

Integrated Lab/Industry Research Project at LBNL

Jordi Cabana

Lawrence Berkeley National Laboratory

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ES102

Overview

Timeline

- Project start Aug. '10
- Project end Sep. '14
- 15% complete

Budget

- Funding FY10: \$1M
- Funding FY11: \$1M

Barriers

- Barriers addressed
 - Gravimetric and volumetric Energy Density
 - Cycle life
 - Safety

Partners

- ILIRP-LBNL team members: V. Srinivasan, V. Battaglia, R. Kostecki, J. Cabana, M.M. Doeff, T.J. Richardson, G. Chen, J.B. Kerr, G. Liu, N.P. Balsara
- ILIRP is a joint project with ANL (Spokesperson: J.T. Vaughey)

Relevance - Objectives

- **General goal:** Enable cycling of lithium metal electrode with good life at practical rates. Fundamental impact on next generation technologies (Li/air, Li/S).

Specific goals:

- Ramping up of the program. Started August '10.
- Develop tools to gain a better understanding of how lithium interacts with its environment in an electrochemical cell.
- Investigate the system responses to experimental conditions that affect lithium electrodeposition/dissolution.
- Develop an understanding of failure mechanisms.
- Search for ceramic phases with high Li^+ conductivity that are stable against the metal electrode. Improve their mechanical properties using composites.
- Understand the ion transfer processes that occur at the liquid/solid electrolyte and solid electrolyte/metal interface.

Milestones

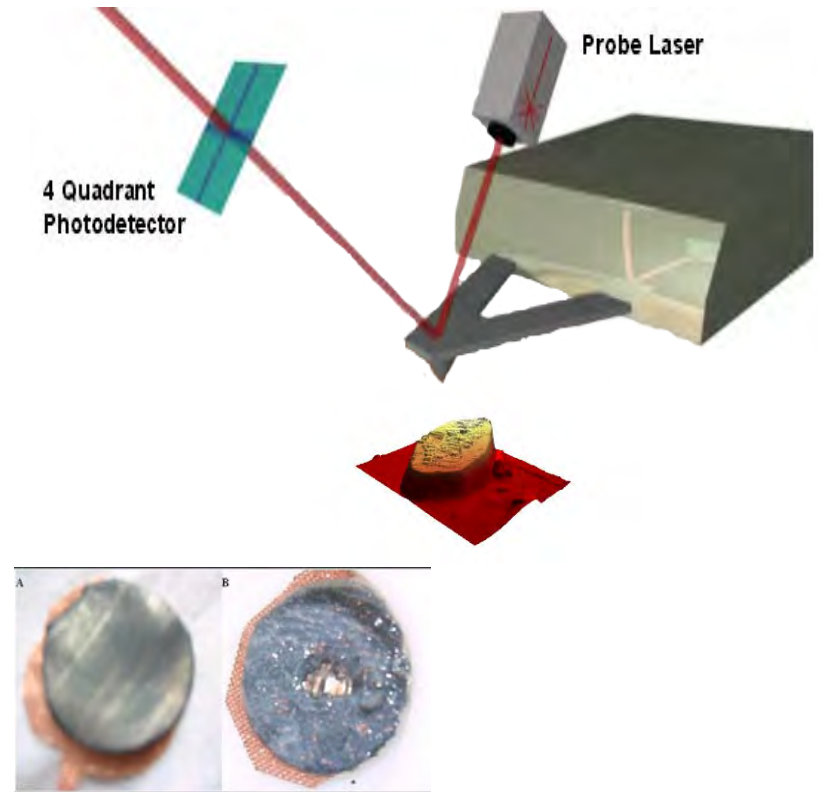
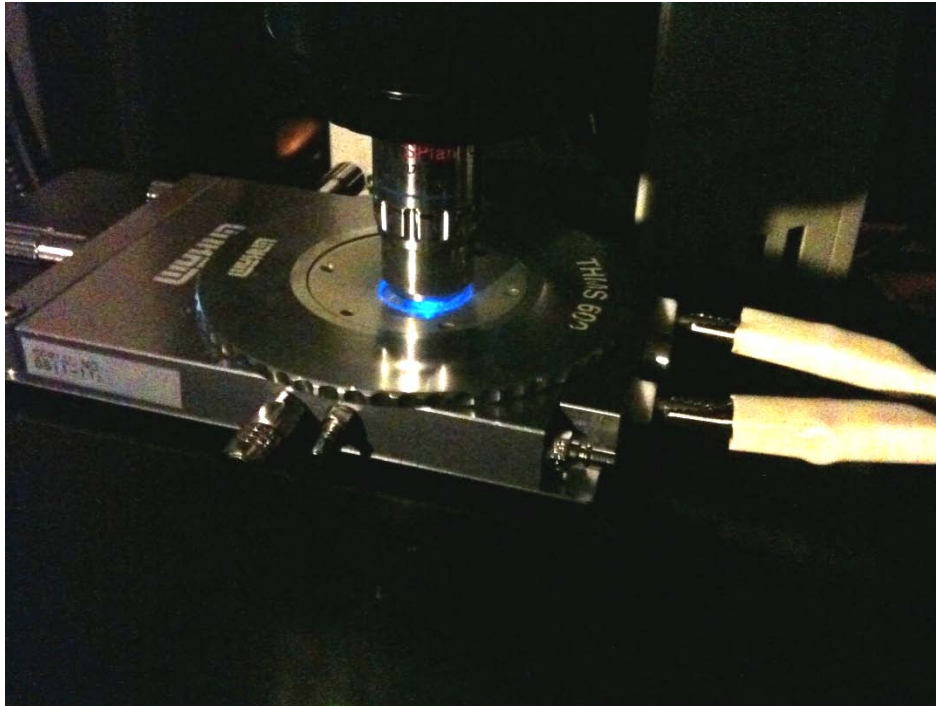
Mar. 11	Report the synthesis of phases in the $\text{Li}_2\text{O-SiO}_2\text{-P}_2\text{O}_5\text{-B}_2\text{O}_3$ system.
Apr. 11	Determine effect of exchange current density and transport properties on dendrite initiation and morphology evolution.
Sep. 11	Develop in situ tools to examine the surface of lithium anodes while cycling.
Sep. 11	Establishment of a baseline electrochemical cell fixture.
Sep. 11	Report on the spectroscopic characterization of coated lithium metal anodes as a function of cycle life.
Sep. 11	Determine effect of physical properties of electrolyte and chemical additives on morphology evolution.
Sep. 11	Report on a protocol for the synthesis of composite ceramic layers .

Approach/Strategy

- **General Approach:** leverage individual expertise at LBNL and ANL to study fundamental processes with critical impact on industrial development of Li-based cells.
- Use microscopy and spectroscopy to study and evaluate changes on lithium metal anode surfaces in different conditions.
 - Develop cells that are suitable for in situ experiments.
- Study morphology changes as a function of electrolyte composition.
 - Determine factors that influence the initiation of dendrite growth, calendar life and cycling efficiency.
- Evaluate Li^+ diffusion within ceramic membranes in a two compartment cell.
 - Investigate charge transfer phenomena upon cation desolvation.
- Explore the existence of conductive crystalline and glassy phases in phase diagrams that are a combination of Li_2O , SiO_2 , P_2O_5 , and B_2O_3 .
 - Evaluate compatibility with lithium metal.
- Build composite architectures using a combination of a mechanically strong and an ionically conducting ceramic.
 - Porous Al_2O_3 chosen as the mechanical support.

Technical accomplishments/Progress:

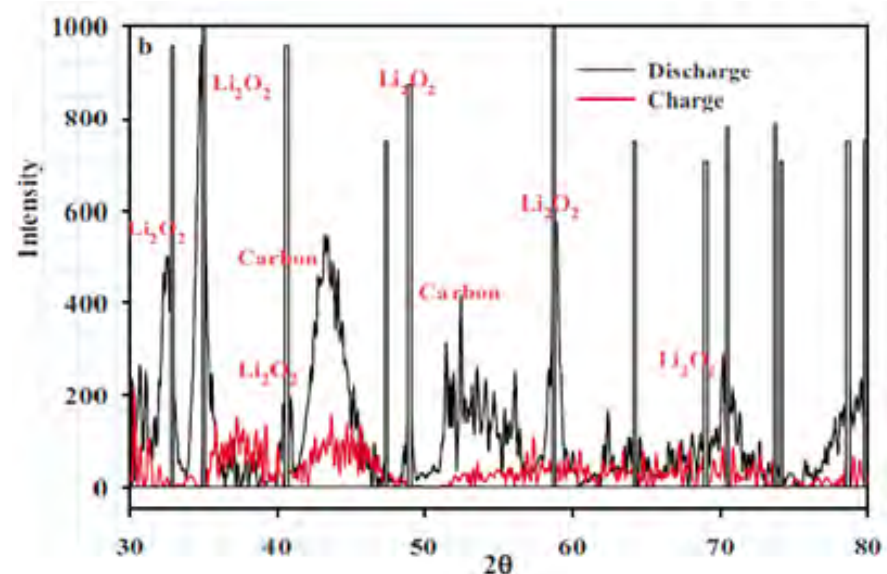
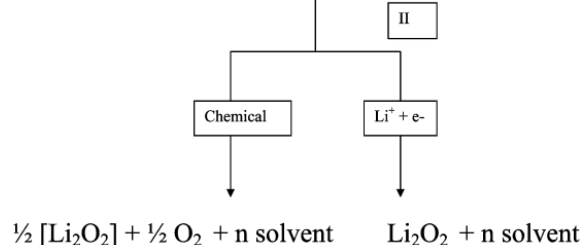
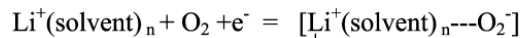
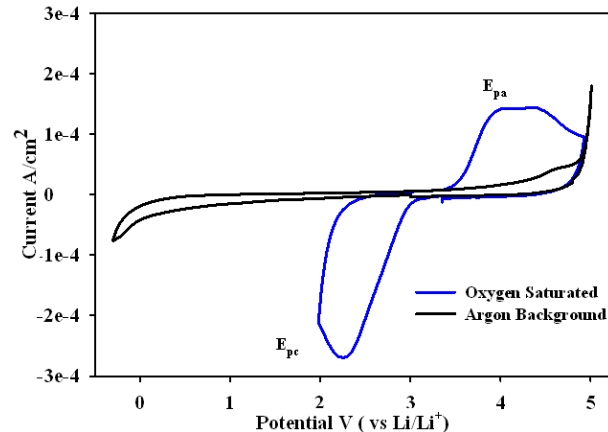
Toward diagnostics cell development



- A universal spectro-electrochemical cell for in situ Raman and FTIR measurements was developed and tested.
- Developed new vibrational spectroscopy and microscopy scanning probe cells for the in situ observation of changes on the surface of lithium metal as a function of cycle life and coating materials.

Technical accomplishments/Progress:

Toward in situ probing of lithium metal

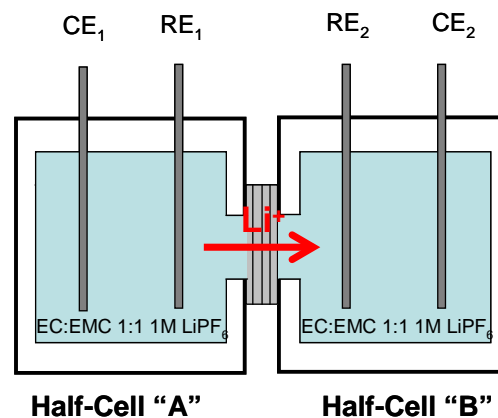


- Tetraglymes have been pitched as suitable solvents for Li-air batteries due to their O₂ solubility. Investigate what their effect is on the lithium anode.
- Interaction between solvent physico-chemical properties and electrode failure mechanisms are crucial to battery success.
- **Synergy:** ANL will provide silane-coated Li metal for studies of morphology-surface changes at LBNL.

Technical accomplishments/Progress:

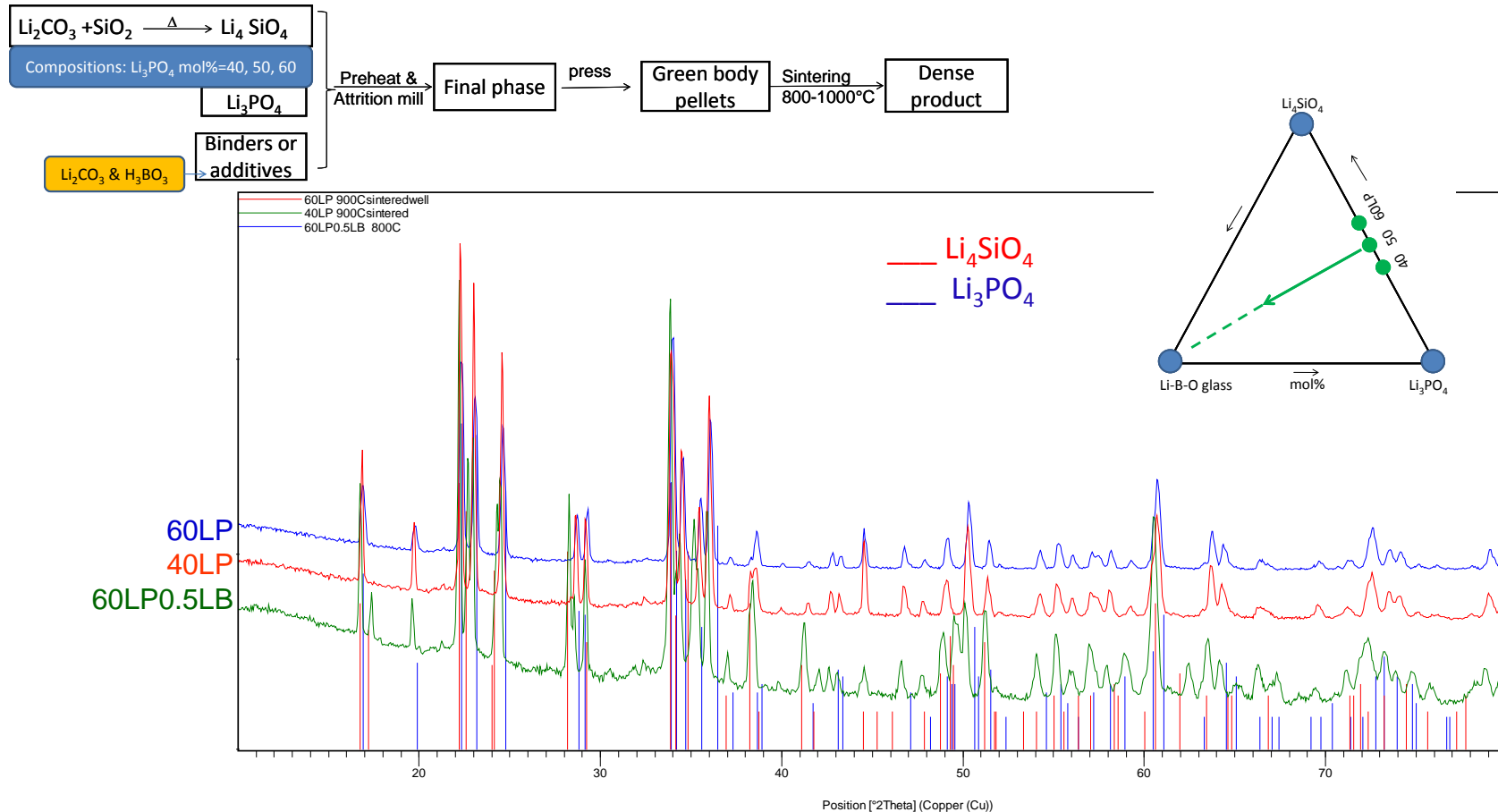
Study of Li^+ transfer at the Solid/Liquid Electrolyte Interface

- Interaction between Li^+ ion and anion affect the charge-transfer process at the interface between solid and liquid electrolytes. *Sagane et al., Chem. Lett. 39 (2010) 826*
- The activation energies are quite large and consistent with the interaction between lithium ion and solvents in an electrolyte as determined by a theoretical calculation. *Abe et al., J. Electrochem Soc., 152 (2005) A2151*
- Rate-determining steps on the interfacial ion transfer can be determined from the concentration dependence of the activation energies. *Sagane et al., J. Phys. Chem. C 2009 113 20135*
- Lithium-ion transfer processes through the liquid/solid electrolyte interface will be examined using a Devanathan-Stachurski cell: 4-probe cell for ac impedance spectroscopy used to study diffusion in ceramic membranes. C. E. and R. E. are both Li metal. 4-probe system eliminates resistances at the Li/liquid electrolyte interface.
- **Synergy:** ANL will provide glass membranes of conductive ceramic. LBNL will perform transport characterization.



Technical accomplishments:

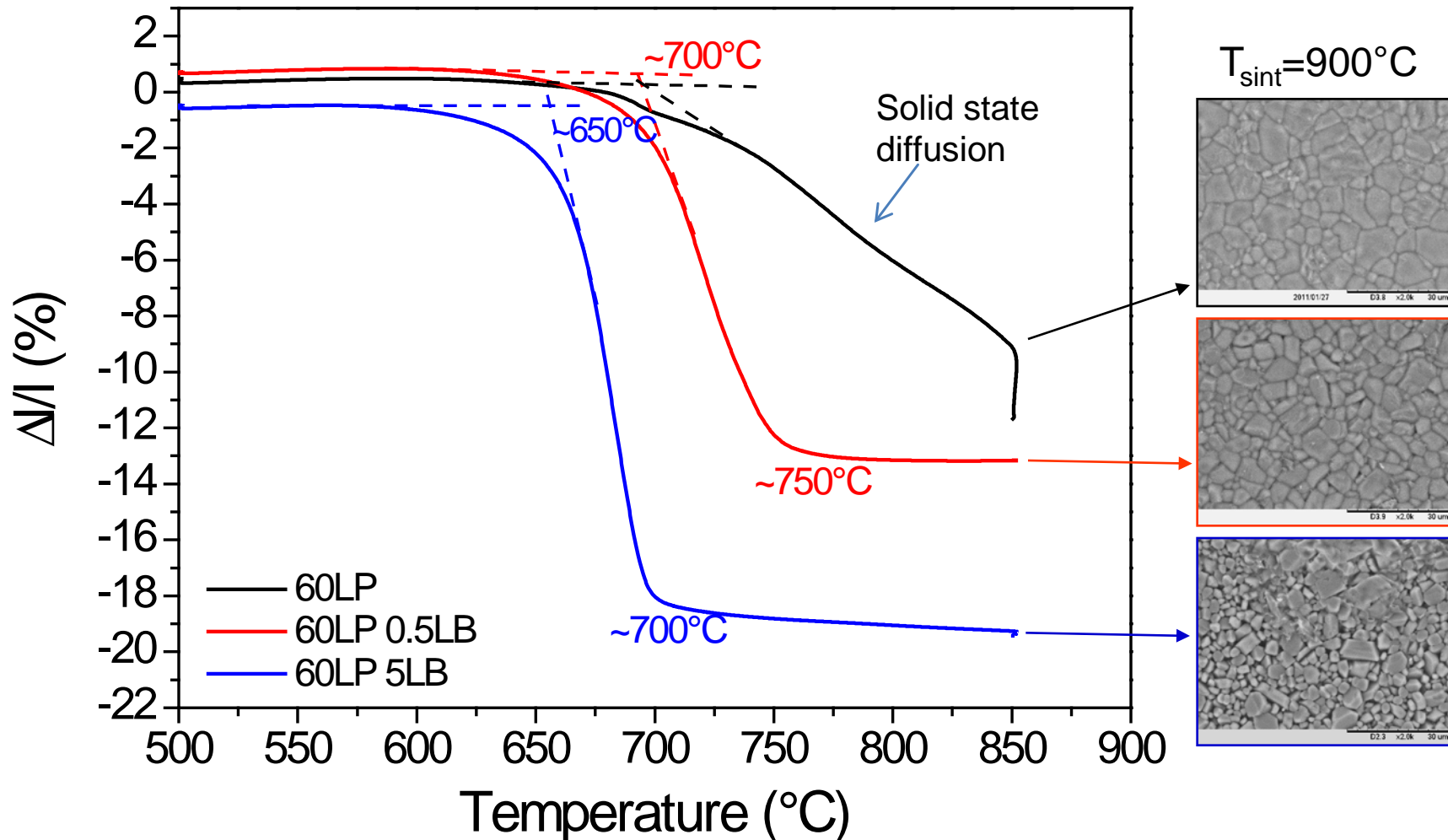
Ceramic conductors, synthesis, XRD



- $x\text{Li}_3\text{PO}_4 \cdot (1-x)\text{Li}_4\text{SiO}_4$ ($x=0.4-0.6$) synthesized by classical solid state method. Addition of LiBO_3 as sintering agent.
- Samples form solid solutions \Rightarrow Li vacancies.

Technical accomplishments:

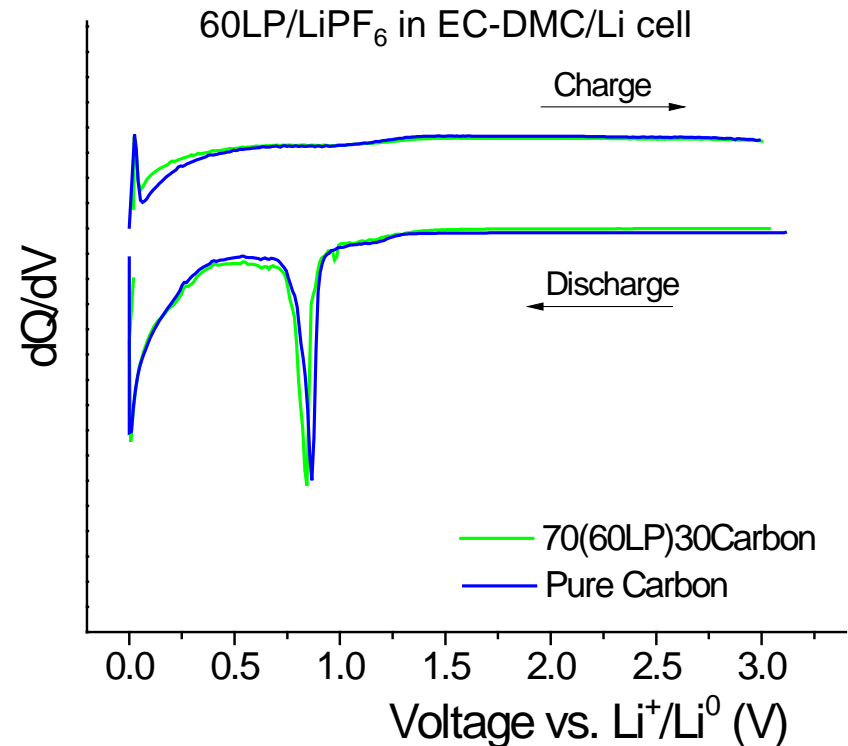
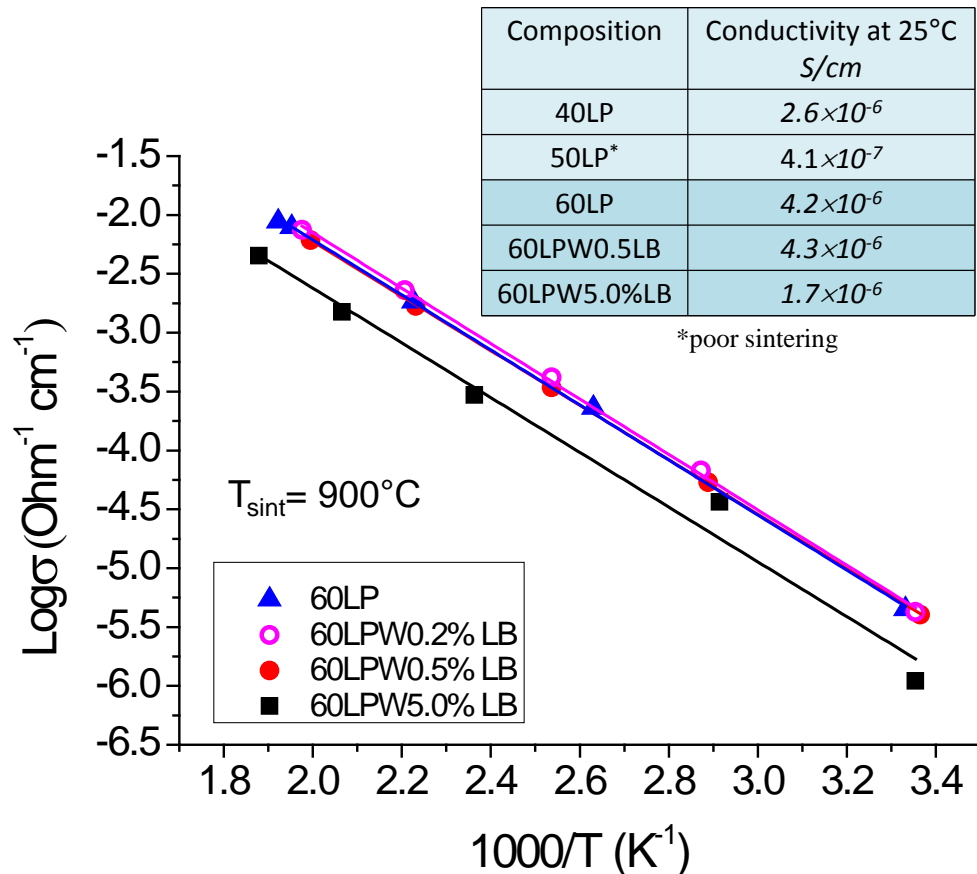
Ceramic conductors, sintering



- Addition of LiBO₃ enhances sintering and lowers densification temperature.
- Larger amounts of LiBO₃ result in porous samples at high T (product evaporation and agglomeration).

Technical accomplishments:

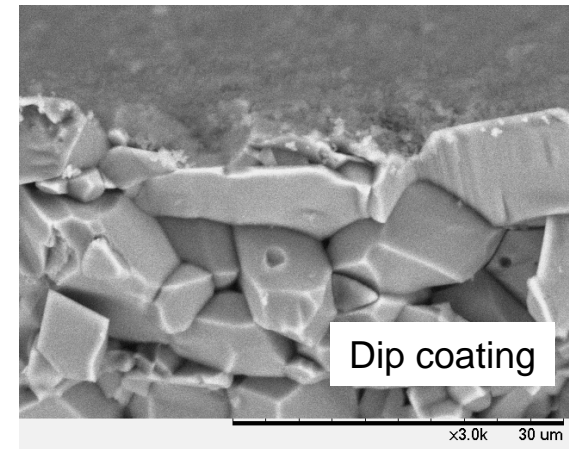
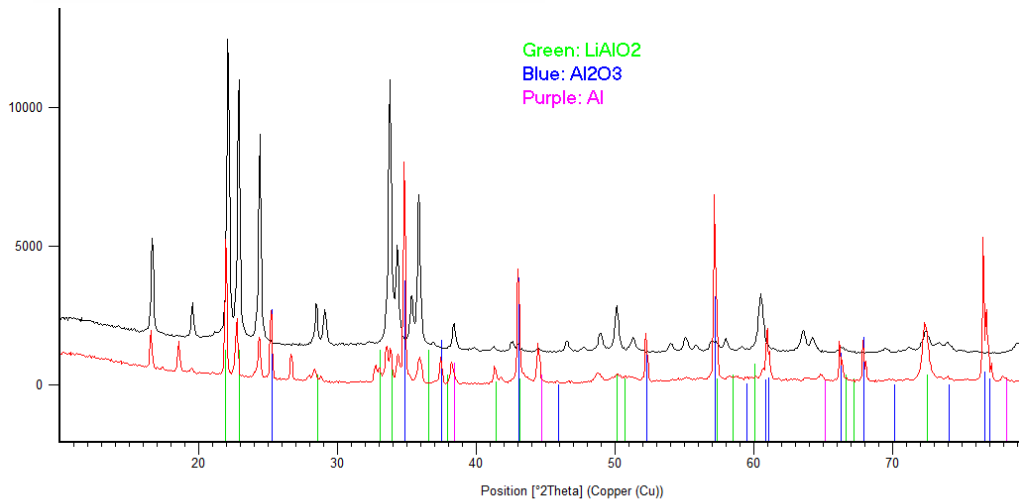
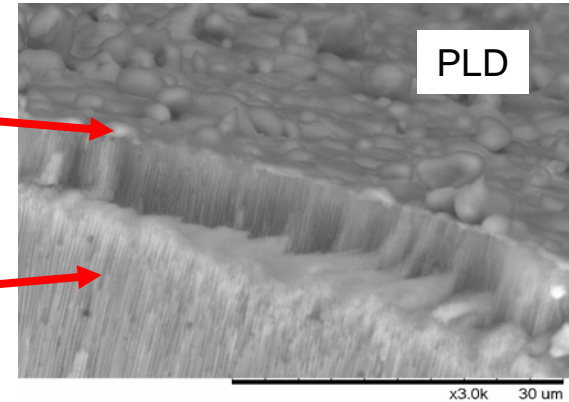
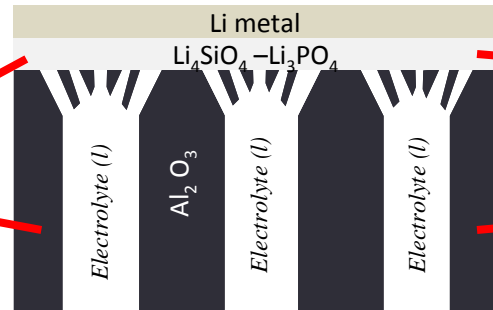
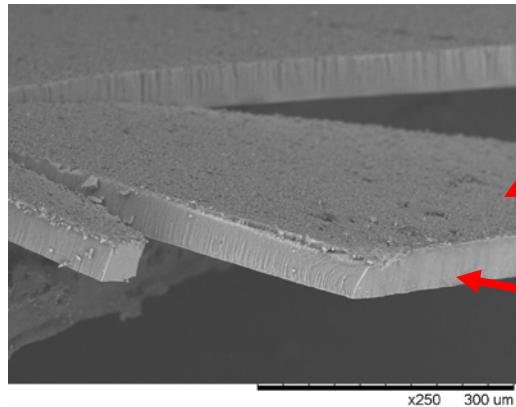
Ceramic conductors, electrical properties



- 60LP (900°C); conductivity at 25°C: $4.2 \times 10^{-6} \text{ S/cm}$, E_a = Activation energy: 0.46 eV. Comparable to LiPON.
- Decrease for 5% LiBO₃ is ascribed to poor sintering.
- No observable reduction is observed above 0 V vs. $\text{Li}^+/\text{Li}^0 \Rightarrow$ stability against Li metal.

Technical accomplishments:

Ceramic conductors, composite layers



- Dense thin film on porous $\text{Al}_2\text{O}_3 \Rightarrow$ Li protection, low impedance loss, high mechanical stability, liquid electrolyte can flow.
- 1st attempts of deposition of 60LP by tape casting, dip coating, pulsed laser deposition.
- Reactivity between substrate and electrolyte found.
- **Synergy:** ANL will custom fabricate Al_2O_3 membranes, LBNL will perform deposition.

Collaboration and Coordination

- Synergy with ANL:
 - ANL supplies silane-coated Li metal for the study of morphology/topology changes during plating/stripping.
 - ANL supplies glass ceramic membranes for the study of transport of Li^+ at the liquid/solid interface.
 - ANL leverages expertise fabricating porous Al_2O_3 membranes for ceramic electrolyte deposition at LBNL (access to PLD, dip coating, RF sputtering).
 - LBNL will deposit thin protective Cu_3N layers on LATP membranes for analysis at ANL.
- Outside ILIRP:
 - Dr. M. Tucker (LBNL): ceramic processing, electrical characterization.
 - Discussions with PolyPlus (Berkeley, CA) to identify fundamental barriers to application of lithium metal electrode, protective layer approach.

Future Work (I)

- Apply *in situ* and *ex situ* instrumental methods to detect and characterize surface processes in Li-metal anodes
 - In situ spectroscopic FTIR/Raman measurements in conjunction with AFM will be carried out to study the SEI layer formation.
 - Cooperate with the ILIRP groups to investigate the effect of ceramic or polymer membrane material structure, morphology, topology on interfacial stability.
 - Investigate correlations between physico-chemical properties of the SEI layer and long-term electrochemical performance of Li-metal electrodes.
- Studies of mass and charge transfer mechanisms at the different interfaces
 - Use the Devanathan-Stachurski spectro-electrochemical cell to study kinetics of Li^+ diffusion through ceramic membrane materials.

Future Work (II)

- Ceramic protective layers:
 - Investigate the conditions for glass formation in $\text{Li}_2\text{O-SiO}_2\text{-P}_2\text{O}_5\text{-B}_2\text{O}_3$ system. Compare transport properties of glass vs. crystalline. Synthesize and characterize glass-crystalline phases.
 - Explore conditions necessary to produce thin ($<1\ \mu\text{m}$), but dense layers of oxide-based ceramics. Use array of methodologies (dip coating, PLD, sputtering).
- Continue and expand integrated activities:
 - Recent visit by R. Kostecki to ANL to explore new synergistic activities.
 - Regular video-conferences are scheduled every two months between the LBNL and ANL teams.
 - Maintain contact with active industrial players (e.g., PolyPlus) to assess the impact of the fundamental developments within ILIRP in the context of application.

Summary (I)

- Integrated Laboratory-Industry Research Project initiated at LBNL August '10.
 - Team of PIs working in synergy with counterparts at ANL. Similar goals, complementary approaches, leverage specific skills.
- Diagnostic equipment and procedures previously developed by LBNL have been adapted to study the processes at the Li electrode.
 - *In situ* spectroscopic cells that can be used to study a variety of interfacial processes as a function of cycle number, additive concentration, polymer cross-linking, ceramic composition, axial pressure, or temperature were developed.
- *In situ* preliminary studies revealed that the nature and kinetics of surface reactions are strongly dependent on the electrode and electrolyte.

Summary (II)

- Started exploration/characterization of crystalline phases in $\text{Li}_2\text{O-SiO}_2\text{-P}_2\text{O}_5\text{-B}_2\text{O}_3$ system.
 - 60LP has conductivity comparable to LiPON (4.2×10^{-6} S/cm). Addition of small amounts of LiBO_3 reduce sintering temperature with good densification.
 - Materials are stable to reduction by Li (also checked in Li symmetric cells).
- Started exploration of conditions required for fabrication of ceramic composites that show good mechanical and transport properties.
 - First composites have been made using PLD and dip coating. Work will continue to improve layer quality.
- Coordinated electrode and electrolyte design must be carried out to achieve interfacial stability of Li anodes in battery applications.