



# Interfacial Processes – Diagnostics

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# Overview



## Timeline

- PI participated in the BATT Program since 1999
- Task #1 started on Aug. 30, 2009 completed on Dec. 30, 2008
- Task #2 initiated on April 1, 2009 70% completed
- Task #3 initiated on May 1 2009 70% completed

## Barriers Addressed

- Inadequate Li-ion battery energy density, and calendar/cycle lifetimes for PHV and EV applications
- Electrode impedance that limits power density

## Budget

- FY11 funding TBD
- FY10 funding \$520K
- FY09 funding \$520K
- FY08 funding \$485K
- FY07 funding \$320K

## Partners

- ANL, HQ, LBNL, SUNY, UP, and UU (BATT Task Group "SEI on Alloys")
- M. Doeff, LBNL (BATT Task Group "Phosphates -  $\text{LiMnPO}_4$ ")
- John Newman (LBNL/UCB) is the program lead

# Objectives



- ❑ Establish direct correlations between BATT baseline electrodes interfacial phenomena and surface chemistry, morphology, topology, and degradation mechanisms.
- ❑ Evaluate and improve the capacity and cycle life of intermetallic anodes and high voltage cathodes
  - Determine physico-chemical properties of the SEI i.e., chemical composition, reactions kinetics, morphology, ionic/electronic conductivity etc.
  - Investigate electrocatalytic behavior of intermetallic anodes in organic electrolytes
  - Provide remedies to interface instability e.g., new alloys and/or structures, electrolyte additives, co-deposition of other metals etc.
  - Characterize degradation modes, improve SEI long-term stability in high-energy Li-ion systems
  - Evaluate the effect of surface composition and architecture on electrochemical behavior of the electrode

# Milestones



1. Evaluate surface and bulk phenomena in  $\text{LiMnPO}_4$  cathodes (July 2009)
  - Accomplished on time. Novel experimental methodology developed ( $\text{O}_2$ -plasma etching) to study *in situ* interfacial phenomena on composite  $\text{LiMnPO}_4$  cathodes.
2. Preliminary results of ellipsometric and optical spectroscopy studies of the SEI formation on Sn and Si thin-film anodes (September 2009).
  - Accomplished on time. Preliminary results corroborate previous AFM studies suggesting that the SEI layer on tin anodes undergoes continuous reformation during cycling.
3. Characterize surface phenomena on  $\text{LiMnPO}_4$  composite cathodes (July-2010)
  - Work in progress ~90% completed
4. Identify the structural and surface changes of Al, Si and Sn-containing anodes during cycling working collaboratively with the BATT SEI Group. (September-2010).
  - Work in progress ~70% completed

# Study of $\text{Li}^+$ Transport in Al Membranes



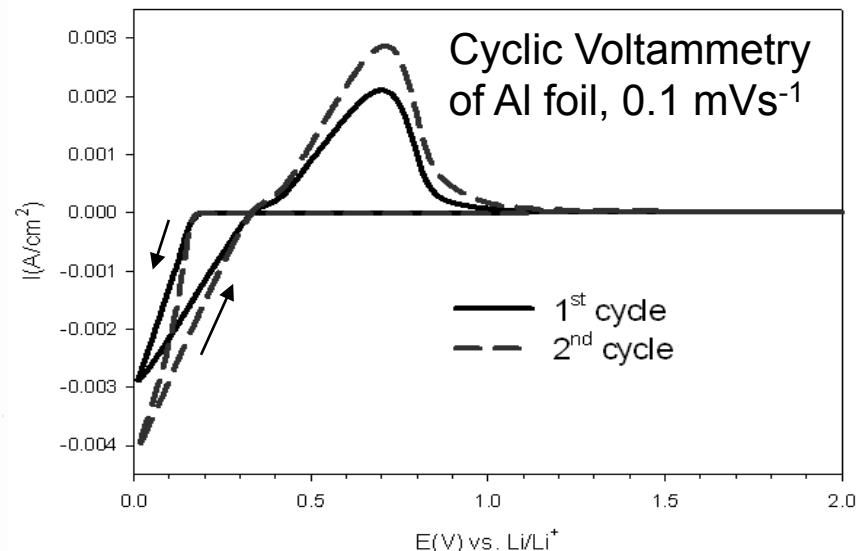
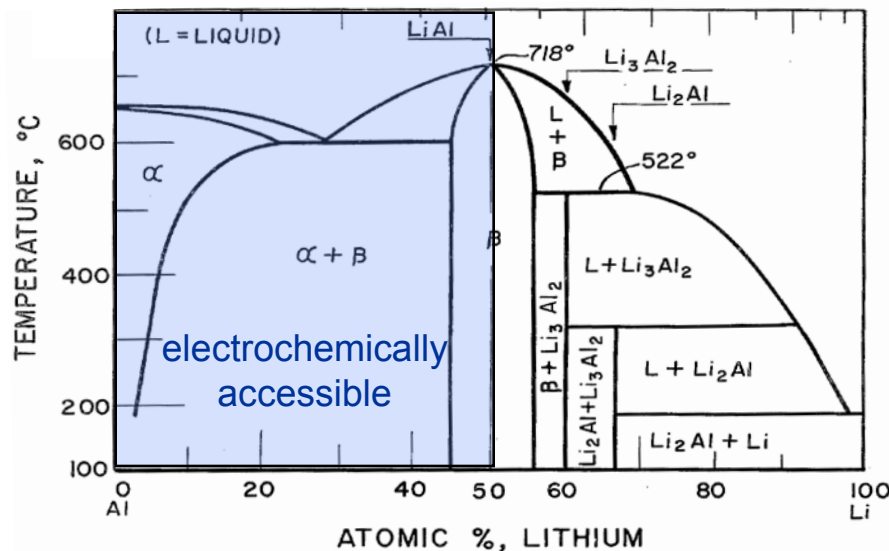
## Approach

- Improve and use an electrochemical cell of the Devanathan-Stachurski type to study mass and charge transfer mechanism in intermetallic anodes.
- Develop a time-dependent mass transport model to validate the observed experimental behavior and determine Li transport parameters in aluminum.
- Characterize surface processes in aluminum anodes

## Accomplishments

- The mechanism of  $\text{Li}^+$  transport in aluminum was revealed and quantified.
- Higher rate of lithium diffusion in thicker membranes originates from the structural damage to Al matrix.
  - Mixed electrolyte/solid solution transport mechanism and shorter diffusion length in  $\text{Li}_x\text{Al}$  phases contribute to this effect.

# Study of $\text{Li}^+$ Transport in Al Membranes



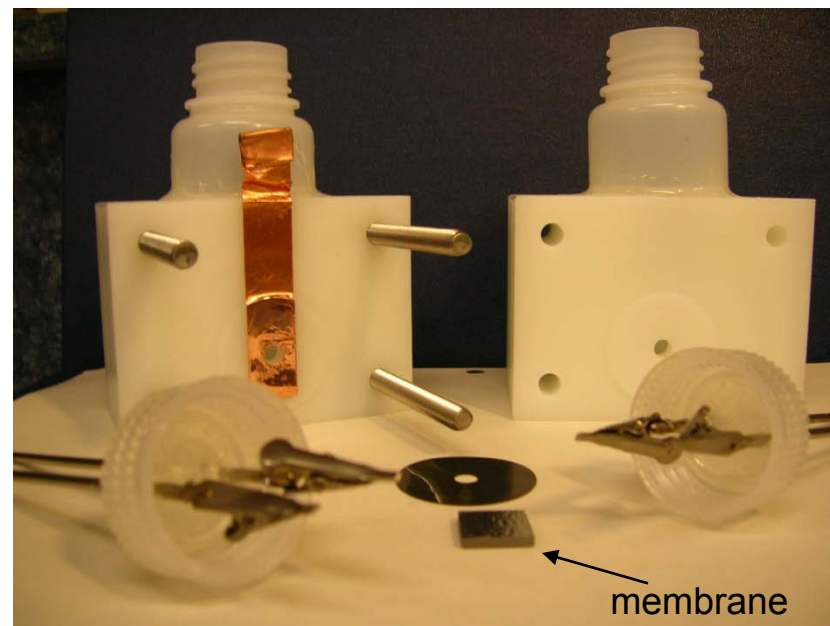
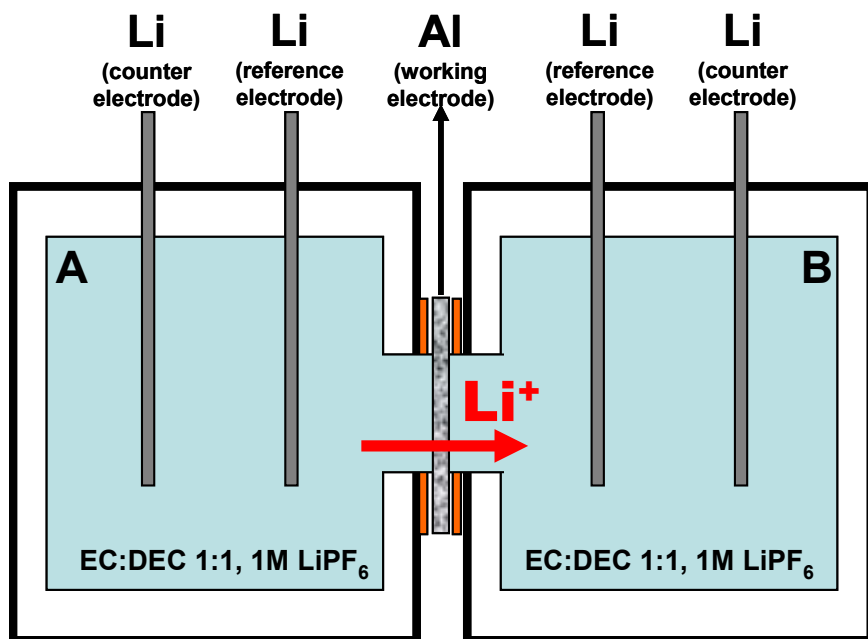
- $\alpha$ -Li<sub>x</sub>Al solid solution (0 < x < 0.1).
- Eutectic mixture of  $\alpha$ - and  $\beta$ -Li<sub>x</sub>Al solid solutions (0.1 < x < 0.5).
- $\beta$ -Li<sub>x</sub>Al solid solution (0.85 < x < 1).

- Threshold of the cathodic current at 0.17 V tends to shift to 0.35 V during the reverse scan.
- Dynamic changes in the mechanism and kinetics of Li insertion in Li<sub>x</sub>Al during cycling.

**What is the mechanism of  $\text{Li}^+$  transport in Al?**

# Study of $\text{Li}^+$ Transport in Al Membranes

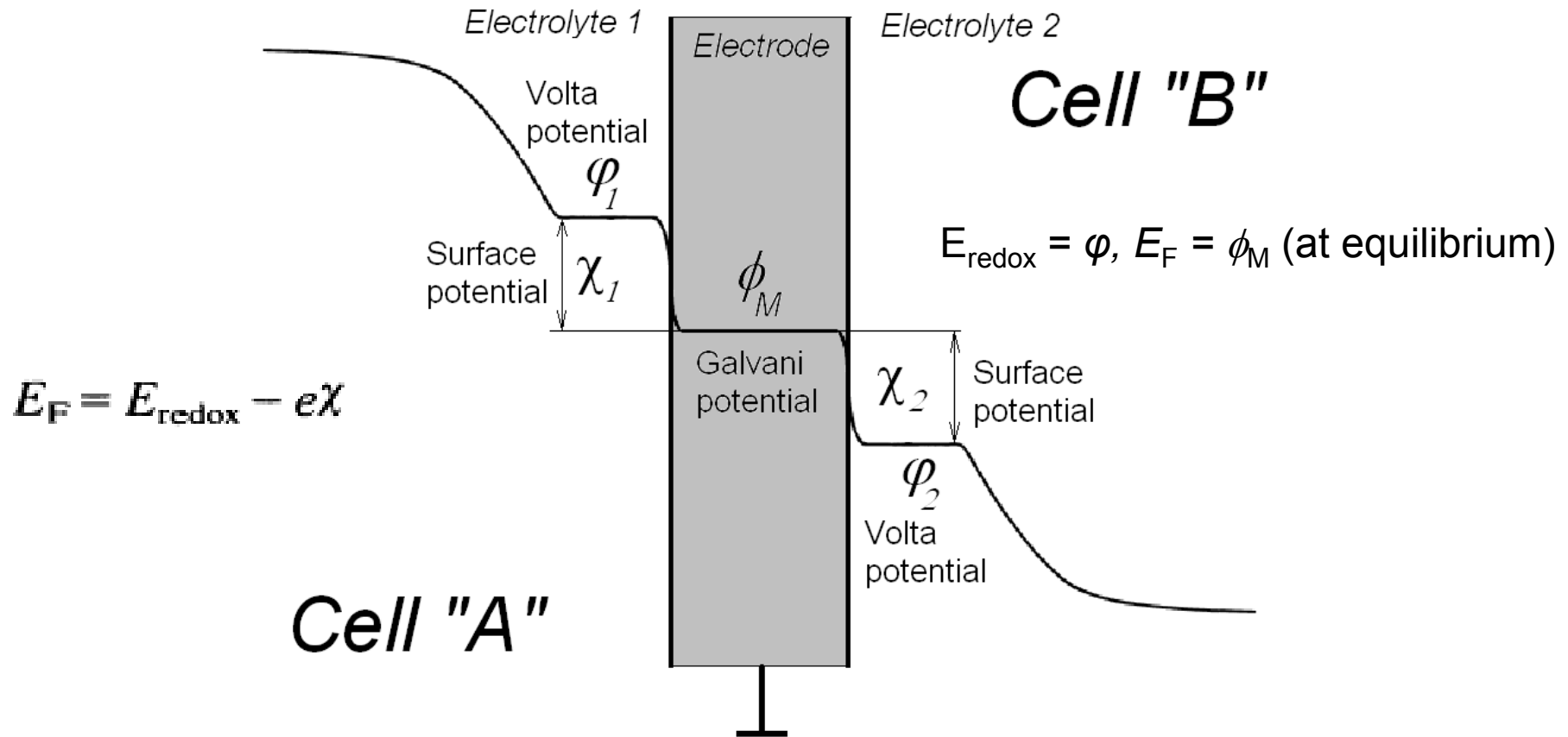
## Devanathan-Stachurski Cell for Studies of $\text{Li}^+$ Transport in Al



**Half-Cell A** –  $\text{Li}^+$  insertion, Al membrane is polarized at  $U = 10 \text{ mV}$  vs.  $\text{Li}/\text{Li}^+$ .

**Half-Cell B** -  $\text{Li}_x\text{Al}$  oxidation, Al membrane is polarized at constant  $U = 3 \text{ V}$  vs.  $\text{Li}/\text{Li}^+$ .

# Metallic Electrode in the Devanathan-Stachurski Cell

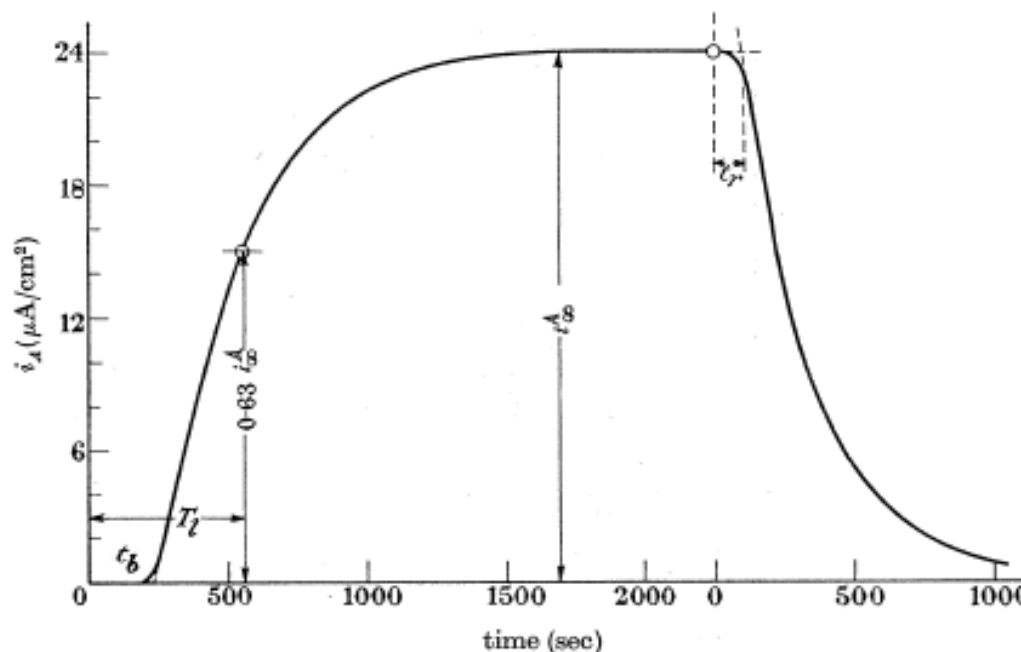


- Density of charge carriers on the electrode surface (potential) in cell "A" and "B" is different
- The charge carriers are forced in or away from the space charge region at the surface by an electric field created in the cell "A" and "B"
- Space charge region in metallic electrodes is very thin ca. a few Å



# Membrane Permeation Rate

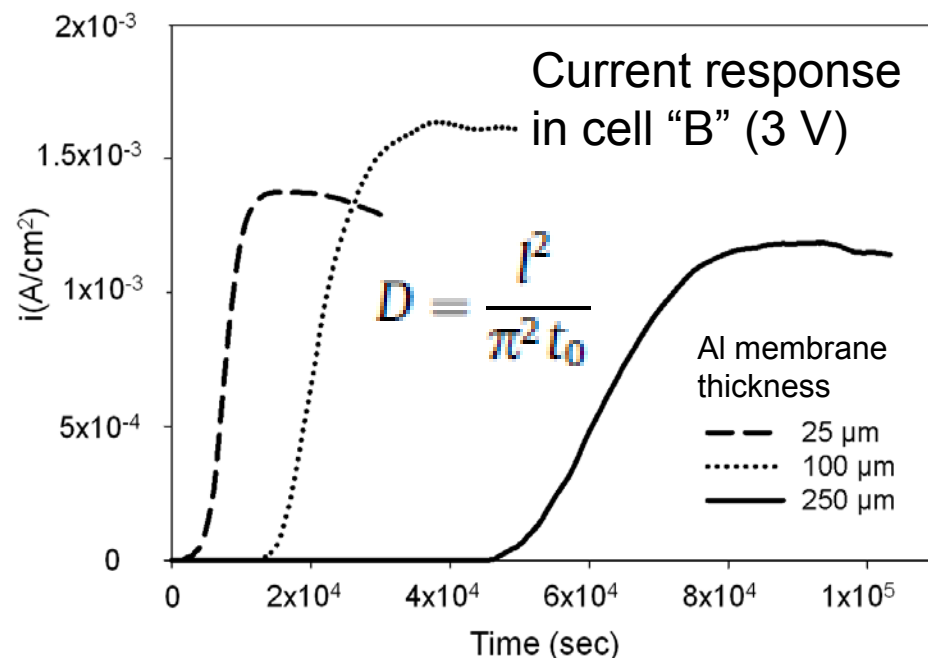
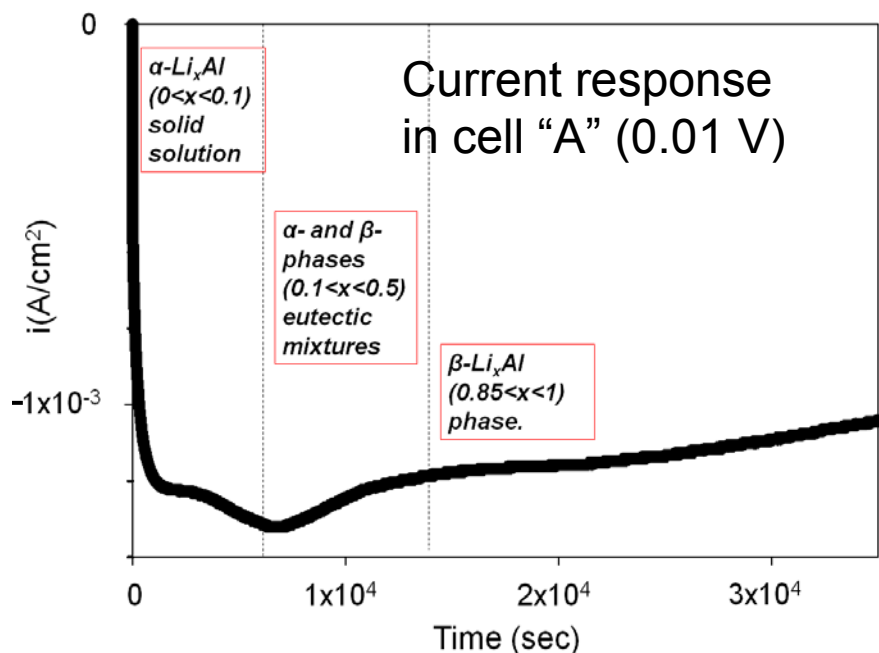
Typical Current Transient in Cell "B"  
(coverage on the cathodic side is constant)



$$t_b = \frac{L^2}{D} \left( \frac{1}{6} - \frac{1}{\pi^2} \right) = \frac{L^2}{15.3 D}$$

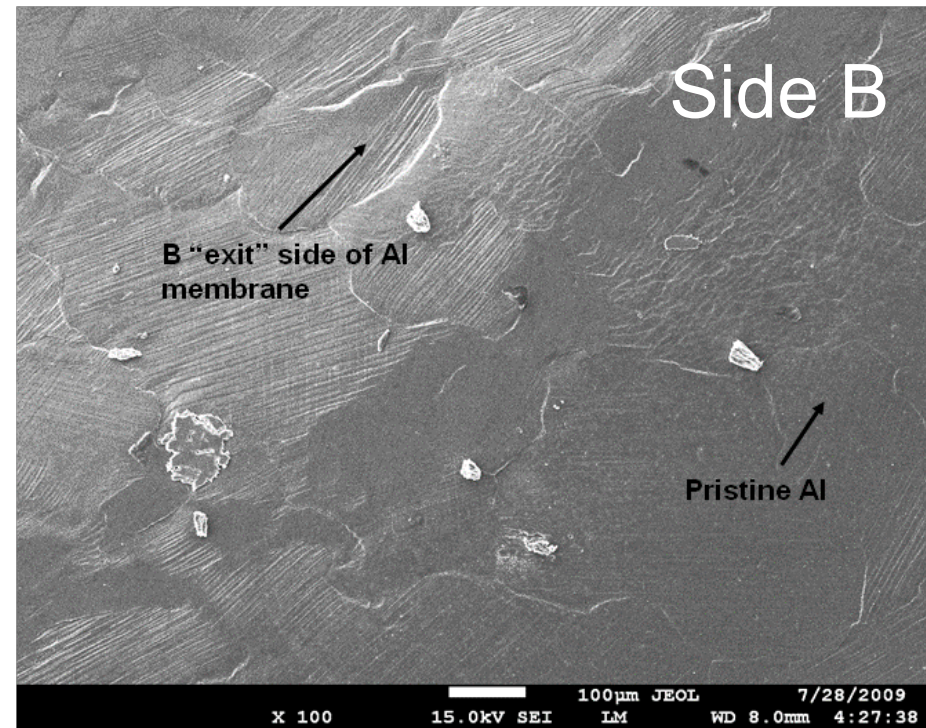
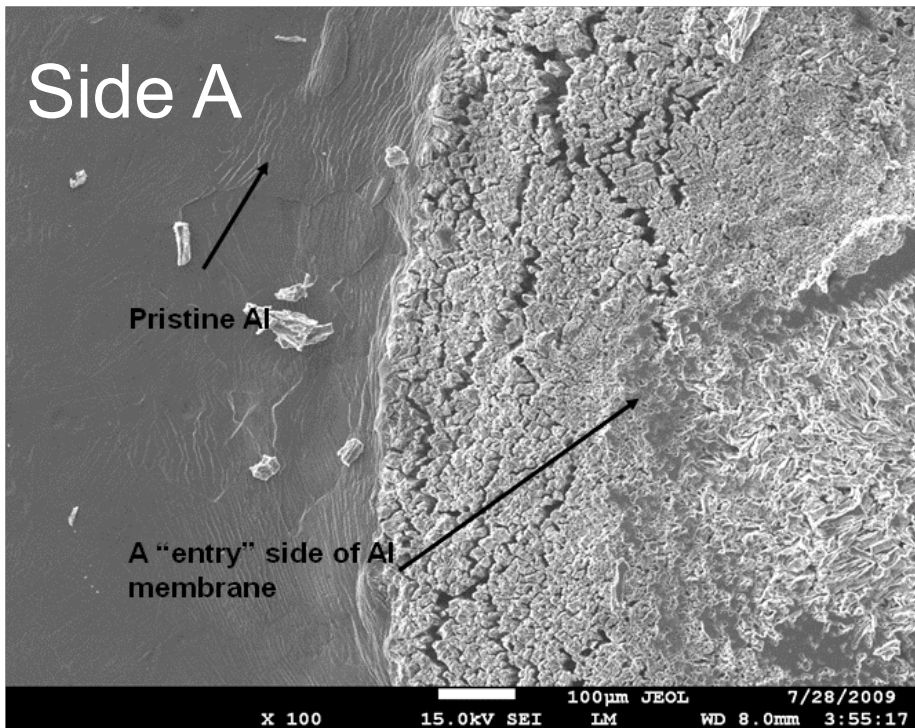
- Permeation is controlled by diffusion in the bulk - the diffusion constant is independent of thickness
- Anomalies in mass transport e.g., phase transitions, structural changes, molecular interactions affect the response signal.

# Study of Li<sup>+</sup> Transport in Al Membranes



- The initial increase of the cathodic current in cell "A" corresponds to formation of  $\alpha\text{-Li}_x\text{Al}$  ( $0 < x < 0.1$ ) solid solution.
- The onset of formation of the  $\beta\text{-Li}_y\text{Al}$  ( $0.85 < y < 1$ ) phase is marked by the current peak observed after 7000 s.
- The onset (rise time  $\tau_0$ ) of the anodic current in cell "B" corresponds to the oxidation of  $\alpha\text{-Li}_x\text{Al}$  after Li<sup>+</sup> reaches side "B" of the membrane.
- The average composition at the steady state conditions reaches ca.  $\text{Li}_{0.28}\text{Al}$

# Surface Analysis of Al Membranes



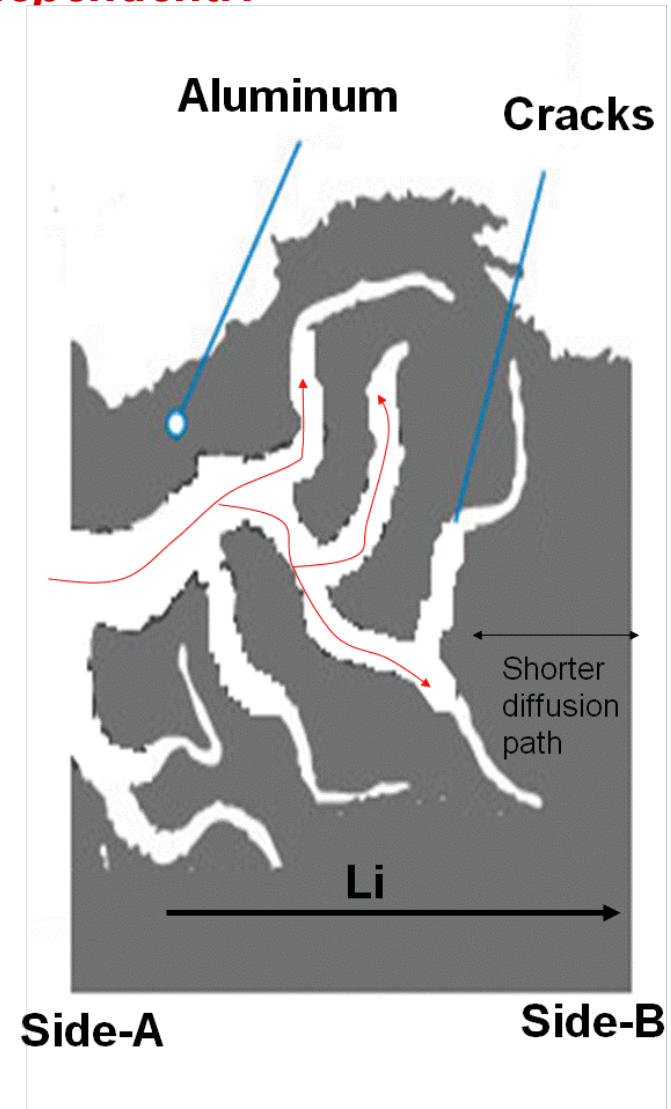
- Deep cracks and crevices form during the course of alloying with Li.
- The "A" side of the Al membrane exhibits significant morphology changes. It consists of pillar-like structures with wide gaps and cracks between them.
- The "B"-side of the Al membrane displays only moderate surface degradation.

# Study of Li<sup>+</sup> Transport in Al Membranes

Membrane thickness (μm)	Diffusion Coefficient (cm <sup>2</sup> s <sup>-1</sup> )
25	4.13*10 <sup>-10</sup>
100	8.6*10 <sup>-10</sup>
250	1.5*10 <sup>-9</sup>

*Why is the diffusion coefficient thickness dependent!?*

- Lithium transport can be treated as diffusion controlled, assuming a constant concentration gradient across the aluminum membrane.
- Formation of β-Li<sub>x</sub>Al (0.85<x<1) is associated with substantial volumetric expansion, which induces local stress and leads to Al crystallites expansion, decrepitation and separation.





# Summary I



- The measured diffusion coefficients appear to be in relatively good agreement with the reported  $D$  values for lithium in Al.
- Observed anomalies in the thickness dependence of the permeation rate of Li in Al suggest a more complicated transport mechanism.
- The amount of mechanical stress is higher in thicker electrodes, which leads to more structural damage.
- The apparent higher rate of lithium diffusion in thicker membranes originates from the mixed electrolyte/solid solution transport mechanism and shorter diffusion length in solid  $\text{Li}_x\text{Al}$  phases.

Careful micro- and nano-design and advanced manufacturing methods of intermetallic materials is required to improve their rate performance and stability in Li-ion battery applications.

# Study of Interfacial Phenomena at Sn Anodes



## Approach

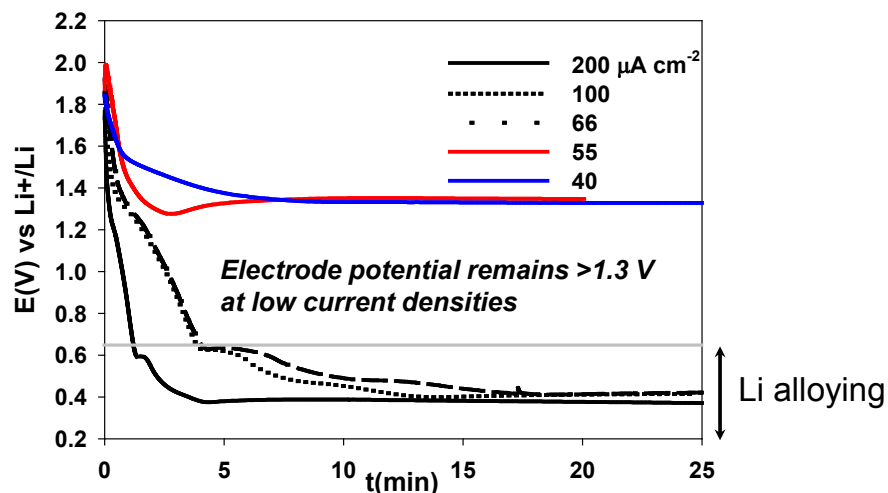
- Apply *in situ* and *ex situ* Raman and FTIR spectroscopy, spectroscopic ellipsometry, AFM, SEM, HRTEM, and electrochemical techniques to detect and characterize surface processes at intermetallic anodes.
- Use model Sn electrodes to detect and monitor early stages of the SEI formation in various electrolytes.
- Determine the nature and kinetics of surface phenomena and their implications for long-term electrochemical performance of the intermetallic anodes in high-energy Li-ion systems.

## Accomplishments

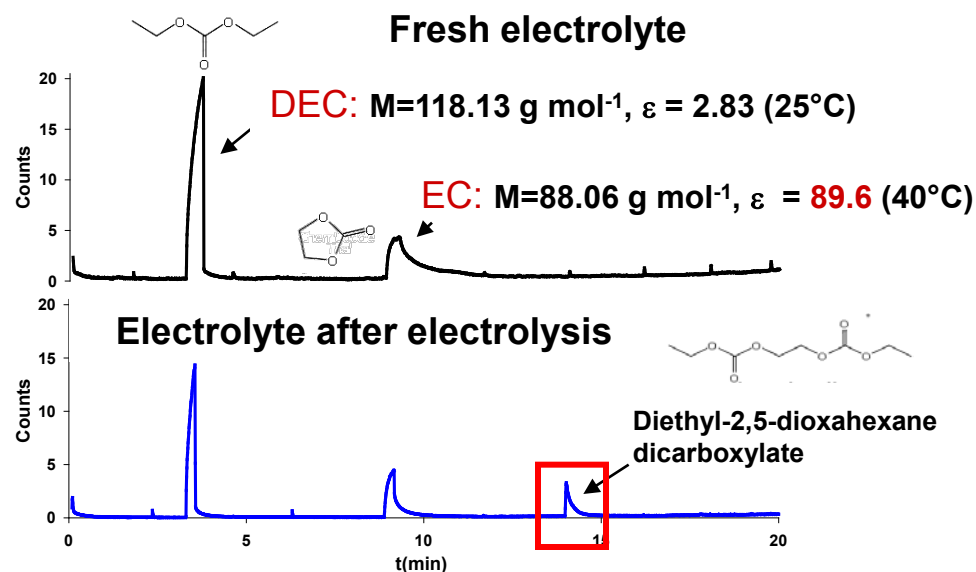
- Full assessment of interfacial processes on Sn electrode was completed.
  - *In situ* studies revealed that an effective SEI layer never forms on polycrystalline Sn in EC-DEC LiPF<sub>6</sub> electrolytes.
  - The mechanisms of interfacial processes were determined and characterized.
- Effective strategies to suppress unwanted surface reactions on Sn electrodes were proposed.

# Study of Interfacial Phenomena at Sn Anodes

## Galvanostatic Polarization of Sn-foil in 1M LiPF<sub>6</sub>, EC:DEC (1:2)



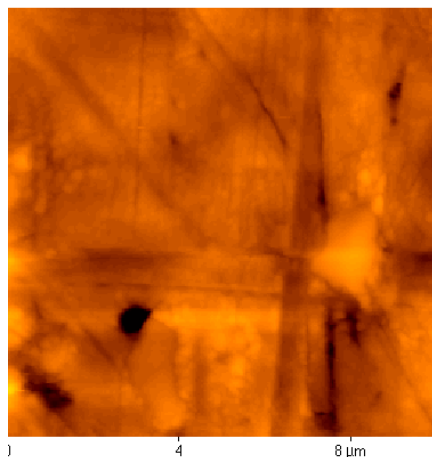
## GC-MS of the Electrolyte



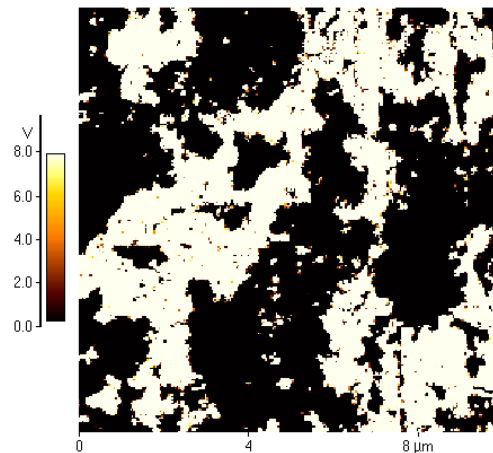
- Effective SEI layer never forms at the surface of Sn in EC/DEC LiPF<sub>6</sub> electrolyte
  - Continuous reduction reactions at 1.3-1.5V consume the electrolyte.
- Formation of soluble high molecular weight diethyl-2,5-dioxahehexane dicarboxylate (DEOHC) is responsible for coulombic inefficiency of Sn anodes.
  - PF<sub>5</sub> catalyzed ring-opening polymerization of EC.
  - Electrochemical and chemical decomposition of DEC.

# Ex situ AFM Study of Interfacial Phenomena at Sn-foil Anodes

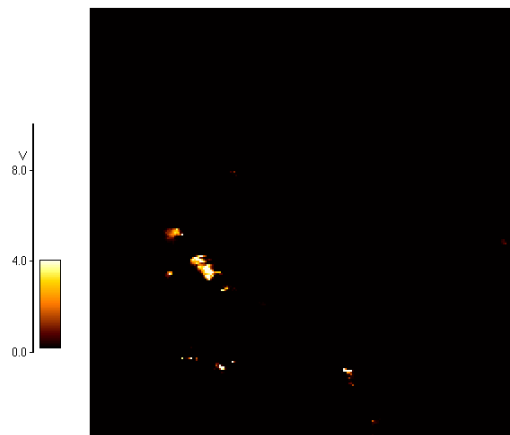
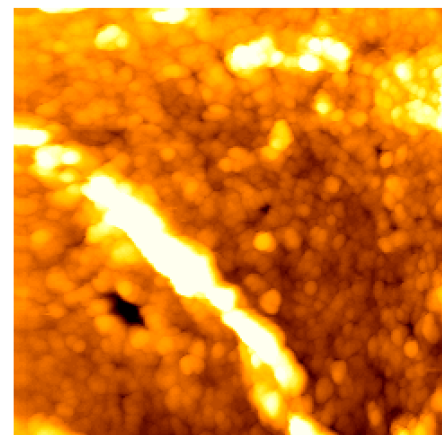
Morphology



Conductance



Fresh Sn-foil electrode



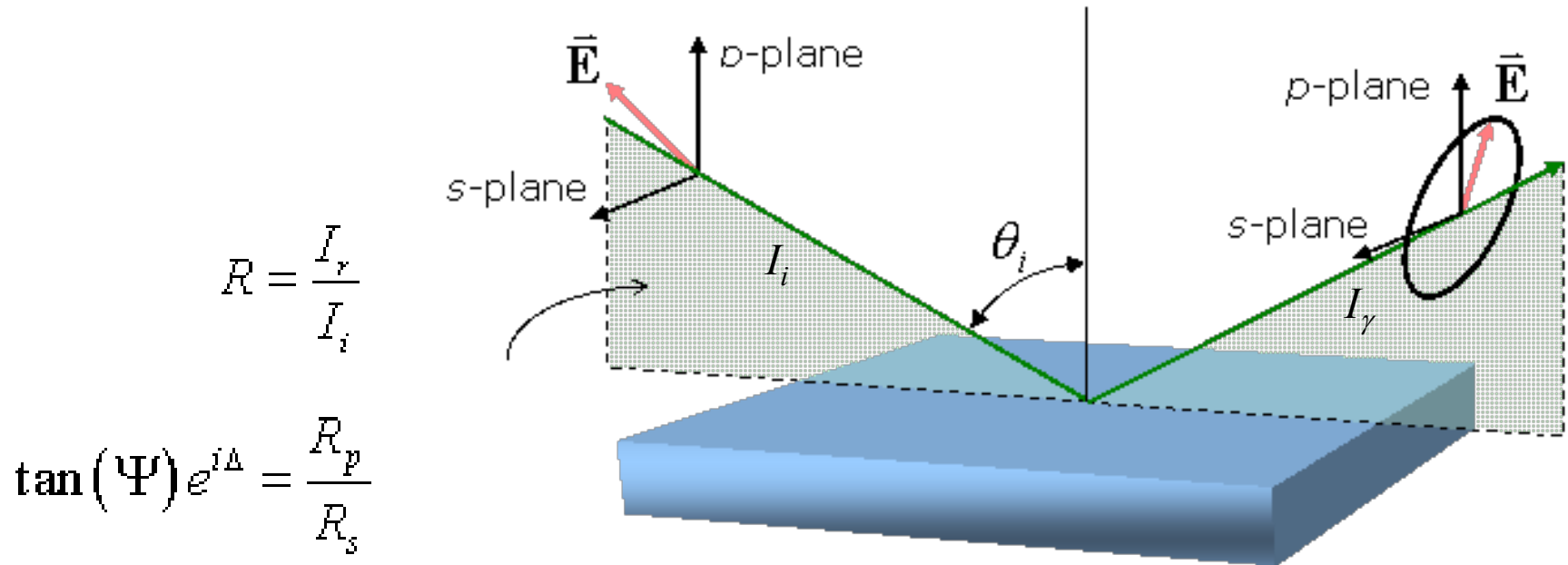
After scan from 2.7  $\rightarrow$  0.8 V in 1M LiPF<sub>6</sub>, EC:DEC (1:2),  $v = 2 \text{ mVs}^{-1}$

(8 x 8 μm images, black color on conductance images represents non-conductive areas )

- The surface layer is electronically insulating
- Pin holes and cracks in the SEI layer reach the surface of the Sn electrode



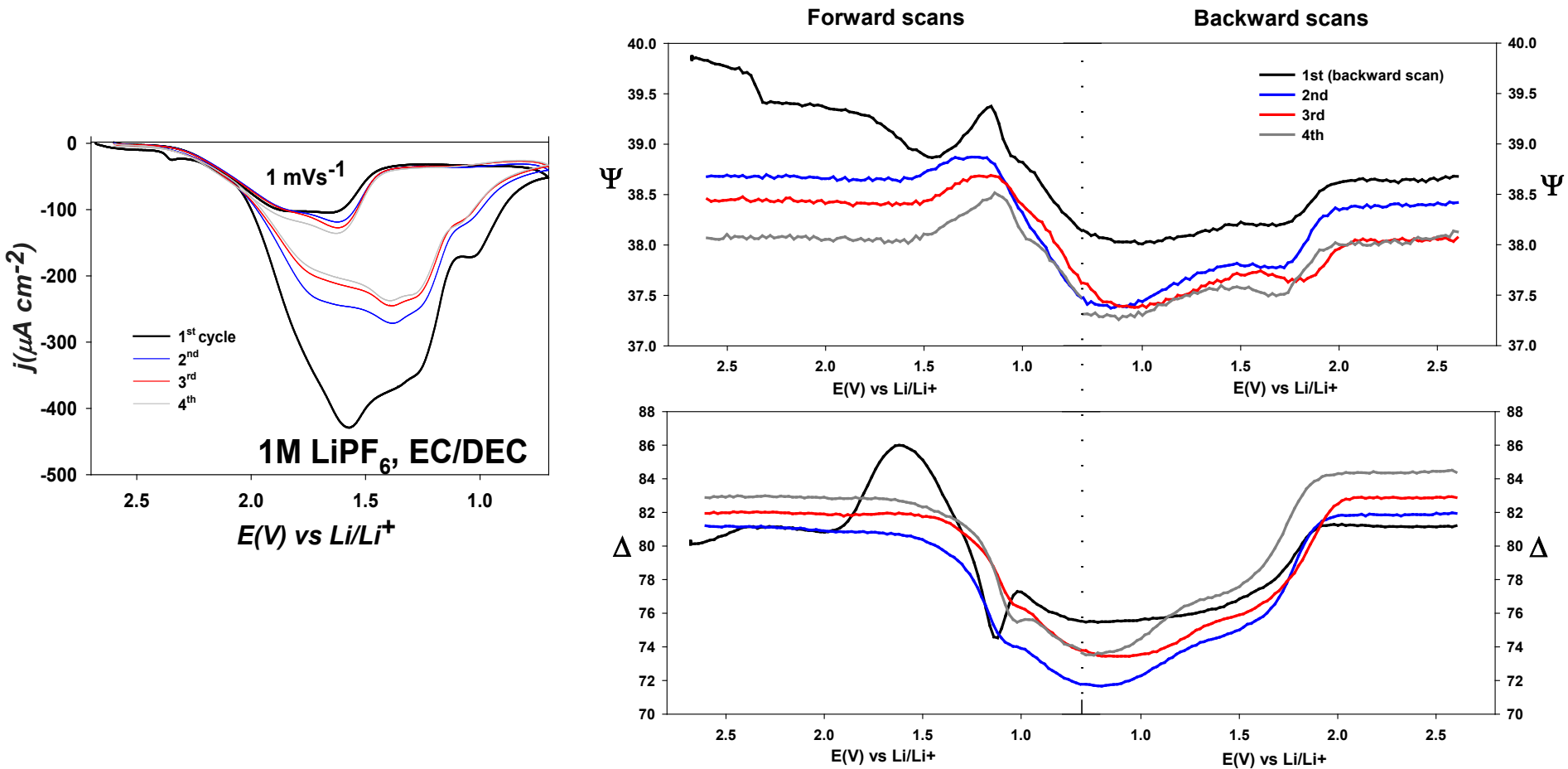
# In situ Spectroscopic Ellipsometry



Ellipsometry measures the change in polarization state of light reflected from the surface of a sample. The measured  $\Delta$  and  $\Psi$  values are related to the ratio of Fresnel reflection coefficients  $R_p$  and  $R_s$  for  $p$  and  $s$ -polarized light, respectively.

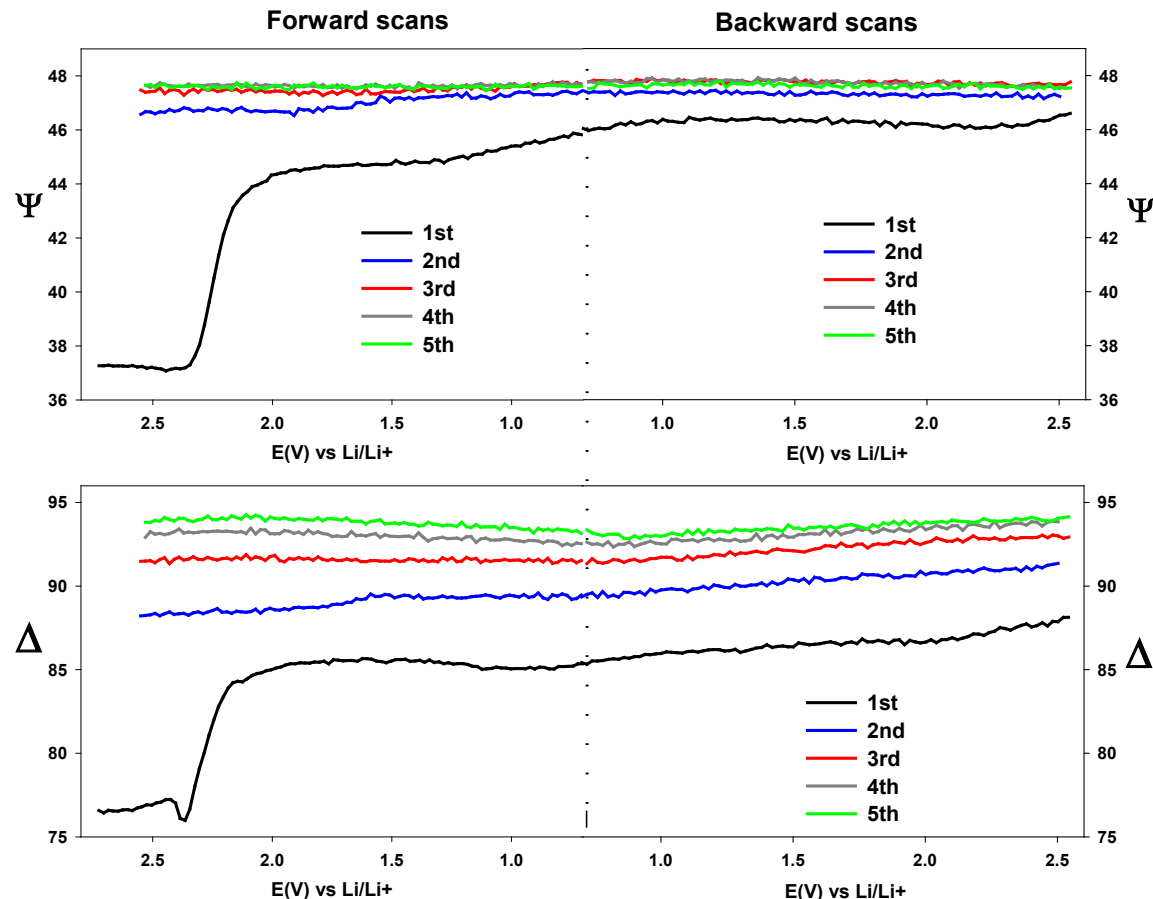
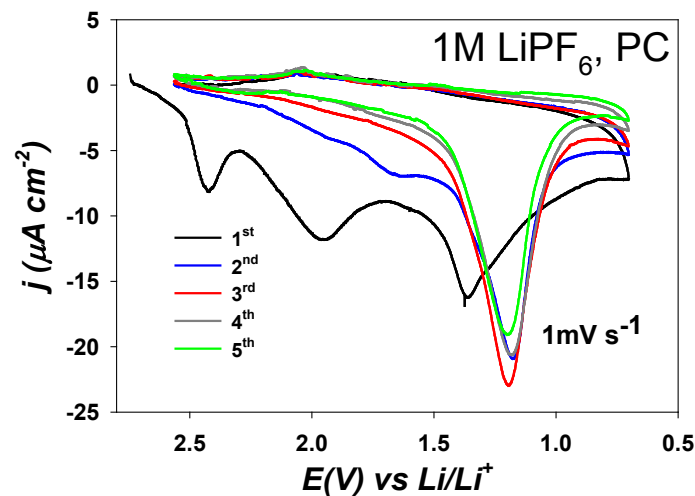
*Interfacial processes can be sensed and monitored in situ at extremely high sensitivity for well defined samples.*

# *In situ* Ellipsometry of Sn-foil Anodes



- Significant changes of  $\Delta$  and  $\Psi$  occur at 2.4 and 1.5 V, which correspond to the initial formation of a surface film and further reduction of the electrolyte
- Continuous reformation of SEI upon cycling gradually shifts  $\Delta$  and  $\Psi$  plots shift to higher and lower values, respectively

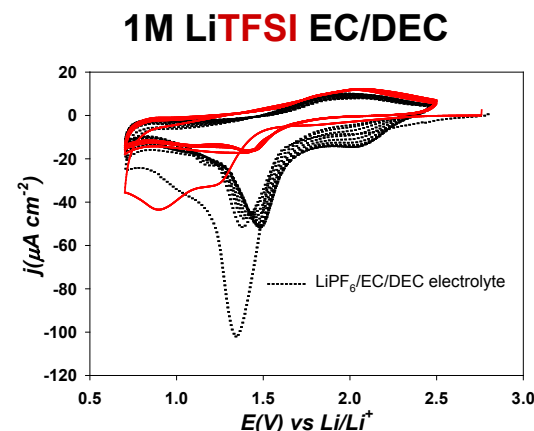
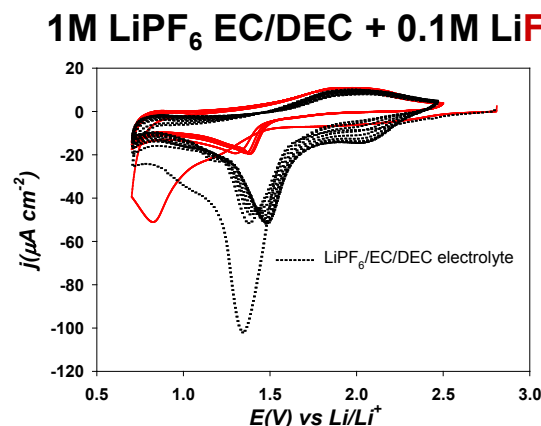
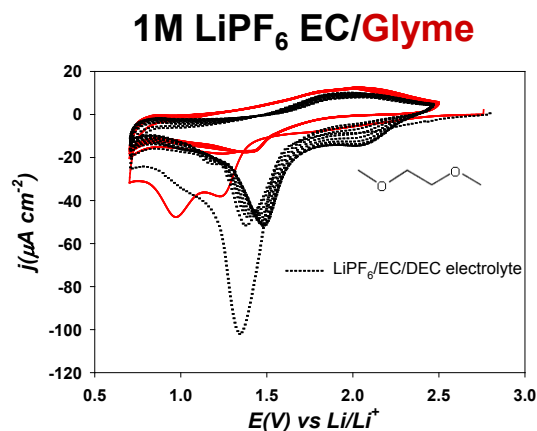
# *In situ* Ellipsometry of Sn-foil Anodes



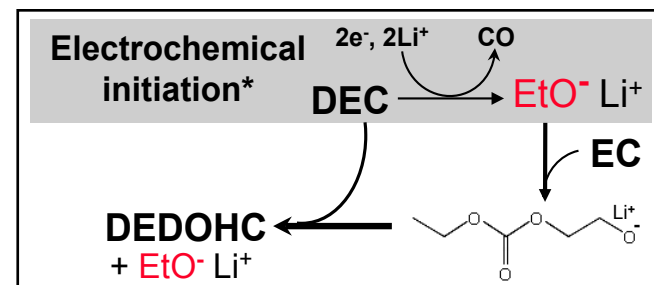
- Significant changes of  $\Delta$  and  $\Psi$  at 2.4 and 1.5 V in PC electrolyte reflect different SEI layer thickness and composition
- Continuous reformation of SEI upon cycling gradually shifts  $\Delta$  and  $\Psi$  plots shift to higher values

# Study of Interfacial Phenomena at Sn Anodes

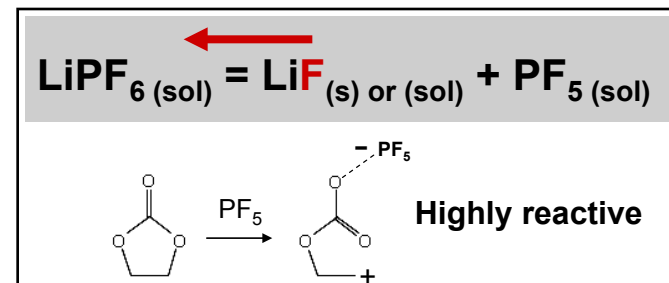
## The Effect of Electrolyte Composition



- The mechanism of 1M LiPF<sub>6</sub> EC/DEC electrolyte reduction involves reduction of DEC to EtO<sup>-</sup> followed by chemical reactions with EC and DEC and PF<sub>6</sub><sup>-</sup>
- Formation of an effective SEI layer on Sn electrodes can be achieved via electrolyte modification solvent(s) (PC, glyme) (LiTFSI) and salt modifications, and additives e.g., LiF, FEC.



Tarascon et al, J. Pow Sources, 178 (2008), 409



Sloop et al, J. Pow. Sources, 119 (2003), 330

# Summary II



- ❑ Preliminary assessment of interfacial processes on Sn electrode was completed
- ❑ *In situ* studies revealed that the nature and kinetics of surface reactions are strongly dependent on the electrode and electrolyte.
  - Effective SEI layer never forms at the surface of polycrystalline Sn in EC-DEC LiPF<sub>6</sub> electrolytes
- ❑ Sn interface instability in organic carbonate electrolytes can be remedied by careful optimization of the electrolyte composition and use of additives that (re)produce a stable SEI layer.

It is critical for the long-term electrochemical performance of intermetallic anodes to suppress unwanted surface reactions. Coordinated electrode and electrolyte design must be carried out to achieve interfacial stability of Sn anodes in Li-ion battery applications.

# Interfacial and Bulk Processes in $\text{LiMnPO}_4$ Cathodes



## Approach

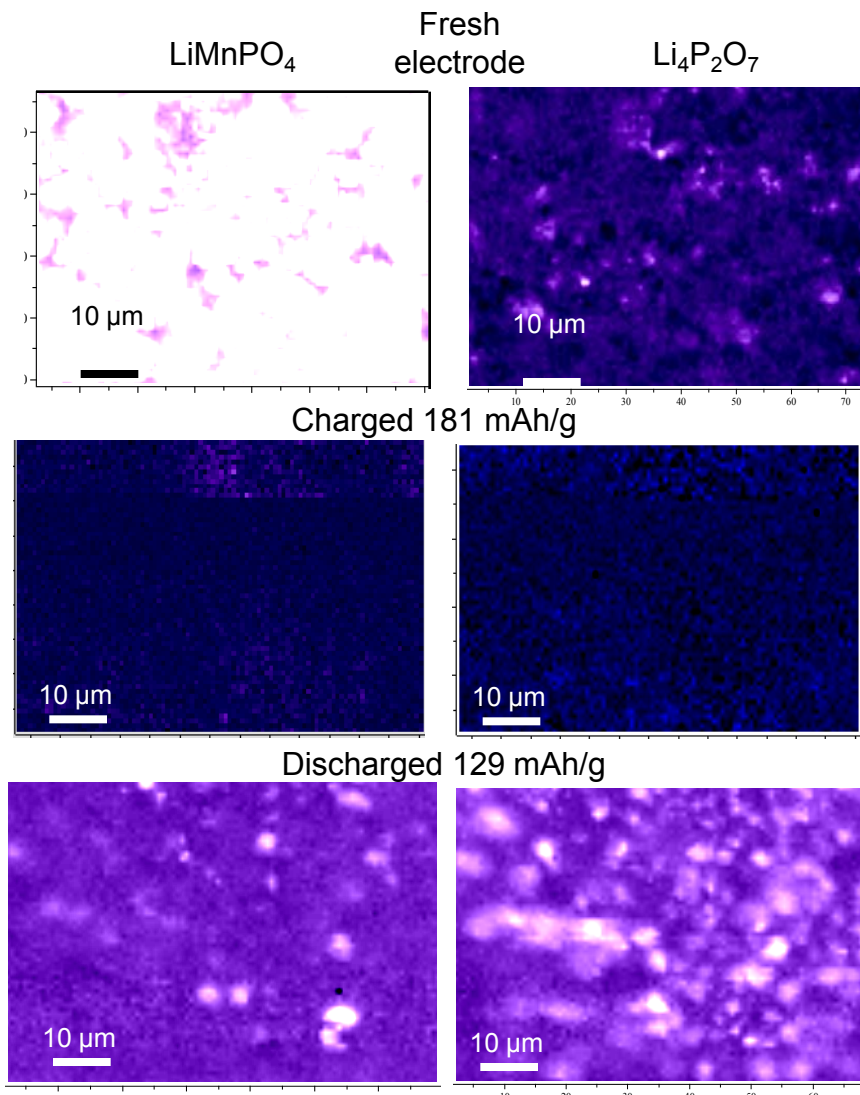
- Apply *in situ* and *ex situ* Raman and FTIR spectroscopy, and electrochemical techniques to detect and characterize chemical and structural changes in  $\text{LiMnPO}_4$ , and interfacial processes on composite  $\text{LiMnPO}_4$  cathodes (HPL).
  - Develop an experimental procedure for surface carbon removal through an  $\text{O}_2$ -plasma etching process to allow microRaman probing of  $\text{LiMnPO}_4$  composite cathodes.
  - Design and construct a spectro-electrochemical cell for *in situ* FTIR-attenuated total reflectance (ATR) microscopy measurements.

## Accomplishments

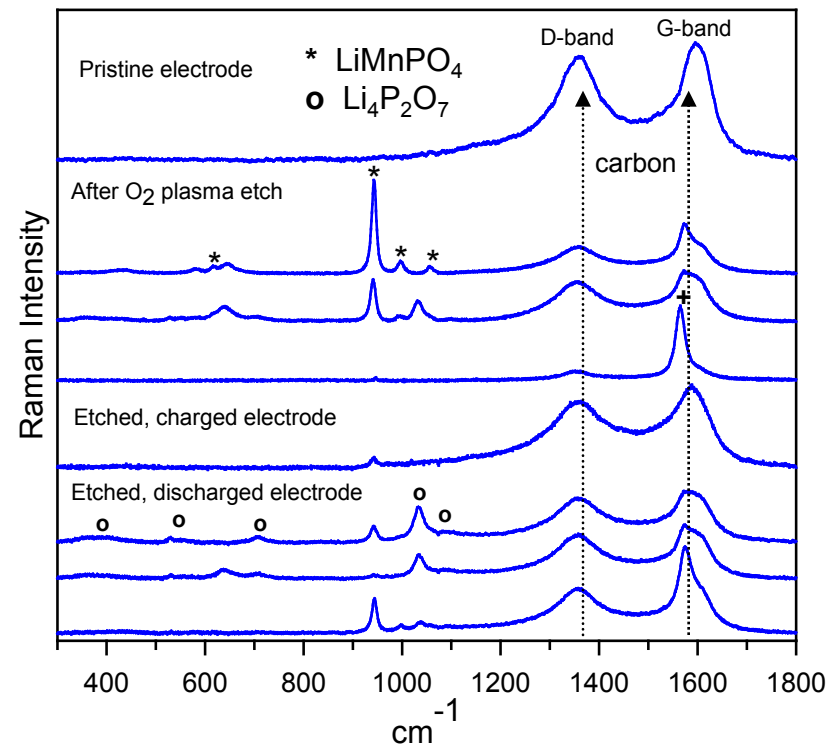
- Bulk and surface characterization of a  $\text{LiMnPO}_4$  electrode was completed.
  - $\text{LiMnPO}_4$  chemical instability upon delithiation was observed and characterized.
  - Formation of surface films on  $\text{LiMnPO}_4$  upon charging was observed and characterized.

# Interfacial and Bulk Processes in $\text{LiMnPO}_4$ Cathodes

## MicroRaman images of $\text{LiMnPO}_4$ composite electrode after $\text{O}_2$ -plasma etching



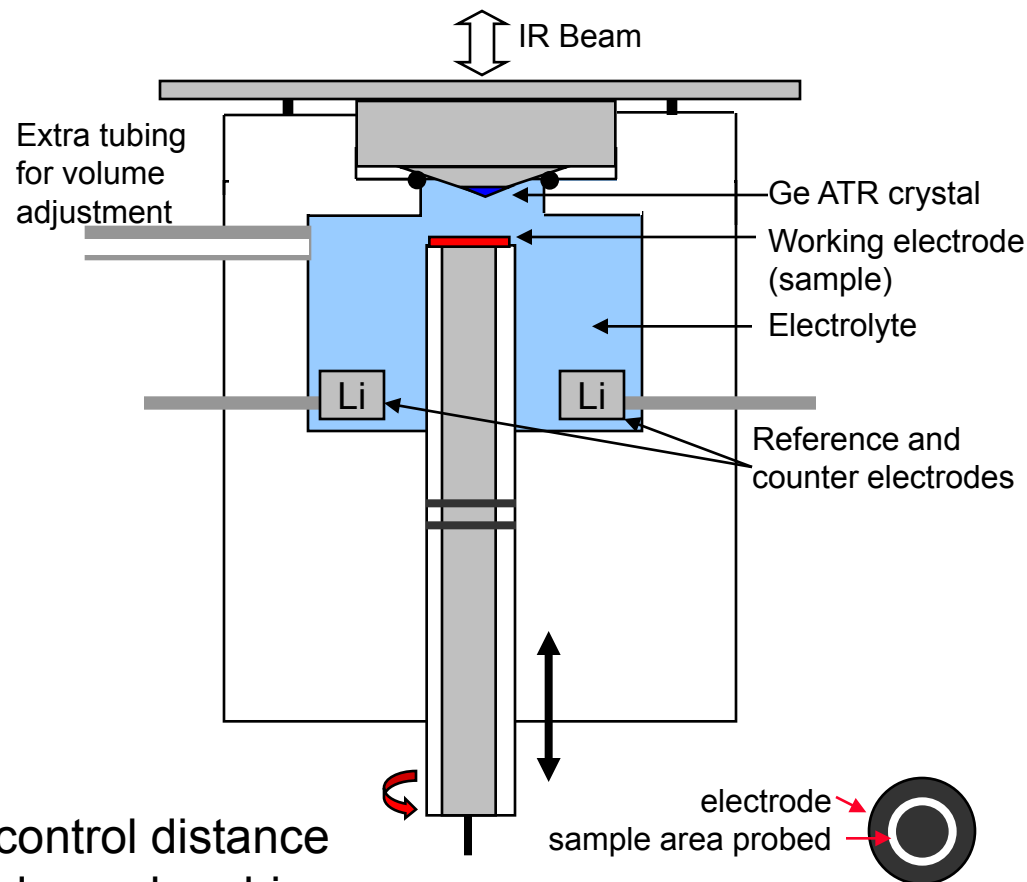
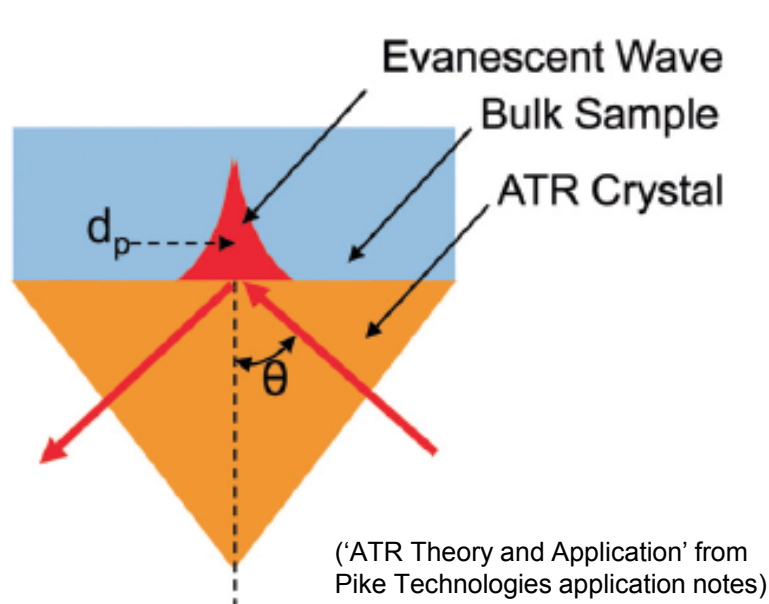
## Selected Raman spectra of $\text{LiMnPO}_4$ composite electrode



- $\gamma_{\text{sym}} \text{PO}_4$  vibration mode disappears upon charging(!?)
- $\text{Li}_4\text{P}_2\text{O}_7$  forms upon  $\text{LiMnPO}_4$  cycling.
  - $\text{MnPO}_4$  is chemically unstable vs. the electrolyte?

# Interfacial and Bulk Processes in $\text{LiMePO}_4$ Cathodes

## FTIR-Attenuated Total Reflectance (ATR) Spectro-electrochemical Cell

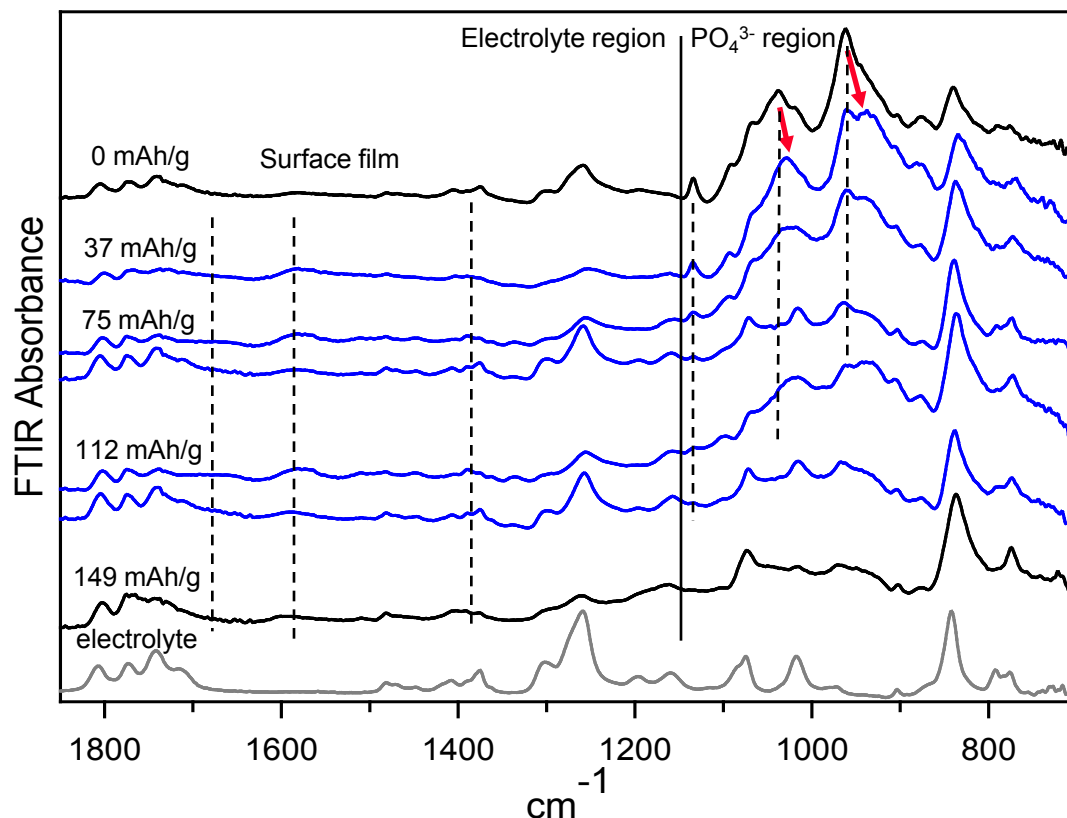


- Approach mechanism (not shown) to control distance between the Ge ATR crystal and sample, and probing location.
- ATR sample penetration depth  $\sim 1 \mu\text{m}$ .

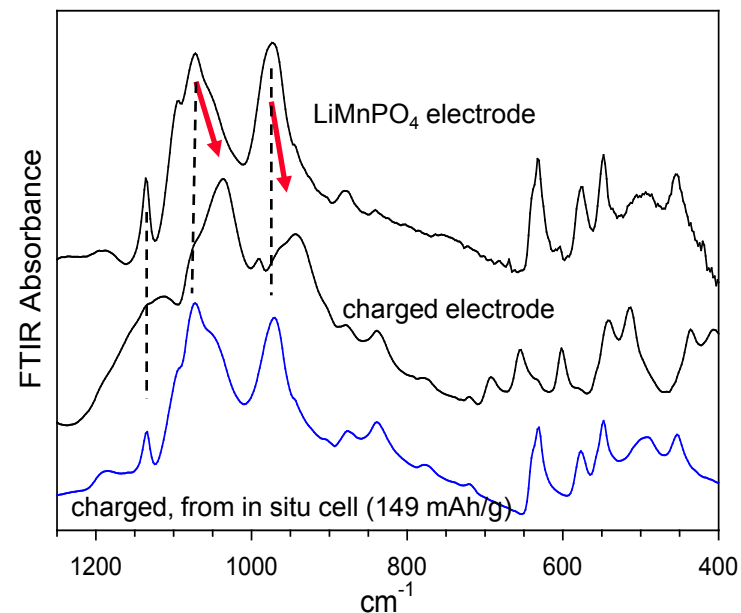


# Interfacial and Bulk Processes in $\text{LiMnPO}_4$ Cathodes

## *In situ* FTIR-ATR spectra



## Transmission FTIR spectra



- $\text{MnPO}_4$  forms early at the surface of the electrode during charging.
- IR bands characteristic for  $\text{PO}_4$  group tend to vanish upon charging. FTIR data are in good agreement with Raman results.
- Non uniform surface film forms on surface of  $\text{LiMnPO}_4$  electrode during charging (no film was detected on pure carbon black electrode at 4.4 V)

# Summary III



- ❑  $\text{Li}_x\text{MnPO}_4$  is unstable vs.  $\text{LiPF}_6$ : organic carbonate electrolytes.
- ❑  $\text{MnPO}_4$  forms early during charging but then tends to undergo chemical and structural changes to convert to  $\text{Li}_4\text{P}_2\text{O}_7$  after the full cycle of Li extraction and insertion is completed.
- ❑ Surface film forms at the exposed  $\text{Li}_x\text{MnPO}_4$  active material. No surface film was detected on carbon black additive.

Instability of delithiated  $\text{Li}_x\text{MnPO}_4$  likely precludes this material from achieving commercial viability without developing routes for stabilizing the active material.

# Future Work



- **Continue studies of mass and charge transfer mechanisms at the electrode-electrolyte interface**
  - Develop multi-task spectro-electrochemical cell of the Devanathan-Stachurski type to study *in situ* and model kinetics of Li intercalation and diffusion through anode and cathode materials (V. Srinivasan)
  - Carry out quantitative measurements of the mass and charge transfer across electrode/electrolyte interfaces.
- **Design and apply *in situ* and *ex situ* experimental methodologies to detect and characterize surface processes in Li-ion intermetallic anodes**
  - Comprehensive fundamental *in situ* spectroscopic ellipsometry in conjunction with AFM and FTIR/Raman surface analysis studies of the SEI layer formation on model monocrystal Sn and Si electrodes will be carried out
  - Cooperate with the BATT Interfacial Studies Group to investigate the effect of material structure, morphology, topology on formation of the SEI layer
  - Investigate correlations between physico-chemical properties of the SEI layer and long-term electrochemical performance of Li-ion electrodes
- **Diagnostic evaluation of detrimental phenomena in high-voltage (>4.3V) cathodes**
  - Apply *in situ* and *ex situ* Raman and FTIR spectroscopy to detect and characterize surface and bulk processes in high voltage cathodes
  - Evaluate the effect of electrode passive additives and impurities on the electrochemical performance and long-term stability of the composite cathodes.