plot along the red line (TM layer) shown in (b). (d) Intensity plot along the yellow line (Li layer) shown in (b). (e) Atomic model of the [100] zone projection of R-3m phase, where the lithium sites at surface region are occupied by the TM ions to form defect spinel structure in [011] projection.

Q1 Patents/Publications/Presentations

1. Understanding and Mitigation of Voltage Fade in High Energy Cathode Materials, Jianming Zheng, Pengfei Yan, Jie Xiao, Chongmin Wang, and Ji-Guang Zhang, presented in 2014 MRS fall meeting in Boston, Dec. 1, 2014.

Task 3.4 – Patrick Looney, Feng Wang (Brookhaven National Laboratory)

In-situ Solvothermal Synthesis of Novel High Capacity Cathodes

PROJECT OBJECTIVE: Develop low-cost cathode materials that offer high energy density (≥ 660 Wh/kg) and electrochemical properties (cycle life, power density, safety) consistent with USABC goals.

PROJECT IMPACT: Present-day Li-ion batteries are incapable of meeting the 40-mile all-electric-range within the weight and volume constraints established for PHEVs by DOE and the USABC. Higher energy density cathodes are needed for Li-ion batteries to be widely commercialized for PHEV applications. This effort will focus on increasing energy density (while maintaining the other performance characteristics of current cathodes) using synthesis methods that have the potential to lower cost. The primary deliverable for this project is a reversible cathode with an energy density of about 660 Wh/kg or higher.

OUT-YEAR GOALS: In FY15, we will continue our work on *in-situ* solvothermal synthesis, structural and electrochemical characterization of V-based (fluoro)phosphates and other high-capacity cathodes. We will also put efforts on technique development for *in-situ* synthesis. The out-year-goals we aim to achieve include:

- Determining the reaction pathway during ion-exchange of $\text{Li}(\text{Na})\text{VPO}_5\text{F}_x$
- Optimizing the ion-exchange procedures to maximize the Li-exchange content in $\text{Li}(\text{Na})\text{VPO}_5\text{F}_x$
- Characterizing the structure of the intermediate and final exchanged products of $\text{Li}(\text{Na})\text{VPO}_5\text{F}_x$ and their electrochemical properties
- Identifying at least one cathode material, with reversible specific capacity higher than 200 mAh/g under moderate cycling conditions
- Developing new *in-situ* reactors that may be applied for different types of synthesis methods (beyond solvothermal) in making phase-pure cathodes
- Building new capabilities for simultaneous *in-situ* measurements of multiple synthesis reactions in the newly built beamlines at NSLS II.

COLLABORATIONS: Jianming Bai, Lijun Wu, Yimei Zhu (Brookhaven Nat. Lab), Peter Khalifha (Stony Brook U.), Kirsuk Kang (Seoul Nat. U.), Nitash Balsara (Lawrence Berkeley Nat. Lab) Arumugam Manthiram (U. Texas at Austin), Brett Lucht (U. Rhode Island), Zaghbir Karim (Hydro-Quebec), Jason Graetz (HRL).

Milestones

- 1) Determine the reaction pathways and phase evolution during hydrothermal ion exchange synthesis of $\text{Li}(\text{Na})\text{VPO}_5\text{F}_x$ cathodes *via in-situ* studies. (12/01/14) **Completed**
- 2) Optimize ion exchange synthesis for preparing $\text{Li}(\text{Na})\text{VPO}_5\text{F}_x$ with maximized Li content, and characterize its structural and electrochemical properties. (03/01/15) *On schedule*
- 3) Develop new reactor design to enable high-throughput synthesis of phase-pure cathode materials. (06/01/15) *On schedule*
- 4) Obtain good cycling stability of one high-capacity cathode in a prototype cell with specific capacity higher than 200 mAh/g. *No-Go* if 80% capacity retention after 50 cycles cannot be achieved. (09/01/15) *On schedule*

Progress Report

In previous quarters, a hydrothermal ion-exchange method was developed for synthesis of Li-containing cathodes from Na counterparts, and utilized to prepare Li(Na)VPO₅F_x (LVOPF), a high-capacity cathode. In order to understand and further optimize the synthesis to obtain materials of desired stoichiometry and electrochemical properties, a study of the synthesis parameters for preparing LVOPF, including temperature, concentration of LiBr solution, Li/Na ratio and heating rate was completed through *in-situ* synthesis. These studies provided detailed insights into the structural evolution and Li⁺/Na⁺ ion exchange pathways.

Figure 18 shows one set of *time-resolved* XRD patterns recorded during ion exchange at fixed temperature. This shows that, instead of proceeding *via* a single facile solid solution (as commonly believed), the Li substitution into LVOPF is more complicated, involving multiple steps (as indicated in Figure 18a). Among them a 2-phase transformation, from tetragonal to orthorhombic structure (of reduced symmetry), is found to be the rate-limiting step. Raising reaction temperature is one way to accelerate the process, as demonstrated by the 3x reduction in time to complete the phase transition at 120°C (compared to 72°C; Figure 18b). Nevertheless, even at elevated temperatures, reactions require sufficient time in order to obtain final phases with high lithium content as both a phase transition and solid solution processes are involved.

Complementary to *in-situ* studies, high-resolution synchrotron X-ray and neutron diffraction measurements were performed to identify the positions and occupancies of Li and Na atoms in the intermediate and final products. The local alkali ion and vacancy ordering (determined by structure refinement), along with the possible diffusion pathways, are illustrated in Figure 18c. The Li⁺/Na⁺ ion exchange is anisotropic, preferentially going along the *a* direction, which leads to a peculiar Na/Li/vacancy ordering. Those one-dimensional Na, Li, and empty channels are alternatively repeated along *b* direction (as indicated by blue boxes). This is an interesting discovery in that the interdiffusion of ions in the solid is rate-determining step, and the empty channels provide the pathway for the Li/Na interdiffusion, which is essential to the ion-exchange process. These results shed light on the kinetics and thermodynamics of ion exchange in LVOPF that may also be applicable to other polyanionic cathodes (with similar 1D diffusion channel). The dependence of exchange process on the synthesis parameters provides guidance to optimizing the synthesis procedures in obtaining the LVOPF electrodes of maximized lithium capacity and improved cycling stability.

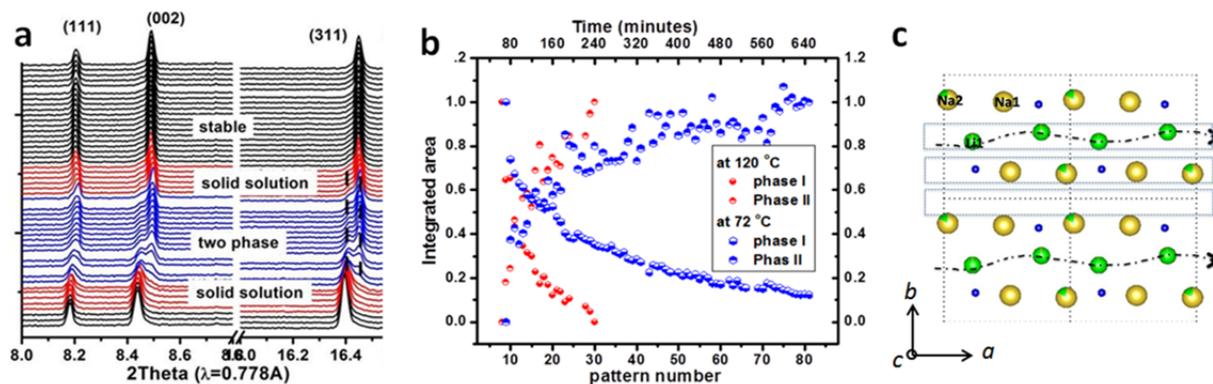


Figure 18: *In-situ* studies of ion exchange in Li(Na)VPO₅F_x. (a) Time-resolved XRD patterns, (b) the integrated Bragg peak intensity of (311) of the Na-phase (phase I) and Li-phase (phase II) at fixed temperatures, 72 °C and 120 °C, (c) illustration of the configuration of Na⁺ ions (golden) and Li⁺ ions (green) in the *ab* plane determined by structure refinement.

Q1 Patents/Publications/Presentations

Publication

1. J. Bai, J. Hong, H. Chen, J. Graetz and F. Wang, Solvothermal Synthesis of $\text{LiMn}_{1-x}\text{Fe}_x\text{PO}_4$ Cathode Materials: A Study of Reaction Mechanisms by Time-resolved In-situ Synchrotron X-ray Diffraction, *J. Phys. Chem. C.* (accepted)

Task 3.5 – Michael M. Thackeray and Jason R. Croy (Argonne National Laboratory)

Exploiting Co and Ni Spinel in Structurally-Integrated Composite Electrodes.

PROJECT OBJECTIVE:

This is a new project, the goal of which is to stabilize high capacity, composite ‘layered-layered’ electrode structures with lithium-cobalt-oxide and lithium-nickel-oxide spinel components (referred to as LCO-S and LNO-S, respectively), or solid solutions thereof (LCNO-S), which can accommodate lithium at approximately 3.5 V vs. metallic lithium. This approach and the motivation to use LCO-S and LNO-S spinel components, about which relatively little is known, is novel. The initial thrust of the project will focus on the design and synthesis of new spinel compositions and structures that operate above 3 V and below 4 V and to determine their structural and electrochemical properties. This information will subsequently be used to select the most promising spinel materials for integration as stabilizers into high capacity composite electrode structures.

PROJECT IMPACT:

State-of-the art lithium-ion batteries are currently unable to satisfy the performance goals for plug-in hybrid- (PHEV) and all-electric (EV) vehicles. If successful, this project will impact the advance of energy storage for electrified transportation as well as other applications, such as portable electronic devices and the electrical grid.

OUT-YEAR-GOALS:

The electrochemical capacity of most high potential lithium-metal oxide insertion electrodes is generally severely compromised by their structural instability and surface reactivity with the electrolyte at low lithium loadings (i.e., at highly charged states). Although some progress has been made by cation substitution and structural modification, the practical capacity of these electrodes is still restricted to approximately 160-170 mAh/g. This project puts forth a new structural and compositional approach with the goal of producing electrode materials that can provide 200-220 mAh/g without significant structural or voltage decay for 500 cycles. If successful, the materials processing technology will be transferred to Argonne’s Materials Engineering and Research Facility (MERF) for scale up and further evaluation.

COLLABORATIONS: Eungje Lee, Brandon R. Long and Joong Sun Park (CSE, ANL), Mali Balasubramanian (APS, ANL), V. Dravid and C. Wolverton (Northwestern University)

Milestones

- 1) Synthesize and optimize LCO-S, LNO-S and LCNO-S spinel compositions and structures and determine their structural and electrochemical properties (Sep-15). **In progress – see text.**
- 2) Devise synthesis techniques to embed the most promising spinel compositions into layered structures (Sep-15).
- 3) Determine the impact of embedding LCO-S or LNO-S components on the electrochemical properties and cycling stability of composite ‘layered-spinel’ or ‘layered-layered-spinel’ structures (Sep-15).
- 4) Use complementary theoretical approaches to further the understanding of the structural and electrochemical properties of LCO-S, LNO-S and LCNO-S electrodes and protective surface layers (Sep-15).

Progress Report

In spite of their alluring characteristics, such as high specific energy density and low materials cost, the practical application of composite ‘layered-layered’ (LL) electrodes has been hampered by several critical problems, for example, structural destabilization during cycling and high impedance at the top of charge and the end of discharge. Over recent years, the BMR team at Argonne has demonstrated that the incorporation of a spinel (S) component into LL structures and control of the operating voltage window can mitigate these problems, the spinel component serving as a stabilizing unit to slow transition metal migration during electrochemical cycling. However, it is difficult to control the structural composition and elemental configurations in ‘layered-layered-spinel’ (LLS) materials, which contain several cations (typically, Li, Mn, Ni, and Co) in highly complex, inhomogeneous arrangements within multiple structural domains. Compared to the extensive understanding of Mn-based spinel materials, relatively little is known about the electrochemical properties of Li-Co-O (LCO-S) and Li-Co-Ni-O (LCNO-S) spinel structures that were first reported by Gummow et al. in the early 1990s.

Low-temperature firing of precursor materials during the solid state synthesis of layered oxides, particularly those with high cobalt content, can result in intermediate structures with quasi-spinel character. This finding raises the possibility of using quasi-spinel precursors for the synthesis of LLS materials. To initiate this project, the electrochemical properties of spinel-related materials in the system $\text{LiCo}_{1-x}\text{Ni}_x\text{O}_2$, prepared by a ‘low-temperature’ (LT) method, were evaluated.

Lithium carbonate was thoroughly mixed with various cobalt and nickel precursors and fired at 400 °C for 3-7 days in air. Phase pure samples were obtained when synthesized from a carbonate precursor; impurity phases such as Co_3O_4 were detected when oxide or hydroxide precursors were used. Figure 19 (a) shows synchrotron high-resolution X-ray diffraction (HR-XRD) patterns for samples with $x = 0$ and 0.1. Compared to layered LiCoO_2 , which is prepared at higher temperature (900 °C), the HR-XRD pattern for LT- LiCoO_2 clearly shows the overlap of the (006) and (012) reflections, and (108) and (110) reflections indicating a spinel-like arrangement of the cobalt ions. The high-resolution data revealed a slight splitting of all the peaks, suggesting a non-uniform distribution of lattice parameters within the samples. In contrast, the HR-XRD pattern of LT- $\text{LiCo}_{0.9}\text{Ni}_{0.1}\text{O}_2$ shows sharp reflection peaks indicating a better-defined lithiated spinel lattice. For $x > 0.2$, a $\text{Li}_x\text{Ni}_{1-x}\text{O}$ rock salt phase appeared (not shown). A comparison of the electrochemistry of the LT- LiCoO_2 vs. LT- $\text{LiCo}_{0.9}\text{Ni}_{0.1}\text{O}_2$ electrodes is shown in Figure 19 (b). It is apparent that Ni substitution significantly improves the capacity and stability of the spinel electrode, the LT- $\text{LiCo}_{0.9}\text{Ni}_{0.1}\text{O}_2$ electrode initially yielding 120 mAh/g at ~3.6 V, relative to LT- LiCoO_2 (80 mAh/g). These early results are encouraging and bode well for further progress in this project.

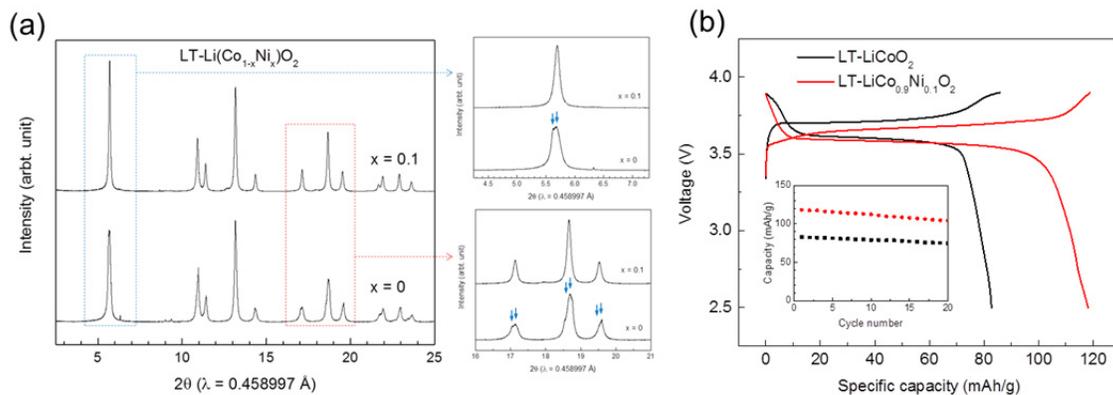


Figure 19: (a) Synchrotron HR-XRD patterns and (b) initial voltage profiles of Li/LT- $\text{LiCo}_{1-x}\text{Ni}_x\text{O}_2$ ($x = 0$ and 0.1) cells cycled between 2.5 and 3.9 V at the rate of 15 mA/g. The selected 2θ ranges in (a), highlighted in separate panes, show the non-uniform distribution of lattice parameters in LT- LiCoO_2 . Inset in (b) compares the cycling stability of LT- LiCoO_2 and LT- $\text{LiCo}_{0.9}\text{Ni}_{0.1}\text{O}_2$.

Q1 Patents/Publications/Presentations

1. M. M. Thackeray, J. R. Croy, and B. R. Long, Lithium Metal Oxide Electrodes for Lithium Batteries, Filed USPTO, December 2014.
2. M. M. Thackeray, J. R. Croy, and B. R. Long, Cobalt Stabilized Lithium Metal Oxide Electrodes for Lithium Batteries, Filed USPTO, December 2014.

Task 3.6 – Arumugam Manthiram (University of Texas, Austin)

High-capacity, High-voltage Cathode Materials for Lithium-ion Batteries

PROJECT OBJECTIVE: A significant increase in capacity and/or operating voltage is needed to make the lithium-ion technology viable for vehicle applications. This project addresses this issue by focusing on the design and development of cathode materials based on polyanions that have the possibility for reversibly inserting/extracting more than one lithium ion per transition-metal ion and/or operating above 4.3 V. Specifically, high-capacity and/or high-voltage lithium transition-metal phosphate, silicate, and carbonophosphate cathodes are investigated. The major issue with the phosphate and silicate cathodes is the poor electronic and ionic transport, which limits their practical capacity and energy and power densities. To overcome these difficulties, novel microwave-assisted solvothermal, microwave-assisted hydrothermal, and template-assisted synthesis approaches are pursued to realize controlled morphology with smaller particle size and to integrate conductive additives like graphene in a single synthesis step.

PROJECT IMPACT: The critical requirements for the widespread adoption of lithium-ion batteries for vehicle applications are high energy, high power, long cycle life, low cost, and acceptable safety. The currently available cathode materials do not adequately fulfill these requirements. The polyanion cathodes, which are synthesized by novel methods in this project, have the potential to significantly increase the energy and power. More importantly, the covalently bonded polyanion groups can offer excellent thermal stability and enhanced safety. The microwave-assisted synthesis could also lower the manufacturing cost of the cathodes through a significant reduction in reaction time and temperature.

OUT-YEAR GOALS: The overall goal is to enhance the electrochemical performances of high-capacity, high-voltage polyanion cathode systems and to develop a fundamental understanding of their structure-composition-performance relationships. Specifically, the project is focused on enhancing the electrochemical performance of systems such as Li_2MSiO_4 (M = Mn, Fe, Co, Ni, and VO), $\text{Li}_2\text{MP}_2\text{O}_7$ (M = Mn, Fe, Co, Ni, and VO), LiMPO_4 (M = Co, Ni, and VO), $\text{Li}_3\text{V}_2(\text{PO}_4)_3$, $\text{Li}_9\text{V}_3(\text{P}_2\text{O}_7)_3(\text{PO}_4)_2$, $\text{Li}_3\text{M}(\text{CO}_3)(\text{PO}_4)$, and their solid solutions. Advanced structural, chemical, surface, and electrochemical characterizations of the materials synthesized by novel approaches are anticipated to provide in-depth understanding of the factors that control the electrochemical properties of the polyanion cathodes and facilitate design of better-performing cathode materials for vehicle applications. For example, understanding the role of conductive graphene integrated into the polyanion cathodes can help to design better-performing cathodes.

COLLABORATIONS: Collaboration/discussion with Wanli Yang (LBNL), Feng Wang (BNL), and Craig Bridges (ORNL) on structural/chemical characterizations of polyanion cathodes.

Milestones

- 1) Demonstrate the synthesis of LiVOPO_4 nanoparticles with > 200 mAh/g capacity by employing ordered macroporous carbon as a hard-template (Dec-14) **Complete**
- 2) Demonstrate aliovalent doping with Ti^{4+} in $\text{LiM}_{1-2x}\text{Ti}_x\text{PO}_4$ with enhanced electrochemical properties by the microwave-assisted solvothermal synthesis. (Mar-15) **Ongoing**
- 3) Demonstrate the synthesis of α - and/or β - LiVOPO_4 /graphene nanocomposites with > 200 mAh/g capacity by the microwave-assisted process. (Jun-15) **Ongoing**
- 4) Go/No-Go: Stop synthesis attempts if aliovalent doping is not possible or if the doped samples exhibit a capacity of < 110 mAh/g. Criteria: Demonstrate the extraction of more than one lithium (> 110 mAh/g) through aliovalent doping in $\text{Li}_2\text{M}_{1-3/2x}\text{V}_x\text{P}_{x/2}\text{O}_7$ by low-temperature synthesis approaches (Sep-15) **Ongoing**

Progress Report

In this quarter, we focused on the preparation of the LiVOPO_4 nanoparticles by employing 3-dimensional ordered macroporous (3-DOM) carbon as a hard-template. The 3-DOM carbon was synthesized with poly(methyl methacrylate) (PMMA) colloidal crystals as the template and glucose as the carbon source and firing at 600°C in Ar. LiVOPO_4 was fabricated *via* a sol-gel process in the presence of the 3-DOM template, followed by firing at 600°C in Ar and air in sequence. The scanning electron microscopy (SEM) images in Figure 20 show that the PMMA crystals are comprised of closed-packed nanospheres, while the 3-DOM carbon has a reverse structure of the PMMA with ordered macropores. The LiVOPO_4 templated from the 3-DOM has a mean particle size of ~ 300 nm due to the confinement by the template. The carbon template was not detected after the sintering process in air. Therefore, carbon coating was conducted by carbonization of sucrose at elevated temperatures. Unfortunately, $\alpha\text{-LiVOPO}_4$ is not stable during this process because it undergoes phase transformation even when the sample is heated at 400°C . Other attempts such as high-speed ball-milling were not successful as well due to similar problems of phase transformation.

In order to achieve the conductive coating on $\alpha\text{-LiVOPO}_4$, a low-temperature approach was developed by employing poly(ethylenedioxythiophene) (PEDOT) as the conductive polymer. First, the V^{4+} in $\alpha\text{-LiVOPO}_4$ was partially oxidized to V^{5+} by chemically extracting $\sim 20\%$ Li^+ ions with NO_2BF_4 in acetonitrile medium. This delithiated sample was a mixture of $\alpha\text{-LiVOPO}_4$ and $\epsilon\text{-VOPO}_4$, as evidenced by the X-ray diffraction (XRD) patterns in Figure 21. Next, ethylenedioxythiophene (EDOT) was oxidized by the V^{5+} to complete the *in-situ* formation of the PEDOT polymer coating. This process is confirmed by the XRD pattern of the $\alpha\text{-LiVOPO}_4/\text{PEDOT}$, where the $\epsilon\text{-VOPO}_4$ phase has disappeared after the polymerization of EDOT. The SEM image of the $\text{LiVOPO}_4/\text{PEDOT}$ composite exhibits a morphology similar to LiVOPO_4 (Figure 1), indicating that PEDOT is uniformly coated on the surface of LiVOPO_4 nanoparticles.

The $\alpha\text{-LiVOPO}_4/\text{PEDOT}$ cathode shows a high capacity of 212 mAh/g during first discharge, equivalent to the insertion of ~ 1.35 Li per vanadium ion (Figure 22). In contrast, the $\alpha\text{-LiVOPO}_4$ prepared without the template and PEDOT coating has a much lower capacity of 70 mAh/g, while the templated $\alpha\text{-LiVOPO}_4$ without PEDOT coating offers a moderate capacity of 140 mAh/g. Additionally, the $\alpha\text{-LiVOPO}_4/\text{PEDOT}$ exhibits much improved cycling

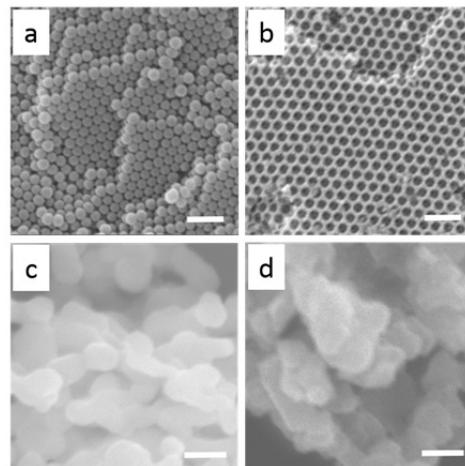


Figure 20: SEM images of the (a) PMMA colloidal crystal, (b) 3-DOM carbon, (c) $\alpha\text{-LiVOPO}_4$, and (d) $\alpha\text{-LiVOPO}_4/\text{PEDOT}$ composite. The scale bars in (a, b) and (c, d) are $1\ \mu\text{m}$ and $500\ \text{nm}$, respectively.

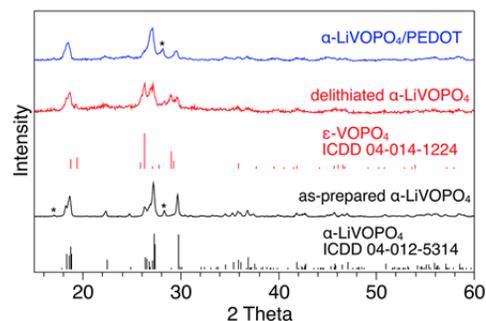


Figure 21: XRD patterns of the as-prepared $\alpha\text{-LiVOPO}_4$, chemically delithiated $\alpha\text{-LiVOPO}_4$, and $\alpha\text{-LiVOPO}_4/\text{PEDOT}$ composite. Asterisks indicate $\beta\text{-LiVOPO}_4$.

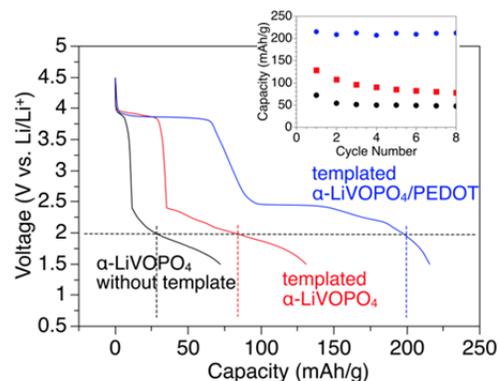


Figure 22: Electrochemical data at C/20 rate of the various $\alpha\text{-LiVOPO}_4$ electrodes.

performance than the other two samples (see the inset in Figure 22). These results clearly demonstrate the importance of structural optimization for the LiVOPO_4 cathodes that suffer from low electrical and ionic conductivities.

Q1 Patents/Publications/Presentations

Publications

1. X. Xiang, J. C. Knight, W. Li, and A. Manthiram, “Understanding the Effect of Co^{3+} Substitution on the Electrochemical Properties of Lithium-Rich Layered Oxide Cathodes for Lithium-Ion Batteries,” *Journal of Physical Chemistry C* **118**, 21826-21833 (2014).
2. X. Xiang, J. C. Knight, W. Li, and A. Manthiram, “Understanding the Influence of Composition and Synthesis Temperature on Oxygen Loss, Reversible Capacity, and Electrochemical Behavior of $x\text{Li}_2\text{MnO}_3-(1-x)\text{LiCoO}_2$ Cathodes in the First Cycle,” *Journal of Physical Chemistry C* **118**, 23553-23558 (2014).
3. J. C. Knight, P. Nandakumar, and A. Manthiram, “Effect of Ru Substitution on the First Charge-Discharge Cycle of Lithium-rich Layered Oxides,” *Journal of Materials Chemistry A* DOI: 10.1039/C4TA05178E (2014).

Presentations

1. A. Manthiram, “From Insertion-compound Electrodes to Conversion-reaction Electrodes for Energy Storage,” Battery Division Research Award Presentation, 226th *Electrochemical Society Meeting*, Cancun, Mexico, October 5 – 10, 2014 (invited).
2. A. Manthiram, “Electrochemical Energy Conversion and Storage: Challenges and Prospects,” Georgia Institute of Technology, Atlanta, GA, October 27, 2014 (invited).
3. A. Manthiram, “Next Generation Rechargeable Battery Chemistries,” 2014 Global Innovation Festival, Daegu Gyeongbuk Institute of Science and Technology, Daegu, South Korea, November 20 – 21, 2014 (invited).

Task 3.7 – Jim Kiggans and Andrew Kercher (Oak Ridge National Laboratory)

Lithium-bearing Mixed Polyanion (LBMP) Glasses as Cathode Materials

PROJECT OBJECTIVE: Develop mixed polyanion (MP) glasses as potential cathode materials for lithium ion batteries with superior performance to lithium iron phosphate for use in electric vehicle applications. Modify MP glass compositions to provide higher electrical conductivities, specific capacities, and specific energies than similar crystalline polyanionic materials. Test MP glasses in coin cells for electrochemical performance and cycleability. The final goal is to develop MP glass compositions for cathodes with specific energies up to near 1,000 Wh/kg.

PROJECT IMPACT: The projected performance of MP glass cathode materials addresses the Vehicle Technology Multi-Year Plan goals of higher energy densities, excellent cycle life, and low cost. MP glasses offer the potential of exceptional cathode energy density up to 1,000 Wh/kg, excellent cycle life from a rigid polyanionic framework, and low cost conventional glass processing.

OUT-YEAR GOALS:

MP glass development will focus on compositions with expected multi-valent intercalation reactions within a desirable voltage window and/or expected high-energy glass-state conversion reactions. Polyanion substitution will be further adjusted to improve glass properties to potentially enable multi-valent intercalation reactions and to improve the discharge voltage and cycleability of glass-state conversion reactions. Cathode processing of the most promising mixed polyanion glasses will be refined to obtain desired cycling and rate performance. These optimized glasses will be disseminated to BATT collaborators for further electrochemical testing and validation.

COLLABORATIONS: No collaborations this quarter

Milestones

- 1) Perform electron microscopy on mixed polyanion glass cathodes at key states of charge. (Dec-14) **Completed 12/04/14**
- 2) Produce and electrochemically test MP glasses designed to have enhanced ionic diffusivity. (Mar-15) **25% complete**
- 3) Produce and electrochemically test an MP glass designed to have enhanced ionic diffusivity and theoretically capable of a multi-valent intercalation reaction. (Jun-15) **In progress.**
- 4) Determine the polyanion substitution effect on a series of non-phosphate glasses. (Sep-15) **In progress.**

Progress Report

Conversion reactions in lithium-ion battery cathodes are well established for crystalline materials, but not for glass materials. Unlike most crystalline materials, glass materials can tolerate wide compositional changes and have substantial free volume. Prior ex-situ x-ray absorption spectroscopy of glass cathodes confirmed the valence changes that would be associated with a conversion reaction. The glass-state conversion reaction mechanism has been further studied by ex-situ electron microscopy and energy dispersive x-ray spectroscopy (EDXS) of nickel phosphate vanadate glass cathodes at fully charged (4V) and fully discharged (1V) states. Thin cross-sections of the cathodes were made using focused ion milling.

The glass particles in the cathodes did not show gross cracking after charge or discharge. (See Figure 23) EDXS of the discharged cathode revealed that the nickel remained uniformly distributed inside the particles. Transmission electron microscopy of the discharged cathode did not reveal signs of nickel nanoparticles inside the glass, but small disordered nickel nanoparticles may possibly be present inside the particles. To our knowledge, the intact particles

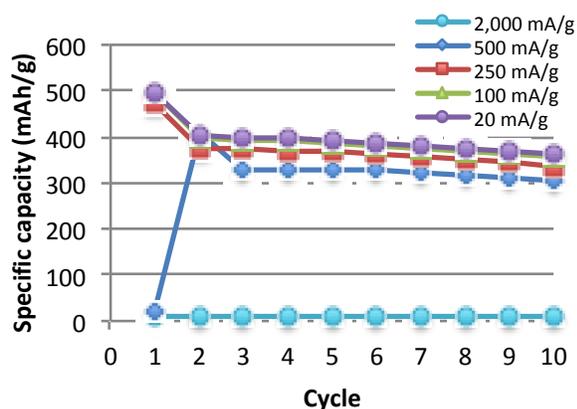


Figure 24: Short 10 cycle tests of an iron-based MP glass cathode material (400 nm particle size) at a wide range of specific currents

but the glass-state conversion reaction was far less dependent on discharge rate. Reduction in particle size (400 nm to 70 nm) was shown to improve capacity of iron phosphate vanadate glass cathodes at high discharge rates ($\sim C$ - $4C$). (See Figure 24.)

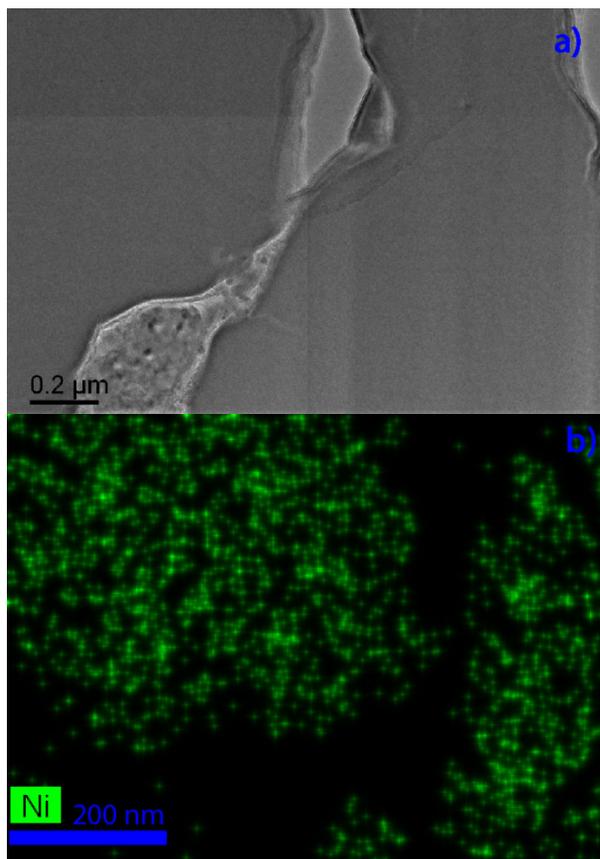


Figure 23: Microscopy showed that a discharged nickel-based glass cathode showed no gross cracking (a: TEM image) and had nickel uniformly distributed inside glass particles (b: EDXS).

containing zero-valence metal found in this glass-state conversion reaction are not observed in crystalline conversion reactions.

Short cycle tests (10 cycles) at multiple specific currents have been performed on nickel, cobalt, iron, and copper-based MP glass cathodes. The capacity of the intercalation reaction has been found to be strongly dependent on discharge rate between 20 mA/g and 500 mA/g ($\sim C/20$ and $\sim C$, respectively),

Q1 Patents/Publications/Presentations

1. Kercher AK, Ramey JO, Carroll KJ, Kiggans JO, Dudney NJ, Meisner RA, Boatner LA, Veith GM. Mixed polyanion glass cathodes: iron phosphate vanadate glasses. *Journal of The Electrochemical Society* 2014; 161(14): A2210-A2215.

Task 3.8 – Marca Doeff (Lawrence Berkeley National Laboratory)

Design of High Performance, High Energy Cathode Materials

PROJECT OBJECTIVE: To develop high energy, high performance cathode materials including composites and coated powders, using spray pyrolysis and other synthesis techniques. The emphasis is on high voltage systems including NMCs designed for higher voltage operation. Experiments are directed towards optimizing the synthesis, improving cycle life, and understanding the behavior of NMCs subjected to high voltage cycling. Particle size and morphology are controlled during spray pyrolysis synthesis by varying residence time, temperature, precursors and other synthetic parameters. By exploiting differences in precursor reactivity, coated materials can be produced, and composites can be prepared by post-processing techniques such as infiltration. These approaches are expected to improve cycling due to reduced side reactions with electrolytes.

PROJECT IMPACT: To increase the energy density of Li ion batteries, cathode materials with higher voltages and/or higher capacities are required, but safety and cycle life cannot be compromised. In the short term, the most promising materials are based on NMCs modified to undergo high voltage cycling that do not require formation cycles or undergo structural transformations during cycling. Spray pyrolysis synthesis results in high quality materials that can be coated (solid particles) or used as the basis for composites (hollow particles) designed to withstand high voltage cycling.

OUT-YEAR GOALS: The objective is to design high capacity NMC cathodes, which can withstand high voltage cycling without bulk structural transformation. Materials will be synthesized by a simple, low cost spray pyrolysis method, which has potential for commercialization. This technique produces phase-pure, unagglomerated powders and allows for excellent control over particle morphologies, sizes and distributions. Coated materials will also be produced in either one or two simple steps by exploiting differing precursor reactivities during the spray pyrolysis procedure, or by first preparing hollow spheres of an electroactive material, infiltrating the spheres with precursors of a second phase (e.g., high voltage spinel), and subsequent thermal treatment. The final result is expected to be a high energy density cathode material with good safety and cycling characteristics suitable for use in vehicular applications, which can be made by a low-cost process that is easily scalable.

COLLABORATIONS: Huolin Xin of Brookhaven National Lab, Dennis Norlund, Yijin Liu, Tsu-Chien Weng and Dimosthenis Sokaras of SLAC National Accelerator Laboratory, Professor M. Asta of U.C. Berkeley, Dr. Chunmei Ban of NREL, Professor Shirley Meng of UCSD.

Milestones

- 1) Complete synchrotron X-ray Raman experiments on representative NMC samples (12/31/14) Status: experiments completed, analysis still required.
- 2) Finish survey of composites made with spray pyrolyzed NMC hollow particles (3/31/15) Status: on track.
- 3) Go/no go decision on feasibility of coating processes using spray pyrolysis methods or molecular layer deposition (6/30/15) Status: on track
- 4) Select best-performing coated or composite material based on capacities and high voltage cycling results (9/30/15). Status: on track

Progress Report

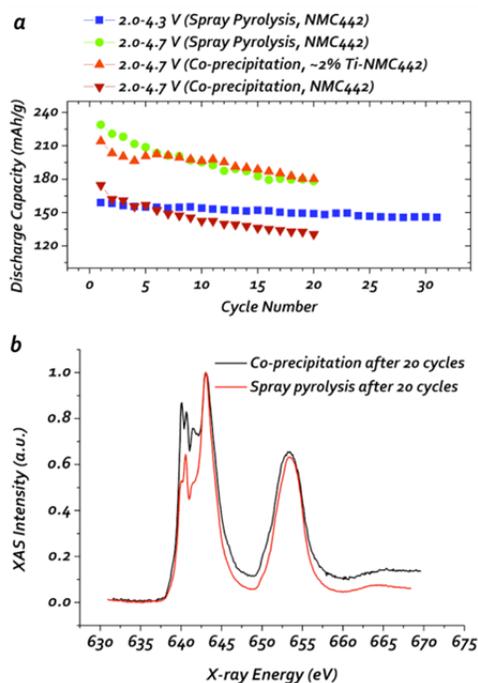


Figure 25: (a) Discharge capacity comparison of NMC materials prepared by spray pyrolysis and co-precipitation; (b) Surface reconstruction comparison of NMC materials prepared by spray pyrolysis and co-precipitation after 20 cycles, represented by Mn oxidation states.

Spray pyrolysis synthesis of cathode materials was continued this quarter with more syntheses, electrochemical measurements and characterization. During this quarter efforts have been attempted to synthesize nickel-rich NMCs (NR-NMCs, e.g., 622) by spray pyrolysis. Evidence showed that the lithium content control is more challenging for NR-NMCs than NMC442. More experiments (lithium content, annealing temperature) are being performed to achieve a goal of 225 mAh/g below 4.7 V vs. Li^+/Li . More experiments were performed on NMC442 materials to verify the good electrochemical performance of spray pyrolyzed samples. Figure 25a shows that spray pyrolyzed samples outperform those made by co-precipitation, even those that are Ti-substituted. Earlier in this project, surface reconstruction on free particles was identified as one of the main failure mechanisms for NMC cathode particles [Nat Commun 2014, 5, 3529], in particular under abuse cycling conditions [J Mater Chem A 2014, 2, 19833]. Figure 25b shows soft XAS results indicating that surface reconstruction after cycling is less severe for the spray pyrolyzed sample than the co-precipitated one. The differences are thought to arise from the improved microstructure of the spray pyrolyzed powders, which consist of small primary particles fused together to form large spherical secondary particles.

Efforts towards understanding the impact of electrochemical cycling conditions on the surface reconstruction have been completed and soft X-ray data show

that cycling conditions indeed dramatically impact the surface reconstruction phenomenon (*data not shown*).

TEM has also been used this quarter to characterize NMC materials, work done in collaboration with Dr. Huolin Xin (BNL). Synchrotron and computational efforts are continued in collaboration with Professor M. Asta (UCB), Dr. Dennis Nordlund (SSRL), Dr. Tsu-Chien Weng (SSRL) and Dr. Dimosthenis Sokaras (SSRL). Atomic layer deposition was performed in collaboration with Dr. Chunmei Ban (NREL). Synchrotron experiments designed to evaluate the different behaviors of NMCs and LMR-NMCs were carried out with Professor Shirley Meng's group, and data is currently under analysis.

Q1 Patents/Publications/Presentations

- 1) 2014 SLAC Open House for CalCharge (Nov 18, 2014), Menlo Park, CA, poster presentation by Feng Lin, "Surface Reconstruction and Chemical Evolution of $\text{LiNi}_x\text{Mn}_x\text{Co}_{1-2x}\text{O}_2$ Cathode Materials in Lithium-Ion Batteries," Feng Lin, Isaac Markus, Dennis Nordlund, Tsu-Chien Weng, Mark Asta, Huolin Xin and Marca Doeff.
- 2) 2014 Society of Hispanic Professional Engineers National Conference (Nov 6, 2014), Detroit, MI, oral presentation by Isaac Markus, "Computational and Experimental Investigation of Ti Substitution in $\text{Li}(\text{Ni}_{1/3}\text{Mn}_{1/3}\text{Co}_{1/3-y}\text{Ti}_y)\text{O}_2$ for Lithium-Ion Battery Cathodes," Isaac Markus, Feng Lin, Kinson Kam, Mark Asta and Marca Doeff.
- 3) "Effect of Surface Microstructure on Electrochemical Performance of Garnet Solid Electrolytes" Lei Cheng, Wei Chen, Martin Kunz, Kristin Persson, Nobumichi Tamura, Guoying Chen and Marca Doeff, ACS Applied Mater. & Interfaces DOI: 10.1021/am508111r (2015).

Task 3.9 – John B. Goodenough (UT Austin)

Lithium Batteries with Higher Capacity and Voltage.

PROJECT OBJECTIVE:

(a) To increase cell energy density for a given cathode and (b) to allow low-cost rechargeable batteries with cathodes other than insertion compounds.

PROJECT IMPACT:

A solid Na^+ or Li^+ -electrolyte separator would permit use of a Li^0 anode, thus maximizing energy density for a given cathode, and liquid flow-through and air cathodes of high capacity as well as high-voltage solid cathodes given two liquid electrolytes having different windows.

OUT-YEAR-GOALS:

(a) To increase cell energy density for a given cathode and (b) to allow low-cost, high-capacity rechargeable batteries with cathodes other than insertion compounds.

COLLABORATIONS: A. Manthiram, UT Austin and Karim Zaghib, Hydro Quebec.

Milestones

- 1) Fabricate oxide/polymer composite membrane as a separator in an alkali-ion (Li^+ , Na^+) battery and optimization of pore size, oxide loading, and thickness for blocking anode dendrites with fast alkali-ion transport. (31 December, 2014) **Ongoing.**
- 2) Investigate membranes that can block a customized soluble redox couple in a flow-through cathode. (31 March, 2015).
- 3) Evaluate Li-ion and Na-ion cells with a metallic Li or Na anode, oxide/polymer membrane as separator, and a flow-through liquid cathode. (30 June, 2015).
- 4) Measure performance of cells with a metallic Li or Na anode, oxide/polymer composite membrane as separator, and an insertion compound as cathode. (31 September, 2015)

Progress Report

Several cross-linked polymer membranes as listed in Figure 26 fabricated by thiol-ene chemistry have been characterized as battery separators. However, strong electrostatic interaction between Li^+ (or Na^+) and polymer backbone could limit facile alkali ion transports through the separator membrane. For example, the size of the stretched polymer mesh between two neighboring tetrathiol crosslinks is about 30 Å when di(ethylene glycol) divinyl ether was used as a monomer source, which could result in slow alkali ion transports because of its smaller pore area.

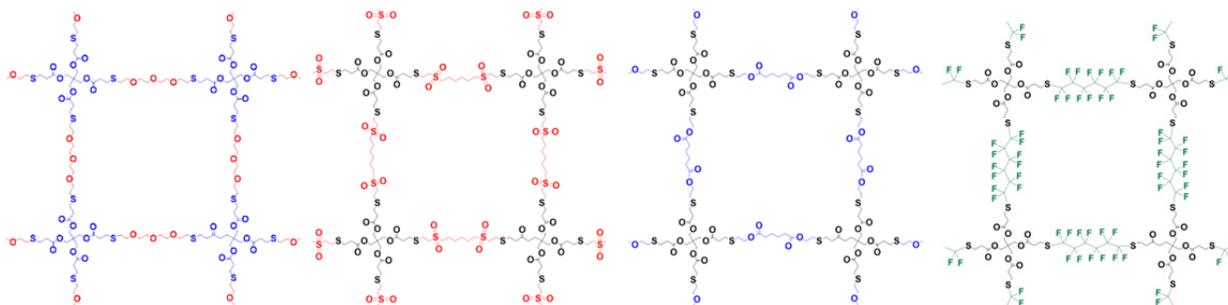


Figure 26: Crosslinked polymer membranes with polyethylene oxide, double vinyl sulfones, double vinyl ester, and perfluorohexane units (from the left).

During the first quarter, we have tried to increase the mesh size, so the membrane has more liquid electrolyte inside and Li^+ (or Na^+) ions have less interaction with the polymer backbones. Poly(ethylene glycol) diacrylate (M_n 700) has been used with tetrathiol crosslinker for thiol-acrylate reaction. The ratio between the acrylate monomer and crosslinker has been optimized to be 4/1 (monomer/crosslinker). Transparent membranes with a thickness of $< 300 \mu\text{m}$ have been fabricated by a photo-polymerization. Thickness of the membranes could be controlled by using a spacer and/or by adding excess tetrahydrofuran (THF) solvent. Final membrane has a density of $1.1 \sim 1.2 \text{ g/cm}^3$ regardless of different amount of THF during the process. It was also characterized with DSC to check crystallinity since excess poly(ethylene glycol) units with $M_n \sim 700$ could be crystallized during the polymerization. In the DSC data, glass transition temperature (T_g) is present at around $-36 \text{ }^\circ\text{C}$, but melting point do not appear below $100 \text{ }^\circ\text{C}$. It suggests that the membrane has very low crystallinity. After soaking the membrane in 1M NaClO_4 in PC (or in EC/DEC) electrolyte overnight, the membrane was tested as a separator. Na metal was used as counter electrode, and rhombohedral $\text{Na}_{1.72}\text{MnFe}(\text{CN})_6$ was adopted as a cathode active material. However, half-cell data shows significant polarization, which suggests that the membrane is inappropriate as a battery separator. It is not clear whether the membrane has side reaction and degradation in a cell or whether it has a problem with uptaking liquid electrolyte.

To improve the physical properties of the membrane, a plasticizer, succinonitrile, was added during the polymerization process. Succinonitrile addition made the membrane more flexible and increased electrolyte uptake. However, a coin half-cell test showed that the succinonitrile-added polymer membranes indeed decompose at high voltage. More tests on different kinds of plasticizer will be continued.

Q1 Patents/Publications/Presentations

None

TASK 4 – ELECTROLYTES FOR HIGH VOLTAGE HIGH ENERGY LITHIUM-ION BATTERIES

The current lithium-ion electrolyte technology is based on LiPF_6 solutions in organic carbonate mixtures with one or more functional additives. Lithium-ion battery chemistries with energy density of 175~250 Wh/Kg are currently the most promising choice. To further increase the energy density, the most efficient way is to raise either the voltage and/or the capacity of the positive materials. Several high energy materials including high-capacity composite cathode $x\text{Li}_2\text{MnO}_3 \cdot (1-x)\text{LiMO}_2$ and high-voltage cathode materials such as $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ (4.8 V) and LiCoPO_4 (5.1 V) have been developed. However, their increased operating voltage during the activation and charging poses great challenges to the conventional electrolytes, whose organic carbonate-based components tend to oxidatively decompose at the threshold beyond 4.5 V vs Li^+/Li .

Other candidate positive materials for PHEV application that have potential of providing high capacity are the layered Ni-rich NCM materials. When charged to a voltage higher than 4.5 V, they can deliver a much higher capacity. For example, $\text{LiNi}_{0.8}\text{Co}_{0.1}\text{Mn}_{0.1}\text{O}_2$ (NCM 811) only utilizes 50% of its theoretical capacity of 275 mAh/g when operating in a voltage window of 4.2 V-3.0 V. Operating voltage higher than 4.4 V would significantly increase the capacity to 220 mAh/g; however, the cell cycle life becomes significantly shortened mainly due to the interfacial reactivity of the charged cathode with the conventional electrolyte. The oxidative voltage instability of the conventional electrolyte essentially prevents the practicality to access the extra capacities of these materials.

To address the above challenges, new electrolytes that have substantially high voltage tolerance at high temperature with improved safety are demanded urgently. Organic compounds with low HOMO (highest occupied molecular orbital) energy level are suitable candidates for high voltage application. Alternative approach to address the electrolyte challenges is to mitigate the surface reactivity of high voltage cathodes by developing cathode passivating additives. Like the indispensable role of SEI on the carbonaceous anodes, cathode electrolyte interphase (CEI) formation additives could kinetically suppress the thermodynamic reaction of the delithiated cathode and electrolyte, thus significantly improve the cycle life and calendar life of the high energy density lithium-ion battery.

An ideal electrolyte for high voltage high energy cathodes also requires high compatibility with anode materials (graphite or silicon). New anode SEI formation additives tailored for the new high voltage electrolyte are equally critical for the high energy lithium-ion battery system. Such an electrolyte should have the following properties: high stability against 4.5-5.0 V charging state, particularly with cathodes exhibiting high surface oxygen activity; high compatibility with a strongly reducing anode under high voltage charging; high Li salt solubility (>1.0 M) and ionic conductivity ($> 6 \times 10^{-3}$ S/cm @ room temperature); non-flammability (no flash point) for improved safety and excellent low temperature performance (-30°C).

Task 4.1 – Zhengcheng Zhang (Argonne National Laboratory)

Fluorinated Electrolyte for 5-V Li-ion Chemistry

PROJECT OBJECTIVE: The objective of this project is to develop a new advanced electrolyte system with outstanding stability at high voltage and high temperature and improved safety characteristic for an electrochemical couple consisting of the high voltage $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ (LNMO) cathode and graphite anode. The specific objectives of this proposal are the design, synthesis and evaluation of (1) non-flammable high voltage solvents to render intrinsic voltage and thermal stability in the entire electrochemical window of the high-voltage cathode materials, and (2) electrolyte additives to enhance the formation of a compact and robust solid electrolyte interphase (SEI) on the surface of the high voltage cathode. A third objective is to gain fundamental understanding of the interaction between electrolyte and high voltage electrode materials, the dependence of SEI functionality on electrolyte composition, and the effect of high temperature on the full Li-ion cells using the advanced electrolyte system.

PROJECT IMPACT: This innovative fluorinated electrolyte is intrinsically more stable in electrochemical oxidation due to the fluorine substitution; therefore it would be also applicable to cathode chemistries based on TM oxides other than LNMO. The results of this project can be further applied to a wide spectrum of high-energy battery systems oriented for PHEVs that operate at high potentials, such as LiMPO_4 (M=Co, Ni, Mn), or battery systems that require a high-voltage activation process, such as the high-capacity Li-Mn-rich $x\text{Li}_2\text{MnO}_3 \cdot (1-x)\text{Li}[\text{Ni}_x\text{Mn}_y\text{Co}_z]\text{O}_2$. This electrolyte innovation will push the U.S. supply base of batteries and battery materials past the technological and cost advantages of foreign competitors, thereby increasing economic value to the USA. ANL's new fluorinated electrolyte material will enable the demand for more PHEVs and EVs, which directly transforms to much less gasoline consumption and less pollutant emissions.

OUT-YEAR-GOALS: The goal of this project is to deliver a new fluorinated electrolyte system with outstanding stability at high voltage and high temperature with improved safety characteristic for an electrochemical couple consisting of 5-V Ni-Mn spinel $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ (LNMO) cathode and graphite anode. The specific objectives of this proposal are the design, synthesis, and evaluation of (1) non-flammable high voltage fluorinated solvents to attain intrinsic voltage stability in the entire electrochemical window of the high-voltage cathode material and (2) effective electrolyte additives that form a compact and robust solid-electrolyte interphase (SEI) on the surfaces of the high voltage cathode and graphitic anode.

COLLABORATIONS: Dr. Kang Xu, U.S. Army Research Laboratory; Dr. Xiao-Qing Yang, Brookhaven National Laboratory; Dr. Brett Lucht, University of Rhode Island; Dr. Andrew Jansen and Dr. Gregory Krumdick, Argonne National Laboratory.

Milestones

- 1) Complete theoretical calculation of electrolyte solvents; Validate the electrochemical properties of the available fluorinated solvents by CV and leakage current experiment. (March-14) **Complete**.
- 2) Synthesize and characterize the Gen-1 electrolyte. (June-14) **Complete**.
- 3) Evaluate the LNMO/graphite cell performance of Gen-1 F-electrolyte. (Sep-14) **Complete**.
- 4) Design and build interim cells and baseline pouch cells. (Jan.-15) **On-going**
- 5) Synthesize and evaluate Gen-2 F-electrolyte based on TF-PC. (Mar.-15) **On Track**
- 6) Develop optimized F-electrolyte containing multinary F-solvents. (Jun.-15) **On Track**
- 7) Design and build final cells. (sep.-15) **On Track**

Progress Report

This quarter, the project focuses on the optimization of fluorinated electrolytes with FEC and F-linear carbonate (FLC) binary solvents. Electrochemical floating test data indicate that when the FEC content increases, the voltage stability improves as shown in Figure 27a. However, such advantage becomes less prominent once FEC content reaches 50%; also, the separator and electrode wetting becomes an issue. A binary system of FEC and FLC with 1:1 weight ratio is chosen for cell performance evaluation. FEC-based formulations showed quite different performance and we have figured out this difference is not caused by the voltage stability of FLC, but the wetting issue with the Celgard separator (Figure 27b) reflected by the low impedance (inset of Figure 27c) and the improved cycling performance by using a compatible glass fiber separator (Figure 27c). It is manifest that to benefit from the voltage stability of F-carbonates, additional efforts beyond the voltage stability are needed to fix the incompatibility of the electrolyte with cell components.

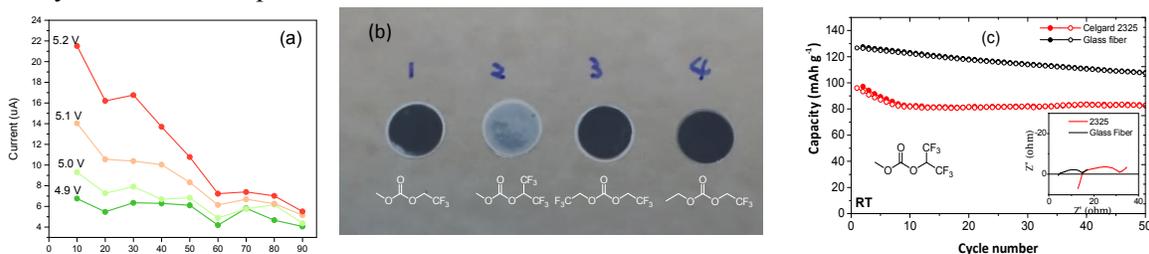


Figure 27: (a) Electrochemical floating test of electrolyte voltage stability with different FEC/DMC ratios with 0.5 M LiPF₆ (leakage current recorded at the end of 10h-hold at potentials of 4.9 to 5.2 V); (b) electrolyte wetting of Celgard 2325 separator (1) FEC/F-EMC=1/1, (2) FEC/F-MiPC/F-EMC=2/1/1, (3) FEC/HF-DEC=1/1, (4) FEC/TF-DEC = 1/1; (c) LNMO/A12 cell cycling performance with electrolyte (2) 1.0 M LiPF₆ in FEC/F-MiPC/F-EMC=2/1/1 with Celgard 2325 separator and glass fiber separator.

The discovery of a symmetrically substituted FLC-based electrolyte (1.0 M FEC/TF-DEC, FEC/F-MiPC) delivered an initial capacity over 130 mAh/g (close to the theoretical capacity of LNMO) using glass fiber separator (Figure 28a). Moreover, TF-DEC and F-MiPC, when mixed with FEC, suppressing the decomposition of the FEC (2, 4 in Figure 28b) as indicated by the ¹H, ¹⁹F and ³¹P-NMR data (not shown).

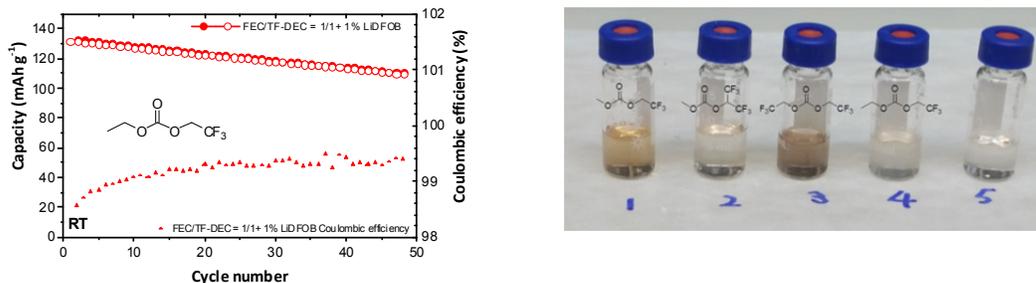


Figure 28: (left) LNMO/A12 cell performance with 1.0 M LiPF₆ in FEC/TF-DEC 1/1 with glass fiber separator; (right) Electrolyte discoloration after storage for a month: 1.0 M LiPF₆ in (1) FEC/F-EMC=1/1, (2) FEC/F-MiPC/F-EMC=2/1/1, (3) FEC/HF-DEC=1/1, (4) FEC/TF-DEC = 1/1 and (5) EC/F-EMC = 1/1.

For the next quarter, our focus will be shifted to fluorinated propylene carbonate (TF-PC). Compared with FEC, TF-PC is chemically inert in the presence of LiPF₆, even at elevated temperatures. To our surprise, like FEC, TF-PC can passivate the graphite surface and enable a reversible Li⁺ interaction chemistry. From the DFT modeling work and our preliminary research, TF-PC is comparably oxidatively stable as FEC with remarkable chemical and thermal stability.

Task 4.2 – Ron Hendershot (Daikin America)

High Voltage Electrolyte

PROJECT OBJECTIVE: Development of a stable (300–1000 cycles), high-voltage (at 4.6 V), and safe (self-extinguishing) formulated electrolyte.

Exploratory Development (Budget Period #1 – October 1, 2013 to January 31, 2015)

- Identify promising electrolyte compositions for high-voltage (4.6 V) electrolytes via the initial experimental screening and testing of selected compositions

Advanced Development (Budget Period #2 – February 1, 2015 to September 31, 2015)

- Detailed studies and testing of the selected high-voltage electrolyte formulations and the fabrication of final demonstration cells

PROJECT IMPACT: Fluorinated small molecules offer the advantage of low viscosity along with high chemical stability due to the strength of the C-F bond. Due to this bond strength, Daikin fluorochemical materials are among the most electrochemical stable materials that still have the needed performance attributes for a practical electrolyte. Such an electrolyte will allow routine operating voltages to be increased to 4.6 V. This technological advance would allow significant cost reduction by reducing the number of cells needed in a particular application and/or allow for greater driving range in PHEV applications.

OUT-YEAR-GOALS: This project has a clearly defined goals for both temperature and voltage performance which are consistent with the deliverables of this proposal. Those goals are to deliver an electrolyte capable of 300-1000 cycles at 3.2-4.6 V at nominal rate with stable performance. An additional goal is to have improved high temperature (> 60 °C) performance. An additional safety goal is to have this electrolyte be self-extinguishing.

COLLABORATIONS: Daikin has begun collaboration with Coulometrics. The collaboration achieves several tasks: fabrication of high voltage electrodes/cells, screening of additive combinations through high precision coulometric techniques described by J. Dahn and extended capability/channels to achieve real time cycle data. Daikin is continuing to pursue a partner to do physical surface analysis.

Milestones

Budget Period #1 – Oct. 1, 2013 to Jan. 31, 2015

- (1) Complete identification of promising electrolyte formulations. Experimental design completed with consistent data sufficient to build models. Promising electrolyte formulations are identified which are suitable for high-voltage battery testing. **Ongoing**
- (2) Successful fabrication of 10 interim cells and delivery of cells to DOE laboratory to be specified. **Ongoing**
- (3) Electrochemical and battery cycle tests are completed and promising results are obtained which demonstrate stable performance at 4.6 V. **Ongoing**

Progress Report

The technical approach to achieve the milestones is based on an iterative plan following a sound scientific method, also sometimes referred to as a Plan-Do-Check-Act (PDCA) cycle, which has been described in detail in previous reports



Figure 29: OCV vs. Gas generation data

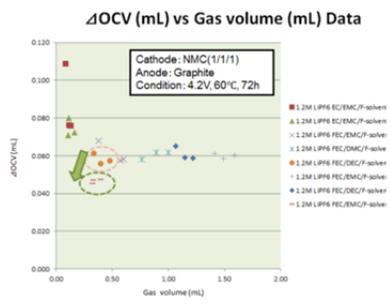


Figure 30: 4.2V 72h 60°C storage data

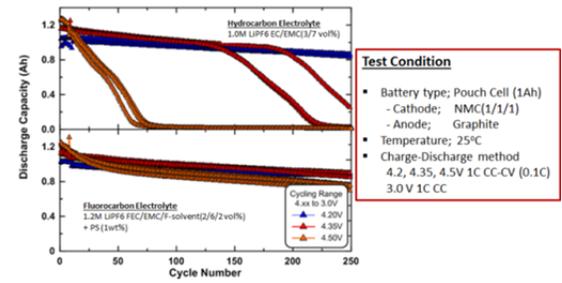


Figure 31: Conventional hydrocarbon electrolyte data

Status: We analyzed the OCV vs Gas generation data (Figure 29) and 4.2 V 72Hr 60 oC storage data (Figure 30) for several compositions of FEC/organic carbonate/F-solvent where organic carbonate can be EMC, DMC or DEC. Based on the battery performance data, base composition for fluorocarbon electrolyte is close to be FEC/EMC/F-solvent (2/6/2, volume). In addition, propane sultone (PS) is found to be the most suitable additive to affect gas generation (Figure 29 and Figure 30). Using the electrolyte (1.2M LiPF6 FEC/EMC/F-solvent (2/6/2)+PS (1.0 wt%)), a significant benefit can be shown for 60°C cycling performance at high voltage (4.35V and 4.50V) as compared to conventional hydrocarbon electrolyte (Figure 31).

The next goal is to reduce gas generation data (less than 0.20ml after 4.50V 72Hr 60°C storage) and achieve better cycle life performance data (more than 80% capacity for initial capacity after 250 cycle at 4.60V 60°C)

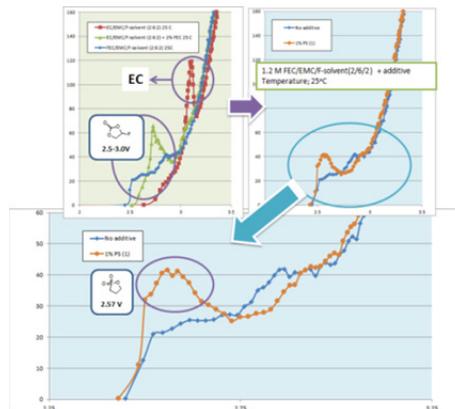


Figure 32: dQ/dV vs. V data.

Additional work has been completed regarding source of gas generation for which we have 3 hypotheses.

1. Mn ion solution from cathode material at high voltage
2. FEC electrochemical decomposition on anode surface (FEC reductive decomposition and then gas generation)
3. FEC chemical decomposition by HF attack.

Regarding hypothesis 2, confirmation of SEI formation voltage has been measured. The dQ/dV vs V data (Figure 32) was measured and analyzed. From this data, the SEI formation for FEC occurs at 2.50 V–3.00 V. Addition of PS, give rise to an additional peak at 2.57 V. It is unclear whether this peak is due to layer formation by PS/FEC or PS alone. It is believed that the decrease in gas volume is attributed to the reductive decomposition being suppressed by this SEI made by PS or PS/FEC.

Additional surface techniques are planned to understand the nature of this layer formation. Additional work regarding gas generation needs to be completed to increase cycle life. The next round of testing will be completed on additional fluorinated additives (Ex. VC, A9, HFEEC, S2 and so on). The fabrication of high voltage electrodes is currently in progress at Coulometrics. The first round of electrodes are LMNO cathode obtained from NEI and Mag D anodes. Efforts are underway to secure several other options to broaden the high voltage profile.

Task 4.3 – Dee Strand (Wildcat Discovery Technologies)

Novel Non-Carbonate Based Electrolytes for Silicon Anodes

PROJECT OBJECTIVE:

The objective of this project is to develop non-carbonate electrolytes that form a stable solid electrolyte interphase (SEI) on silicon alloy anodes, enabling substantial improvements in energy density and cost relative to current lithium ion batteries (LIBs). These improvements are vital for mass market adoption of electric vehicles. At present, commercial vehicle batteries employ cells based on LiMO_2 ($M = \text{Mn, Ni, Co}$), LiMn_2O_4 , and/or LiFePO_4 coupled with graphite anodes. Next generation cathode candidates include materials with higher specific capacity or higher operating voltage, with a goal of improving overall cell energy density. However, to achieve substantial increases in cell energy density, a higher energy density anode material is also required. Silicon anodes demonstrate very high specific capacities, with a theoretical limit of 4200 mAh/g and state-of-the-art electrodes exhibiting capacities greater than 1000 mAh/g. While these types of anodes can help achieve target energy densities, their current cycle life is inadequate for automotive applications. In graphite anodes, carbonate electrolyte formulations reductively decompose during the first cycle lithiation, forming a passivation layer that allows lithium transport, yet is electrically insulating to prevent further reduction of bulk electrolyte. However, the volumetric changes in silicon upon cycling are substantially larger than graphite, requiring a much more mechanically robust SEI film.

PROJECT IMPACT:

Silicon alloy anodes enable substantial improvements in energy density and cost relative to current lithium ion batteries. These improvements are vital for mass market adoption of electric vehicles, which would significantly reduce CO_2 emissions as well as eliminate the US dependence on energy imports.

OUT-YEAR-GOALS:

Development of non-carbonate electrolyte formulations that

- form stable SEIs on 3M silicon alloy anode, enabling coulombic efficiency > 99.9% and cycle life > 500 cycles (80% capacity) with NMC cathodes;
- have comparable ionic conductivity to carbonate formulations, enabling high power at room temperature and low temperature;
- are oxidatively stable to 4.6V, enabling the use of high energy NMC cathodes in the future; and
- do not increase cell costs over today's carbonate formulations.

COLLABORATIONS:

Wildcat is working with 3M on this project. To date, 3M is supplying the silicon alloy anode films and NMC cathode films for use in Wildcat cells.

Milestones

- 1) Assemble materials, establish baseline performance with 3M materials (Dec-13) **Complete**
- 2) Develop initial additive package using non-SEI forming solvent. (Mar-14) **Complete**
- 3) Screen initial solvents with initial additive package. (Jun-14) **Complete**
- 4) Design/build interim cells for DOE (Sep-14) **Complete**
- 5) Improve performance with noncarbonate solvents and new SEI additives (Mar-15) **On Track**
- 6) Optimize formulations (Aug-15)
- 7) Design/build final cells for DOE (Dec-15)

Progress Report

This quarter, the project focused on two primary efforts. First, screening of noncarbonated solvents was extended to include additional candidates. Second, an extensive study on the effect of salt composition was performed. Last quarter, a number of promising high dielectric (HD) and low viscosity (LV) combinations were identified with promising cycle life. This work was extended to include additional solvents, with results shown in Figure 33. The control carbonate electrolyte 1st cycle capacity and capacity retention at 100 cycles are shown as the gray bands. Several of the newly identified combinations of HD/LV solvents show comparable performance to the control.

Now that promising solvents have been identified (last two quarters), formulation effects need to be determined. Screening of the new solvents was done using a set formulation (salt, additives). Therefore, we focused first on the effect of salt on the new solvent performance. Salt composition has been determined to affect the ratio of the inorganic/organic composition of the SEI and would, therefore, be expected to impact the mechanical robustness of the SEI on a silicon anode particle. In this study, 11 of the most promising new solvent mixtures were studied with six different lithium ion salts with and without an SEI additive.

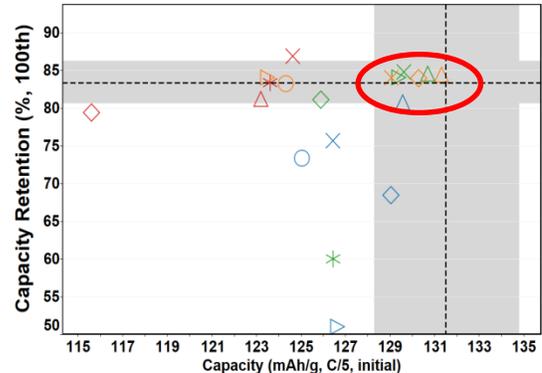


Figure 33: Several promising HD/LV combinations show performance comparable to the carbonate control electrolyte

Figure 35 shows an example of performance (1st cycle capacity and capacity retention at 100 cycles) for one of the noncarbonate solvent combinations with varying salt composition. Several salts result in non-carbonate formulations performing similarly to the carbonate control. Further improvement is observed at longer cycles, as shown in Figure 34.

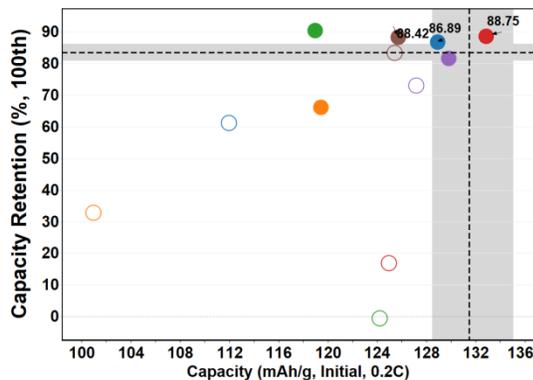


Figure 35: Noncarbonate formulation performance (colors = different salts; open/close = without/with SEI additive)

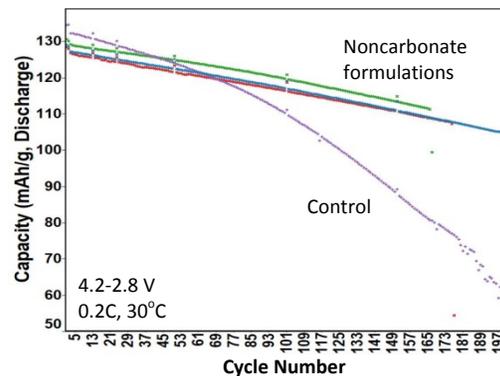


Figure 34: Significant cycle life improvement at 200 cycles for the noncarbonate formulation over an EC/EMC control

The next phase of work will consist of extensive testing of novel SEI additives in the promising noncarbonate solvent combinations. As originally proposed, these will consist of molecules expected to promote good film formation with flexible structures to create more mechanically robust SEI layers on the silicon anode.

Patents/Publications/Presentations

1. Provisional patent application on most promising additives filed 4/15/2014.
2. Three additional provisional patent applications in process.
3. Poster, DOE AMR, 6/2014.
4. “Development of Non-Carbonate Based Electrolytes for Silicon Anodes,” The Battery Show, Novi, MI, 9/2014.

TASK 5 – DIAGNOSTICS

In order to meet the goals of Vehicle Technology Program's (VTP's) Multi Year Program Plan (MYPP) and develop lower-cost, abuse-tolerant batteries with higher energy density, higher power, better low-temperature operation, and longer lifetimes for the next-generation of HEVs, PHEVs, and EVs, there is a strong need to identify and understand structure-property-electrochemical performance relationships in materials, life-limiting and performance-limiting processes, and various failure modes to guide battery development activities and scale-up efforts. In the pursuit of Li-ion cells with high energy density, high cell operating voltages and demanding cycling requirements lead to unprecedented chemical and mechanical instabilities in cell components. Successful implementation of newer materials such as Si anode and high voltage cathodes also requires better understanding of fundamental processes, especially those at the solid/electrolyte interface of both anode and cathode. The Advanced Diagnostics team seeks to utilize model systems, ex-situ, in situ and operando approaches combined with a suite of start-of-the-art analytical tools, including atomic resolution transmission electron microscopy (TEM) and electron energy loss spectroscopy (EELS), X-ray photoelectron spectroscopy (XPS), X-ray and neutron diffraction, pair distribution function analysis, X-ray absorption, emission and scattering, nuclear magnetic resonance (NMR), mass spectrometry, optical and vibrational spectroscopies, to correlate materials' physical properties and reaction mechanisms to their performance and stability in batteries, investigate compositional, structural and morphological changes of electrode materials, and reveal fundamental, atomic-scale processes that are behind the observed limitations in performance and lifetime. The effort produces a wealth of knowledge that is key to the design and development of next-generation batteries. For example, a better understanding of electrode surface processes and reactions at electrode/electrolyte interface would provide guidance on the strategies of using electrode surface modifications, bulk substitutions, and electrolyte additives to induce a stable interface critical for battery longevity. Furthermore, the research advances analytical techniques and tools that have a far-reaching effect on material and device development in a variety of fields.

Featured Highlight

✚ Grey's group developed an *in situ* NMR method for tracking Li-ion transport during cycling.

Task 5.1 – Guoying Chen (Lawrence Berkeley National Laboratory)

Design and Synthesis of Advanced High-Energy Cathode Materials

PROJECT OBJECTIVE: The successful development of next-generation electrode materials requires particle-level knowledge of the relationships between materials' specific physical properties and reaction mechanisms to their performance and stability. This single-crystal-based project was developed specifically for this purpose and it has the following objectives: 1) obtain new insights into electrode materials by utilizing state-of-the-art analytical techniques that are mostly inapplicable on conventional, aggregated secondary particles, 2) gain fundamental understanding on structural, chemical and morphological instabilities during Li extraction/insertion and prolonged cycling, 3) establish and control the interfacial chemistry between the cathode and electrolyte at high operating voltages, 4) determine transport limitations at both particle and electrode levels, and 5) develop next-generation electrode materials based on rational design as opposed to more conventional empirical approaches.

PROJECT IMPACT: This project will reveal performance-limiting physical properties, phase-transition mechanisms, parasitic reactions, and transport processes based on the advanced diagnostic studies on well-formed single crystals. The findings will establish rational, non-empirical design methods that will improve the commercial viability of next-generation $\text{Li}_{1+x}\text{M}_{1-x}\text{O}_2$ (M=Mn, Ni and Co) and spinel $\text{LiNi}_x\text{Mn}_{2-x}\text{O}_4$ cathode materials.

OUT-YEAR GOALS:

- Synthesize single-crystal samples of lithium transition-metal oxide cathode materials.
- Characterize structural and morphological changes and establish their correlation to rate performance and cycling stability.
- Determine crystal-plane specific reactivity between cathode particles and the electrolyte.
- Measure lithium-concentration dependent transport and kinetic properties.
- Define performance-limiting fundamental properties and mechanisms and outline mitigating approaches. Design, synthesize, and evaluate the improved electrode materials.

COLLABORATIONS: Drs. R. Kostecki, M. Doeff, K. Persson, V. Zorba, T. Tyliczszak and Z. Liu (LBNL), Prof. C. Grey (Cambridge), Prof. B. Lucht (URI), and Prof. Y.-M. Chiang (MIT).

Milestones

- 1) Characterize Ni/Mn spinel solid solutions and determine the impact of phase transformation and phase boundary on rate capability. (Dec-14) **Completed**
- 2) Complete the investigation on crystal-plane specific reactivity between Li-rich layered composites and the electrolyte. Determine morphology effect in layered oxide side reactions. (Mar-15) **On schedule**
- 3) Develop new techniques to characterize reactions and processes at the cathode-electrolyte interface. Evaluate the effect of surface compositions and modifications on side reactions and interface stability. (Jun-15) **On schedule**
- 4) Go/No-Go: Continue the approach of using synthesis conditions to vary surface composition if significant structural and performance differences are observed. (Sep-15) **On schedule**

Progress Report

Phase transition and rate capability in $\text{LiNi}_x\text{Mn}_{2-x}\text{O}_4$: During the charge and discharge of intercalation cathodes, solid solution transformation is commonly involved even in the materials where two-phase transition dominates the processes. The relationship between the extend of solid solution involvement and rate capability, therefore, is important knowledge in material design. To this end, ordered $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ (LMNO) crystals, previously synthesized by a molten-salt method, was disordered by rapid thermal annealing at 720 °C followed by fast cooling. The dQ/dV profile show a peak separation of about 60 mV at 4.7 V, similar to that observed in $\text{LiNi}_{0.3}\text{Mn}_{1.7}\text{O}_4$ (Figure 36a), confirming the disordered nature of both samples. Synchrotron in situ XRD experiments were performed at beamline 11-3 at SSRL, and the phase composition at a given Li content during discharge was obtained from full-pattern Rietveld refinement and shown in Figure 36b and Figure 36c. While three cubic phases and two two-phase transitions were involved in $x=0.5$, indicating presence of extensive phase boundaries, the sample with $x=0.3$ transformed through two cubic phases with a large solid solution domain covering nearly 50% of the Li content. The rate capability obtained from varying-rate cycling of half-cells between 3.0 and 5.0 V is compared in Figure 36d. At C/22 rate, both spinels delivered a discharge capacity close to the theoretical value of 147 mAh g^{-1} . Compared to the sample with $x=0.3$, slight improvement was observed on $x=0.5$ at all rates, despite a lower Mn^{3+} content and a smaller presence of solid solution in the sample. In cathodes where two-phase transition is involved and phase boundaries are present, direct correlation between kinetics and the extent of solid solution transformation was not found. The kinetic advantage of solid solution transformation in the entire Li content range, in the absence of phase boundary, however, is unclear from the study.

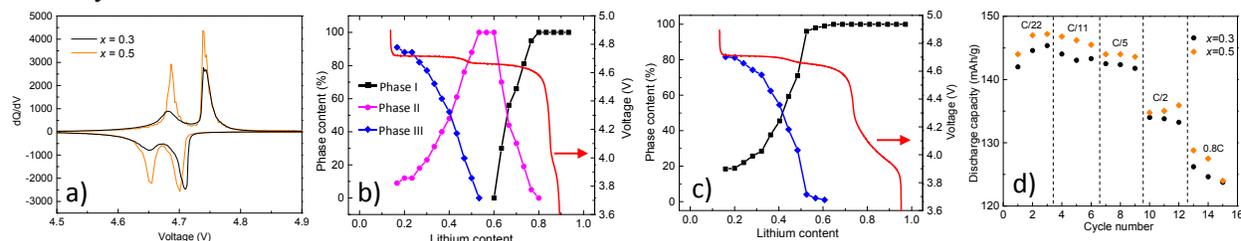


Figure 36: a) dQ/dV profiles, b) and c) percentage of the phases present during in situ discharge of $x=0.5$ and $x=0.3$, and d) rate capability of the crystal samples.

Properties of $\text{Li}_x\text{Ni}_{0.5}\text{Mn}_{1.5}\text{O}_4$ solid solutions: Room-temperature, phase-pure $\text{Li}_x\text{Ni}_{0.5}\text{Mn}_{1.5}\text{O}_4$ (Li_xMNO , $x \geq 0.71$) solid solutions, previously synthesized through a controlled thermal treatment process, was characterized in detail to probe their physical properties and understand their roles in kinetics. On the Raman spectrum of pristine LMNO (Figure 37a), the peaks at 404 and 496 cm^{-1} are commonly attributed to E_g and $F_{2g}^{(2)}$ Ni^{2+} -O stretching modes. The peaks between 570 and 650 cm^{-1} are assigned as A_{1g} and $F_{2g}^{(1)}$ Mn-O modes in the MnO_6 octahedron, with their position and relative intensity ratio closely related to Mn-O bond length, MnO_6 distortion, and Mn oxidation state. The well-resolved split of the $F_{2g}^{(1)}$ bands at 593 and 612 cm^{-1} is consistent with the ordering of the transition-metal cations. The A_{1g} band at 635 cm^{-1} is related to both Mn^{4+} -O and Mn^{3+} -O vibrations. No significant differences were observed when comparing the spectra of Li_xMNO solid solutions with $0.71 \leq x < 1$, all of which resembled that of pristine LMNO. The corresponding FTIR spectra of the Li_xMNO samples are shown in Figure 37b. The presence of the same eight well-defined bands at 430, 468, 480, 501, 557, 594, 621, and 650 cm^{-1} in all spectra further confirm the retention of spinel local symmetry in the thermally-induced solid solutions and phase purity of the samples. Neutron profiles obtained from the LMNO and $\text{Li}_{0.82}\text{MNO}$ suggest that both samples are fully ordered with a space group of $P4_332$ and a nearly identical lattice parameter of 8.1666 ± 0.0006 Å.

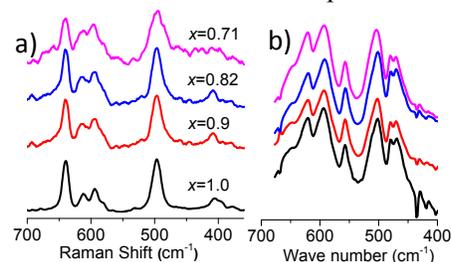


Figure 37: a) Raman and b) FTIR of Li_xMNO .

Q1 Patents/Publications/Presentations

1. S. Kuppan, A. Jarry, R. Kostecki, and G. Chen, “A study of room-temperature $\text{Li}_x\text{Mn}_{1.5}\text{Ni}_{0.5}\text{O}_4$ solid solutions” *Scientific Reports*, 2014, accepted.
2. J. S. Park, L. Cheng, , V. Zorba, A. Mehta, , J. Cabana, G. Chen, M. M. Doeff, T. J. Richardson, J. H. Park, J.-W. Son, W.-S. Hong, “Effects of Crystallinity and Impurities on the Electrical Conductivity of Li-La-Zr-O Thin Films” *Thin Solid Films*, 2014, in press.
3. L. Cheng, W. Chen, M. Kunz, K. Persson, N. Tamura, G. Chen, and M. M. Doeff, “Effect of Surface Microstructure on Electrochemical Performance of Garnet Solid Electrolytes,” *ACS Applied Materials & Interfaces*, 2014, accepted.
4. S. Kuppan and G. Chen, “Thermal Behavior of $\text{Li}_x\text{Mn}_{1.5}\text{Ni}_{0.5}\text{O}_4$ ($0 \leq x \leq 1$) and Isolation of Room-Temperature Solid Solutions,” 2014 CalCharge open house, SLAC National Accelerator Laboratory, Menlo Park, CA, November 2014.
5. A. K. Shukla, Q. Ramasse, C. Ophus, A. Darbal, H. Duncan, and G. Chen, “Unfolding the bulk and defect structure of lithium-rich layered oxides using multi-scale electron microscopy and spectroscopy techniques for high-capacity lithium-ion batteries,” 2014 BERCC Energy Summit, Berkeley, CA, October 2014.

Task 5.2 – Robert Kostecki (Lawrence Berkeley National Laboratory)

Interfacial Processes – Diagnostics

PROJECT OBJECTIVE: The main objective of this task is to obtain detailed insight into the dynamic behavior of molecules, atoms, and electrons at electrode/electrolyte interfaces of intermetallic anodes (Si) and high voltage Ni/Mn-based materials at a spatial resolution that corresponds to the size of basic chemical or structural building blocks. The aim of these studies is to unveil the structure and reactivity at hidden or buried interfaces and interphases that determine battery performance and failure modes. To accomplish these goals novel far- and near-field optical multifunctional probes must be developed and deployed *in situ*. The proposed work constitutes an integral part of the concerted effort within the BATT Program and it attempts to establish clear connections between diagnostics, theory/modelling, materials synthesis, and cell development efforts.

PROJECT IMPACT: This project provides better understanding of the underlying principles that govern the function and operation of battery materials, interfaces and interphases, which is inextricably linked with successful implementation of high energy density materials such as Si and high voltage cathodes in Li-ion cells for PHEVs and EVs. This task also involves the development and application of novel innovative experimental methodologies to study and understand the basic function and mechanism of operation of materials, composite electrodes, and Li-ion battery systems for PHEV and EV applications.

OUT-YEAR GOALS: Design and employ novel and sophisticated *in situ* analytical methods to address the key problems of the BATT baseline chemistries. The proposed experimental strategies combine imaging with spectroscopy aimed at probing electrodes at an atom, molecular, or nanoparticulate level to unveil structure and reactivity at hidden or buried interfaces and determine electrode performance and failure modes in baseline Li_xSi -anodes and high-voltage LMNO cathodes. The main goal is to gain insight into the mechanism of surface phenomena on thin-film and monocrystal Sn and Si intermetallic anodes and evaluate their impact on the electrode long-term electrochemical behavior. Comprehensive fundamental study of the early stages of SEI layer formation on polycrystalline and single crystal face Sn and Si electrodes will be carried out. *In situ* and *ex situ* far- and near-field scanning probe spectroscopy and LIBS will be employed to detect and monitor surface phenomena at the intermetallic anodes and high-voltage (>4.3V) model and composite cathodes.

COLLABORATIONS: Please list current collaborations in this section, whether inside or outside the BATT Program. Vincent Battaglia, Ban Chunmei, Vassilia Zorba, Bryan D. McCloskey

Milestones

- 1) Determine the mechanism of formation of the metal complexes species that are produced at high-energy Li-ion cathodes (Dec-14) **Status completed**
- 2) Resolve SEI layer chemistry of coated Si single crystal and thin film anodes (collaboration with Chunmei Ban). (Mar-15) **Status on schedule**
- 3) Determine the mechanism of SEI layer poisoning by Ni and Mn coordination compounds (collaboration with the Bryan D. McCloskey). (Jun-15) **Status on schedule**
- 4) Go/No-Go: Demonstrate feasibility of *in situ* near-field and LIBS techniques at Li-ion electrodes (collaboration with Vassilia Zorba). Criteria: Stop development of near-field and LIBS techniques, if the experiments fail to deliver adequate sensitivity. (Sep-15) **Status on schedule**

Progress Report

In the first quarter of FY2015 the mechanism of Mn and Ni dissolution from $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ cathode was studied. Previous reports (Q1 and Q3 FY2014) revealed the formation of Mn fluorescent species at the $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ /electrolyte interface by electrochemical oxidation as well as the deposition of a mixture of Mn(II)(acac)_2 and Mn(II) oxalate at the graphite electrode surface, with Mn(II)(acac)_2 as the major species. Similarly, the presence of Ni(II)(acac)_2 and Ni(II) carbonates in the SEI were also detected. Metal oxalates and carbonates are commonly formed by decarboxylation reactions of EC and frequently observed in Ni/Mn oxide-based battery system. On the other hand, the mechanism of interaction between the metal site at the $\text{Li}_x\text{Ni}_{0.5}\text{Mn}_{1.5}\text{O}_4$ surface and the electrolyte during oxidation, which leads to the formation of metal complexes, is unknown. A plausible formation pathway, presented in figure 1, involves two proton and two electron transfers as well as a propagation mechanism and is accompanied by desorption of water.

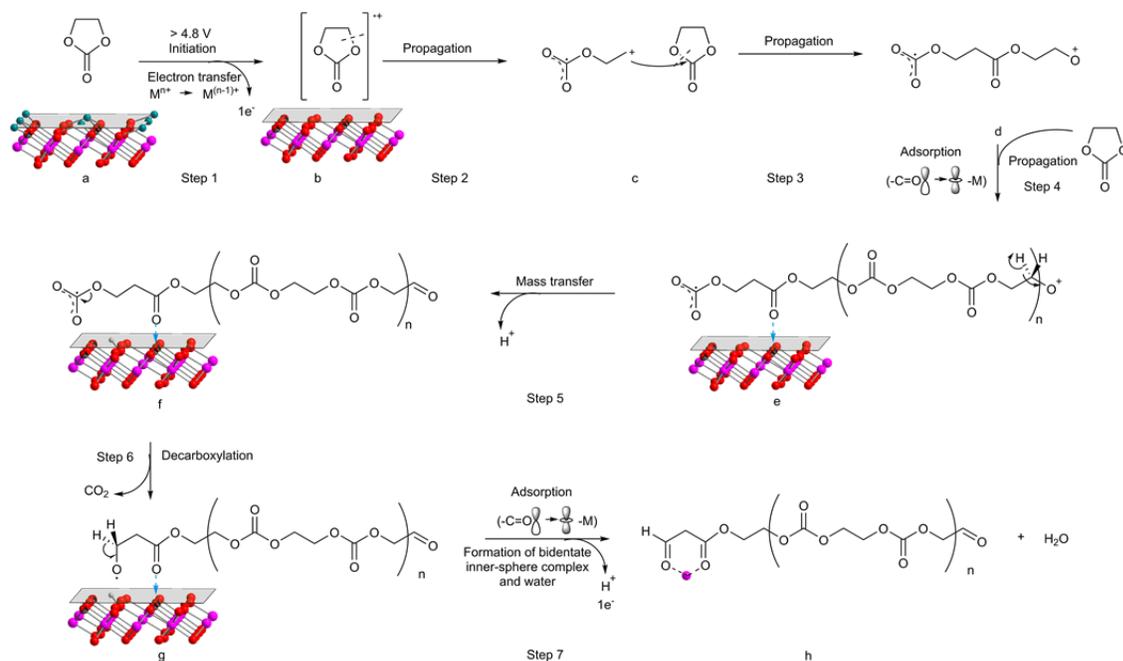


Figure 38: Possible formation pathway of the metal complexes upon EC oxidation at the $\text{Li}_x\text{Ni}_{0.5}\text{Mn}_{1.5}\text{O}_4$ surface by an electron transfer, propagation, proton transfer and a proton coupled electron transfer (PCET) mechanism.

The propagation mechanism results in longer side chains which decrease the solubility of the resultant metal complexes. Therefore a variety of soluble and insoluble fluorescent compounds is observed in aged/cycled Li-ion cells. The M^{II} β -diketone complexes with longer alkoxide side precipitate to form surface films at the cathode side whereas the M^{II} β -diketone complexes with shorter chains diffuse in the electrolyte and get incorporated in the SEI layer on the graphite electrode. These results suggest that the adsorption of β -diketone chelate ligands at $\text{Mn}^{\text{IV/III}}$ and Ni^{IV} sites is primarily responsible for the observed metal dissolution and that the rate of these reactions is accelerated by the continuous formation of oxygen vacancies. This implies that manganese and nickel diffuse as complex species and not as free Mn(II) and Ni(II) ions. Further investigations concerning the Mn, Ni and Co species' role in Li-ion systems' failure mechanism are underway (milestone 3). Studies regarding the influence of coating the Si anode on SEI formation and its impact on the Li-ion system's long-term stability are also carried out (milestone 2).

Q1 Patents/Publications/Presentations

1. M. Ayache, J. Syzdek, I. Lucas, N. Norberg and R. Kostecki, “Interfacial Studies of the SEI Layer on a Tin Electrode”, 2014 ECS and SMEQ Joint International Meeting Cancun, October 5-9, 2014
2. Maurice Ayache, Simon Lux, and Robert Kostecki, “Nanoscale Chemical Mapping of the Solid Electrolyte Interphase in Li-ion Systems”, SciX Conference, September 29, 2014, Reno, Nv (invited talk)

Task 5.3 – Xiao-Qing Yang and Xiqian Yu (Brookhaven National Laboratory)

Advanced *In-situ* Diagnostic Techniques for Battery Materials

PROJECT OBJECTIVE: The primary objective of this proposed project is to develop new advanced in situ material characterization techniques and to apply these techniques to support the development of new cathode and anode materials for the next generation of lithium-ion batteries (LIBs) for plug-in hybrid electric vehicles (PHEV). In order to meet the challenges of powering the PHEV, LIBs with high energy and power density, low cost, good abuse tolerance, and long calendar and cycle life must be developed.

PROJECT IMPACT: In the Multi Year Program Plan (MYPP) of Vehicle Technology Program (VTP), the goals for battery were described as: “Specifically, lower-cost, abuse-tolerant batteries with higher energy density, higher power, better low-temperature operation, and longer lifetimes are needed for the development of the next-generation of HEVs, PHEVs, and EVs.” If this project is successfully carried out, the knowledge learned from diagnostic studies and collaborations with US industries and international research institutions through this project will help US industries to develop new materials and processes for new generation of lithium-ion batteries in their efforts to reach these VTP goals.

OUT-YEAR GOALS: For the high voltage spinel $\text{LiMn}_{1.5}\text{Ni}_{0.5}\text{O}_4$, the high voltage charge and discharge cycling is a serious challenge for the electrolyte oxidation decomposition. The studies on the improvement of the thermal stability are quite important for the better safety characteristics. For the high energy density $\text{Li}(\text{NiMnCo})\text{O}_2$ composite materials, the problem of poor rate capability during charge and discharge and performance degradation during charge-discharge cycling are issues need to be addressed..

COLLABORATIONS: The BNL team will work closely with material synthesis groups at ANL (Drs. Thackeray and Amine) for the high energy composite; at UT Austin (Prof. Manthiram) for the high voltage spinel; and at PNNL (Drs. Liu and Zhang) for the Si-based anode materials. Such interaction between the diagnostic team at BNL and synthesis groups of these other BATT members will catalyze innovative design and synthesis of advanced cathode and anode materials. We will also collaborate with industrial partners at General Motors (Dr. Wu), Duracell (Dr. Bae), and Johnson Controls (Drs. Cho and Bonhomme) to obtain feedback information as battery end users.

Milestones

- 1) Complete the thermal stability studies of a series of blended LiMn_2O_4 (LMO) - $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$ (NCM) cathode materials with different weight ratios using in situ time-resolved x-ray diffraction (XRD) and mass spectroscopy techniques in the temperature range of 25°C to 580°C (Dec-14).
Completed
- 2) Complete the In situ XRD studies of the structural evolution of $\text{Li}_{2-x}\text{MoO}_3$ ($0 \leq x \leq 2$) high energy density cathode material during charge-discharge cycling between 2.0 and 4.8 V. (Mar-15) **In progress**
- 3) Complete the x-ray absorption near edge structure (XANES) and extended x-ray absorption fine structure (EXAFS) studies at Mo K-edge of Li_2MoO_3 at different charge-discharge states. (Jun-15) **In progress**
- 4) Complete the preliminary studies of elemental distribution of Fe substituted high voltage spinel cathode materials using transmission x-ray microscopy (TXM). (Sep-15) **In progress**

Progress Report

In the 1st quarter of FY2015, the milestones for the 1st quarter of FY2014 had been completed and progress towards other milestones has been made.

In the 1st quarter of FY2015, BNL has been focused on studying the thermal stability in the blended LiMn_2O_4 - $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$ (LMO-NCM) cathode materials using in situ Time-resolved XRD and Mass Spectroscopy.

Figure 39 shows the XRD-MS results for the mixture with a weight ratio of LMO:NCM = 3:1. In terms of phase transition, it differs from that of pure LMO in three major aspects, namely, high temperature phases, phase transition route and CO_2 release profile. First, a close look at the XRD pattern at 580 °C reveals two kinds of rock-salt at high temperature. In addition to the MnO in pure LMO, the other phase with lattice parameter shorter than MnO but longer than those for CoO and NiO, suggesting a solid-solution type rock-salt phase. It is denoted as (Mn, Co, Ni)O. This assignment is supported by the fact that in the CO_2 profile, multiple peaks were observed at high temperatures for this mixture, in contrast to that for LMO, where only a singular peak was observed. Secondly, as can be seen from the third stage Fig. 1, rock-salt phases were formed through the decomposition of Mn_3O_4 only. Thirdly, the onset temperature of CO_2 release is lowered from above 200°C in LMO to around 175°C. This is presumably caused by the introduction of Ni in NCM. It is possible to identify which part contributes to the early stage oxygen release. Interestingly, it is clearly seen that peaks from the hexagonal phase are gradually disappearing while those from the cubic phase still remain as temperature is increased in the early stage of heating. This indicates the NCM part reacts first, suggesting its poorer thermal stability than the LMO.

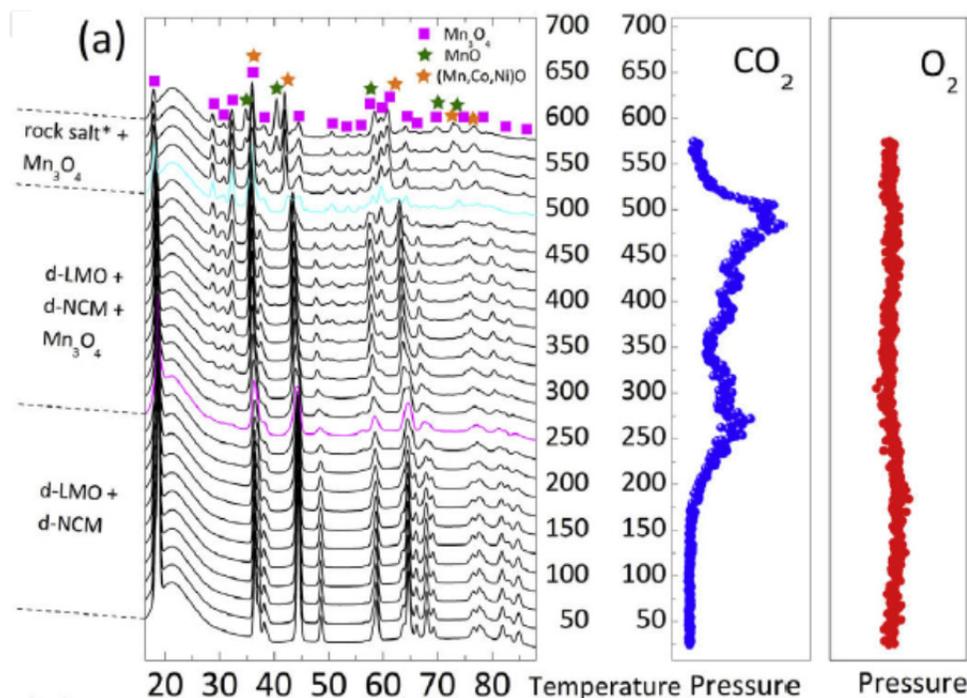


Figure 39: *In situ* XRD-MS data of electrochemically delithiated LMO and NCM mixture with weight ratio of 3:1.

Q1 Patents/Publications/Presentations

1. Yong-Ning Zhou, Jun Ma, Enyuan Hu, Xiqian Yu, Lin Gu, Kyung-Wan Nam, Liquan Chen, Zhaoxiang Wang, and Xiao-Qing Yang, “Tuning Charge-discharge Induced Unit-cell-breathing through Metal-Metal Bonding in Layer-structured Cathode Materials for Lithium-ion Batteries”, NATURE COMMUNICATIONS, Volume: 5, DOI: 10.1038/ncomms6381, Published: NOV 2014
2. Won-Sub Yoon, Otto Haas, Shoaib Muhammad, Hyunchul Kim, Wontae Lee, Donghwi Kim, Daniel A. Fischer, Cherno Jaye, Xiao-Qing Yang, Mahalingam Balasubramanian, Kyung-Wan Nam, “In situ soft XAS study on nickel-based layered cathode material at elevated temperatures: A novel approach to study thermal stability”, SCIENTIFIC REPORTS Volume: 4 Article Number: 6827 Published: OCT 29 2014
3. Yongning Zhou, Enyuan Hu, Xiqian Yu, Seongmin Bak, Xiao-Qing Yang, Hung-Sui Lee, Jun Ma, Zhaoxiang Wang, Lin Gu and Liquan Chen, and Kyung-Wan Nam, “Structural Changes of Li_2MoO_3 As Cathode Material for Li-Ion Batteries during Initial Charge-Discharge Studied By Synchrotron-Based X-Ray Diffraction and Absorption”, presented at the 226th ECS Meeting, October 6th, 2014, Cancun, Mexico, **Invited**

Task 5.4 – Clare Grey (Cambridge University)

NMR and Pulse Field Gradient Studies of SEI and Electrode Structure

PROJECT OBJECTIVE: The formation of a stable surface electrode interphase (SEI) is critical to the long-term performance of a battery, since the continued growth of the SEI on cycling/aging results in capacity fade (due to Li consumption) and reduced rate performance due to increased interfacial resistance. Although arguably a (largely) solved problem with graphitic anodes/lower voltage cathodes, this is not the case for newer, much higher capacity anodes such as silicon, which suffer from large volume expansions on lithiation, and for cathodes operating above 4.3 V. Thus it is essential to identify how to design a stable SEI. The objectives are to identify major SEI components, and their spatial proximity, and how they change with cycling. SEI formation on Si vs. graphite and high voltage cathodes will be contrasted. Li⁺ diffusivity in particles and composite electrodes will be correlated with rate. The SEI study will be complemented by investigations of local structural changes of high voltage/high capacity electrodes on cycling.

PROJECT IMPACT: The first impact of this project will be an improved, molecular based understanding of the surface passivation (SEI) layers that form on electrode materials, which are critical to the operation of the battery. Second, we will provide direct evidence for how additives to the electrolyte modify the SEI. Third, we will provide insight to guide and optimize the design of more stable SEIs on electrodes beyond LiCoO₂/graphite.

OUT-YEAR GOALS: The goals of this project are to identify the major components of the SEI as a function of state of charge and cycle number different forms of silicon. We will determine how the surface oxide coating affects the SEI structure and establish how the SEI on Si differs from that on graphite and high voltage cathodes. We will determine how the additives that have been shown to improve SEI stability affect the SEI structure and explore the effect of different additives that react directly with exposed fresh silicon surfaces on SEI structure. Via this program, we will develop new NMR based methods for identifying different components in the SEI and their spatial proximities within the SEI, which will be broadly applicable to the study SEI formation on a much wider range of electrodes. These studies will be complemented by studies of electrode bulk and surface structure to develop a fuller model with which to describe how these electrodes function.

COLLABORATIONS: Ram Seshadri and Anton van der Ven, UCSB, Brett Lucht, Rhode Island, Kristin Persson, LBNL, Jordi Cabana, UICC, M. S. Whittingham, Bingampton, S. Meng, UCSD, Stephan Hoffman and Andrew Morris, Cambridge.

Milestones

Quarter	Milestones/Deliverables Description and Due Date	Go/No-Go Description and Due Date
Q1	Complete initial Si SEI work and submit for publication. Work complete; publication in final stages of preparation. Complete 4Vspinel work (<i>in situ</i> NMR) and submit for publication. Work complete; thesis written and papers are now being written up.	
Q2	Identify differences in Si SEI after one and multiple cycles.	
Q3	Identify major organic components on the SEIs formed on high surface area carbons by NMR.	
Q4	Complete initial carbon-SEI interfacial studies	Determine whether NMR has the sensitivity to probe organics on the cathode side in paramagnetic systems.

Progress Report

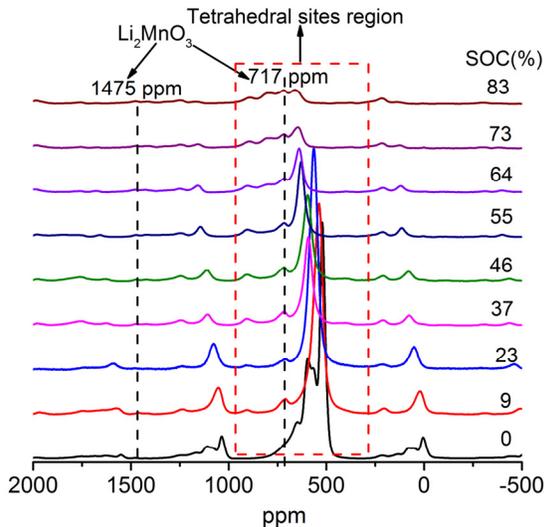


Figure 40: ${}^7\text{Li}$ MAS NMR spectra of $\text{Li}_{1.08}\text{Mn}_{1.92}\text{O}_4$ electrodes at different state of charge (SOC). The spectra were acquired at 4.7 T with MAS frequency of 40 kHz. The impurity Li_2MnO_3 (marked on the spectra) is electrochemically inactive upon charging. The isotropic shift regions are marked with a red dashed square; the other spectral regions are dominated by the spinning sidebands.

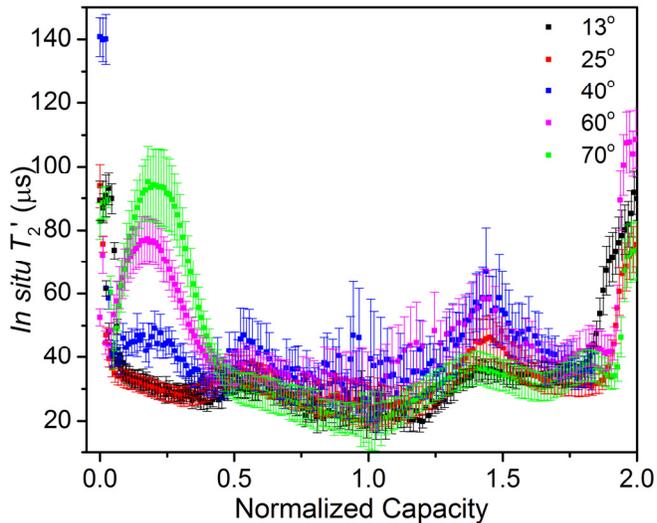


Figure 41: ${}^7\text{Li}$ NMR T_2' measurements of $\text{Li}_{1.08}\text{Mn}_{1.92}\text{O}_4$ measured during battery cycling over two cycles (1st cycle 0 – 1; 2nd cycle 1- 2). The measurements were performed at 13, 25, 40, 60 and 70 °C.

Detailed in- and ex-situ NMR studies of spinels have been performed to determine the sensitivity of the NMR experiment to ionic motion during battery cycling. Figure 40 shows the ex-situ ${}^7\text{Li}$ MAS NMR experiment performed for a sample of nominal stoichiometry $\text{Li}_{1.08}\text{Mn}_{1.92}\text{O}_4$. Interestingly, the partially charged samples show weak resonances at 1475 and 717 ppm, which are clear signatures for trace Li_2MnO_3 impurities, indicating that the Li content of the spinel sample is lower than implied by the nominal composition. The second observation is the clear collapse of the fine structure between 500 – 750 ppm, assigned to Li ions in tetrahedral regions, as has been discussed extensively in our prior publications. This collapse is indicative of motion on a timescale that is faster than the separation between the various resonances. Assuming a separation of chemical shifts of approx. 150 ppm, this implies a Li hopping frequency of > 12 kHz. The increase in Li^+ ion motion is facilitated by the presence of Li^+ vacancies, created by charging.

Rapid Li^+ mobility is observed until approximately 73 SOC, although weaker peaks suggest that there are trapped Li^+ sites in the structure in addition to the mobile components. Mobility has been explored by performing T_2' (spin-spin relaxation) measurements *in situ* during battery cycling (Figure 41), the T_2' providing an indirect measurement of motion on the kHz timescale.

The *in situ* data reveal distinct mobility regimes. A dramatic reduction in T_2' is seen initially which correlates with the mobility seen *ex situ*, simulations showing that this is consistent with Li hop rates on the order of 10 kHz. Interestingly, the T_2' increases again, the increase increasing with increased temperature. This provides evidence for motion approaching the fast regime. Again simulations suggest motion of $\gg 60$ kHz. Motion slows down at 50% SOC, a phenomenon that more clearly observed at lower temperatures, consistent with

at least partial ordering at this composition. The approach provides a simple method for tracking Li-ion transport during cycling.

Task 5.5 – Shirley Meng (UC San Diego)

Optimization of Ion Transport in High-Energy Composite Cathodes

PROJECT OBJECTIVE: This project aims to probe and control the atomic-level kinetic processes that govern the performance limitations (rate capability and voltage stability) in a class of high energy composite electrodes. A systematic study with powerful suite of analytical tools (including atomic resolution scanning transmission electron microscopy (a-STEM) & Electron energy loss spectroscopy (EELS), X-ray photoelectron spectroscopy (XPS) and first principles (FP) computation) will be used to pin down the mechanism and determine the optimum bulk compositions and surface characteristics for high rate and long life. Moreover, to help the synthesis efforts to produce the materials at large scale with consistently good performance. It is also aimed to extend the suite of surface-sensitive tools to diagnose the silicon anodes types.

PROJECT IMPACT: If successful, this research will provide a major breakthrough in commercial applications of the class of high energy density cathode material for lithium ion batteries. Additionally, it will provide in-depth understanding of the role of surface modifications and bulk substitution in the high voltage composite materials. The diagnostic tools developed here can also be leveraged to study a wide variety of cathode and anode materials for rechargeable batteries.

OUT-YEAR GOALS: Careful engineering of the surface (coating) and bulk compositions (substitution) of the high energy composite cathode materials can lead to significant improvement on ion transport and voltage stability. The goals are to establish the STEM/EELS and XPS as quantities diagnostic tools for surface and interface characterization and to enable quick identification of causes of surface instability (or stability) in various types of cathode materials. It is also planned to identify ways to extend the techniques for anode materials, such as silicon anode.

COLLABORATIONS:

- Michael Sailor (UCSD) – porous silicon and carbonization of silicon based anodes.
- Keith Stevenson (UT Austin) – XPS and TOF-SIMS
- Nancy Dudney and Juchuan Li (Oak Ridge National Lab) – silicon thin film fabrication
- Chunmei Ban (National Renewable Energy Laboratory- Molecular Layer Deposition)

Milestones

- 1) Identify ways to extend the STEM/EELS and XPS techniques for anode materials, such as silicon anode. (09/30/14) **On Track (STEM/EELS operational in Jan 2015)**
- 2) Identify at least two high voltage cathode materials that deliver 200mAh/g reversible capacity when charged to high voltages (12/31/14) **Complete**
- 3) Obtain the optimum surface coating and substitution compositions in lithium rich layered oxides when charged up to 4.8V (or 5.0 V) (3/31/15) **On Track**
- 4) Identify the appropriate SEI characteristics and microstructure for improving first cycle irreversible capacity of silicon anode. (Improve to 85-95%) (6/30/15) **On Track**
- 5) Identify the mechanisms of ALD and MLD coated silicon anode for their improved chemical stability upon long cycling. (9/30/15) **On Track**

Progress Report

Effect of FEC additive on the electrochemistry and surface chemistry on DC-sputtered a-Si thin film electrodes

It is widely accepted that silicon suffers from mechanical and chemical degradation. In order to mitigate the mechanical degradation and focus on the forming a stable SEI, a-Si 50 nm thin film was cycled with traditional electrolyte (1:1 (wt%) ethylene carbonate (EC):diethylene carbonate (DEC)) and FEC-containing electrolyte (45:45:10 (wt%) EC:DEC:FEC) for 100 cycles. To understand how inclusion of FEC in the electrolyte affects SEI structure and evolution we attempt to reconcile these differing accounts of the reduction mechanism of FEC, by extending

previously developed anoxic and anhydrous analytical characterization techniques (XPS and TOF-SIMS) on a-Si thin film electrodes. Figure 42 presents the electrochemical data for the electrodes cycled with the traditional electrolyte and FEC containing electrolyte. After 100 cycles, the FEC containing electrolyte helps maintain capacity retention above 3000 mAhg⁻¹ after the 100th delithiation. Conversely, the film in the traditional electrolyte suffers from severe capacity fading; after 100 cycles the delithiated capacity is only 1252 mAhg⁻¹. The high capacity and coulombic efficiency retained in the electrode cycled with FEC is largely due to the evolution of a stable SEI.

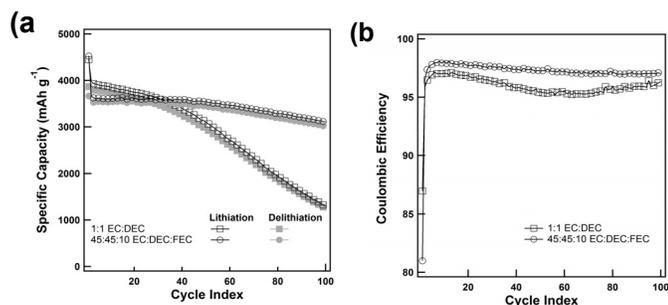


Figure 42: (a) Specific capacity versus cycling for galvanostatic cycling of a-Si thin films at C/2 rate and (b) Coulombic efficiency comparison of cells cycled with traditional electrolyte, 1:1 EC:DEC (squares), and FEC-containing electrolyte, 45:45:10 EC:DEC:FEC (circles).

The XPS and TOF-SIMS were used to investigate the differences in SEI formation as a function of electrolyte additive. DC-sputtered silicon electrodes in the same two electrolyte mixtures underwent the

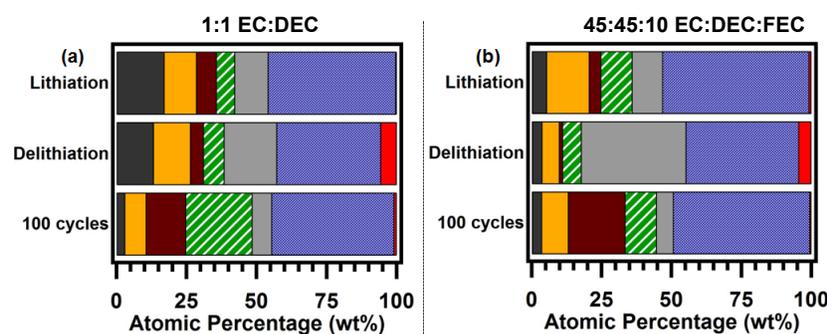


Figure 43: A relative composition of the 10nm outer SEI after: first lithiation; first delithiation; and 100 cycles. The layer resulted from and was in fluid communication with electrolyte comprising (a) 1:1 EC:DEC and (b) 45:45:10 EC:DEC:FEC.

following galvanostatic conditions: (1) a single lithiation event; (2) one complete lithiation and delithiation cycle and; (3) 100 cycles. The relative chemical compositions were determined by XPS analysis, and are shown in Figure 43. We observed subtle yet critical changes in the chemical composition and structure between the SEI resulting from the two electrolytes. First, from the XPS, the SEI resulting from the FEC-containing electrolyte shows increase in inorganic species, specifically LiF which little change throughout cycling. Moreover, after 100 cycles the electrode cycled with the FEC-containing electrolyte, contains more ester and carboxylates (ROCO) and fewer carbonate species than its counterpart. These subtle differences allows for a more stable SEI in the FEC-containing electrolyte. With regards to the structure of the SEI, the TOF-SIMS shows that there is an increase signal from the Si₂⁻ secondary ion indicating the SEI/silicon active material interface. During the first lithiation, the SEI on the electrode cycled with FEC is thicker compared to the electrode cycled with the traditional electrolyte. There is a high degree of overlap between organics and inorganics during the delithiated state in both electrolytes. A more detailed analysis is underway.

Improvement on first cycle columbic efficiency for optimized Si powder (50nm) based electrode

We have optimized various mixing parameters in order to achieve a high performance electrode based on 50nm Si powder. The electrode has an active mass loading of 0.5 mgcm^{-2} and cycled with the traditional electrolyte (without FEC). The electrode exhibited an initial coulombic efficiency of 88.8 % with a charge capacity of 1.46 mAhcm^{-2} . The SEI formation on 50 nm crystalline silicon nanoparticles and carboxymethyl cellulose (250,000 MW) as a binder will be studied using STEM/EELS.

Task 5.6 – Gabor Somorjai (UC Berkeley), Phil Ross (Lawrence Berkeley National Laboratory)

Analysis of Film Formation Chemistry on Silicon Anodes by Advanced *In Situ* and *Operando* Vibrational Spectroscopy

PROJECT OBJECTIVE: Understand the composition, structure, and formation/degradation mechanisms of the solid electrolyte interface (SEI) on the surfaces of Si anodes during charge/discharge cycles by applying advanced *in-situ* vibrational spectroscopies. Determine how the properties of the SEI contribute to failure of Si anodes in Li-ion batteries in vehicular applications. Use this understanding to develop electrolyte additives and/or surface modification methods to improve Si anode capacity loss and cycling behavior.

PROJECT IMPACT: A high capacity alternative to graphitic carbon anodes is Si, which stores 3.75 Li per Si versus 1 Li per 6 C yielding a theoretical capacity of 4008 mAh/g versus 372 mAh/g for C. But Si anodes suffer from large first cycle irreversible capacity loss and continued parasitic capacity loss upon cycling leading to battery failure. Electrolyte additives and/or surface modification developed from new understanding of failure modes will be applied to reduce irreversible capacity loss, improve long term stability and cyclability of Si anodes for vehicular applications.

OUT-YEAR GOALS: Extend the study of interfacial processes with advanced vibrational spectroscopies to high voltage oxide cathode materials. The particular oxide to study will be chosen based on materials of interest at that time and availability of the material in a form suitable for these studies, e.g. sufficiently large crystals or sufficiently smooth/reflective thin films. The effect of electrolyte composition, electrolyte additives, and surface coatings will be determined and new strategies for improving cycle life developed.

COLLABORATIONS:

Chunmei Ban (NREL) Functionalization of Si by Atomic Layer Deposition (ALD): Effect of functionalization on electrolyte reduction

Gao Liu (LBNL) Surface electrochemistry of electrolyte additives on model Si electrodes

Milestones

- 1) Determine the reduction products of the electrolyte additive FEC on a characteristic Si electrode and relate composition to the function in cycling. (Dec-14)**Completed**
- 2) Determine the role of $-O_x$ and $-OR$ ($R = H, CH_3, C_2H_5$, etc.) surface functional groups on baseline electrolyte reduction chemistry (Mar-15)**On schedule**
- 3) Determine role of the Si surface morphology, e.g. roughness, on the SEI formation structure and cycling properties (Jun-15)**On schedule**
- 4) Go/No-Go: Feasibility of surface functionalization to improve SEI structure and properties. Criteria: Functionalize a model Si anode surface and determine how SEI formation is changed. (Sep-15)**On schedule**

Progress Report

In Q1, additive molecular (VC, FEC) decomposition mechanism on Li foil was investigated. The surface reaction initiated when the native surface layer on metallic Li foil was scrapped off in VC and FEC solvent with/without LiPF₆ salt, with emersion time of 1 min. The whole procedure was performed in Ar filled glove box. After removing the Li foil from the electrolyte solvent, the samples were transferred to FTIR spectrometer under Ar environment, ensuring no air exposure.

To improve the understanding of passive film formation on battery electrode in organic electrolyte with additives (like VC, FEC), it is crucial to analyze the decomposition mechanisms of these additives on Li foil. As shown in Figure 44, based on the synthesized poly-VC standard spectra, the VC additive reduction compound has been assigned to poly-VC or its oligomer, which is similar to the spectra taken from Si electrode. Moreover, the additional peaks shown up at ~2921, 2851, 1677 and 1268 cm⁻¹ may come from ROCO₂Li or oxalate fragment, indicating that the reaction path of VC decomposition on Li surface can go through ring-opening as well. For the surface species formed on Li foil after exposed in FEC solvent, most obvious new features are the at ~2921, 2851cm⁻¹ and 1653, 1319cm⁻¹. Comparing to the spectra from VC, the decomposition product of FEC seems to be dominated by the ROCO₂Li. Though the specific product is not clear yet, we found that the surface species was similar to pure EC decomposition on Li. In both VC and FEC tests, the addition of LiPF₆ does not affect the reaction on the Li foil.

With low vapor pressure of VC and FEC, it is challenging to remove residual signal. However, we are still able to obtain good FTIR signal of additive VC and FEC decomposition product on Li surface without disturbance from other organic co-solvent. Additional characterizations are required to better interpret VC and FEC decomposition mechanism.

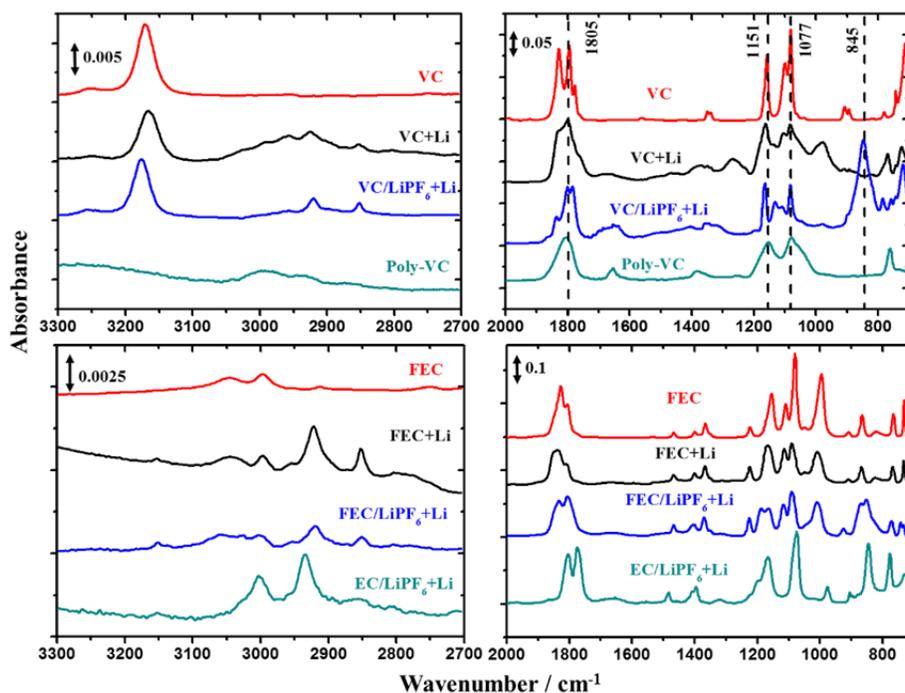


Figure 44: FTIR spectra of surface film formed by reacting metallic Li with VC, VC/LiPF₆, FEC, FEC/LiPF₆ and EC/LiPF₆ solvents in comparison with pure VC, FEC, and poly-VC.

Task 5.7 – Chongmin Wang (Pacific Northwest National Laboratory)

Project Title: Microscopy Investigation on the fading mechanism of electrode materials

PROJECT OBJECTIVE:

The objective of this work is to use *ex-situ*, *in situ* and *operando* high-resolution transmission electron microscopy (TEM) and spectroscopy to probe the fading mechanism of electrode materials. The focus of the work will be on using *in situ* TEM under real battery operating conditions to probe the structural evolution of electrodes and interfaces between the electrode and electrolyte and correlate this structural and chemical evolution with battery performance. The following three questions will be addressed:

- How do the structure and chemistry of electrode materials evolve at a dimension ranging from atomic-scale to meso-scale during the charge and discharge cycles?
- What is the correlation of the structural and chemical change to the fading and failure of lithium (Li)-ion batteries?
- How does the interface evolve between the electrode and the electrolyte and their dependence on the chemistry of electrolytes?

PROJECT IMPACT:

- Most previous microscopic investigations on solid-electrolyte interphase (SEI) layer formation and morphology evolution on electrodes are either *ex situ* studies or used low-vapor-pressure electrolytes so they cannot reveal the details of the dynamic information under practical conditions. We have developed new *operando* characterization tools to characterize SEI formation and electrode/electrolyte interaction using practical electrolyte that are critical for making new breakthroughs in this field. The success of this work will increase the energy density of Li-ion batteries and accelerate market acceptance of electrical vehicles (EV), especially for plug-in hybrid electrical vehicles (PHEV) required by the EV Everywhere Grand Challenge proposed by DOE/EERE.

OUT-YEAR-GOALS:

- Extended the *in situ* TEM capability for energy storage technology beyond Li ions, such as Li-S, Li-air, Li-metal, sodium ions, and multi-valence ions
- Multi-scale (i.e., ranging from atomic scale to meso-scale) *in situ* TEM investigation of failure mechanisms for energy-storage materials and devices (both cathode and anode)
- Integration of the *in situ* TEM capability with other microscopy and spectroscopy methods to study energy-storage materials, such as *in situ* SEM, *in situ* SIMS, and *in situ* x-ray diffraction
- Atomic-level *in situ* TEM and scanning transmission electron microscopy (STEM) imaging to help develop a fundamental understanding of electrochemical energy-storage processes and kinetics of both cathodes and anode

COLLABORATIONS: Dr. Chunmei Ban (NREL); Dr. Gao Liu (LBNL); Dr. Khalil Amine (ANL); Professor Yi Cui (Stanford); Dr. Jason Zhang (PNNL); Dr. Jun Liu (PNNL); Guoying Chen (LBNL). Dr. Xingcheng Xiao (GM).

Milestones

- 1) Establish the methodology that enables reliably positioning of a nanowire on the chip to assembly the closed liquid cell. Complete the *in-situ* TEM study of the behavior of native oxide layer during lithiation and delithiation (12/31/2014). **Completed.**
- 2) Complete quantitative measurement of coating layer and SEI layer thickness as a function of cycle number on a Si anode in a liquid cell with a practical electrolyte (03/31/2015). **Ongoing.**
- 3) Complete the *operando* TEM study of cathode materials with/without coating layer and the SEI layer formation (9/30/2015). **Ongoing.**

Progress Report

Using S/TEM equipped with HAADF/ABF detectors, EDS and EELS, the direct correlation between structural and electrochemical degradation of Li_2MnO_3 has been systematically investigated. Based on atomic level structural imaging, elemental mapping of the pristine and cycled samples (1-cycle, 10-cycles, 45-cycles) with the pristine sample and density functional theory calculations, it is found that structural degradation occurs from the very first cycle and is spatially initiated from the surface of the particle and propagates towards the inner bulk as cyclic number increase, featuring the formation of the surface phase transformation layer and gradual thickening of this layer. The structure degradation is found to follow a sequential phase transformation: monoclinic $\text{C2/m} \rightarrow$ tetragonal $\text{I4}_1 \rightarrow$ cubic spinel, which is consistently supported by the decreasing lattice formation energy based on DFT calculations. For the first time, high spatial resolution quantitative chemical analysis reveals that 20% oxygen in the surface phase transformation layer is removed and such newly developed surface layer is a Li-depleted layer with reduced Mn cations (Figure 45).

EELS analysis indicates that the surface phase transformation layer (including I4_1 and spinel phases) has little Li content and the tetravalent Mn cations are partially reduced to lower valence states. By combining the TEM microanalysis with electrochemical data, along with DFT calculations, the relationship between the structure degradation and cell performance degradation of Li_2MnO_3 cathode has been clarified. Since Li_2MnO_3 cathode is the parent compound for LMR cathode, this work will enhance our understanding on the degradation mechanism of LMR cathode materials during cycling.

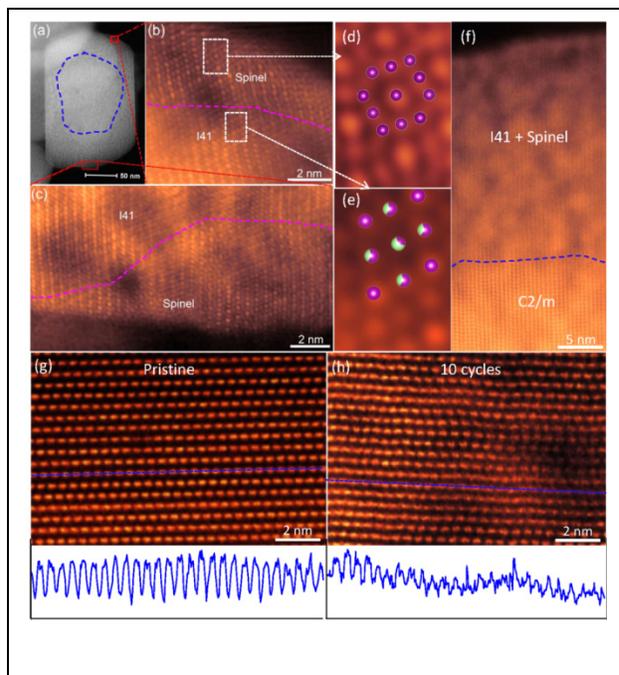


Figure 45: (a-c) [010] zone STEM-HAADF images to show a 10-cycles Li_2MnO_3 particle and its outer surface lattice structure. (d) and (e) highlight the lattice difference between Mn_3O_4 -spinel and I4_1 structure. Purple and green indicate Mn and Li, respectively. (f) [100] zone STEM-HAADF image of the surface layer after 10 cycles. STEM-HAADF images to show inner bulk lattice structure of pristine sample (g) and 10-cycles sample (h). The intensity profile along the blue lines in (g) and (h) are shown in each figure.

Q1 Patents/Publications/Presentations

1. Yang He, Chunmei Ban, Arda Genc, Lee Pullan, Jun Liu, Ji-Guang Zhang, Scott Mao, and Chongmin Wang, “In-Situ Transmission Electron Microscopy Probing of Native Oxide and Artificial Coating Layer on Silicon Nanoparticles for Lithium Ion Batteries”, ACS Nano, 8, 11816-11823, 2014.
2. Pengfei Yan, Anmin Nie, Jianming Zheng, Yungang Zhou, Dongping Lu, Xiaofeng Zhang, Rui Xu, Ilias Belharouak, Xiaotao Zu, Jie Xiao, Khalil Amine, Jun Liu, Fei Gao, Reza Shahbazian-Yassar, Ji-Guang Zhang, and Chong-Min Wang, “Evolution of lattice structure and chemical composition of the surface reconstruction layer in $\text{Li}_{1.2}\text{Ni}_{0.2}\text{Mn}_{0.6}\text{O}_2$ cathode material for Lithium ion batteries”, Nano Letter. 14, published on line, 2014.
3. Pengfei Yan, Jiguang Zhang, Chongmin Wang, “Microscopic Characterization of Structural and Chemical Evolution of $\text{Li}_{1.2}\text{Ni}_{0.2}\text{Mn}_{0.6}\text{O}_2$ Cathode Material upon Cycling”, Presented at MRS 2014 Fall Meeting, Boston, November 29, 2014.

Task 5.8 – Michael M. Thackeray and Jason R. Croy (Argonne National Laboratory)

Energy Storage Materials Research using DOE's User Facilities

PROJECT OBJECTIVE:

The primary objective of this project is to explore the fundamental, atomic-scale processes which are most relevant to the challenges of next-generation, energy-storage technologies. To this end, a wide array of unique capabilities available at user facilities throughout the US National Laboratory system will be brought together to focus on challenging experimental problems. X-ray and neutron diffraction, pair distribution function analysis, and X-ray absorption, emission and scattering, and high resolution transmission electron microscopy can be combined to give an unparalleled look into the structural, electrochemical and chemical mechanisms at play in complex electrode/electrolyte systems. A deeper understanding of these systems will rely on novel and challenging experimental work; work that is only possible through unique user-facility resources. The goal of this project is therefore to capitalize on these facilities to advance the field through cutting-edge science, collaborations, and multi-disciplinary efforts.

PROJECT IMPACT:

This project is being implemented because the user facilities of DOE's National Laboratories possess capabilities, scientists, and technologies which are not available on such a scale anywhere else in the world. Capitalizing on, and exploiting the DOE's user facilities and infrastructure (including skilled and trained personnel) will produce knowledge of fundamental importance to the advancement of energy-storage technologies. Specifically, the gathering of a fundamental understanding of structure-electrochemical property relationships and degradation mechanisms will contribute significantly to meeting the near-to-long term goals of EV and PHEV technologies. This knowledge can only be achieved through projects such as this which are less feasible for large-scale battery developers or through smaller-scale, university projects.

OUT-YEAR-GOALS:

- Gain new, fundamental insights into complex structures and degradation mechanisms of composite cathode materials from novel, probing experiments carried out at user facilities.
- Establish structure-property relationships that will provide insight into the design of improved cathode materials.
- Develop and scale up advanced cathode materials in practical lithium-ion prototype cells, based on the knowledge and understanding gained from this project.

COLLABORATIONS: Mahalingam Balasubramanian (ANL-APS); Dean Miller (ANL-EMC); Bill David and Tom Wood (Rutherford Appleton Laboratory, UK).

Milestones

- 1) Evaluation of lithium-ion battery electrodes using DOE User Facilities at Argonne (APS, EMC and ALCF) and facilities elsewhere, e.g., neutron spallation sources at SNS (Oak Ridge) and ISIS, Rutherford Laboratory (UK). (Sep-15). **In progress.**
- 2) Evaluation of Li_2MnO_3 end member and composite $\text{Li}_2\text{MnO}_3 \bullet (1-x)\text{LiMO}_2$ (M = Mn, Ni, Co) structures by combined neutron/X-ray diffraction. (Sep-15). **In progress.**
- 3) Evaluation of transition metal migration in lithium-metal-oxide insertion electrodes. (Sep-15). **In progress. (See text)**
- 4) Analysis, interpretation, and dissemination of collected data for publication and presentation. (Sep-15).

Progress Report

An underlying emphasis of this project, as listed in the Out-Year-Goals, is to understand structure property relationships and atomic-scale processes that control performance and degradation of cathode materials. Model systems and experiments can be useful to give insights into the mechanisms at play in more complex systems. Cation migration in layered cathode materials appears to be a general phenomenon related to cation charge as well as lithium vacancy concentrations. In addition, small concentrations of dopant atoms are often incorporated as stabilizing constituents. However, the mechanisms of stabilization are not clear for all dopant types, active vs. non-redox active, and much of the theory available is generated from highly delithiated structures, for example, $x \geq 0.5$ in $\text{Li}_{1-x}\text{MO}_2$. A study has been undertaken on the model system, LiCoO_2 , with and without non-redox active Ga doping. Small amounts of Ga can be uniformly doped into the transition metal layers of the R3-m LiCoO_2 structure and the local environments during charge and discharge can be well-distinguished in X-ray absorption (XAS) experiments.

Figure 46(a) shows the magnitude of the Fourier-transformed, Ga K-edge EXAFS for $\text{Li}/\text{LiCo}_{1-x}\text{Ga}_x\text{O}_2$ cells with $x=0.05$, collected in fluorescence geometry, charged and discharged to the noted capacities. For the as-prepared sample, fits of the local Ga environment [Figure 46 (b)] reveals coordination numbers (~ 6) and bond distances ($\text{Ga-O} \approx 2.0 \text{ \AA}$, $\text{Ga-Metal} \approx 2.9 \text{ \AA}$) consistent with uniform doping into the LiCoO_2 matrix. An interesting observation is that when charged to just 30 mAh/g ($\sim 10\%$ of theoretical) significant Ga migration into the tetrahedral sites of the lithium layers is observed. This is revealed through severe damping of the Ga-Metal correlations at $\sim 2.5 \text{ \AA}$ (uncorrected for photoelectron wave phase shift) and the growth of a new peak just above 3 \AA , also corroborated through the fits shown in Figure 46 (b) giving Ga-Co distances of $\sim 3.3 \text{ \AA}$. When charged to 150 mAh/g, $\sim 100\%$ of the Ga is observed to migrate into the tetrahedral sites. Upon discharge, the best fit scenario reveals that, again, $\sim 100\%$ of the migrated Ga is returned to the octahedral sites of the transition metal layers. The migration of Ga, while seemingly reversible, results in a $\sim 40\%$ increase in the disorder parameter, σ^2 , of the octahedral-octahedral bonds of the $\text{LiCo}_{0.95}\text{Ga}_{0.05}\text{O}_2$ structure. Similar results were obtained for the $x=0.075$ sample.

Figure 46 (c) shows electrochemical cycling to 20 mAh/g at 0.2 mA/g for $x=0, 0.05$, and 0.075 . Compared to the undoped LiCoO_2 , Ga doping changes the initial lithium extraction processes occurring in the electrode. In agreement with the EXAFS data, changes in the doped samples relative to the pure LiCoO_2 are observed at very low levels of delithiation shown for cycle 2 in Figure 46 (c).

Nuclear magnetic resonance (NMR) combined with theory and simulations are currently being explored to better understand the processes and implications of these data and the role of active vs. non-redox active dopants in cathode structures. This information will provide greater insight into the migration of transition metal ions and voltage decay in lithium-rich, high capacity NMC electrodes.

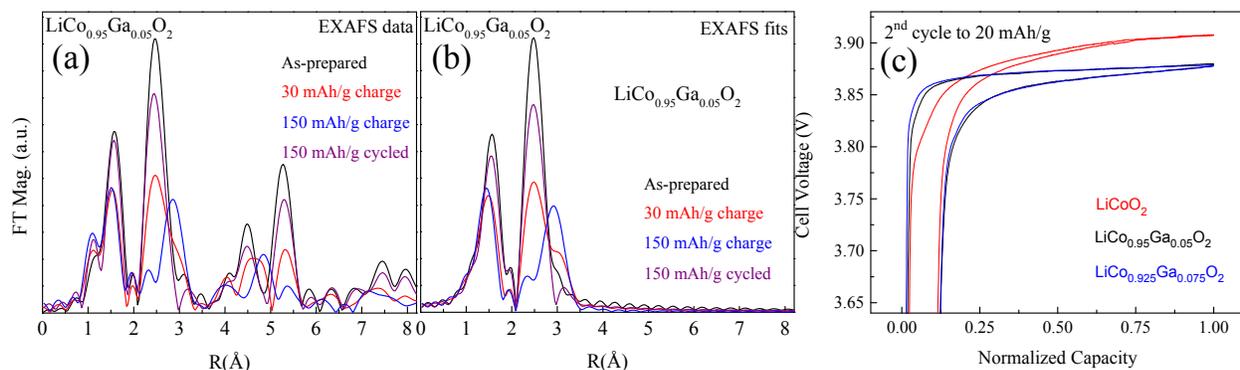


Figure 46: (a) Ga K-edge EXAFS and (b) corresponding fits of cycled $\text{Li}/\text{LiCo}_{0.95}\text{Ga}_{0.05}\text{O}_2$ cells. (c) A comparison of delithiation behavior on cycle 2 for $\text{Li}/\text{LiCo}_{1-x}\text{Ga}_x\text{O}_2$ cells ($x=0, 0.05$, and 0.075) cycled to 20 mAh/g at 0.2 mA/g.

Q1 Patents/Publications/Presentations

None.

TASK 6 – MODELING ADVANCED ELECTRODE MATERIALS

Summary and Highlights

Achieving the performance, life, and cost targets outlined in the *EV Everywhere* grand challenge will require moving to next generation chemistries, such as higher capacity Li-ion intercalation cathodes, silicon and other alloy-based anodes, lithium metal anode, and sulfur cathodes. However, numerous problems plague the development of these systems, from material level challenges in ensuring reversibility to electrode level issues in accommodating volume changes, to cell-level challenges in preventing cross talk between the electrodes. In this task, a mathematical perspective is applied to these challenges in order to provide an understanding of the underlying phenomenon and to suggest solutions that can be implemented by the material synthesis and electrode architecture groups.

The effort spans multiple length scales from *ab initio* methods to continuum-scale techniques. Models are combined with experiments and extensive collaborations are established with experimental groups to ensure that the predictions match reality. Efforts are also focused on obtaining the parameters needed for the models either from lower length scale methods or from experiments. Projects also emphasize pushing the boundaries of the modeling techniques used to ensure that the task stays on the cutting edge.

In the area of intercalation cathodes, the effort is focused on understanding the working principles of the high Ni layered materials with an aim of understanding structural changes and the associated changes in transport properties. In addition, focus is paid to the assembling of porous electrodes with particles to predict the conduction behavior and developing tools to measure electronic conduction.

In the area of silicon anodes, the effort is focused on understanding the interfacial instability and suggesting ways to improve the cycleability of the system. Additional effort is focused on designing artificial SEI layers that can accommodate the volume change, and in understanding the ideal properties for a binder to accommodate the volume change without delamination.

In the area of sulfur cathodes, the focus is on developing better models for the chemistry with the aim of describing the precipitation reactions accurately. Efforts are focused on performing the necessary experiments to obtain a physical picture of the phase transformations in the system and in measuring the relevant thermodynamic, transport, and kinetic properties. In addition, changes in the morphology of the electrode are described and tested experimentally.

Finally, microstructure models are an area of focus to ensure that the predictions move away from average techniques to more sophisticated descriptions of processes inside electrodes. Efforts are focused on understanding conduction within the electrode and also on simulating the full electrode that describe the intricate physics inside the battery electrode. These efforts are combined with tomography information as input into the models.

Task 6.1 – Venkat Srinivasan (Lawrence Berkeley National Laboratory)

Electrode Materials Design and Failure Prediction

PROJECT OBJECTIVE: The goal of this project is to use continuum-level mathematical models along with controlled experiments on model cells to (i) understand the performance and failure models associated with next-generation battery materials, and (ii) design battery materials and electrodes to alleviate these challenges. The focus of the research will be on the Li-S battery chemistry and on microscale modeling of electrodes. The initial work on the Li-S system will include developing a mathematical model for the chemistry along with obtaining the necessary experimental data using a single ion conductor (SIC) as a protective layer to prevent polysulfide migration to the Li anode. The initial work on microscale modeling will use the well-understood $\text{Li}(\text{NiMnCo})_{1/3}\text{O}_2$ (NMC) electrode to establish a baseline for modeling next-generation electrodes.

PROJECT IMPACT: Li-S cells promise to increase the energy density and decrease the cost of batteries compared to the state-of-the-art. If the performance and cycling challenges can be alleviated, these systems hold the promise for meeting the EV-Everywhere targets.

OUT-YEAR-GOALS: At the end of this project, a mathematical model will be developed that can address the power and cycling performance of next-generation battery systems. The present focus is on microscale modeling of electrodes and Li-S cells however, the project will adapt to newer systems if appropriate. The models will serve as a guide for better design of materials, such as, the kinetics and solubility needed to decrease the morphological changes in sulfur cells and increase the power performance.

COLLABORATIONS: Gao Liu (LBNL), Nitash Balsara (LBNL), Dula Parkinson (ALS).

Milestones

- 1) Develop a model of a Li-S cell incorporating concentration solution framework (Due on 12/31/14). **Status: Complete**
- 2) Develop a custom Li-S electrochemical cell with small (~200 μm) catholyte layer incorporating a SIC. (Due on 3/31/15) Stop custom cell development if unable to prevent SIC damage during cell assembly. **Status: In progress**
- 3) Use custom cell to perform rate experiments (Due on 6/30/15). If unsuccessful in developing custom cell, develop cell without SIC and measure shuttle current. **Status: Waiting for outcome of Q2**
- 4) Compare microscale and macroscale simulation results and experimental data to determine the importance of microstructural detail (Due on 9/30/15). **Status: In progress**

Progress Report

Li-S cell modeling: In this quarter, a theoretical model based on concentrated solution theory, involving concentration-dependent transport properties has been developed. While much needed model parameters are not yet available, this comprehensive model will be updated as more parameters are determined through our complementary experimental work. Figure 47 compares the solid Li_2S distribution profile at the end of a relatively fast discharge (3.5C) as computed by two models: an updated model with measured electrolyte conductivity (“Updated”) and a model based on dilute solution theory (“Dilute”), demonstrating the importance of incorporating accurate transport properties. The sulfur loading of the simulated cell is 1.36 mg/cm^2 , with a cathode thickness of $41 \mu\text{m}$. The dilute model simulation shows almost uniform Li_2S distribution, while the updated model predicts a stronger tendency for Li_2S to deposit near the separator. The latter result is qualitatively consistent with previous experimental studies at high discharge rates. This suggests that the updated model is a better predictor of cell performance. The development of this updated model fulfills the Q1 milestone.

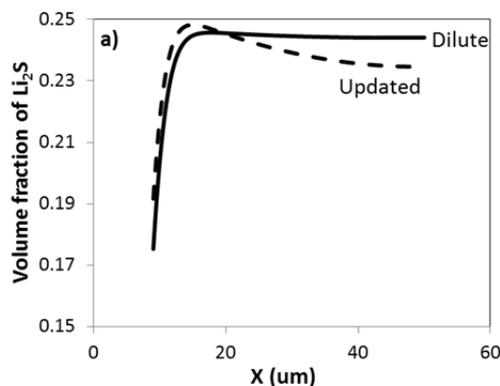


Figure 47: Updated model (Updated) and Dilute model (Dilute) predictions of Li_2S deposition at 3.5 C discharge current throughout cathode at the end of discharge

Custom Li-S cell with small catholyte layer: An initial design for a novel Li-S cell has been developed. It incorporates and mechanically protects a fragile single-ion conductor (SIC) while maintaining a catholyte layer much smaller than $200 \mu\text{m}$. In the next quarter, an iterative process of fabrication and design modification will be used in order to create the custom cell described in the Q2 milestone, which will then be used for the rate experiments planned for the Q3 milestone.

Microscale simulation: A tentative workflow for obtaining X-ray tomography images of NMC porous electrodes (generated at the Advanced Light Source at LBNL) and processing the data into simulation domains has been developed. Simple simulations on sample microstructural domains have been successfully performed on the Lawrence Livermore cluster at LBNL. These processes will require further refinement and will be united into a single workflow in order to perform the microscale simulations required by the Q4 milestone.

Task 6.2 – Kristin Persson (Lawrence Berkeley National Laboratory)

Predicting and Understanding Novel Electrode Materials from First-Principles

PROJECT OBJECTIVE: The aim of the Project is to model and predict novel electrode materials from first-principles by focusing on 1) understanding the atomistic interactions behind the behavior and performance of the high-capacity lithium excess and related composite cathode materials and 2) predict new materials using the recently developed Materials Project high-throughput computational capabilities at LBNL. More materials and new capabilities will be added to the Materials Project Lithium Battery Explorer App (www.materialsproject.org/apps/battery_explorer/).

PROJECT IMPACT: The project will result in a profound understanding of the atomistic mechanisms underlying the behavior and performance of the Li-excess as well as related composite cathode materials. The models of the composite materials will result in prediction of voltage profiles and structural stability; the ultimate goal being to suggest improvements based on the fundamental understanding that will increase the life and safety of these materials. The Materials Project aspect of the work will result in improved data and calculated electrode properties to aid predictions of new materials for target chemistries relevant for ongoing ABMR projects.

OUT-YEAR GOALS: During year 1-2, the bulk phase diagram will be established – including bulk defect phases in layered Li_2MnO_3 , layered LiMO_2 ($M = \text{Co}, \text{Ni}, \text{and Mn}$) and LiMn_2O_4 spinel to map out the stable defect intermediate phases as a function of possible transition metal rearrangements. Modeling of defect materials (mainly Li_2MnO_3) under stress/strain will be undertaken to simulate effect of composite nano-domains. The composite voltage profiles as function of structural change and Li content will be obtained. In year 2-4, the project will focus on obtaining Li activation barriers for the most favorable TM migration paths as a function of Li content. Year 2-4 will also focus on electronic DOS as a function of Li content for the most stable defect structures identified in year 1-2. Furthermore, stable crystal facets of the layered and spinel phases will be explored, as a function of O_2 release from surface and oxygen chemical potential. Within the Materials Project, hundreds of novel Li intercalation materials will be calculated and made available.

COLLABORATIONS: Gerbrand Ceder (MIT), Clare Grey (U Cambridge, UK). Mike Thackarey (ANL), Guoying Chen (LBNL).

Milestones

- 1) Mn mobilities as a function of Li content in layered Li_xMnO_3 and related defect spinel and layered phases (3/31/14) **Delayed**
- 2) Surface facets calculated and validated for Li_2MnO_3 (3/31/14) **Ongoing**
- 3) Calculate stable crystal facets. Determine whether facet stabilization is possible through morphology tuning. (6/30/14) **Ongoing**
- 4) Go/No-Go: Stop this approach if facet stabilization cannot be achieved. (6/30/14)
- 5) Li mobilities as a function of Li content in layered Li_xMnO_3 and related defect spinel and layered phases (9/30/14) **Ongoing**

Progress Report

We are continuing to work toward understanding the fundamental limitations of the layered Li excess materials performance, primarily Li_2MnO_3 and related $\{\text{Co},\text{Ni}\}$ solid solution phases. In the previous year, we established the thermodynamic landscape of stable structures in this class of materials, spanning the layered, defect-layered and spinel-defect phases. While the layered Li_2MnO_3 is stable at high Li content, it is rendered highly unstable against Mn migration into the Li layer when more than 1 Li/TM is removed (Figure 48). The Mn activation barriers are found to support this migration, at medium to low Li content. We also elucidated that, in the pure Mn material, the charging process largely resides on the oxygen ion. Oxygen oxidation has been observed in other Li intercalation materials – such as LiCoO_2 – however, at smaller scale and always in hybridization with the transition metal. We found that oxygen release is thermodynamically favorable at Li content less than 1/TM, however, oxygen migration barriers remain high throughout the composition range, which limits the oxygen release process to the surface region.

During FY 2015, we are focusing on understanding Li diffusion bottlenecks, particularly related to the Li content, and the impact of Mn migration into the Li layer. We are also starting to investigate the surface morphology of Li_2MnO_3 phases and their instability towards oxygen release, Mn dissolution etc.

This effort has been somewhat delayed due to the hiring of a replacement postdoctoral associate (arriving Jan 22, 2015). However, the first Li migration barriers have been calculated in the pristine layered phase as well as under some Mn defect formation. The existing cluster expansion will be used as a basis for a kinetic Monte Carlo investigation of Li diffusivity as a function of Li concentration and Mn defect formation.

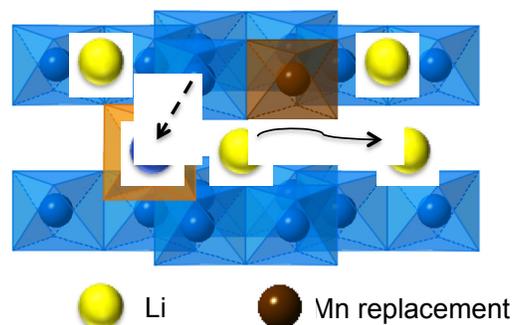


Figure 48: A schematic of a migrated TM impacting Li migration in the Li layer.

Task 6.3 – Gerbrand Ceder (MIT)

First Principles Calculations of Existing and Novel Electrode Materials

PROJECT OBJECTIVE: Identify the structure of layered cathodes that leads to high capacity. Clarify the role of the initial structure as well as structural changes upon first charge and discharge. Give insight into the role of Li-excess and develop methods to predict ion migration in layered cathodes upon cycling and during overcharge. Develop predictive modeling of oxygen charge transfer and oxygen loss. Give insight into the factors that control the capacity and rate of Na-intercalation electrodes, as well as Na-vacancy ordering. Develop very high capacity layered cathodes with high structural stability (> 250 mAh/g).

PROJECT IMPACT: The project will lead to insight in how Li excess materials work and ultimately to higher capacity cathode materials for Li-ion batteries. The project will help in the design of high capacity cathode materials that are tolerant to transition metal migration.

OUT-YEAR GOALS: Higher capacity Li-ion cathode materials, and novel chemistries for higher energy density storage devices. Guide the field in the search for higher energy density Li-ion materials..

COLLABORATIONS: Persson (LBNL), Grey (Cambridge U).

Milestones

- 1) Demonstrate capability to accurately predict oxygen redox activity in cathode materials by comparing calculations to spectroscopic data. (Dec-31) **Completed**
- 2) Develop model for effect of Li-excess in $\text{Li}(\text{Li},\text{Ni},\text{Sb})\text{O}_2$. **Ongoing**
- 3) Develop model for Na-vacancy ordering in Na-intercalation compounds. **Ongoing**
- 4) Identify at least one other disordered material with high reversible capacity. **Ongoing**

Progress Report

As part of our objective to identify the structure of layered cathodes that leads to high capacity, we have developed an accurate first-principles calculation methodology this quarter for predictive modeling of oxygen redox activity, which has been proposed as a possible source of the excess lithium extraction capacity in lithium-rich TM oxide intercalation materials.

The observed electrochemical capacity in Li-excess materials can often exceed that dictated by their transition metal (TM) redox content unlike in common stoichiometric Li-ion cathode materials such as LiCoO_2 , LiMn_2O_4 , or LiFePO_4 . To conclusively isolate the source of “excess” capacity with first-principles calculations, however, improvements in accuracy over traditional density function theory (DFT) techniques on the level of the general gradient approximation *GGA* and *GGA+U* are required. Specifically, a materials system that undergoes possibly both TM and oxygen redox requires investigation with a reliable computational methodology that can accurately predict the charge transfer between oxygen, lithium, and TM atoms as well as their redox potentials.

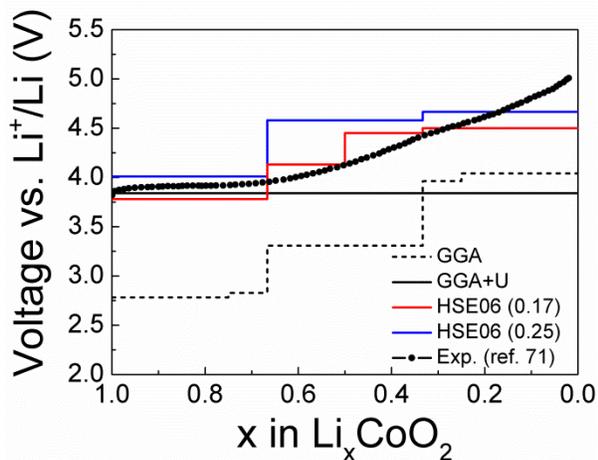


Figure 50: Computed voltage profiles of $\text{Li}_{1-x}\text{CoO}_2$ ($0 \leq x \leq 1$), as predicted by *GGA*, *GGA+U*, and *HSE* with different mixing parameters in comparison to the experimental reference.

This quarter, we have proposed and successfully benchmarked a new methodology for the accurate prediction of electronic structure properties of TM oxides and lithium TM oxides based on hybrid-functional calculations with optimized mixing parameters. Toward our project objective, our next task is to apply this methodology to lithium excess TM materials and accurately predict both the TM and oxygen redox potentials.

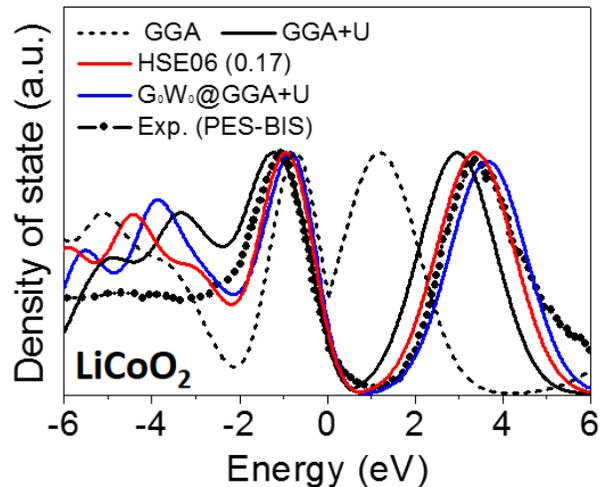


Figure 49: Density of states (DOS) of LiCoO_2 as predicted by various electronic structure methods in comparison to experimental spectroscopic measurement.

Our strategy has been to employ hybrid functionals (*HSE06*), which produce a more accurate representation of the electronic structure due to adding some amount of Hartree-Fock exchange through a tunable mixing parameter α , specifically optimized to reproduce experimental band gaps (or when unavailable, more computationally expensive but accurate *GW* calculations). Benchmarking the electronic structure of LiCoO_2 , the optimal α is found to be 0.17 (red line in Figure 49) and provides very good agreement with experiment in comparison to the *GGA* and *GGA+U* calculations which both underestimate the band gap. The computed voltage profiles for $\text{Li}_{1-x}\text{CoO}_2$ shown in Figure 50 show that *HSE06* with the optimized α (red line) also most accurately reproduces the experimental voltage curve.

Task 6.4 – Perla Balbuena (Texas A&M University)

First Principles Modeling of SEI Formation on Bare and Surface/Additive Modified Silicon Anode

PROJECT OBJECTIVE: This project aims to develop fundamental understanding of the molecular processes that lead to the formation of a solid electrolyte interphase (SEI) layer due to electrolyte decomposition on Si anodes; we will use such new knowledge in a rational selection of additives and/or coatings. The focus is on SEI layer formation and evolution during cycling and subsequent effects on capacity fade through two concatenated problems: 1) SEI layers formed on lithiated Si surfaces, and 2) SEI layers formed on coated surfaces. Key issues that this project addresses include the dynamic evolution of the system and electron transfer through solid-liquid interfaces.

PROJECT IMPACT: Finding the correspondence between electrolyte molecular properties and SEI formation mechanism, structure, and properties will allow the identification of new/improved additives. Studies of SEI layer formation on modified surfaces will allow the identification of effective coatings able to overcome the intrinsic deficiencies of SEI layers on bare surfaces.

OUT-YEAR GOALS: Investigating the SEI layer formed on modified Si surfaces involves: analysis of the interfacial structure and properties of specific coating(s) deposited over the Si anode surface, characterization of the corresponding surface properties before and after lithiation – especially how such modified surfaces may interact with electrolyte systems (solvent/salt/additive), and what SEI layer structure, composition, and properties may result from such interaction. This study will allow identification of effective additives and coatings able to overcome the intrinsic deficiencies of SEI layers on bare surfaces. Once the SEI layer is formed on bare or modified surfaces, it is exposed to cycling effects that influence its overall structure (including the anode), chemical, and mechanical stability. Elucidating such effects using a molecular level approach will help establish their relationship with capacity fading, which will lead to revisiting additive and/or coating design.

COLLABORATIONS: Work with Chunmei Ban (NREL, BATT) consists in modelling the deposition-reaction of trimethylaluminum and glycerol on Si surfaces and their reactivity. Work with B. Lucht (URI, BATT) relates to finding the best additives for optimum SEI formation on Si anodes. Reduction of solvents and additives on Si surfaces were studied in collaboration with K. Leung and S. Rempe (Sandia National Labs). Collaboration with Dr. Partha Mukherjee (TAMU) involved the development of a multi-scale model to describe the SEI growth on Si anodes.

Milestones

- 1) Identification of lithiation and SEI formation mechanisms through alucon coatings on Si surfaces.. (Dec-14) **Completed**
- 2) Clarify role of additives VC vs. FEC vs. solvent without additive on SEI properties. (Mar-15). **In progress**
- 3) Characterization of SEI mosaic formation from building blocks. (Jun-15) **In progress**
- 4) Go/No-Go: Prediction of irreversible capacity loss and electron transfer mechanisms through the SEI layer. Criteria: Stop KMC approach if no new physical insights are obtained (Sep-15) **In progress**

Progress Report

Lithiation and SEI formation mechanisms on silicon surfaces covered by alucon coatings: DFT evaluations of formation reactions of alucone coatings on hydroxylated Si surfaces showed that they are thermodynamically favorable. The structure of the film, estimated from the coupling of the basic units according to the experimental density, suggests the presence of many cross-links and branched chains. DFT analysis reveals that Al atoms can have 3-O and 4-O coordinations and various strong Li^+ binding structures with energies ranging from -2.6 to -3.3 eV. The binding of Li ions was found to be dependent on the position along the film thickness, but in all cases, the binding of Li to the film was found to be stronger than that to the silicon substrate. AIMD simulations showed that EC molecules are strongly adsorbed on the film surface when the carbonyl oxygen bonded with Al atoms from the film. However, in a low-lithiated film, no decomposition reaction is captured during the simulation period (4.5ps). Further studies on the lithiation of the film indicated that the film becomes saturated once all the favorable sites are occupied with Li; at that point further Li addition is not favorable. DFT-Green's function analysis of electron transfer through such highly lithiated film indicated that electron transfer is possible at those conditions, and new AIMD simulations of the Si electrode covered by the highly lithiated film showed the decomposition of EC molecules on its surface. Thus, the analysis clearly shows how a passivation layer could be formed on the surface of the highly lithiated film covering the electrode. All the results were discussed in collaboration with Chunmei Ban from NREL; manuscript is in preparation.

Role of additives vs. solvent on SEI properties: AIMD simulations demonstrated that SEI reduction reactions depend strongly on the composition of the electrolyte. Though the salt should reduce first, due to its higher reduction potential, the reduction reaction usually happens via electron transfer from the surface. It also depends on the proximity of the anion to the Li active surface sites. The other factor is the polarity of the solvent: solutions containing low-polar solvents, such as DEC, may decrease the frequency of salt dissociation and subsequent reduction. Once the PF_6^- anion is reduced, the first product is the radical PF_3 which is found to be relatively stable, remaining intact for a few to tens of picoseconds. The other products of the initial dissociation are F radicals that rapidly combine to form LiF on the surface. The radical PF_3 has various forms of further reaction with the P atom becoming reduced and ending association with Si atoms of the surface, or with other fragments of the solvent/additive decomposition. These simulations also revealed the existence of an alternative pathway for VC decomposition yielding CO_2 and other radical fragments that further react with the PF_3^- radical anion. Similar reactions of fragments of FEC decomposition with salt fragments are also observed. Finally, this work also showed for the first time the generation of radical O species as products of solvent or additive decomposition that interact with the surface and can be precursors of formation of Li oxides and Li silicate species. New AIMD simulations have revealed mechanisms of lithiation of SiO_2 films. As a result of these studies, a clear picture of SEI formation has emerged.

Voltage effects: Instantaneous voltages of bare or amorphous LiF_x -coated $\text{Li}_{3.25}\text{Si}$ (010) covered surfaces were evaluated with roughly a liquid monolayer of 9 EC molecules. The thin LiF_x coating slows down electron tunneling responsible for SEI formation, but it also changes the average voltage. For $x=1.14, 1.00, 0.93, 0.80$, and no LiF_x coating, the zero temperature voltages of $\text{Li}_{3.25}\text{Si}$ (010) are predicted to be 1.35, 0.86, 0.71, 0.63, and 1.28 V vs. $\text{Li}^+/\text{Li}(s)$, respectively, in the absence of EC molecules. On $\text{LiF}_{0.80}$ -coated $\text{Li}_{3.25}\text{Si}$ (010) covered surfaces with the 9-EC liquid film, the initial voltage is extremely low, and 2 EC molecules decompose rapidly. Conversely, the $\text{LiF}_{1.14}$ -coated surface induces no EC decomposition after 5 ps. This trend is consistent with voltage increases with F-content even in the absence of EC. This correlation arises because an increase of Li^+ content in the LiF_x film increases the surface dipole moment pointing inwards towards the electrode. The resulting surface dipole density lowers the voltage. In real liquid electrolytes, the Li:F ratio should be determined by the Li^+ chemical potential and is not free to vary. Instead, the voltage is controlled by counter anion density in the liquid region. Nevertheless, the control of voltage in the model system offers an electrostatic-based design principle that may improve artificial SEIs. Voltage calibration will be carried out for the alucon surface coatings.

Task 6.5 – Xingcheng Xiao (General Motors), Yue Qi (Michigan State University)

A Combined Experimental and Modeling Approach for the Design of High Current Efficiency Si Electrodes

PROJECT OBJECTIVE: The use of high capacity Si based electrodes has been hampered by its mechanical degradation due to the large volume expansion/contraction during cycling. Nanostructured Si can effectively avoid Si cracking/fracture. Unfortunately, the high surface to volume ratio in nanostructures leads to unacceptable amount of solid-electrolyte interphase (SEI) formation and growth, thereby low current/coulombic efficiency and short life. Based on mechanics models we demonstrate that the artificial SEI coating can be mechanically stable despite the volume change in Si, if the material properties, thickness of the SEI, and the size/shape of Si are optimized. Therefore, the objective of this project is to develop an integrated modeling and experimental approach to understand, design, and make coated Si anode structures with high current efficiency and stability.

PROJECT IMPACT: The validated model will ultimately be used to guide the synthesis of surface coatings and the optimization of Si size/geometry that can mitigate SEI breakdown. The optimized structures will eventually enable a negative electrode with a 10x improvement in capacity (compared to graphite) while providing a >99.99% coulombic efficiency, which could significantly improve the energy/power density of current LIB.

OUT-YEAR GOALS: The out year goal is to develop a well validated mechanics model that will directly import material properties either measured from experiments or computed from atomic simulations. The predicted SEI induced stress evolution and other critical phenomena will be validated against in-situ experiments in a simplified thin-film system. This comparison will also allow fundamental understanding of the mechanical and chemical stability of artificial SEI in electrochemical environments and the correlation between the coulombic efficiency and the dynamic process of SEI evolution. Thus, the size and geometry of coated Si nanostructures can be optimized in order to mitigate SEI breakdown, and therefore provide high current efficiency.

COLLABORATIONS: LBNL, PNNL.

Milestones

- 1) Identify SEI failure mode by using combined in-situ electrochemical experiments and modeling techniques developed in 2014 (12/31/14) (**Indented some failure modes, continue comparing individual SEI components**)
- 2) Reveal detailed SEI failure mode by using MD simulations with ReaxFF for Li-Si-Al-O-C system to model the deformation of SEI on a Si as it undergoes large strain. (3/31/15)
- 3) Correlate and determine the desirable material properties for stable SEI by applying the continuum model and experimental nanomechanics. Establish the material property design methodology for stabilizing SEI on Si. (6/30/15)
- 4) Make Go/No-Go decision on whether to select oxide, fluoridated, or carbon artificial SEI chemistry based on comparisons of their mechanical stability and transport properties. (9/30/15)

Progress Report

1) Identified the strain state and the lithiation voltage corresponding to the SEI mechanical failure and the subsequent SEI growth. A novel approach based on patterned Si islands, with complimenting measurements that include modified galvanostatic cycling, EIS, *in situ* optical microcopy, TOF-SIMS, and *in situ* stress states, was developed. By calibrating the expansion and contraction of these Si islands, and comparing with continuous Si films, the impact of large volume changes on the SEI stability was investigated. It was observed that because of lateral expansion and contraction of patterned Si islands, the SEI becomes unstable around 0.25V. TOF-SIMS data showed that the intensity of Li_2CO_3 , LiF and electrolyte reduction products is higher in case of Si islands compared to continuous film which complements the larger irreversible capacity of the continuous film. (See Figure 51.)

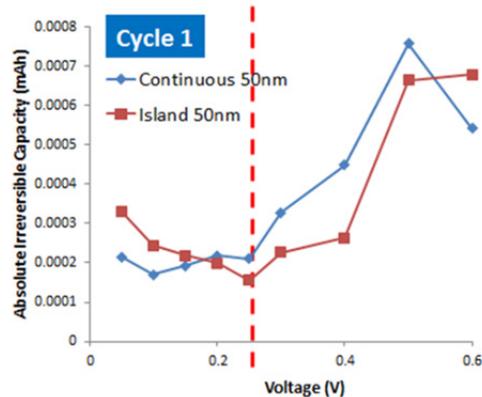


Figure 51: Investigation of large-volume changes on SEI stability

2) Investigated the contribution of pure LiF, Li_2CO_3 , and Li_2O as the artificial SEI layers to the cycle efficiency of Si film electrodes. The comparisons show these artificial SEI layers improve the cycling stability. The electrode coated with LiF has the highest Coulombic efficiency for Si without significant increase of electrochemical impedance. It is concluded that LiF plays an important role in stabilizing the SEI on Si for enabling long cycle stability.

3) Investigated the electron transport in the major components of SEI in order to avoid the excess electrolyte molecule decomposition. In this quarter, the study was focused on small polarons (e.g., F_2^- molecular ions) in LiF. A new method has been developed by using hybrid DFT. This method was able to isolate polaron on a F_2^- molecular ion (VK center) and the distance of two F atoms ($\sim 1.95 \text{ \AA}$) is very close to experimentally value. The lowest polaron hopping barrier is about 2.05 eV associated with the 60° pathway, much lower than the band gap.

4) Atomic simulation of lithiation of Si-core/ Al_2O_3 and Si-core/ SiO_2 -shell nanowires revealed Al_2O_3 is a more mechanically stable coating. Finished the development of Li-Si-Al-O parameters of ReaxFF. The coating structural integrity and stability improved as coating thickness increases. Upon lithiation of thin coatings, the oxide shell was immediately lithiated without much volume expansion, followed by the lithiation of Si core; then the SiO_2 shell spread out and lost its structural integrity. When the thickness of the oxide coating is comparable to the radius of Si, its mechanical integrity is maintained, and fully lithiated Si is undercompression. However more cracks were observed in SiO_2 coating than Al_2O_3 coating at the same thickness. This is attributed to the lithiation induced softening in Al_2O_3 coatings.

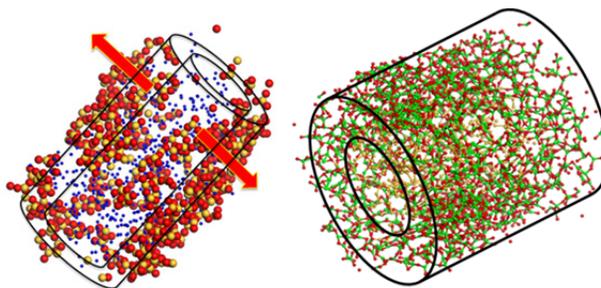


Figure 52: Lithiation of oxide shell

Task 6.6 – Dean Wheeler and Brian Mazzeo (Brigham Young University)

Predicting Microstructure and Performance for Optimal Cell Fabrication

PROJECT OBJECTIVE: This work uses microstructural modeling coupled with extensive experimental validation and diagnostics to understand and optimize fabrication processes for composite particle-based electrodes. The first main outcome will be revolutionary methods to assess electronic and ionic conductivities of porous electrodes attached to current collectors, including heterogeneities and anisotropic effects. The second main outcome is a particle-dynamics model parameterized with fundamental physical properties that can predict electrode morphology and transport pathways resulting from particular fabrication steps. These two outcomes will enable the third, which is an understanding of the effects of processing conditions on microscopic and macroscopic properties of electrodes.

PROJECT IMPACT: This work will result in new diagnostic tools for rapidly and conveniently interrogating electronic and ionic pathways in porous electrodes. A new mesoscale 3D microstructure prediction model, validated by experimental structures and electrode-performance metrics, will be developed. The model will enable virtual exploration of process improvements that currently can only be explored empirically.

OUT-YEAR GOALS: This project was initiated April 2013 and concludes March 2017. Goals by fiscal year are as follows.

- 2013: Fabricate first-generation micro-four-line probe and complete associated computer model.
- 2014: Assess conductivity variability in electrodes; characterize microstructures of multiple electrodes.
- 2015: Fabricate first-gen ionic conductivity probe, N-line probe, and dynamic particle packing (DPP) model.
- 2016: Fabricate second-gen N-line probe and DPP model; assess effect of processing variables.
- 2017: Use conductivity predictions in full electrochemical model; evaluate effect of innovative processing conditions.

COLLABORATIONS: Bryant Polzin (ANL) and Karim Zaghib (Hydro-Québec) provided battery materials. Transfer of our technology to A123 to improve their electrode production process is in process. There are ongoing collaborations with Simon Thiele (IMTEK, University of Freiburg) and Mårten Behm (KTH, Sweden)

Milestones

- 1) Develop localized ionic conductivity probe and demonstrate method by testing two candidate electrode materials (Dec-14). **Partially complete – new completion date Mar-15**
- 2) Use dynamic particle-packing (DPP) model to predict electrode morphology of Toda 523 material (Mar-15). **Ongoing**
- 3) Develop fabrication process of micro-N-line probe and demonstrate method by testing two candidate electrode materials (Jun-15). **Ongoing**
- 4) Go/No-Go: Discontinue dynamic particle-packing (DPP) model if predictions are not suitable match to real electrode materials (Sep-15). **Ongoing**

Progress Report

Milestone 1 (Partially complete)

The first activity of FY2015 is to extend the micro-four-line probe (μ 4LP) apparatus to enable measurement of local effective ionic conductivity of thin-film battery electrodes. (See Figure 53.) An electrolyte containing a redox shuttle is used to flow ions between the probe lines and the sample. This milestone is meant to be preliminary and the development of this technology will continue into FY 2016.

The milestone as written is only partially complete. Work began on this milestone in June 2014, but has been more difficult than expected. Full completion will require testing the method on two battery electrode sample materials, which will take place by March 2015.

The current status is as follows. After extensive experimentation with different redox shuttle molecules, supporting electrolyte, and solvents, we have selected a suitable solution that enables current to be carried between the outer lines of the probe through the sample, without electrochemically altering the probe.

So far tests have been completed with stacked disks of Celguard 2400 separator (25 μ m thick) acting as a proxy for battery electrode films. Rings of Celguard were also used as spacers to allow a defined thickness of pure liquid electrolyte next to the probe surface. The disks or rings are placed on the surface along with electrolyte and an acrylic cover layer is added, squeezing out any excess liquid (Fig. 1). A four-line DC experiment is conducted and an apparent resistance is determined for a sampling volume on the order of 1-3 μ L. This is converted to an effective ionic conductivity through use of a shape factor, computed using an algorithm developed previously for electronic conductivity measurements with the μ 4LP.

Measurements using the apparatus indicate that the conductivity of the electrolyte is 38 mS/m and of Celguard with electrolyte is 7.5 mS/m, which corresponds to a tortuosity of 1.87. This is about 40% below expectation, based on earlier tortuosity experiments with Celguard 2400. The cause of this discrepancy is currently being investigated. Once this is done, tests will begin with battery electrode films.

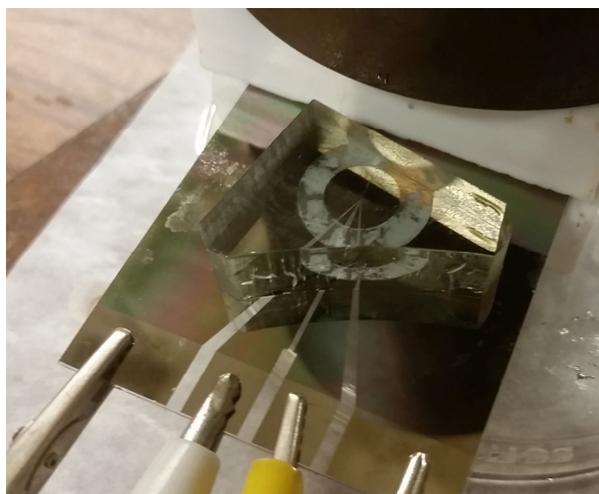


Figure 53: Photo of apparatus with μ 4LP (contact pads on the bottom), with a piece of clear acrylic covering the sampling window and keeping electrolyte from evaporating.

TASK 7 – METALLIC LITHIUM AND SOLID ELECTROLYTES

The use of a metallic lithium anode is required for advanced battery chemistries like Li-air and Li-S in order to realize dramatic improvements in energy density, vehicle range, cost requirements and safety. However, the use of metallic Li with liquid and polymer electrolytes has been so far limited due to parasitic SEI reactions and dendrite formation. Adding excess lithium to compensate for such losses effectively negates the high energy density for lithium in the first place. For a long lifetime and safe anode, it is essential that no lithium capacity is lost to either physical isolation from roughening, dendrites or delamination processes, or to chemical isolation from side reactions. The key risk and current limitation for this technology is the gradual loss of lithium over the cycle life of the battery.

To date there are no examples of battery materials and architectures that realize such highly efficient cycling of metallic lithium anodes for a lifetime of 1000 cycles due to degradation of the Li-electrolyte interface. A much deeper analysis of the degradation processes is needed, so that materials can be engineered to fulfill the target level of performance for EV, namely 1000 cycles and a 15 year lifetime, with adequate pulse power. Projecting the performance required in terms of just the Li anode, this requires a high rate of lithium deposition and stripping reactions, specifically about 40 μ m Li per cycle, with pulse rates up to 10 and 20 nm/s charge and discharge, respectively. This is a conservative estimate, yet daunting in the total mass and rate of material transport. While such cycling has been achieved for state-of-the-art batteries using *molten* Na in Na-S and zebra cells, solid Na and Li anodes are proving more difficult.

The efficient and safe use of metallic lithium for rechargeable batteries is then a great challenge, one that has eluded R&D efforts for many years. The Battery Materials Research Task 7, takes a broad look at this challenge for both solid state batteries and batteries continuing to use liquid electrolytes. Four of the projects are new endeavors; two are ongoing. For the liquid electrolyte batteries, PNNL researchers are examining the use of cesium salts and organic additives to the typical organic carbonate electrolytes to impede dendrite formation at both the lithium and graphite anodes. If successful, this is the simplest to implement. At Stanford, novel coatings of carbon and boron nitride with a 3D structure are applied to the lithium surface and appear to suppress roughening and lengthen cycle life. A relatively new family of solid electrolytes with a garnet crystal structure show superionic conductivity and good electrochemical stability. Four programs chose this family of solid electrolytes for investigation. Aspects of the processing of this ceramic garnet electrolyte are addressed at University of Maryland and University of Michigan with attention to effect of flaws and composition. Computational models will complement their experiments to better understand interfaces and reduce the electrode area specific resistance (ASR). At Oak Ridge National Laboratory, composite electrolytes composed of ceramic and polymer phases are being investigated, anticipating that the mixed phase structures may provide additional means to adjust the mechanical and transport properties. The last project takes on the challenge to used nanoindentation methods to measure the mechanical properties of the solid electrolyte, the lithium metal anode, and the interface of an active electrode. Each of these projects have a collaborative team of experts with the skills needed to address the challenging materials studies of this dynamic electrochemical system.

Task 7.1 – Nancy Dudney (ORNL), Erik Herbert (UTK), Jeff Sakamoto (UM)

Mechanical Properties at the Protected Lithium Interface

PROJECT OBJECTIVE: This project will develop the understanding of the Li metal-solid electrolyte interface through state of the art mechanical nanoindentation methods coupled with solid electrolyte fabrication and electrochemical cycling. Our goal is to provide the critical information that will enable transformative insights into the complex coupling between the microstructure, its defects and the mechanical behavior of Li metal anodes.

PROJECT IMPACT: Instability and/or high resistance at the interface of lithium metal with various solid electrolytes limit the use of the metallic anode for batteries with high energy density batteries, such as Li-air and Li-S. The critical impact of this endeavor will be a much deeper analysis of the degradation, so that materials can be engineered to fulfill the target level of performance for EV batteries, namely 1000 cycles and 15 year lifetime, with adequate pulse power.

APPROACH: Mechanical properties studies through state of the art nanoindentation techniques will be used to probe the surface properties of the solid electrolyte and the changes to the lithium that result from prolonged electrodeposition and dissolution at the interface. An understanding of the degradation processes will guide future electrolyte and anode designs for robust performance. In the first year, the team will address the two critical and poorly understood aspects of the protected Li metal anode assembly: (1) the mechanical properties of the solid electrolyte and (2) the morphology of the cycled Li metal.

OUT-YEAR GOALS: Work will progress toward study of the electrode assembly during electrochemical cycling of the anode. We hope to capture the formation and annealing of vacancies and other defects in the lithium and correlate this with the properties of the solid electrolyte and the interface.

COLLABORATIONS: This project funds work at Oak Ridge National Laboratory, University of Tennessee at Knoxville, and University of Michigan. Asma Sharafi (UM Ph. D. student), Dr. Robert Schmidt (UM) also contribute to the project. Steve Visco (PolyPlus) will serve as a technical advisor.

Milestones

- 1) Four nano-indentation maps showing grain boundary regions of the crystalline LLZO and the glass ceramic material from Ohara (Q1) **(Initiated January 2015)**
- 2) Two or three indentation studies with as-fabricated, air reacted and polished surfaces (Q2)
- 3) Demonstrate capability to transfer and then map viscoelastic properties of Li films and rolled lithium foils in vacuum system of sem (Q3) **(Initiated)**
- 4) Determine elastic properties of battery grade lithium from different sources and preparation, comparing to values from the reference literature (Q4)

Progress Report

Subcontracts were completed, but not until January. Instrument feedthroughs were designed. Preliminary results were limited to one study, shown below, of a cycled garnet ceramic electrolyte pellet.

Cubic LLZO (Lithium Lanthanum Zirconium Oxide) powder was prepared using solid state synthesis. 0.27 mol of Al was added to stabilize the cubic garnet phase. The powder was densified using rapid induction hot pressing (RIHP) at 1100 °C. As shown in Figure 54, the LLZO pellet had high phase purity after hot pressing. Scanning electron microscopy (Figure 55) shows the low porosity (3 %) and transgranular fracture; evidence of relatively high grain boundary adhesion.

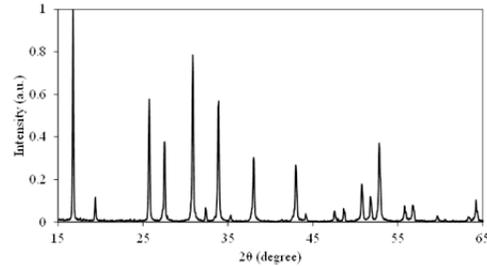


Figure 54: XRD of the LLZO pellet after hot pressing. There is no evidence of impurities.

For cycling, the surface of LLZO pellet was dry-polished in an Ar glove box. The LLZO pellet was placed between two lithium foil disks under constant pressure (316 kPa). After preconditioning, the cell was cycled at 70 °C at varying current densities. While the cell potential remained stable and followed Ohmic behavior between 5 and 50 $\mu\text{A}\cdot\text{cm}^{-2}$, at higher current densities, the cell voltage became erratic and dropped to nearly 0 V. Black spots and lenticular shapes propagated from pellet face to pellet face.

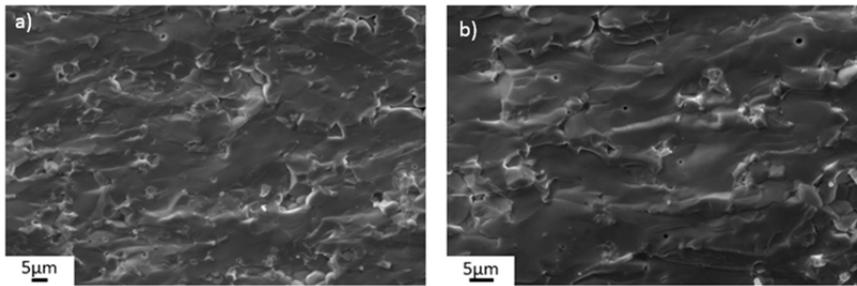


Figure 55: Scanning electron microscopy of a typical hot pressed LLZO pellet: (a) 500 X, and b) 2000 X.

Rapid nanoindentation mapping of the cycled LLZO pellet was conducted with the sample protected from air by mineral oil. The surface was mapped in 17 separate regions with a 10x10 point array at each. A statistically significant difference was found for regions near sites of the degradation forming the visible black features. While the average modulus was independent of the damage, the average hardness, shown in Figure 56, was approximately 25% higher for the damaged regions.

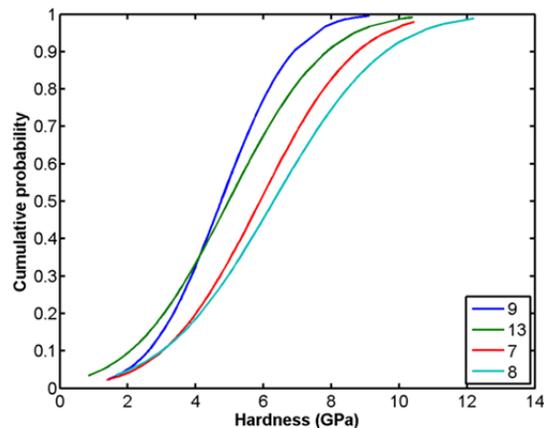


Figure 56: Cumulative hardness for selected maps. Areas 7 and 8 had visible dark areas; areas 9 and 13 were still white.

Patents/Publications/Presentations

None this quarter.

Task 7.2 – Jeff Sakamoto (Univ. of Michigan)

Solid electrolytes for solid-state and lithium-sulfur batteries

PROJECT OBJECTIVES: *Enable advanced Li-ion solid-state and lithium-sulfur EV batteries using LLZO solid-electrolyte membrane technology.* Owing to its combination of fast ion conductivity, stability, and high elastic modulus, LLZO exhibits promise as an advanced solid-state electrolyte. To demonstrate relevance in EV battery technology, several objectives must be met. First, LLZO membranes must withstand current densities approaching $\sim 1 \text{ mA/cm}^2$ (commensurate with EV battery charging and discharging rates). Second, low area specific resistance (ASR) between Li and LLZO must be achieved to achieve cell impedance comparable to conventional Li-ion technology ($\sim 10 \text{ Ohms/cm}^2$). Third, low ASR and stability between LLZO and sulfur cathodes must be demonstrated.

PROJECT IMPACT: The expected outcomes will: (i) enable Li metal protection, (ii) augment DOE's access to fast ion conductors and/or hybrid electrolytes, (iii) mitigate Li-polysulfide dissolution and deleterious passivation of Li metal anodes, and (iv) prevent dendrite formation. Demonstrating these aspects could enable Li-S batteries with unprecedented end-of-life, cell-level performance: $\geq 500 \text{ Wh/kg}$, $\geq 1080 \text{ Wh/l}$, ≥ 1000 cycles, lasting ≥ 15 years.

APPROACH: Our effort will focus on the promising new electrolyte known as LLZO ($\text{Li}_7\text{La}_3\text{Zr}_2\text{O}_{12}$). LLZO is the first bulk-scale ceramic electrolyte to simultaneously exhibit the favorable combination of high conductivity ($\sim 1 \text{ mS/cm}$ at 298K), high shear modulus (61 GPa) to suppress Li dendrite penetration, and apparent electrochemical stability (0-6V vs Li/Li⁺). While these attributes are encouraging, additional R&D is needed to demonstrate that LLZO can tolerate current densities in excess of 1 mA/cm^2 , thereby establishing its relevance for PHEV/EV applications. We hypothesize that defects and the polycrystalline nature of realistic LLZO membranes can limit the critical current density. However, the relative importance of the many possible defect types (porosity, grain boundaries, interfaces, surface & bulk impurities), and the mechanisms by which they impact current density, have not been identified. Using our experience with the synthesis and processing of LLZO (Sakamoto and Wolfenstine), combined with sophisticated materials characterization (Nanda), we will precisely control atomic and microstructural defects and correlate their concentration with the critical current density. These data will inform multi-scale computation models (Siegel and Monroe) which will isolate and quantify the role(s) that each defect plays in controlling the current density. By bridging the knowledge gap between composition, structure, and performance we will determine if LLZO can achieve the current densities required for vehicle applications.

COLLABORATIONS: Don Siegel (UM atomistic modeling), Chuck Monroe (UM, continuum scale modeling), Jagjit Nanda (ORNL sulfur chemical and electrochemical spectroscopy), Jeff Wolfenstine (ARL atomic force microscopy of Li-LLZO interfaces).

Milestones

- 1) **M1.1 Milestone (to be completed Q2):** Demonstrate ability to vary porosity from 1 to 15 volume %. Correlate critical current density with scale and volume of porosity. **Started January 1, 2015.**
- 2) **M1.2 Milestone (to be completed Q3):** Establish baseline atomistic and continuum theory to predict the maximum critical current density based on pore size and volume. Fabricate ceramic-polymer composite sheets with 20-60 vol% ceramic to determine the composition dependence of the conductivity as the structure. **Started January 1, 2015.**

Progress Report

1. Officially on contract as of January 1, 2015.
2. All collaborators have staffed respective projects/tasks.
3. Sakamoto group transition to U of M 100% complete as of January 1, 2015.

Patents/Publications/Presentations

Invited Presentations

1. J. Sakamoto, “Fast ion conducting ceramic electrolyte based on $Li_7La_3Zr_2O_{12}$ garnet”, Materials Science Department Seminar, University of Michigan, Ann Arbor, MI (October, 2014).
2. J. Sakamoto, “Keeping up with the increasing demands for electrical vehicle energy storage: Ceramic electrolytes enabling Beyond Li-ion batteries”, *The Battery Show*, Novi, MI (October, 2014).
3. J. Sakamoto, National Academy of Engineering, “Battery Anxiety” Session, Beckman Center, Irvine, CA (September, 2014).

Task 7.3 – Nancy Dudney and Sergiy Kalnaus (Oak Ridge National Laboratory)

Composite Electrolytes to Stabilize Metallic Lithium Anodes

PROJECT OBJECTIVE: Prepare composites of representative polymer and ceramic electrolyte materials to achieve thin membranes which have the unique combination of electrochemical and mechanical properties required to stabilize the metallic lithium anode while providing for good power performance and long cycle life. Understand the lithium ion transport at the interface between polymer and ceramic solid electrolytes which is critical to the effective conductivity of the composite membrane. Identify key features of the composite composition, architecture and fabrication that optimize the performance. Fabricate thin electrolyte membranes to use with a thin metallic lithium anode that provide good power performance and long cycle life.

PROJECT IMPACT: A stable lithium anode is critical to achieve high energy density with excellent safety, lifetime and cycling efficiency. This study will identify the key design strategies that should be used to prepare composite electrolytes to meet the challenging combination of physical and chemical and manufacturing requirements to protect and stabilize the lithium metal anode for advanced batteries. By utilizing well characterized and controlled component phases, the design rules developed for the composite structures will be generally applicable toward the substitution of alternative and improved solid electrolyte component phases as they become available. Success in this program will enable these specific DOE technical targets: 500-700Wh/kg, 3000-5000 deep discharge cycles, robust operation.

APPROACH: This program seeks to develop practical solid electrolytes that will provide stable and long-lived protection for the lithium metal anode. Current electrolytes all have serious challenges when used alone: oxide ceramics are brittle, sulfide ceramics are air sensitive, polymers are too resistive and soft, and many electrolytes react with lithium. Composites provide a clear route to address these issues. This program does not seek discovery of new electrolytes, rather the goal is to study combinations of current well known electrolytes. The program emphasizes the investigation of polymer-ceramic interfaces formed as bilayers and as simple composite mixtures where the effects of the interface properties can be readily isolated. In general, the ceramic phase is several orders of magnitude more conductive than the polymer electrolyte, and interfaces can contribute an additional source of resistance. Using finite element simulations as a guide, composites with promising compositions and architectures are fabricated and evaluated for lithium transport properties using AC impedance and DC cycling with lithium in symmetric or half cells. General design rules will be determined that can be widely applied to other combinations of solid electrolytes.

OUT-YEAR GOAL: Use advanced manufacturing processes where the architecture of the composite membrane can be developed and tailored to maximize performance and cost-effective manufacturing.

COLLABORATIONS: Electrolytes currently under investigation include a garnet electrolyte from Jeff Sakamoto (Michigan State University) and a block styrene copolymer from Nitash Balsara (U.C. Berkeley). Staff at Corning Corporation will serve as our industrial consultant.

Milestones

Q1: Compare the vapor absorption (rate and equilibrium) of small molecules in a single phase polymer and a corresponding ceramic/polymer composite electrolyte. (Complete)

Q2: Compare Li cycling contacting Li with only a Ni current collector tab versus full Cu anode contact.

Q3: By generating a database with at least 5 compositions, determine if the presence of trace solvent molecules that enhance the ionic conductivity is also detrimental to the stability and cycleability of a lithium metal electrode, and if the effect can be altered by adding an intermediate films (SMART)

Q4: Demonstrate a practical processing route to a thin, dense membrane 100 μ m x 50cm².

Progress Report

Work this quarter addressed quantitative analysis of the reaction of small organic solvent molecules the polymer electrolyte and polymer-ceramic electrolyte composite. What controls the organic adsorption rate, and what is the equilibrium or saturated composition? We have already determined, and reported, that several plasticizing molecules have a profound influence on the ionic conductivity and plasticity, but the reactions have not been well controlled. In this work, the vapor pressure, the total amount of solvent available, and the reaction time are investigated; this report shows the results for dimethyl carbonate (DMC) which is likely present at the highest vapor pressure at our battery coin cell crimping systems.

The results in Figure 57 are for composites formed as thin disks containing 40vol% ceramic powder from Ohara dispersed in a PEO + LiTFSI polymer matrix. The x-axis concentration assumes that the sample adsorbs all of the DMC in the sealed container overnight. The highest concentrations (>0.1 , solid blue symbols) were both achieved by treating in Ar initially saturated with DMC ($P_{eq}=18$ torr at 21°C); and lower concentrations from more dilute gas mixtures. These results indicate that the vapor pressure of the DMC does not control the amount adsorbed by the polymer-ceramic composite, rather the material continues to adsorb available DMC with no indication of saturation. The shorter exposure to the saturated gas mix does not allow sufficient time for complete adsorption of the available DMC; the rate limiting step could be diffusion in

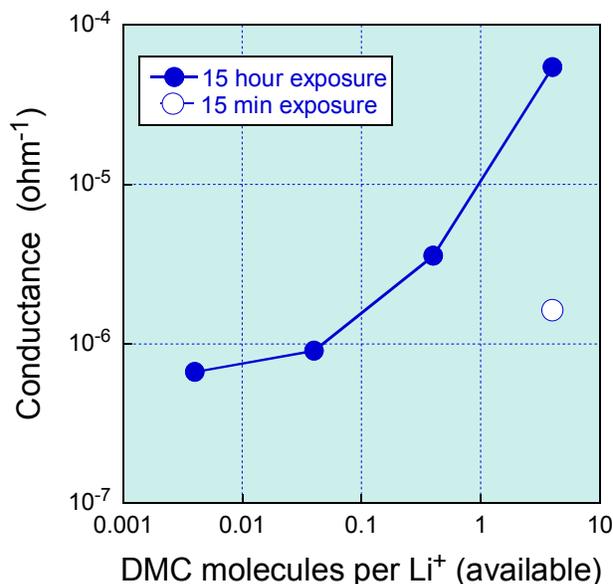


Figure 57: Cumulative hardness for selected maps. Areas 7 and 8 had visible dark areas; areas 9 and 13 were still white.

the solid, surface adsorption from the vapor, or evaporation of liquid DMC. After the vapor treatment, samples were sealed in crimped coin cells with blocking stainless contacts for the impedance study giving the conductance in the figure. The impedance changed little with either room temperature aging or with temperature scans to 90 and 100°C . When contacted with a Li metal electrode, the composite electrode turned black through the thickness of the sample and showed significant contact resistance. It is no surprise that DMC would promote a degradation reaction with the lithium.

The result of the 15minute exposure however, was unexpected. The impedance (white point in figure) was steady within a factor of 2 for several weeks showed no indication of aging. This is in contrast to the curious observations that first suggested that inadvertent contamination was causing an enhanced conductivity (reported earlier). For a number of samples, a short exposure within our standard glovebox housing the crimping machine initiated a slow increase in conductivity or 2-3 orders of magnitude over a few weeks following crimping. While here, the short exposure to a controlled DMC in Ar gas mix does not produce the same effect. The aging effect must be due to something other than a slow DMC adsorption or redistribution in the composite. We will continue to seek the cause of this behavior, as it seems to correlate with standard Li-ion fabrication environment, although this is a lower priority.

Patents/Publications/Presentations

None this quarter.

Task 7.4 – Eric Wachsman, Liangbing Hu, Yifei Mo (University of Maryland, College Park)

OVERCOMING INTERFACIAL IMPEDANCE IN SOLID-STATE BATTERIES

PROJECT OBJECTIVE: Develop a multifaceted and integrated (experimental and computational) approach to solve the key issue in solid-state Li-ion batteries (SSLiBs), interfacial impedance, with a focus on Garnet-based solid-state electrolytes (SSEs), the knowledge of which can be applied to other SSE chemistries. The focus is to develop methods to decrease the impedance across interfaces with the solid electrolyte, and ultimately demonstrate a high power/energy density battery employing the best of these methods.

PROJECT IMPACT: Garnet electrolytes have shown great promises for safer and higher energy density batteries due to their stability to both high voltage cathodes and Li metal anodes, as well as their inherent non-flammability. The success of the proposed research can lead to dramatic progress on the development of SSLiBs based on Garnet electrolytes. With regard to the fundamental science, our methodology by combining computations and experiments can lead to an understanding of the thermodynamics, kinetics and structural stability and evolution of SSLiBs with the Garnet electrolytes. Due to the ceramic nature of Garnet electrolyte, being brittle and hard, Garnet electrolyte particles intrinsically lead to poor contacts among themselves or with electrode materials. A fundamental understanding at the nanoscale and through computations, especially with interface layers, can guide improvements to their design and eventually lead to the commercial use of such technologies.

APPROACH: SSLiB interfaces are typically planar resulting in high impedance due to low specific surface area, and attempts to make 3D high surface area interfaces can also result in high impedance due to poor contact at the electrode-electrolyte interface that hinder ion transport or degrade due to expansion/contraction with voltage cycling. We will experimentally and computationally determine the interfacial structure-impedance relationship in SSLiBs to obtain fundamental insight into design parameters to overcome this issue. Furthermore, we will investigate interfacial modification (layers between SSE and electrode) to see if we can extend these structure-property relationships to higher performance.

COLLABORATIONS: We are in collaboration with Dr. Venkataraman Thangadurai on garnet synthesis. We will collaborate with Dr. Leonid A. Bendersky and Dr. Howard Wang at NIST to use Neutron scattering to investigate the lithium profile across the bilayer interface with different charge-discharge rates.

Milestones

1. Synthesize garnet and electrode materials – Complete.
2. Determine frequency dependence of garnet and electrode impedances – in process
3. Develop computation models for garnet based interfaces – in process
4. Identify gel or PFPE based electrolyte with a stable voltage window (0V-4.2 V) – not started

Progress Report

Contract signed (12/15/14) and graduate students and postdocs hired.

Garnet $\text{Li}_7\text{La}_{2.75}\text{Ca}_{0.25}\text{Zr}_{1.75}\text{Nb}_{0.25}\text{O}_{12}$ electrolyte pellets were fabricated. 30 g of precursors with 10% weight excess Li was ball milled overnight in isopropyl alcohol. After drying the slurry in a 100 °C oven the powder was calcined at 900 °C for 4 h with a 5 °C/min ramp rate. 0.5 g of calcined powder was pressed in a 10 mm form at 2 metric tons for 1 minute. The pellets were then sintered in calcined powder at 1050 °C for 12 h with 3 °C/min ramp. XRD confirms that cubic garnet was created (Figure 58).

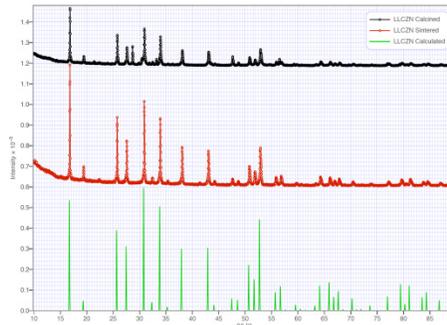


Figure 58: XRD of synthesized garnet

$\text{Li}_2\text{FeMn}_3\text{O}_8$ (LFMO) cathode powders were prepared using the glycine nitrate combustion technique. Lithium nitrate, cobalt nitrate, iron nitrate and manganese nitrate were mixed in the required molar ratio and dissolved in de-ionized water. Glycine was then dissolved in de-ionized water and added in to the nitrate solution under stirring. The mixture solution was heated to 300 °C and a sudden ignition occurred after a complete evaporation of water, leaving black powders. After being collected and annealed at 700 °C in air for 2 h, the powders were ball-milled for 20 h in order to further decrease particle size. Figure 59 shows the XRD pattern of as-prepared (un-doped) LFMO powder. The XRD spectrum is in agreement with JCPDS#48-0258, indicating a phase-pure spinel with lattice constant $a=8.2508\text{\AA}$ in the cubic space group $Fd3m$.

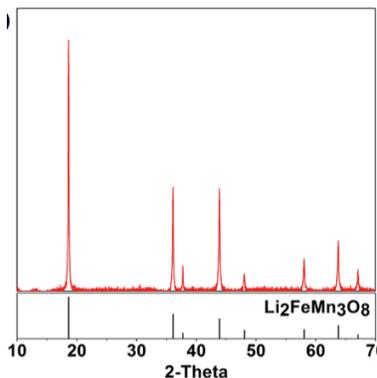


Figure 59: XRD pattern of $\text{Li}_2\text{FeMn}_3\text{O}_8$

Initiated first principles modeling of garnet solid electrolyte materials were performed on both tetragonal and cubic LLZ phases. The ordering of Li was determined using computational methods, and the ground state ordering of Li was determined. The Li grand canonical phase diagram of the Li-La-Zr-O system based on first principles computation methods. The interfacial stability of the garnet materials against Li metal was determined. (See Figure 60.)

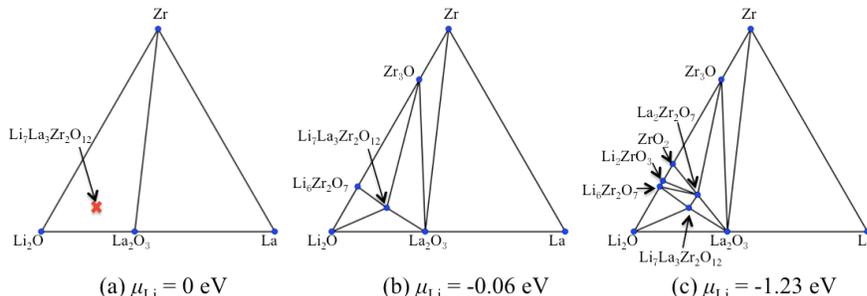


Figure 60: First principles calculated Li grand canonical phase diagram of a Li-La-Zr-O system

Patents/Publications/Presentations

“Solid State Batteries and Fuel Cells,” Defense Strategies Institute, Military Mobile Power Summit, January 13-14, 2015, Alexandria VA

Task 7.5 – Yi Cui (Stanford University)

Nanoscale Interfacial Engineering for Stable Lithium Metal Anodes

PROJECT OBJECTIVE:

This study aims to render lithium metal anode with high capacity and reliability by developing chemically and mechanically stable interfacial layers between lithium metal and electrolytes, which is essential to couple with sulfur cathode for high-energy lithium-sulfur batteries. With the nanoscale interfacial engineering approach, various kinds of advanced thin films will be introduced to overcome the issues related to dendritic growth, reactive surface and virtually “infinite” volume expansion of lithium metal anode.

PROJECT IMPACT: The cycling life and stability of lithium metal anode will be dramatically increased. The success of this project, together with breakthroughs of sulfur cathode, will significantly increase the specific capacity of lithium batteries and decrease the cost as well, therefore stimulating the popularity of electric vehicles.

OUT-YEAR GOALS: Along with suppressing dendrite growth, the cycle life, Coulombic efficiency as well as the current density of lithium metal anode will be greatly improved (No dendrite growth for current density up to 3.0 mA/cm², with Coulombic efficiency >99%) by choosing the appropriate interfacial nanomaterial.

Milestones

- 1) Fabrication of interconnected carbon hollow spheres with various sizes (3/31/2015) **on going**
- 2) Synthesize of layered hexagonal boron nitride and graphene with different thicknesses and defect levels (3/31/2015) **on going**
- 3) Demonstrate the improved cycling life and Coulombic efficiency of lithium metal anode with nanoscale interfacial engineering (9/30/2015) **on going**
- 4) Demonstrate the improved cycling performance of lithium metal anode with different current density and areal capacity (9/30/2015) **on going**

Progress Report

We stabilized lithium metal anode by applying interfacial layers between lithium metal and electrolyte. As two typical demonstrations, interconnected carbon hollow spheres and layered hexagonal boron nitride are selected, featuring with the extraordinary chemical and mechanical stability, the essential lithium ion conductivity, as well as the easy release from the substrate. Lithium metal will insert between the layer and substrate upon deposition, leading to a sandwiched structure with top surface isolated from the electrolyte.

The interconnected hollow carbon spheres are fabricated by direct deposition of amorphous carbon onto polystyrene nanospheres template (Figure 61(a)). The hollow structure (Figure 61 (b)) allowed for both easy release from substrate and huge space for lithium metal storage underneath. The porous nature of amorphous carbon guaranteed essential conductivity for lithium ion. Comparing with bare substrate, the electrode modified with carbon spheres exhibited longer cycling life (>150 cycles) with higher Coulombic efficiency (~98%, Figure 61 (c)) in ether based electrolyte.

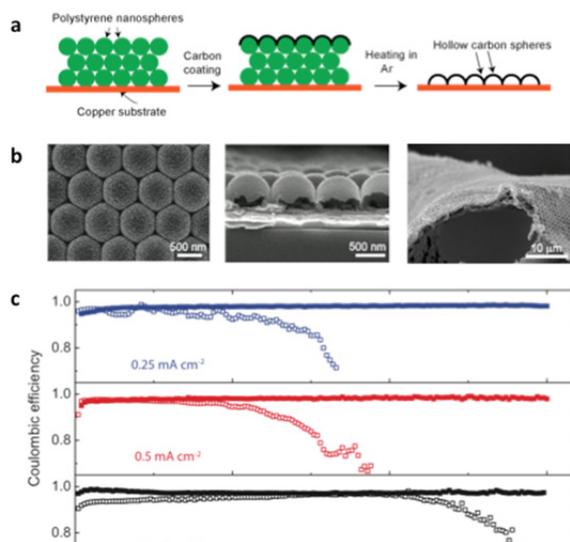


Figure 61: Stable lithium metal cycling enabled by interconnected carbon hollow spheres. (a) Fabrication process (b) SEM images. (c) Cycling performance of lithium metal with (solid) and without (open) hollow carbon coating at different current densities

Hexagonal boron nitride serves as another choice here based on the same working principle. Featured with the two-dimensional nature, h-BN could be easily peeled off the substrate by lithium metal and subsequently isolates lithium metal from electrolyte. Few layered h-BN with arbitrary size could be easily produced by chemical vapor deposition, at a temperature down to 600°C. The surface morphology of

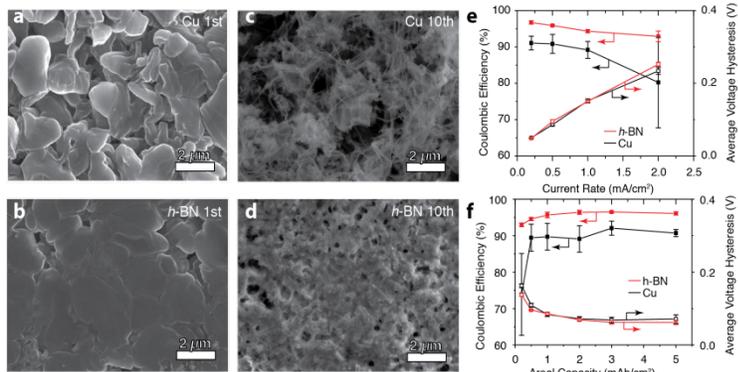


Figure 62: h-BN as interfacial layer for lithium metal. Morphologies of lithium metal surface without (a and c) and with (b and d) h-BN coating at first cycle (a and b) and tenth cycle (c and d). (e) and (f) Coulombic efficiency and average voltage hysteresis of lithium metal anode upon cycling, with and without h-BN coating at different current densities and areal capacities

lithium metal is significantly regulated by the h-BN film as seen in Figure 62a-d. Especially, the hazardous thin lithium filament does not appear in the prolonged cycles when h-BN exists. The Coulombic efficiency remained high comparing with bare copper at different current densities (Figure 62e), even in more corrosive organic carbonate electrolyte. More importantly, the unique working mechanism that the interfacial layer always sits on top of lithium metal allows for stable cycling with various areal capacities up to 5 mAh/cm².

TASK 8 – LI – S BATTERIES

The development of a number of plug-in hybrid and fully electric vehicles (EV) using lithium-ion technology and their favorable market response is the harbinger of a long-awaited transition in automotive technology. However, with the increasing demand in the EV industry for low cost, low weight and high energy storage batteries to meet the *EV everywhere grand challenge*, there is still a genuine need for increasing the energy densities for achieving a successful transition to EVs. Advances in lithium-ion technology thus far have been stymied by the challenges posed in developing high capacity cathodes and stable anodes. This necessitates the development of alternate battery technologies with superior energy densities and cycling capabilities. Lithium sulfur batteries have been touted to hold much promise on account of their attractive theoretical specific energy densities of 2567 Wh/kg. Therefore, the current focus of research has shifted towards the development of lithium sulfur (Li-S) batteries owing to the high theoretical specific capacity exhibited by sulfur compared to other cathode materials currently available. Li-S battery shows a theoretical capacity of 1675 mAh/g corresponding to the formation of Li_2S which renders sulfur a promising cathode. Moreover, the abundance of sulfur in the earth's crust, combined with the ubiquitous availability of sulfur as a byproduct in the extractive and petrochemical industry, together with the ease of processing, makes it a more economical proposition compared to currently existing cathode materials systems. The system however suffers from major drawbacks as elucidated in the following.

Limitations of current Li-S systems

- 1) Limited inherent electronic conductivity of sulfur and sulfur compound based cathodes.
- 2) Volumetric expansion and contraction of both the sulfur cathode and lithium anode.
- 3) Soluble polysulfide formation/dissolution and sluggish kinetics of subsequent conversion of polysulfides to Li_2S resulting in poor cycling life.
- 4) Particle fracture and delamination as a result of the repeated volumetric expansion and contraction.
- 5) Irreversible loss of lithium at the sulfur cathode resulting in poor coulombic efficiency.
- 6) High diffusivity of polysulfides in the electrolyte resulting in plating at the anode and consequent loss in driving force i.e. drop in cell voltage.

The above major issues lead to loss of sulfur from the cathode causing mechanical disintegration of the cathode. This combined with surface passivation of both the anode and cathode systems in the battery result in a decrease in the overall specific capacity and coulombic efficiency (CE) upon cycling. As a result, the battery becomes inactive within the first few charge-discharge cycles.

The major desirable goals of the program is thus to successfully demonstrate functioning electrodes and electrolytes for Li-S battery applications in order to achieve the following targets. Gravimetric and volumetric energy densities exceeding or equal to 350 Wh/kg and 750Wh/l, respectively with a cost target of \$125/kWh and cycle life of at least 1000 cycles; temperature range of -35°C to $+52^\circ\text{C}$, and a calendar life of 15 years to meet the *EV everywhere* blueprint.

Task 8.1 – Prashant N. Kumta (University of Pittsburgh)

New Lamination and doping Concepts for Enhanced Li – S Battery Performance

PROJECT OBJECTIVE: To successfully demonstrate generation of novel sulfur cathodes for Li-S batteries meeting the targeted gravimetric energy densities ≥ 350 Wh/kg and ≥ 750 Wh/l with a cost target \$125/kWh and cycle life of at least 1000 cycles for meeting the *EV everywhere* blueprint. The proposed approach will yield sulfur cathodes with specific capacity ≥ 1400 mAh/g, at ≥ 2.2 V generating ~ 460 Wh/kg energy density higher than the target. Full cells meeting the required deliverables will also be made.

PROJECT IMPACT: Identification of new laminated Sulfur cathode based systems displaying higher gravimetric and volumetric energy densities than conventional lithium ion batteries will likely result in new commercial battery systems that are more robust, capable of delivering better energy and power densities and will be more lightweight than current Li-ion battery packs. New lithium ion conductor (LIC)-coated sulfur cathodes based strategies and configurations will also lead to more compact battery designs for the same energy and power density specifications as current Li-ion systems. Commercialization of these new S cathode based Li-ion battery packs will represent fundamentally, a major hallmark contribution of the DOE-OVT Program and the battery community.

OUT-YEAR GOALS: This is a multi-year project comprising of three major phases to be successfully completed in three years. Phase – 1 (Year 1): Synthesis, Characterization and Scale up of suitable LIC matrix materials and multilayer composite sulfur cathodes. This phase is currently ongoing. Phase – 2 (Year 2): Development of LIC coated sulfur nanoparticles, scale up of high capacity engineered LIC coated multilayer composite electrodes and doping strategies for improving electronic conductivity of sulfur. Phase-3 (Year 3): Advanced high energy density, high rate, extremely cyclable cell development.

COLLABORATIONS: The project will involve collaboration with following members with the corresponding expertise:

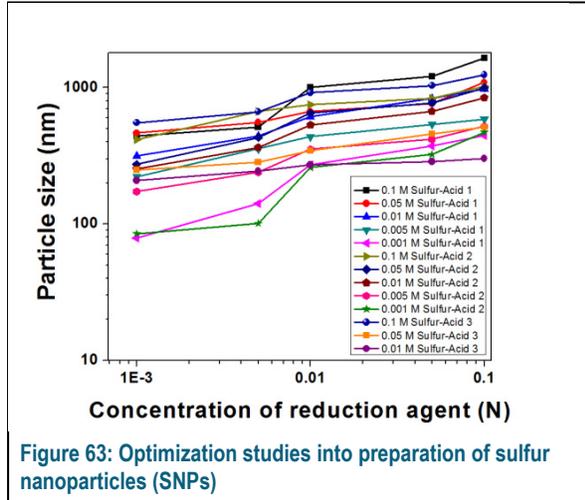
- Dr. Moni Datta (University of Pittsburgh) for expertise on experimental generation of nanoscale composites; Dr. Oleg Velikokhatnyi (University of Pittsburgh) for expertise on density functional theory and first principles studies; Dr. Spandan Maiti (University of Pittsburgh) for expertise on mechanical stability and computational multi-scale modeling; Dr. A. Manivannan (NETL) for expertise on x-ray photoelectron spectroscopy (XPS) for surface characterization; Dr. D. Krishnan Achary (University of Pittsburgh) for expertise on solid-state nuclear magnetic resonance (MAS-NMR) characterization.

Milestones

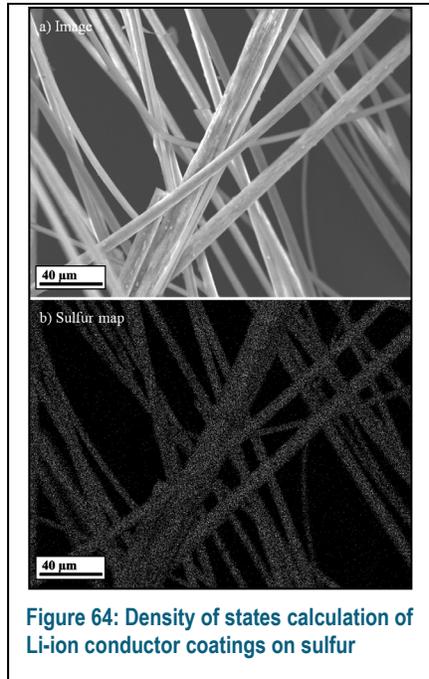
1. Demonstrate synthesis of finely dispersed nanoparticles of sulfur (December 2014) – **Completed**
2. Develop novel lithium-ion conducting membrane systems using *ab-initio* methods displaying impermeability to sulfur diffusion (December 2014) – **Completed**
3. Demonstrate capabilities for generation of novel sulfur 1-D, 2-D and 3-D morphologies exhibiting superior stability and capacity (June 2015) – **On-going**
4. Novel encapsulation and sheathing techniques and exploration of unique architectures and generation of 3-D composites displaying superior Li-ion conduction, reversible capacity and stability (June 2015) – **On-going**

Progress Report

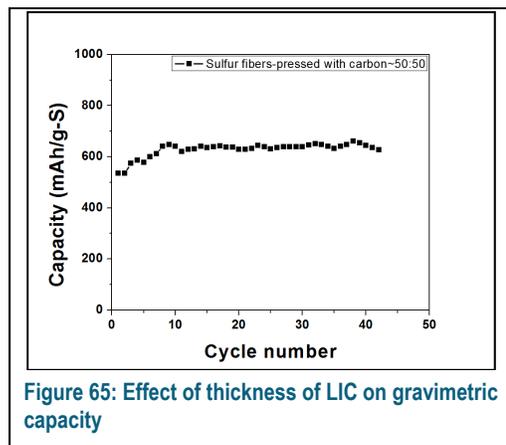
Research in the first quarter involved identification of strategies to improve the characteristics of Li-ion conducting (LIC) coated multilayer composite electrodes with superior areal capacities reported by the PI earlier¹. A two-pronged approach was proposed to address the same during Phase-1 of this project.



Among the several approaches identified first approach was to decrease the sulfur nanoparticles (SNPs) size to increase the capacity approaching theoretical limits of ~1400 mAh/g-Sulfur. Figure 63 shows the effect of various molecular acids and their concentration on the SNP size generated. Different concentrations of various molecular acids resulted in colloidal SNPs of various sizes determined by dynamic light scattering. The average particle size was observed to decrease with lower concentration of the dissolved sulfur solution and also with the decrease in the normality of the acid solution used for generating the colloidal SNPs. Nanoparticles (~80 nm) in size have been generated and the electrochemical analysis are currently on-going. It is expected that the significant size reduction



contrasted with those presented in the PI's previous report¹ (~600 nm) will aid in improving the capacity to ~1400 mAh/g. The second approach involves the first principles driven design and experimental development of suitable LIC materials to improve cycling capability¹. The work also involves the development of unique 2-D and 3-D morphologies in order to improve cycling characteristics of sulfur electrodes. Figure 64 displays the unique fiber like sulfur morphology obtained for the first time making the material very amenable for use in flexible batteries. Figure 65 depicts the superior charge storage characteristics of the sulfur fibers. The sulfur fibers demonstrate a stable capacity of ~650 mAh/g over 40+ cycles. Extended testing is ongoing. Similar structures are also being explored and experimental work is currently ongoing to optimize the thickness and porosity in addition to identification and coating of new LIC materials guided by theory.



Optimization of the LIC thickness and nature of the LIC coating material is an important component of subsequent studies that will be reported in the quarterly reports to follow and there is a need to optimize thickness and porosity to maximize the capacity, while simultaneously minimizing cycling fade. Current LIC thickness allow for capacities of ~700 mAh/g with a major impetus to achieve ~1400 mAh/g, a target to be reached by end of Q3. No change in FY 15 key goals and expected outcomes are anticipated.

Q1 Patents/Publications/Presentations

1. P. J. Hanumantha, B. Gattu, et al., Journal of The Electrochemical Society, 2014, 161, A1173-A1180.

Task 8.2 – Nitash Balsara (Lawrence Berkeley National Laboratory)

Simulations and X-ray Spectroscopy of Li-S Chemistry

PROJECT OBJECTIVE: Lithium-sulfur cells are attractive targets for energy storage applications as their theoretical specific energy of 2600 Wh/kg is much greater than the theoretical specific energy of current lithium-ion batteries. Unfortunately, the cycle-life of lithium-sulfur cells is limited due to migration of species generated at the sulfur cathode. These species, collectively known as polysulfides, can transform spontaneously, depending on the environment, and it has thus proven difficult to determine the nature of redox reactions that occur at the sulfur electrode. The objective of this project is to use X-ray spectroscopy to track species formation and consumption during charge-discharge reactions in a lithium-sulfur cell. Molecular simulations will be used to obtain X-ray spectroscopy signatures of different polysulfide species, and to determine reaction pathways and diffusion in the sulfur cathode. The long-term objective of this project is to use the mechanistic information to build high specific energy lithium-sulfur cells.

PROJECT IMPACT: Enabling rechargeable lithium-sulfur cells has the potential to change the landscape of rechargeable batteries for large-scale applications beyond personal electronics due to: (1) high specific energy, (2) simplicity and low cost of cathode (the most expensive component of current lithium-ion batteries), and (3) earth abundance of sulfur. The proposed diagnostic approach also has significant potential impact as it represents a new path for determining the species that form during charge-discharge reactions in a battery electrode.

OUT-YEAR GOALS: Year 1 Goals: Simulations of sulfur and polysulfides (PSL) in oligomeric polyethylene oxide (PEO) solvent. Prediction of X-ray spectroscopy signatures of PSL/PEO mixtures. Measurement of X-ray spectroscopy signatures PSL/PEO mixtures. Year 2 Goals: Use comparisons between theory and experiment to refine simulation parameters. Determine speciation in PSL/PEO mixtures without resorting to ad hoc assumptions. Year 3 Goals: Build an all-solid lithium-sulfur cell that enables measurement of X-ray spectra *in situ*. Conduct simulations of reduction of sulfur cathode. Year 4 Goals: Use comparisons between theory and experiment to determine the mechanism of sulfur reduction and Li₂S oxidation in all-solid lithium-sulfur cell. Use this information to build lithium-sulfur cells with improved life-time.

COLLABORATIONS:

Tsu-Chien Weng, Dimosthenis Sokaras and Dennis Nordlund, Stanford Synchrotron Radiation Lightsource, SLAC National Accelerator Laboratory, Stanford, California 94720, USA.

Milestones

- 1) Extend theoretical calculations of XAS to finite polysulfide concentrations. (12/1/14) **Completed.**
- 2) Experimental study of the effect of polysulfide concentration on XAS spectra. (2/15/15) **On schedule.**
- 3) Quantitative comparison of experimental and theoretical XAS spectra. (5/20/15) **On schedule.**
- 4) Build and test cell for in situ XAS analysis. (8/23/15) **On schedule.**

Progress Report

Milestone (1) has been completed. A schematic of the Li-S cell used for XAS experiments appears in Figure 66. We have found that the XAS fingerprints of aggregated polysulfides are very similar to those calculated for individual molecules. In addition, the measured XAS spectra have a weak concentration dependence [Milestone (2)] and comparisons with theoretical predictions are underway [Milestone (3)]. This is very powerful result as we can use XAS to determine the existence of species regardless of concentration. Encouraged by these results, we designed and built an *in situ* XAS of Li-S cells [Milestone (4)]. Li-S cells were discharged to specific points in the voltage profile, discharge was stopped, and cells were allowed to sit at operating temperature (90°C) for three days to allow polysulfide diffusion to occur. XAS was then performed in an attempt to determine what species are present in the electrolyte after ample time has been given for diffusion. The voltage profiles for cells (A), (B), and (C) are shown in Figure 67. The corresponding XAS of each cell is shown in Figure 68. Interestingly, cell (A) shows a spectral feature at 2469.2 eV, evidence of polysulfide radical anion species (as they previously determined via theoretical XAS calculations of S₃⁻ radical species dissolved in TEGDME). The result shows that not only radical species are formed during discharge, but that the radical species are still present at a significant concentration after the cell has been allowed to reach thermodynamic equilibrium. We are now in the process of quantifying the electrolyte composition by using linear combinations of theoretically calculated XAS for the different polysulfide (dianion and radical) species.

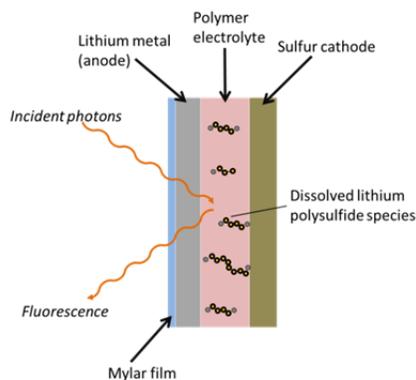


Figure 66: Schematic of Li-S cell used for XAS experiments

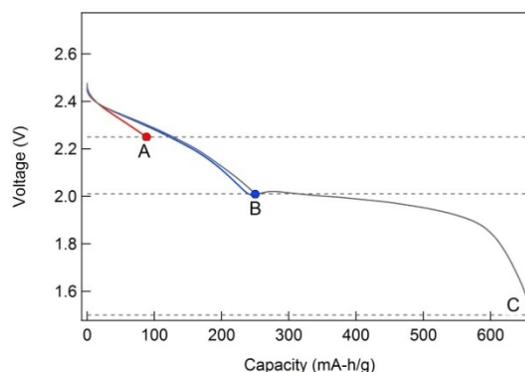


Figure 67: Voltage profiles for three Li-S cells

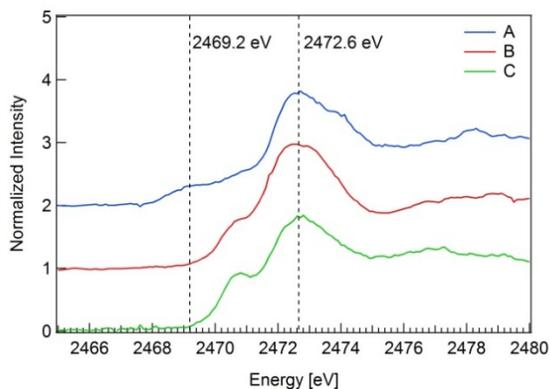


Figure 68: XAS for Li-S cells (A), (B), and (C)

Q1 Patents/Publications/Presentations

1. Presentations
 - a. None.

2. Publications

- a. “Probing the Charge State of Lithium Polysulfides using X-ray Absorption Spectroscopy”,
Tod A Pascal, CD Pemmaraju and David Prendergast, Under Revision Phys. Chem. Chem.
Phys.

Task 8.3 – Khalil Amine (Argonne National Laboratory)

PROJECT OBJECTIVE: The objective of this project is to develop a novel SeS_x cathode material for rechargeable lithium batteries with high energy density, long life along with low cost and high safety.

PROJECT IMPACT: Developing a new battery chemistry that is promising to support the goal of PHEV and EV applications.

OUT-YEAR GOALS: When this new cathode is optimized, the following result can be achieved:

- A cell with nominal voltage of 2 V and energy density of 600 Wh/kg;
- A battery capable of operating for 500 cycles with low capacity fade.

COLLABORATIONS: Prof. Chunsheng Wang of University of Maryland
Dr. Yang Ren and Dr. Chengjun Sun of APS at ANL

Milestones

The following are the milestones for each Quarter during FY15:

1. Investigate the phase stability of SeS_x (September 2015)-**Ongoing**
2. Confine Se, SeS in different carbon matrix including porous organic polymer to suppress the dissolution of lithium polysulfides and polyselenide (April 2016)-**Ongoing**
3. Understand the specific interaction between S (and Se) with porous substrate and their dissolution in different solvents (September 2016)-**Ongoing**
4. Develop new capsulation strategy to further suppress the dissolution of lithium polysulfides or polyselenide (September 2016)-**Ongoing**

Progress Report

A new sulfur electrode embedded in an easily available porous organic polymer (POP) network, which represents a new class of amorphous polymeric materials with tuneable permanent porosity to act as a host to encapsulate sulfur and to suppress the dissolution of lithium polysulfides (see Figure 69). POPs in this study have much higher surface area (up to $3143 \text{ m}^2 \text{ g}^{-1}$) than the porous carbon materials. Moreover, these POPs exhibit dominant micropores with pore size less than 1 nm as calculated from the Non-Local Density Functional Theory (NLDFT). The highly strained tetrahedral monomer in POPs extends the network three dimensionally thus enables the formation of a robust network with less penetration and high surface area.

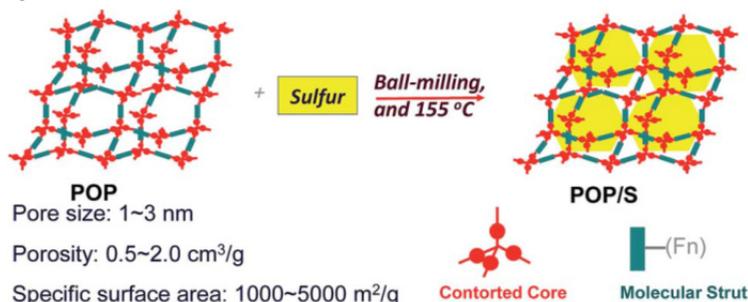


Figure 69: Preparation of POP–sulfur composites with micropores as host materials for accommodation of nanosized sulfur particles.

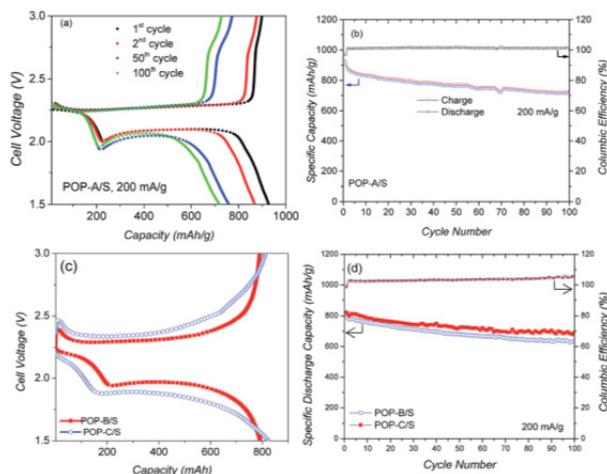


Figure 70: Figure 2 Li–S cells with POP–sulfur composite cathodes cycled between 1.5 and 3.0 V at a current density of 200 mA g^{-1} current. Voltage profiles (a), and capacity retention (b) of POP–A–S composite cell; 1st cycle charge discharge profiles of POP–B–S and POP–C–S composite cells (c), and cycling performance of POP–B–S and POP–C–S composite cells (d). (Electrolyte: 1 M LiTFSI in 1,3-dioxolane (DOL) and $\text{CHF}_2\text{CF}_2\text{CH}_2\text{OCF}_2\text{CF}_2\text{H}$ in a 1 : 2 volume ratio.)

POP-B and POP-C composite cells can achieve high coulombic efficiency in the initial cycle and the values are close to 100% in the following cycles, indicating that the shuttle mechanism was completely suppressed in the POP-B and POP-C systems.

In the future, this new approach will be used for impregnating the Se and SeS system to minimize the dissolution issue. We will also investigate the role of electrolyte in preventing dissolution issues in S, Se and SeS systems.

The charge–discharge voltage profiles of Li–S cells containing POP–sulfur composite are presented in Figure 2. Figure 2a shows the first charge and discharge voltage profiles for POP–A–sulfur cell. The discharge capacity is 927 mAh g^{-1} at a current density of 200 mA g^{-1} and the subsequent charge capacity is 898 mAh g^{-1} , corresponding to a high coulombic efficiency of 97%. As shown in Figure 2b, the high coulombic efficiency for POP–A–sulfur cell is maintained even after 100 cycles, suggesting the successful restraint of polysulfide dissolution and the redox shuttling effect. Such a high coulombic efficiency in the whole cycle range for a sulfur cathode is quite rare. Li–S cell testing data for POP–B–sulfur and POP–C–sulfur composites are shown in Figures 2c and 2d. It is notable that the charge and discharge voltage profiles of POP–sulfur composites showed different potential polarization, which might be caused by the different porous structure and the pore volume reduction after the sulfur infusion. As shown in Figure 2d, both

Q1 Patents/Publications/Presentations

1. Improved cyclability of a lithium–sulfur battery using POP–Sulfur composite materials, Wei Weng, Shengwen Yuan, Nasim Azimi, Zhang Jiang, Yuzi Liu, Yang Ren, Ali Abouimrane and Zhengcheng Zhang, *RSC Adv.*, **2014**, 4, 27518.

Task 8.4 – Hong Gan (Brookhaven National Laboratory); Co-PI: Esther Takeuchi (Brookhaven National Laboratory and Stony Brook University)

Multi-Functional Cathode Additives (MFCA) for Li-S Battery Technology

PROJECT OBJECTIVE: Develop a low cost battery technology for PEV application utilizing Li-S electrochemical system by incorporating multifunctional cathode additives (MFCA), consistent with the long term goals of DOE EV Everywhere Blueprint.

PROJECT IMPACT: The Li-S battery system has gained significant interest due to its low material cost potential (35% cathode cost reduction over Li-ion) and its attractive 2.8x (volumetric) to 6.4x (gravimetric) higher theoretical energy density compared to conventional Li-ion benchmark systems. Commercialization of this technology requires overcoming several technical challenges. This effort will focus on improving the cathode energy density, power capability and cycling stability by introducing multifunctional cathode additives (MFCA). The primary deliverable of this project is to identify and characterize the best MFCA for Li-S cell technology development.

OUT-YEAR GOALS: This is a multi-year project comprised of two major phases to be successfully completed in three years. Phase 1 includes cathode and MFCA investigation, and Phase 2 will include cell component interaction studies and full cell optimization. The work scope for year 1 will focus on the cathode and cathode additive studies. The proof of concept and feasibility studies will be completed for the Multi-Functional Cathode Additives. By year end, multiple types of additives will be identified and prepared, including the synthesis of the non-commercially available additives. The electrochemical testing of all selected MFCA will be initiated.

COLLABORATIONS: Amy Marschilok (SBU), Kenneth Takeuchi (SBU), Dong Su (BNL) and Can Erdonmez (BNL).

Milestones

The following are the milestones for each Quarter during FY15:

1. Baseline Li/MFCA cell demonstration. (Dec-14) **Completed**
2. Baseline Li/S cell demonstration. (Mar-15) **Ongoing**
3. Li/Sulfur-MFCA concept cell demonstration. (Jun-15) **Ongoing**
4. Synthesis of MFCA. (Sep-15) **Ongoing**

Progress Report

Baseline Li-MFCA cell demonstration: Metal sulfides are proposed as the multifunctional cathode additives (MFCA) in Li-S battery electrochemical system. For this task, commercially available Copper Sulfide (CuS) and Pyrite (FeS₂) are selected for coin cell construction and electrochemical cycling testing. Figure 71 shows the Li/CuS coin cell 1st discharge voltage profile under a C/10 discharge rate to 1.0V where 2 voltage plateaus are apparent to 483 mAh/g (86% of theoretical capacity). Cycling the CuS coin cells between 3.0V and 1.0V resulted in fast capacity fade. However, when the cells cycled between 3.0V and 1.8V, reversible cell cycling was achieved, Figure 72, consistent with the literature reported value (B. Jache, B. Mogwitz, F. Klein, P. Adelhelm, *Journal of Power Sources* 247 (2014) 703-711). The structure of the commercially obtained CuS was confirmed as Covellite by XRD. For the cathodes discharged to 1.0V, both Li₂S and Cu (0) are clearly identified as reduction products.

Commercially obtained FeS₂ (Pyrite) has the Cubic crystal structure confirmed by XRD. The 1st and 2nd discharge/charge profiles of FeS₂ coin cell under C/10 rate are shown in Figure 73. Unlike the CuS, a single sloped voltage profile at ~1.4V is observed for the 1st cycle with 800 mAh/g capacity delivered to a 1.1V cut off (~90% of theoretical capacity). However, in the 2nd cycle the voltage profiles show two voltage plateaus, indicating a material structural change and delivering lower capacity. The results are in good agreement with literature reported observations (E. Strauss, D. Golodnitsky, E. Peled, *Electrochimica Acta* 2000, 45, 1519). Interestingly, this new phase material demonstrated good cycleability with cycling capacity maintained at 78% of the 2nd cycle discharge capacity over 40 cycles, Figure 74.

During this period, the coin cell capability in testing the selected metal sulfide MFCA candidates has been established. Depending on the additive material selected, the cell cycling potential ranges need to be carefully considered when working on the Sulfur/MFCA hybrid cathode system. For CuS and FeS₂ containing systems, 1.8V and 1.1V discharge voltage cut offs will be used respectively to maintain good system cycleability. Additional studies to understand the reaction mechanism of these electrochemical systems are underway. The principles learned from these two system will be applied to other additive studies.

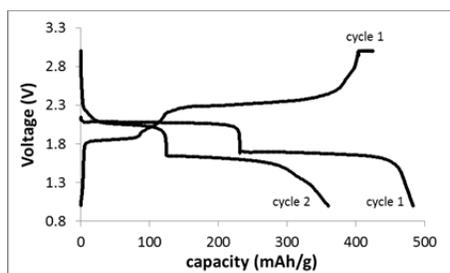


Figure 71: Li/CuS discharge voltage profile

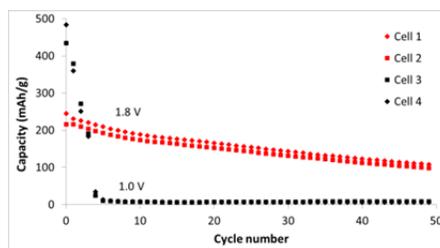


Figure 72: Li/CuS cell cycle test under two different voltage windows

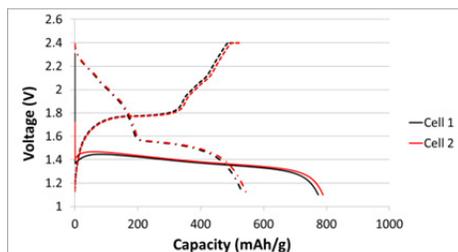


Figure 73: Li/FeS₂ discharge voltage profile

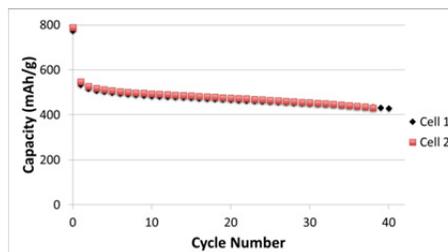


Figure 74: Li/FeS₂ discharge voltage profile

Q1 Patents/Publications/Presentations

None.

Task 8.5 – Jie Xiao and Jun Liu (Pacific Northwest National Laboratory)

Project Title: Development of High-Energy Lithium-Sulfur Batteries

PROJECT OBJECTIVE:

The objective of this project is to develop high-energy, low-cost lithium sulfur (Li-S) batteries with long lifespan. All proposed work will employ thick sulfur cathode (≥ 2 mAh/cm² of sulfur) at a relevant scale for practical applications. The diffusion process of soluble polysulfide out of the thick cathode will be revisited to investigate the cell failure mechanism at different cycling. Alternative anode will be explored to address the lithium anode issue. The fundamental reaction mechanism of polysulfide under the electrical field will be explored by applying advanced characterization techniques to accelerate the development of Li-S battery technology.

PROJECT IMPACT:

The theoretical specific energy of Li-S batteries is ~ 2300 Wh/kg, which is almost three times higher than that of state-of-art Li-ion batteries. The major challenge for Li-S batteries is polysulfide shuttle reactions, which initiate a series of chain reactions that significantly shorten the battery life. The proposed work will design novel approaches to enable Li-S battery technology and accelerate market acceptance of long-range electrical vehicles (EV) required by the EV Everywhere Grand Challenge proposed by DOE/EERE.

OUT-YEAR-GOALS:

- Fabricate Li-S pouch cells with thick electrodes to understand sulfur chemistry/electrochemistry in the environments similar to the real application.
- Leverage the Li-metal protection project funded by DOE and PNNL's advanced characterization facilities to accelerate the development of Li-S battery technology.
- Develop Li-S batteries with a specific energy of 400 Wh/kg at cell level, 1000 deep-discharge cycles, improved abuse tolerance, and less than 20% capacity fade over a 10-year period to accelerate commercialization of electrical vehicles.

COLLABORATIONS:

- Dr. Xiao-Qing Yang (LBNL) – *In situ* characterization
- Dr. Bryant Polzin (ANL) – Electrode fabrication
- Dr. Xingcheng Xiao (GM) – materials testing

Milestones

- 1) Optimization of sulfur loading to reach 3-4 mAh/cm² areal specific capacity on the cathode (12/31/2014). **Completed**
- 2) Complete the investigation on the fundamental reaction mechanism of Li-S batteries (3/31/2015). **On going**
- 3) Identify alternative anode to stabilize the interface reactions on the anode side (6/30/2014). **On going**
- 4) Demonstrate the stable cycling of sulfur batteries (2-4 mAh/cm²) with less than 20% degradation for 200 cycles. (9/30/2015). **On going**

Progress Report

In FY14, an innovative approach has been developed (patent application #: 61/521,191) to fabricate large-area pinhole-free thick sulfur electrodes, while still maintaining the nanostructures of sulfur/carbon composite to obtain high utilization rate of sulfur. In this quarter, the detailed study on the calendar pressure, electrode thickness and the corresponding areal specific capacity was reported. The Q1 milestone of 3-4 mAh/cm² loading has been completed.

Figure 75a compared the deliverable areal capacity from sulfur electrodes with different areal loading of sulfur. The balanced utilization rate of sulfur and conductivity (both ionic and electronic) of the whole electrode was reached at ca. 3.5 mg/cm² sulfur loading, leading to a peak capacity of 4.5 mAh/cm² at 0.1C. Figure 75b showed the thickness changes of a thick sulfur electrode (5.8 mg/cm²) under different pressures. Even a small pressure of 0.25 T induced significant thickness decrease from 150 to 90 μm, indicating relatively loose structure of the electrode comprised of sulfur/carbon composite. Further increase of pressure to above 1 T only slightly decreased the electrode thickness. The purpose of this step was to adjust the porosity of as-prepared electrodes.

Accordingly, the specific areal capacity displayed significant dependence on the rolling pressure e.g. porosity of electrode (Figure 75c). As the pressure increased from 0 to 1.5 T, the areal capacity deliverable from the same electrode did not change much and kept between 3.5-4 mAh/cm². The electrode thickness reduction benefited the final volumetric energy density of the cell; while the slightly decreased porosity helped to reduce the electrolyte amount needed to wet the entire electrodes but still maintained a decent utilization rate of sulfur. Further increasing the pressure to greater than 2 T, a large capacity reduction was seen. However, if the pressure applied was greater than 2 T, the continuous electrolyte diffusion pathway was blocked in the highly densified electrodes. Therefore, not only the electrolyte wetting became an issue at the beginning, the ionic conductivity of whole electrode also largely decreased, leading to a much lower capacity (Figure 75c). For thick electrode preparation, both the areal mass loading and rolling pressure needed be balanced carefully, which may vary with different types of carbon materials and sulfur fractions.

The thick electrode (3.5 mg cm⁻² of sulfur, pressed at 0.2 T) showed a pretty good cycling stability (Figure 75d), comparable or even better than the thin-film Li-S cells for the first 100 cycles. At 0.1 C, the S80/IKB delivered a capacity of 750 mAh g⁻¹ after 100 cycles. After 100 cycles, the limiting step of cycling was transferred to the anode side as discussed in our previous reports last year.

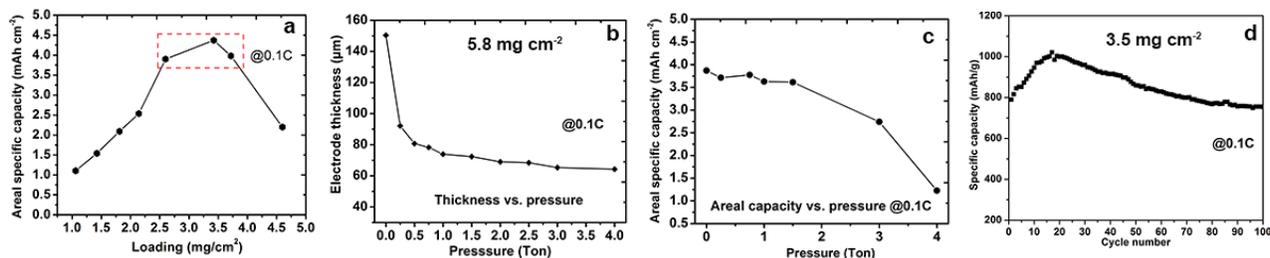


Figure 75: (a) Areal specific capacity in dependence of the sulfur loading obtained at 0.1C, (b) electrode thickness as a function of pressure, (c) areal capacity in dependence of pressure applied for calendaring the electrode, and (d) cycling stability of cell cycled at 0.1C (1C=1000 mAh/g)

Q1 Patents/Publications/Presentations

1. “Preformation of stable solid electrolyte interface (SEI) film on graphite anode”, Application #: **14/529,840**
2. “Electrolyte for lithium-sulfur batteries employing graphite as the anode”, Application #: **14/530,562**

Task 8.6 – Yi Cui (Stanford University)

Nanostructured Design of Sulfur Cathodes for High Energy Lithium-Sulfur Batteries

PROJECT OBJECTIVE: The charge capacity limitations of conventional transition metal oxide cathodes are overcome by designing optimized nano-architected sulfur cathodes.

This study aims to enable sulfur cathodes with high capacity and long cycle life by developing sulfur cathodes from the perspective of nanostructured materials design, which will be used to combine with lithium metal anodes to generate high-energy lithium-sulfur batteries. Novel sulfur nanostructures as well as multifunctional coatings will be designed and fabricated to overcome the issues related to volume expansion, polysulfide dissolution and insulating nature of sulfur.

PROJECT IMPACT: The capacity and the cycling stability of sulfur cathode will be dramatically increased. This project's success will make lithium-sulfur batteries to power electric vehicles and decrease the high cost of batteries.

OUT-YEAR GOALS: The cycle life, capacity retention as well as the capacity loading of sulfur cathodes will be greatly improved (200 cycles with 80% capacity retention, >0.3 mAh/cm² capacity loading) by optimizing material design, synthesis and electrode assembly.

COLLABORATIONS:

- BATT program PI's
- SLAC: In-situ X-ray, Dr. Michael Toney.
- Stanford: Prof. Nix, mechanics; Prof. Bao, materials.

Milestones

- 1) Demonstrate synthesis to generate monodisperse sulfur nanoparticles with/without hollow space (Oct-13) **Completed**
- 2) Develop surface coating with one type of polymers and one type of inorganic materials (Jan-14) **Completed**
- 3) Develop surface coating with several types of polymers; Understand amphiphilic interaction of sulfur and sulfide species (Apr-14) **Completed**
- 4) Demonstrate sulfur cathodes with 200 cycles with 80% capacity retention and 0.3mAh/cm² capacity loading (July-14) **Completed**
- 5) Demonstrate Li₂S cathodes capped by layered metal disulfides (Dec. 2014). **On going**

Progress Report

High-performance lithium sulfide (Li_2S) cathodes based on encapsulation using two-dimensional layered transition metal disulfides have been designed. In particular, the use of titanium disulfide (TiS_2), a 2D layered material, as an effective encapsulation material for Li_2S cathodes has been demonstrated. Compared to sulfur, fully-lithiated Li_2S , with its high theoretical specific capacity of $1,166 \text{ mAh g}^{-1}$, represents a more attractive cathode material because of its compatibility with safer lithium metal-free anodes. The vast majority of previous work on encapsulation of Li_2S cathodes use electronically-conductive carbon-based materials such as graphene and porous carbon for encapsulation. However, their non-polar nature leads to weak interaction with polar Li_2S_n species, which greatly weakens their trapping effect. As a result, the use of TiS_2 as an effective encapsulation material for Li_2S cathodes has been

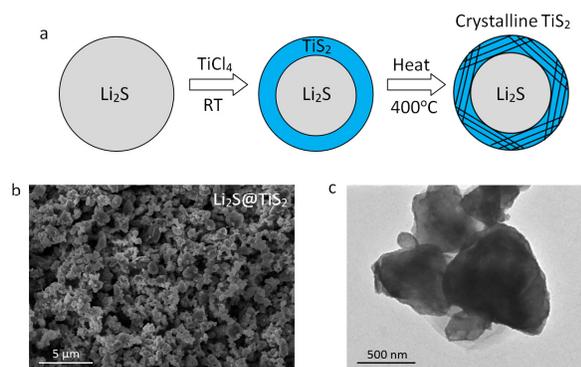


Figure 76: (a) Schematic of the synthesis process, (b) SEM image and (c) TEM image of $\text{Li}_2\text{S}@ \text{TiS}_2$ structures.

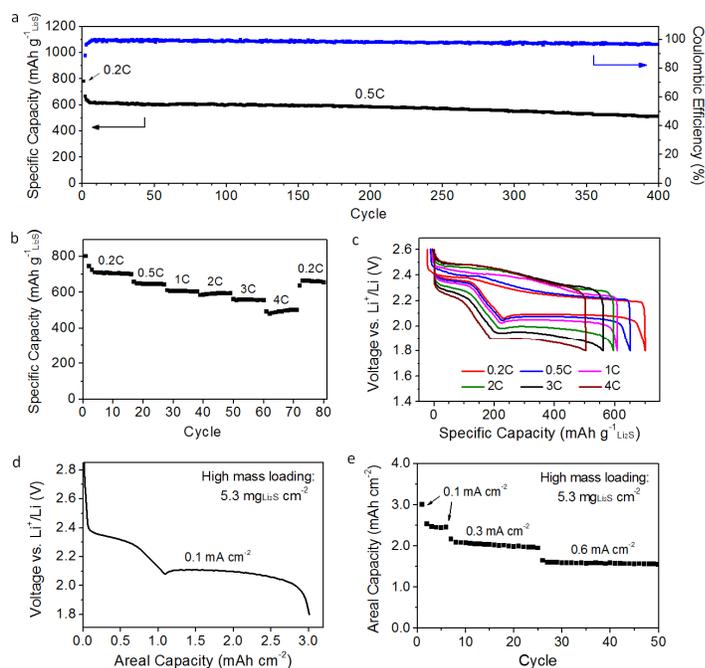


Figure 77: (a) Specific capacity and Coulombic efficiency of $\text{Li}_2\text{S}@ \text{TiS}_2$ cathodes upon prolonged 400 charge-discharge cycles at 0.5C (b) Specific capacity and (c) charge-discharge voltage profiles of $\text{Li}_2\text{S}@ \text{TiS}_2$ cathodes cycled from 0.2C to 4C . (d) First cycle discharge voltage profile and (e) areal capacity of $\text{Li}_2\text{S}@ \text{TiS}_2$ cathodes with high mass loading cycled from 0.1 to 0.6 mA cm^{-2} .

demonstrated. TiS_2 possesses a combination of high electronic conductivity ($\sim 10^3 \text{ S/cm}$) and polar Ti-S groups which can potentially interact strongly with $\text{Li}_2\text{S}/\text{Li}_2\text{S}_n$ species. We synthesized $\text{Li}_2\text{S}@ \text{TiS}_2$ core-shell nanostructures (Figure 76) which exhibited 10 orders of magnitude higher electronic conductivity compared to pure Li_2S . The results of *ab initio* simulations also show strong binding between Li_2S and TiS_2 , with a calculated binding energy 10 times higher than that between Li_2S and carbon-based graphene, a very common encapsulation material used in the literature.

Using the $\text{Li}_2\text{S}@ \text{TiS}_2$ nanostructures as a cathode material, stable cycling performance at 0.5C over 400 charge-discharge cycles (Figure 77a) has been achieved. Relative to the initial specific capacity of $666 \text{ mAh g}^{-1}_{\text{Li}_2\text{S}}$ ($\sim 956 \text{ mAh g}^{-1}_{\text{s}}$) at 0.5C , the cells retained 77% of their capacity at the end of 400 cycles, which corresponds to a small average capacity decay of 0.058% per cycle. The average Coulombic efficiency was calculated to be 98% . Furthermore, an unprecedented specific capacity of $503 \text{ mAh g}^{-1}_{\text{Li}_2\text{S}}$ under high C-rate conditions (4C), as well as unprecedented areal capacity of 3.0 mAh cm^{-2} under high mass loading conditions ($5.3 \text{ mg}_{\text{Li}_2\text{S}} \text{ cm}^{-2}$), both of which are the highest values reported to date for Li_2S cathodes (Figure 77b-e) have been achieved.

Task 8.7 – Perla Balbuena (Texas A&M University)

Addressing Internal “Shuttle” Effect: Electrolyte Design and Cathode Morphology Evolution in Li-S Batteries

PROJECT OBJECTIVE: The objective of this project is to overcome the lithium-metal anode deterioration issues through advanced Li-anode protection/stabilization strategies including (i) in-situ chemical formation of a protective passivation layer and (ii) alleviation of the “aggressiveness” of the environment at the anode by minimizing the polysulfide shuttle with advanced cathode structure design.

PROJECT IMPACT: Through formulation of alternative electrolyte chemistries and design, fabrication, and test of improved cathode architectures it is expected that this project will deliver Li/S cells operating for 500 cycles at efficiency greater than 80%.

OUT-YEAR GOALS: By determining reasons for successes or failures of specific electrolyte chemistries, and assessing relative effects of composite cathode microstructure and internal shuttle chemistry vs. that of electrolyte chemistry on cell performance, expected results are : 1) Develop an improved understanding of the Li/S chemistry and ways to control it; 2) Develop electrolyte formulations able to stabilize the Li anode; 3) Develop new composite cathode microstructures with enhanced cathode performance; 4) Develop a Li/S cell operating for 500 cycles at an efficiency > 80%.

COLLABORATIONS: This is a collaborative work combining first-principles modelling (Perla Balbuena, Texas A&M University), mesoscopic level modelling (Partha Mukherjee, Texas A&M University), and synthesis, fabrication, and test of Li/S materials and cells (Vilas Pol, Purdue University). Balbuena is also a PI in the BATT program.

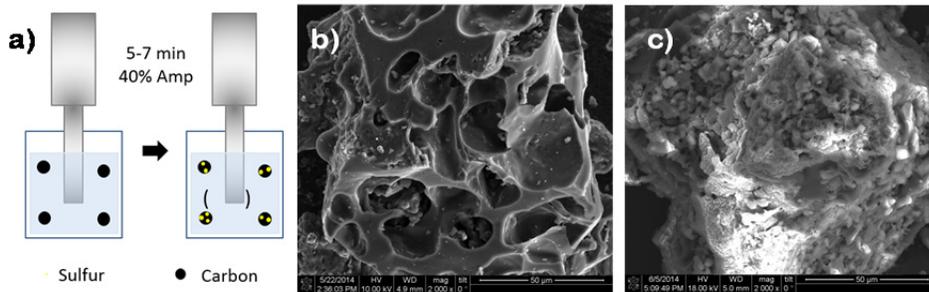
Milestones

- 1) Synthesis of the C/S cathode hybrid materials: Develop lab-scale Li-S composite.(Dec-14) **Completed-** Perform advanced characterization- **On-going** (Mar-15)
- 2) Determination of the structure of the PS/Li Interface: Characterization of thermodynamics of nucleation and growth of PS deposits on the Li surface. (Mar-15) **On-going**
- 3) Determination of the chemistry of the C/S composite cathode: Characterize dissolution, reduction, and lithiation of S in the composite cathode microstructure. (Jun-15) **On-going**
- 4) Study of electrode morphology evolution and mesostructure transport interaction: Study cathode mesostructure impact on product formation and deposition. Go/No-Go: Comparative analysis of the mesoscale model and experimental characterization. (Sep-15) **On-going**

Progress Report

Electrolyte decomposition at the Li anode surface: Ab initio molecular dynamics simulations (AIMD) showed a significantly distinct behavior among the reactivity of solvents: ethylene carbonate (EC), 1,3-dioxolane (DOL), and 1,2-dimethoxyethane (DME) in contact with the Li (100) surface. Simulations show a large reconstruction of the Li surface upon EC reduction followed by ring opening and fragmentation of the radical anions, whereas DOL and DME solutions were found not to be reduced during the simulation time (~15 ps). The significant differences of the reactivity of the solvents are in agreement with experimental observations regarding dendrite formation in the order $EC \gg DME / DOL$, which follows the same order of their polarities, although their reduction potentials are similar.

Synthesis of cathode materials: New carbon cavities were developed for encapsulation of non-conducting sulfur. The solid-state synthesis of the carbon substrate is an environmentally-friendly, economical, and single-step procedure. A bio-mass derived precursor is pyrolytically heat-treated to high temperatures between 500°C – 1000°C in an inert gas atmosphere. The synthesis process of the carbon-sulfur composites utilizes sonochemistry, the application of ultrasound waves that produce high velocity



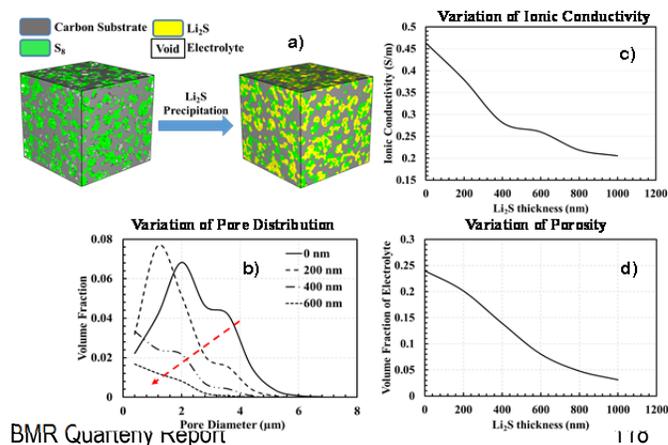
jet-streams of bubbles according to the acoustic cavitation effect. The total time for ultra-sonication is approximately 5-7 minutes. Lab scale 500 mg C/S composite synthesis is

illustrated in

Figure 78.

Figure 78: a) Procedure for synthesizing carbon-sulfur composites, b) SEM of carbon micro-compartment as a substrate for nanosulfur loading, c) SEM of carbon micro-compartment after sonochemical loading of sulfur nanoparticles.

Modeling of cathode microstructure: First-principles thermodynamic analysis of adsorption of insoluble lithium polysulfides (Li_2S and Li_2S_2) on the Li_2S (111) surface indicates that direct Li_2S deposition is energetically favored over Li_2S_2 deposition and reduction processes. The evolution of the thickness of the deposited Li_2S film in the C/S composite cathode determined from a Kinetic Monte Carlo model suggests



a linear growth. Based on this information, the porosity is found to decrease 80% when the thickness grows from 0 nm to 100 nm. The pore size distribution correlates with the microstructure change (Figure 79). The precipitation-induced microstructure change is found to vary the ionic conductivity in the microstructure. For Li_2S thickness < 400 nm the ionic conductivity change is mainly due to porosity change. For Li_2S thickness > 400 nm, the change becomes smaller due to the decrease of the ionic transport path and

isolation of void spaces which reduce the influence of porosity change on the properties.

Figure 79: a) Precipitation-induced microstructure change, b) Pore size distribution, c) Ionic conductivity, d) Porosity with different precipitation thicknesses.

TASK 9 – LI-AIR BATTERIES

High-density energy storage systems are critical for electric vehicles (EV) required by the EV Everywhere Grand Challenge proposed by DOE/EERE. Conventional Li-ion batteries still cannot fully satisfy the ever-increasing needs because of their limited energy density, high cost, and safety concerns. As an alternative, the rechargeable Li-O₂ battery has the potential to be used for long range EVs. The practical energy density of a Li-O₂ battery is expected to be ~ 800 Wh kg⁻¹. The advantages of Li-O₂ batteries come from their open structure; that is, they can absorb the active cathode material (oxygen) from the surrounding environment instead of carrying it within the batteries. However, the open structure of Li-O₂ batteries also leads to several disadvantages. The energy density of Li-O₂ batteries will be much lower if oxygen has to be provided by an onboard container. Although significant progresses have been made in recent years on the fundamental properties of Li-O₂ batteries, the research in this field is still at its early stage and many barriers have to be overcome before their practical applications. The main barriers in this field include:

- 1) Instability of electrolytes. Superoxide species generated during discharge or O₂ reduction process is highly reactive with electrolyte and other components in the battery. Electrolyte decomposition during charge or O₂ evolution process is also significant due to high over-potentials.
- 2) Instability of air electrode (dominated by carbonaceous materials) and other battery components (such as separators and binders) during charge/discharge processes in an oxygen-rich environment.
- 3) Limited cyclability of the battery associated with instability of the electrolyte and other components of the batteries.
- 4) Low energy efficiency associated with large over-potential and poor cyclability of Li-O₂ batteries.
- 5) Low power rate capability due to electrode blocking by the reaction products.
- 6) Absence of a low cost, high efficiency oxygen supply system (such as oxygen selective membrane).

THE MAIN GOAL OF THIS PROJECT IS TO PROVIDE A BETTER UNDERSTANDING ON THE FUNDAMENTAL REACTION MECHANISMS OF LI-O₂ BATTERIES AND IDENTIFY THE REQUIRED COMPONENTS (ESPECIALLY ELECTROLYTES AND ELECTRODES) FOR STABLE OPERATION OF LI-O₂ BATTERIES. THE NEW COMPONENTS DEVELOPED IN THIS WORK CAN ALSO BE USED IN OTHER ELECTROCHEMICAL SYSTEMS OPERATED IN AN OXYGEN-RICH ENVIRONMENT. BETTER BI-FUNCTIONAL CATALYST DEVELOPED IN THIS WORK CAN LOWER THE OVER-POTENTIALS AND IMPROVE THE STABILITY OF THE COMPONENTS OF LI-O₂ BATTERIES. THEY CAN ALSO BE USED IN OTHER METAL-AIR BATTERIES TO IMPROVE THEIR REVERSIBILITY AND POWER RATES. SUCCESS OF THIS PROJECT WILL ESTABLISH A SOLID FOUNDATION FOR FURTHER DEVELOPMENT OF LI-O₂ BATTERIES TOWARDS THEIR PRACTICAL APPLICATIONS FOR LONG RANGE EVS. THE FUNDAMENTAL UNDERSTANDING AND BREAKTHROUGH IN LI-O₂ BATTERIES MAY ALSO PROVIDE INSIGHT ON IMPROVING THE PERFORMANCE OF LI-S BATTERIES AND OTHER ENERGY STORAGE SYSTEMS BASED ON CHEMICAL CONVERSION PROCESSES.

Task 9.1 – Ji-Guang Zhang and Wu Xu (Pacific Northwest National Laboratory)

Rechargeable Lithium-Air Batteries

PROJECT OBJECTIVE:

The objective of this work is to develop stable electrolyte and oxygen evolution reaction (OER) catalysts to reduce the charging overvoltage of lithium (Li)-air batteries and improve the cycling stability of rechargeable Li-air batteries. New catalysts will be synthesized to improve the capacity and cycling stability of Li-O₂ batteries. New electrolytes will be investigated to ensure their oxygen-stability during Li-O₂ reaction.

PROJECT IMPACT:

Li-air batteries have a theoretical specific energy that is more than five times of state of the art Li-ion batteries and are potential candidates for use in next-generation, long-range electric vehicles (EV). However, the poor cycling stability and low Coulombic efficiency of Li-air batteries have prevented their practical application to date. This work will explore a new electrolyte and electrode that could lead to long cyclability and high Coulombic efficiencies in Li-air batteries that can be used in the next generation EVs required by the EV Everywhere Grand Challenge proposed by DOE/EERE.

OUT-YEAR-GOALS:

- The long-term goal of the proposed work is to enable rechargeable Li-air batteries with a specific energy of 800 Wh/kg at cell level, 1000 deep-discharge cycles with less than 20% capacity fade, and improved abuse tolerance over a 10-year period to accelerate commercialization of long-range EVs.

COLLABORATIONS:

- Chunmei Ben (NREL) – Metal oxide coated glassy carbon electrode
- Bryant Polzin (ANL) – NCA, NMC and graphite electrodes
- Apparao M. Rao (Clemson University)– Carbon-based air electrodes
- Yangchuan (Chad) Xing (University of Missouri) – metal oxide coated glassy carbon electrode.

Milestones

- 1) Synthesize and characterize the modified glyme solvent and the dual transition metal oxide catalyst (12/31/2014). **Completed**
- 2) Improve the stability of solvent using conventional carbon air electrode (3/31/2015). **Ongoing**
- 3) Identify the solvent to be stable for at least 50 cycles on modified air electrode. (6/30/2015). **Ongoing**
- 4) Integrate the new electrolyte and modified air electrode to assemble Li-O₂ batteries with at least 120 cycles stable operation (9/30/2015). **Ongoing**

Progress Report

In this quarter, the cycling stability of three air electrodes based on carbon nanotube and fibers (from Prof. Rao's group) were evaluated in Li-O₂ cells with electrolyte of 1 M LiTf in tetraglyme. The structure and pore size data of the air electrodes are shown in Figure 80a and Figure 80b, respectively. The Li-O₂ cells were tested in 1 atm O₂ pressure at a current density of 0.10 mA/cm². Figure 80c shows the discharge/charge voltage profiles of Li-O₂ cells with BAG-50 and the cycling stability results of three BAG electrodes are shown in Figure 80d. The BAG electrodes show typical behavior of carbon air electrodes, i.e. the discharge voltage plateau is at 2.5-2.6 V and charging requires > 4 V. The BAG-10 has much higher initial capacity because of higher surface area and pore volume but it drops very quickly. All three BAG air electrodes exhibit stable cycling with low capacity after first few cycles at ~ 400 mAh/g.

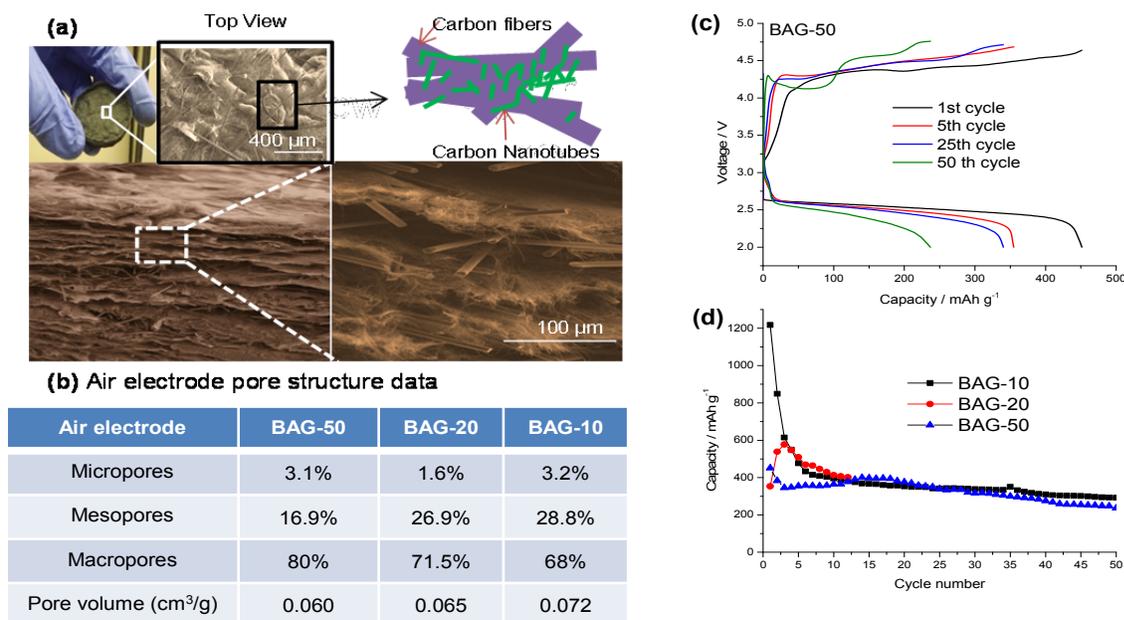


Figure 80: (a) Structural morphology (b) and pore data information of three BAG air electrodes. (c) Voltage profiles of BAG-50 and (d) cycling stability of the three BAG electrodes in Li-O₂ cells.

A new electrolyte (2,3-dimethoxy-2,3-dimethylbutane, which is the methylated DME) solvent was synthesized for the Li-O₂ study. However, the solubility of Li salt (e.g. LiTFSI) in this solvent is very poor. The performance of this solvent will be tested in mixed solvent system with other ethers or glymes.

In a separate effort, nano-structured ZnCo₂O₄ (ZCO) on the surface of carbon cloth (Figure 81b) was synthesized and used it as a catalyst/carbon composite air electrode. Although the ZCO-based electrode led to lower initial discharge capacity due to its heavy weight, the ZCO could reduce the OER potential by about 0.6 V and maintain a higher discharge capacity and capacity retention than the pristine carbon cloth electrode.

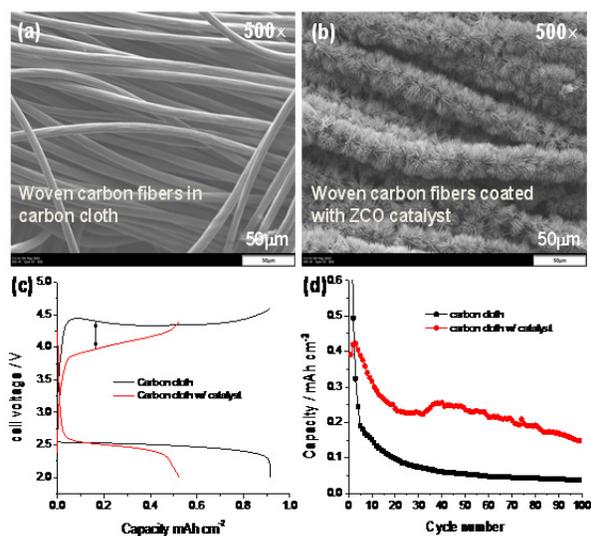


Figure 81: SEM images of (a) carbon cloth and (b) ZCO-coated carbon cloth, and voltage profiles (c) and cycling stability (d) of the Li-O₂ cells with the carbon cloth electrodes w and w/o ZCO.

Q1 Patents/Publications/Presentations

1. E. Nasybulin, W. Xu*, B. L. Mehdi, E. Thomsen, M. H. Engelhard, R. C. Massé, P. Bhattacharya, M. Gu, W. Bennett, Z. Nie, C. Wang, N. D. Browning, J.-G. Zhang*, **“Formation of Interfacial Layer and Long-Term Cycability of Li-O₂ Batteries”**, ACS Applied Materials & Interfaces, 2014, **6**, 14141-14151.

Taks 9.2 – Vincent Giordani (Liox)

Efficient Rechargeable Li/O₂ Batteries Utilizing Stable Inorganic Molten Salt Electrolytes

PROJECT OBJECTIVE: The objective of this project is to develop high specific energy, rechargeable Li-air batteries having lower overpotential and improved robustness under ambient air compared to current Li-air batteries. The technical approach involves replacing traditional organic and aqueous electrolytes with a nonvolatile, inorganic molten salt comprising nitrate anions and operating the cell at elevated temperature (>80 °C). The research methodology includes powerful *in situ* spectroscopic techniques coupled to electrochemical measurements (e.g. electrochemical mass spectrometry) designed to provide quantitative information about the nature of chemical and electrochemical reactions occurring in the air electrode.

PROJECT IMPACT: If successful, this project will solve particularly intractable problems relating to air electrode efficiency, stability and tolerance to the ambient environment. Furthermore, these solutions may translate into reduced complexity in the design of a Li-air stack and system, which in turn may improve prospects for use of Li-air batteries in EVs. Additionally, the project will provide materials and technical concepts relevant for the development of other medium temperature molten salt Li battery systems of high specific energy, which may also have attractive features for EVs.

OUT-YEAR-GOALS: The long term goal of this project is to develop Li-air batteries comprising inorganic molten salt electrolytes and protected Li anodes which demonstrate high (>500 Wh/kg) specific energy and efficient cyclability in ambient air. By the end of the project it is anticipated that problems hindering the use of both the Li anode and air electrode will be overcome due to materials advances and strategies enabled within the intermediate (>80 °C) operating temperature range of the system under development.

COLLABORATIONS:

- Bryan McCloskey (LBNL): Analysis of air electrode and electrolyte
- Julia Greer (Caltech): Design of air electrode materials and structures

Milestones

- 1) Demonstrate eutectic compositions having eutectic points below 120 °C. (Dec. 14) **Complete**
- 2) Measure ionic conductivity and Li⁺ transference number in eutectic compositions. (Dec. 14) **Complete**
- 3) Measure diffusion coefficients and solubilities of O₂, Li₂O₂ and Li₂O (Mar. 15) **Ongoing**
- 4) Synthesize oxidation-resistant carbons (Jun. 15) **Ongoing**
- 5) **Go/No-Go:** Demonstrate suitability of analytical approach for elevated temperature molten salt metal-O₂ cells. **Criteria:** Quantify Li₂O₂ yield, e⁻/O₂ and OER/ORR ratios for baseline carbon air electrodes. (Jun 15) **Ongoing**
- 6) Quantify Li₂O₂ yield, e⁻/O₂ and OER/ORR ratios for oxidation-resistant carbon air electrodes. (Jun. 15) **Ongoing**
- 7) Measure diffusion coefficients and solubilities of H₂O, CO₂, LiOH and Li₂CO₃ (Sept. 15)
- 8) Synthesize metals and metal alloys of high air electrode stability and/or catalytic activity. (Sept. 15) **Ongoing**

Progress Report

Q1 Milestones 1 and 2 include demonstration of eutectic compositions have melting points below 120 °C and measurement of conductivity and Li^+ transference number in said eutectics, respectively. Phase diagrams for a large space of inorganic molten salt compositions comprising alkali metal cations along with nitrate and nitrite anions were explored. Results for an exemplary eutectic composition which achieves Milestone 1 are shown below. This composition is composed of LiNO_3 , KNO_2 and CsNO_3 mixed in a ratio of 37:39:24 mol.%. A melting point of ~ 90 °C is observed via differential scanning calorimetry (Figure 82a).

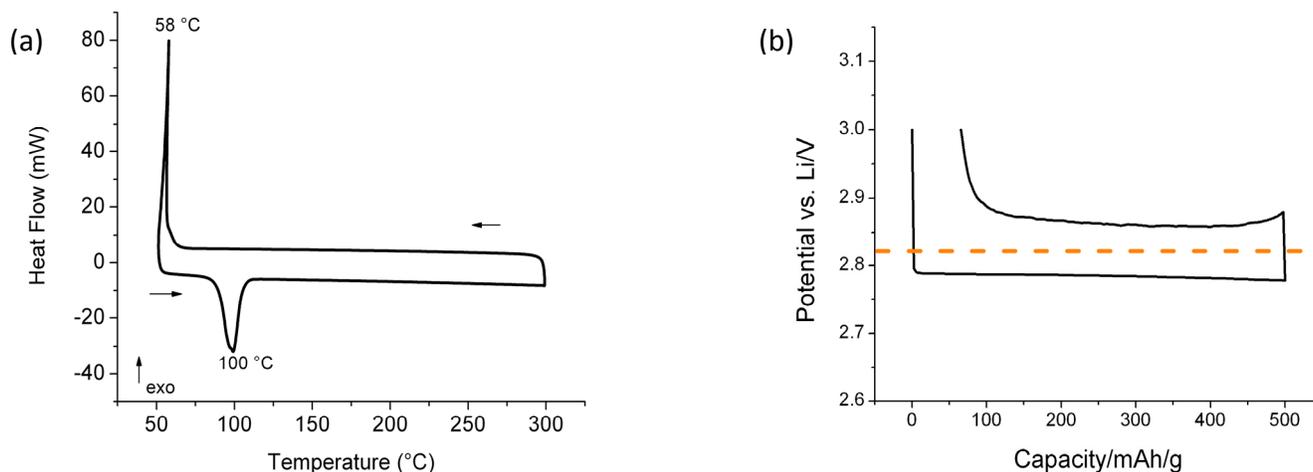


Figure 82: (a) DSC of $\text{LiNO}_3\text{:KNO}_2\text{:CsNO}_3$ eutectic (10 °C/min, Ar). (b) Voltage profile of the tenth cycle of a cell with this eutectic 2 mAh discharge at 0.2 mA/cm² and a PTFE bonded Super P carbon cathode.

Cells employing this eutectic at 120 °C exhibited similar cycling characteristics (Figure 82b) as cells operating at 150 °C with an electrolyte consisting of LiNO_3 and KNO_3 . Features include very low (~ 50 mV) overpotential at a current density of 0.2 mA/cm² that is approximately symmetric for discharge and charge and improving coulombic efficiency (~ 70 % for cycle 1 and ~ 90 % for cycle 10). Fulfilling Milestone 2, conductivity and Li^+ transference number measurements were performed at 150 °C, summarized in the table below for the $\text{LiNO}_3\text{:KNO}_3$ and $\text{LiNO}_3\text{:KNO}_2\text{:CsNO}_3$ eutectics.

Eutectic	M.P. (°C)	T^+	Conductivity (mS/cm)
$\text{LiNO}_3\text{-KNO}_3$	128	0.68	88
$\text{LiNO}_3\text{-KNO}_2\text{-CsNO}_3$	90	0.28	115

Extensive TEM, SEM and XRD analysis was performed on carbon O_2 cathodes at various stages of cycling in order to improve understanding of the composition and structure of discharge products in this electrolyte. Of note, a new morphology of Li_2O_2 was observed empirically for the first time which consists of stacks of hexagonal layers. Intriguingly, this conforms to theoretical predictions of the equilibrium Wulff construction of Li_2O_2 as a hexagonal prism. Additionally, trace amounts of Li_2CO_3 are observed due to reaction between the carbon electrode and Li_2O_2 consistent with ambient temperature organic electrolyte Li/O_2 cells, highlighting the importance of the project task of identifying alternative air electrode materials.

Significant results were obtained during Q1 relating to alternative catalytic electrode materials. These results are presently confidential.

Q1 Patents/Publications/Presentations

1. Presentation by Dan Addison at Lithium Mobil Power Conference in Washington D.C.
2. Confidential unpublished utility patent application

Task 9.3 – Khalil Amine (Argonne National Laboratory)

Li-air batteries

PROJECT OBJECTIVE:

- Develop new cathode materials and electrolytes for lithium-air batteries for long cycle life, high capacity, and high efficiency.
- Use state-of-the-art characterization techniques to understand the charge and discharge chemistries.
- Use state-of-the-art computational methodologies to understand and design new materials and electrolytes for Li-air batteries.

PROJECT IMPACT:

- New electrolytes that are stable and increase cycle life
- New cathode materials that increase cycle life and reduce overpotentials
- Increased cycle life

OUT-YEAR-GOALS:

The out-year goals of this work is to find catalysts that promote discharge product morphologies that reduce charge potentials and find electrolytes for long cycle life through testing and design.

COLLABORATIONS:

Milestones

The following are the milestones for each Quarter during FY15:

1. Characterize the stability of the LiO_2 component of the activated carbon cathode using Raman techniques. Use DFT calculations to model the stability of the LiO_2 component of the LiO_2 component of the activated carbon cathode to explain the Raman results.
2. Investigate the role of impurities in the performance of activated carbon and how they can promote the formation of LiO_2 and reduce charge overpotentials. Use DFT calculations to help understand how the impurities affect the morphologies.
3. Investigate addition of metal nanoparticle catalysts to high surface area carbons such as reduced graphene oxides to promote growth of morphologies with higher LiO_2 contents to reduce charge overpotentials. Use DFT calculations to model the nanoparticle catalysts.
4. Use one of the metal catalyst/carbon systems with good performance to start investigations of how electrolytes can be used to improve the performance (cycle life) of the Li-air battery. Use DFT calculations to help design new electrolytes for the Li-air batteries.

Progress Report

A Raman spectroscopic technique that can focus on individual toroids has been used to investigate the spectra as a function of current density and charge cutoff voltage in a Li-O₂ cell based on a high surface area AC cathode. Three important conclusions can be drawn from this study.

1) The trends in the Raman data for Li₂O₂ and LiO₂-like species as a function of discharge current density shown in Figure 83 and charge cutoff voltage provide evidence that the toroids are made up of an outer LiO₂-like component and an inner Li₂O₂ component, which is consistent with a late stage disproportionation formation mechanism for Li₂O₂ from LiO₂ during discharge for the AC cathode.

2) A new peak in the Raman spectra has been identified between the G and D bands of disordered graphitic carbon. The new peak at ~1505 cm⁻¹ appears only when the peak of LiO₂-like species at 1123 cm⁻¹ is present and the intensities of both peaks are correlated. The new peak could be considered a signature of the presence of a LiO₂-like species in the discharge product.

3) Density function calculations of LiO₂ on a graphitic fragment shown in Figure 84 suggest that the new peak at 1505 cm⁻¹ is due to the interface between the LiO₂-like component and the carbon surface. The calculations also show a metallic-like feature in DOS suggesting the toroids should have good electronic contact with the carbon. The results provide evidence that a late stage disproportionation mechanism for Li₂O₂ formation as illustrated in Figure 85 is possible during discharge and adds new understanding to the complexities of possible processes occurring in Li-O₂ batteries needed to make further advances in this advanced electrical energy storage system.

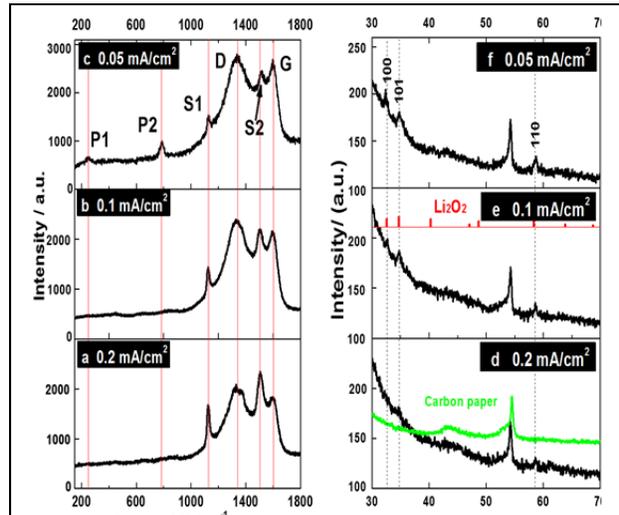


Figure 83: Raman and XRD data for the activated carbon showing dependence of the LiO₂ component of current density

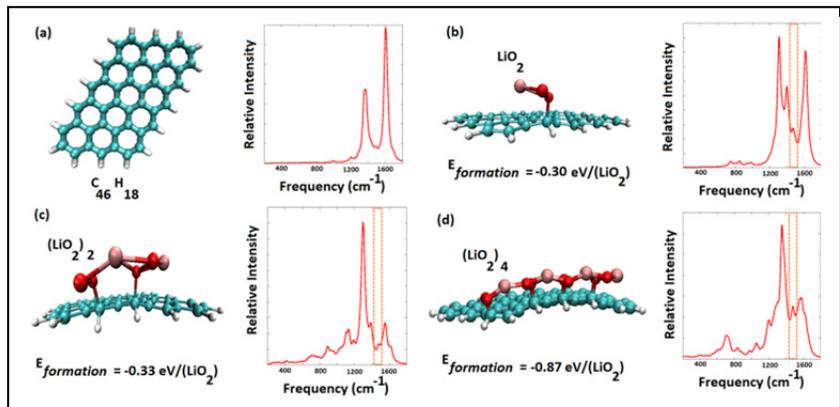


Figure 84: DFT calculations showing that the origin of the 1505 cm⁻¹ peak is due to the LiO₂-carbon interaction.

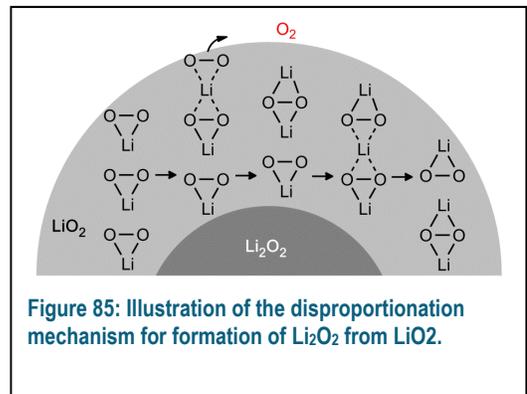


Figure 85: Illustration of the disproportionation mechanism for formation of Li₂O₂ from LiO₂.

Q1 Patents/Publications/Presentations

- Raman Evidence for Late Stage Disproportionation in a Li–O₂ Battery, D. Zhai, H.-H. Wang, K. C. Lau, J. Gao, P. C. Redfern, F. Kang, B. Li, E. Indacochea, U. Das, H.-H. Sun, H.-J. Sun, Khalil Amine, and L. A. Curtiss, *J. Phys. Chem. Lett.* 5, 2705–2710 (2014)
- Molecular-Level Insights into the Reactivity of Siloxane-Based Electrolytes at a Lithium-Metal Anode, R. S. Assary, J. Lu, X. Y. Luo, X. Y. Zhang, Y. Ren, H. M. Wu, H. M. Albishri, D. Abd El-Hady, A. S. Al-Bogami, L. A. Curtiss, K. Amine, *ChemPhysChem* 15 2077-2083 (2014) DOI: 10.1002/cphc.201402130
- Polymer supported organic catalysts for O₂ reduction in Li-O₂ batteries, W. Weng, C. J. Barile, P. Du, A. Abouimrane, R. S. Assary, A. A. Gewirth, L. A. Curtiss, K. Amine, *Electrochimica Acta*, 119, 138-143 (2014)

Task 9.4 – Deyang Qu (UMASS Boston) and Xiao-Qing Yang (Brookhaven National Laboratory)

Overcome the Obstacles for the Rechargeable Li-air Batteries

PROJECT OBJECTIVE: The primary objective is to investigate the root causes of the major obstacles of the air cathode in the Li-air batteries, which impede the realization of high energy, high power, long cycle life Li-air batteries, and understand the mechanisms of such barriers and eventually overcome those obstacles. In this objective, special attentions will be paid to the investigation of high surface carbon material use in the gas diffusion electrode (GDE), establishment of 2-phase interface on the GDE, catalysts, electrolyte and additives stable in Li-air system and with capability to dissolve Li oxide and peroxide. The electrolyte investigation and development will closely collaborate with Brookhaven National Laboratory. The secondary objectives is to engineering design of a Li-air battery with high energy, high rate, long cycle life and high round-trip efficiency, special attention will be paid to Li-air flow cell.

PROJECT IMPACT: Li-air chemistry represents the highest energy density among chemical energy systems. The successful implementation of the technology in the electric vehicles would not only reduce the cost of electrochemical energy storage system but also provide long driving distance per charge by significantly increase the energy density. The attributes would enable cost effective market entry of electric vehicles for US automakers.

OUT-YEAR GOALS: The specific research in the project year will be continuously focused on the fundamental mechanisms of oxygen reduction in non-aqueous electrolytes and the re-oxidization of the soluble boron-peroxide complex, multiple boron complexes will be synthesized in BNL and tested in UMB. The impact of carbon surface structure on the O₂ reduction will be investigated. The unique flow-cell design will be further optimized by means of the inclusion of boron additives.

INDUSTRY COLLABORTOR: The UMASS Boston and BNL team has close collaboration with Johnson Controls' scientists and engineers. The collaboration enables the team to validate the outcomes of fundamental research in pilot scale cells. This team has been closely working with top scientists on new material synthesis at ANL, LBNL, and PNNL, with US industrial collaborators at General Motor, Duracell, and Johnson Control; as well as international collaborators in Japan and South Korea. These collaborations will be strengthened and expanded to give this project a vision on both today's state of art technology and tomorrow' technology under development and the feed-back from the material designer and synthesizers at upstream, as well as from the industrial end users at downstream.

Milestones

1. Complete the studies of the impact of carbon surface structure on the O₂ reduction. (Dec. 14) **Completed**
2. Complete the kinetics studies of catalytic disproportionation of superoxide (determination of reaction order and reaction constant). (March 15) **In progress**
3. Complete the test of the Li-air flow cell. (June 15). **In progress**
4. Complete *in-situ* electrochemical study for the oxygen reduction in various boron additives. (September 15). **In progress**

Progress Report

In the first quarter of FY2015, oxygen reduction and re-oxidation on the surface of carbon with different structure and functionality have been investigated. The results concluded that unlike oxygen reduction in alkaline electrolyte, the surface structure has little impact on the reaction in non-aqueous electrolytes. Figure 86 shows the comparison between the oxygen reduction on the carbon electrodes with different surface crystal structure. Clearly, edge orientation which demonstrated superior O_2 reduction catalysis in alkaline electrolyte, did not show the same catalytic effects in non-aqueous electrolyte. Interestingly, even Pt electrode did not demonstrate better catalytic activity for O_2 reduction. The same conclusion can also be reached for the re-oxidation of H_2O_2 and LiO_2 in alkaline and acetonitrile, respectively.

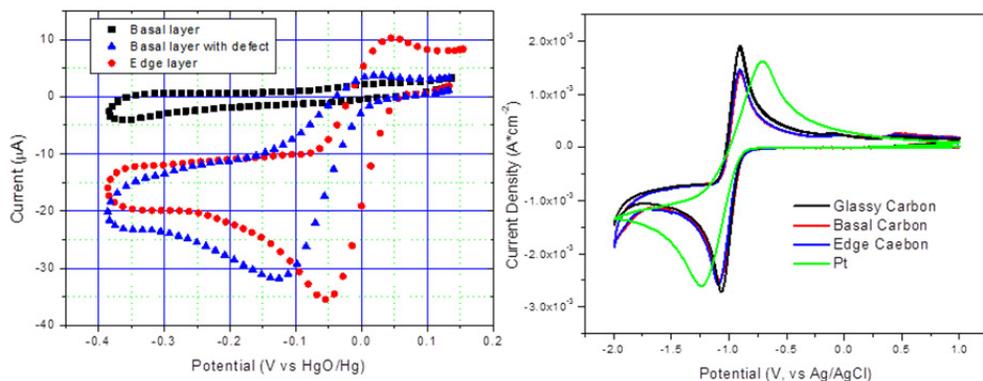


Figure 86: Cyclic voltammety for O_2 reduction on different carbon electrodes in alkaline electrolyte (D.Qu Carbon 45(2007)1296-1301) and in Acetonitrile.

During the research in FY2014, it was found that LiO_2 can become rapidly disproportionate with borate additive and the soluble borate-peroxide ($B-O_2^{2-}$) complex can be easily re-oxidized. In Q1 of FY2015, it was further confirmed that the re-oxidation of the soluble $B-O_2^{2-}$ is sensitive to the surface condition of carbon electrode as shown in Figure 87.

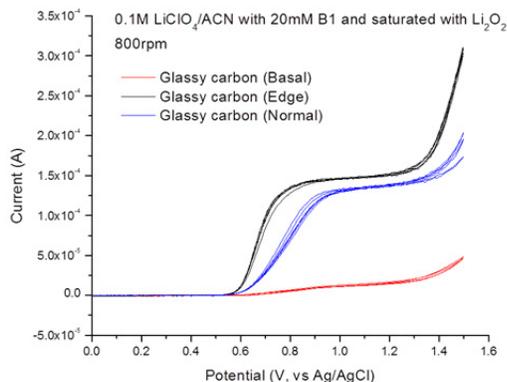


Figure 87: Re-oxidation of $B-O_2^{2-}$ complex in acetonitrile electrolyte.

Q1 Patents/Publications/Presentations

1. Q. Wang, D. Zheng, M.E. McKinnon, X.Q. Yang, D.Y. Qu, “Kinetic Investigation of Catalytic Disproportionation of Superoxide Ions in the Non-aqueous Electrolyte used in Li-Air Batteries”, *J. Power Sources* 274(2015)1005-1008.

TASK 10 – NA-ION BATTERIES

In order to meet the challenges of powering the PHEV, next generation of rechargeable battery systems with higher energy and power density, lower cost, better safety characteristics, and longer calendar and cycle life beyond lithium-ion batteries, which is today's state-of-art technology, need to be developed. Recently, Na-ion battery systems have attracted more and more attentions due to the more abundant and less expensive nature of Na resource. The issue is not insufficient lithium on a global scale, but what fraction can be used and still be economically effective. Most untapped lithium reserves occur in remote or politically sensitive areas. Scale-up will require a long lead time, involve heavy capital investment in mining, and may require the extraction and processing of lower quality resources, which could drive extraction costs higher. Currently, high costs remain a critical barrier to the widespread scale-up of battery energy storage. Recent computational studies on voltage, stability and diffusion barrier of Na-ion and Li-ion materials indicate that Na-ion systems can be competitive with Li-ion systems.

Barriers and Limitations of current state of art of Na-ion systems

1. Building a sodium battery requires redesigning battery technology to accommodate the chemical reactivity and larger size of sodium ions.
2. Lithium batteries pack more energy than sodium batteries per unit mass. Therefore, for sodium batteries to reach energy densities similar to lithium ones, the positive electrode in the sodium battery need to hold more ions.
3. Since Na-ion batteries are an emerging technology, new materials to enable Na electrochemistry and the discovery of new redox couples, and the diagnostic studies of these new materials and redox couples are quite important.
4. In sodium electrochemical systems, the greatest technical hurdles to overcome are the lack of high-performance electrode and electrolyte materials that are easy to synthesize, safe, non-toxic, with long calendar and cycling life and low cost.
5. Furthermore, fundamental scientific questions need to be further elucidated, including including (1) the difference in transport and kinetic behaviors between Na and Li in analogous electrodes; (2) Na insertion/extraction mechanism; (3) solid electrolyte interphase (SEI) layer on the electrodes from different electrolyte systems; and (4) charge transfer in the electrolyte-electrode interface and Na⁺ ion transport through the SEI layer.

This task will use the synchrotron based in situ x-ray techniques and other diagnostic tools to evaluate the new materials and redox couples, to explore fundamental understanding of the mechanisms governing the performance of these materials and provide guidance for new material developments. This task will also be focused on developing advanced diagnostic characterization techniques to investigate these issues, providing solutions and guidance to solve the problems. The synchrotron based in situ X-ray techniques (x-ray diffraction and hard and soft x-ray absorption) will be combined with other imaging and spectroscopic tools such as high resolution transmission electron microscopy (HRTEM), mass spectroscopy (MS), and transmission x-ray microscopy (TXM)

Task 10.1 – Xiao-Qing Yang and Xiqian Yu (Brookhaven National Laboratory)

Exploratory studies of novel sodium-ion battery systems

PROJECT OBJECTIVE: The primary objective of this proposed project is to develop new advanced in situ material characterization techniques and to apply these techniques to explore the potentials, challenges, and feasibility of new rechargeable battery systems beyond the lithium-ion batteries (LIBs), namely the sodium-ion battery systems for plug-in hybrid electric vehicles (PHEV). In order to meet the challenges of powering the PHEV, new rechargeable battery systems with high energy and power density, low cost, good abuse tolerance, and long calendar and cycle life need to be developed. This project will use the synchrotron based in situ x-ray diagnostic tools developed at BNL to evaluate the new materials and redox couples, to explore in fundamental understanding of the mechanisms governing the performance of these materials and provide guidance for new material and new technology developments regarding Na-ion battery systems

PROJECT IMPACT: In the Multi Year Program Plan (MYPP) of Vehicle Technology Program (VTP), the goals for battery were described as: “Specifically, lower-cost, abuse-tolerant batteries with higher energy density, higher power, better low-temperature operation, and longer lifetimes are needed for the development of the next-generation of HEVs, PHEVs, and EVs.” If this project is successfully carried out, the knowledge learned from diagnostic studies and collaborations with US industries and international research institutions through this project will help US industries to develop new materials and processes for new generation of rechargeable battery systems beyond lithium-ion batteries, such as Na-ion battery systems in their efforts to reach these VTP goals.

OUT-YEAR GOALS: Complete the in situ x-ray diffraction and absorption studies of sodium iron ferrocyanide (Prussian Blue Analogous) as cathode materials for Na-ion batteries during charge-discharge cycling.

COLLABORATIONS: BNL team has been closely working with top scientists on new material synthesis at ANL, LBNL, and PNNL, with US industrial collaborators at General Motor, Duracell, and Johnson Control; as well as international collaborators in Japan and South Korea. These collaborations will be strengthened and expanded to give this project a vision on both today’s state of art technology and tomorrow’ technology under development and the feed-back from the material designer and synthesizers at upstream, as well as from the industrial end users at downstream.

Milestones

- 1) Complete the particle size effects on kinetic properties of $\text{Li}_4\text{Ti}_5\text{O}_{12}$ as anode materials for Na-ion batteries using synchrotron based in situ x-ray diffraction (Dec-14) **Completed**
- 2) Complete the in situ x-ray diffraction studies of sodium iron ferrocyanide (Prussian Blue Analogous) as cathode materials for Na-ion batteries during charge-discharge cycling (Mar-15), **In progress**
- 3) Complete the in situ x-ray diffraction studies of NaCrO_2 during electrochemical chemical de-sodiation. NaCrO_2 is considered as a potential cathode material for Na-ion batteries. (Jun-15) **In progress**
- 4) Complete the x-ray absorption studies of NaCrO_2 at different sodiation levels.. (Sep-15) **In progress**

Progress Report

In the 1st quarter of FY2015, the first milestones for FY2015 had been completed.

In the 1st quarter of FY2015, BNL has been focused on the structural studies of $\text{Li}_4\text{Ti}_5\text{O}_{12}$ during chemically sodium insertion using synchrotron based *in situ* X-ray diffraction (XRD). The sodium insertion behavior into $\text{Li}_4\text{Ti}_5\text{O}_{12}$ is strongly size dependent. A solid solution reaction behavior in a wide range has been revealed during sodium insertion into the nano-sized $\text{Li}_4\text{Ti}_5\text{O}_{12}$ (~44 nm), which is quite different from the well-known two-phase reaction of $\text{Li}_4\text{Ti}_5\text{O}_{12}/\text{Li}_7\text{Ti}_5\text{O}_{12}$ system during lithium insertion, and also has not been fully addressed in the literature so far.

Figure 88 (a), (b) and (c) show the SEM images and the crystallite size distribution of nano-size ($r=44$ nm, $r=120$ nm) and sub micro-size ($r=440$ nm) $\text{Li}_4\text{Ti}_5\text{O}_{12}$; Figure 88 (d) shows the *in situ* XRD patterns collected during chemical sodiation of the nano-size 44nm (top), 120nm (middle) and sub micro-size (bottom) $\text{Li}_4\text{Ti}_5\text{O}_{12}$, the sodium insertion caused phase transition behavior is strongly related to the particle size of the material. Fully sodium insertion can be finished within 2 hours for 44nm nano-sized $\text{Li}_4\text{Ti}_5\text{O}_{12}$, while for the sub micro- sized $\text{Li}_4\text{Ti}_5\text{O}_{12}$, no new phase can be observed within the initial 8 hours during chemical sodiation. Figure 88 (e) shows the enlarged view of the (111) reflections for the pristine $\text{Li}_4\text{Ti}_5\text{O}_{12}$ with different particle sizes. Fig. 1 (f) shows XRD patterns of the sub micro-sized $\text{Li}_4\text{Ti}_5\text{O}_{12}$ collected after chemical sodiation of 20 h, 40 h and 80 h respectively, new $\text{Na}_6\text{LiTi}_5\text{O}_{12}$ phase emerged after long time reaction. Full sodiation was obtained in 2h and 24h respectively for 44nm and 120nm $\text{Li}_4\text{Ti}_5\text{O}_{12}$. Figure 88 (g) shows the charge-discharge curve (1st: dash line and 30th: solid line) of Na insertion and extraction into $\text{Li}_4\text{Ti}_5\text{O}_{12}$ (0.1C, 0.5 V-3 V).

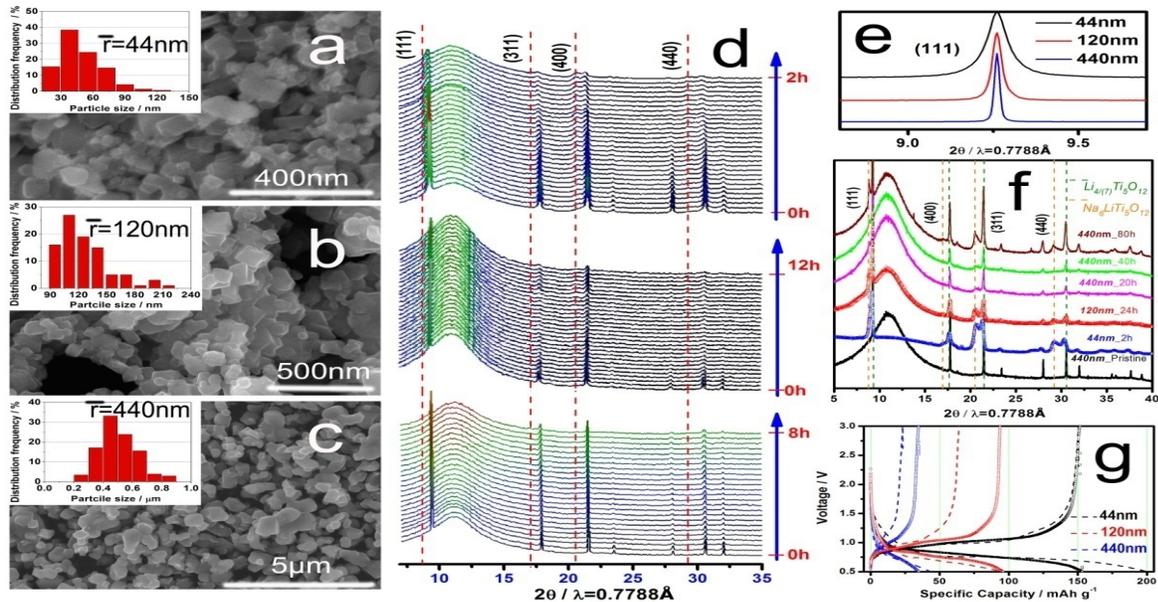


Figure 88: (a) Cr K-edge XANES spectra of pristine ($x = 0$), half charged ($x = 0.25$), fully charged ($x = 0.5$) $\text{Na}_{1-x}\text{CrO}_2$ and CrO_x references (Cr_2O_3 , CrO_2 and CrO_3); (b) Least-square fits of calculated FT-EXAFS phase and amplitude functions (solid red lines) to the experimental EXAFS spectra (solid and open circles) for pristine ($x = 0$), half charged ($x = 0.25$) and fully charged ($x = 0.5$) $\text{Na}_{1-x}\text{CrO}_2$. Phase shift was not corrected in the FT magnitude of EXAFS spectra.

Q1 Patents/Publications/Presentations

Publications

Yong-Ning Zhou, Mahsa Sina, Nathalie Pereira, Xiqian Yu, Glenn G. Amatucci, Xiao-Qing Yang, Frederic Cosandey, and Kyung-Wan Nam, “FeO_{0.7}F_{1.3}/C nanocomposite as a high capacity cathode material for sodium-ion batteries“, *Advanced Functional Materials*, Accepted

Presentations:

Yong-Ning Zhou, Enyuan Hu, Xiqian Yu, Seongmin Bak, Xiao-Qing Yang, Hung-Sui Lee, Jun Ma, Zhaoxiang Wang, Lin Gu and Liquan Chen, Kyung-Wan Nam, and Yijin Liu. “Using synchrotron based advanced characterization techniques to study new electrode materials for lithium-ion batteries”, presented at the 2014 MRS Fall Meeting, November 30 – December 5, 2014, Boston, USA, **Invited**

