Interfacial Processes – Diagnostics

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Overview

Timeline

- PI participated in the BATT Program since 1999
- Task #1 started on Oct. 1, 2010 60% completed
- Task #2 initiated on April 1, 2009 60% 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

- FY12 funding TBD
- FY11 funding $520K
- FY10 funding $520K
- FY09 funding $520K
- FY08 funding $485K
- FY07 funding $320K

Partners

- ANL, LBNL, SUNY, UP, and UU
- HQ, HPL
- J.Kerr, J. Cabana, G. Chen, M.Doeff, K. Persson (LBNL)
- V. Srinivasan (LBNL) 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. Characterize surface phenomena on $LiMnPO_4$ composite cathodes (July, 2010)
   - Accomplished on time. Custom-designed electrochemical cell allowed *in situ* FTIR-ATR measurements to *observe in situ* interfacial behavior of $LiMnPO_4$
2. Identify the structural and surface changes of Al, Si and Sn-containing anodes during cycling working collaboratively with the BATT SEI Group. (September, 2010)
   - Accomplished on time. *In situ* studies revealed that the nature and kinetics of surface reactions are strongly dependent on the electrode and electrolyte composition
3. Identify the structural and surface changes of Si and Sn model anodes working collaboratively with the BATT Anode Group (July, 2011)
   - Work in progress ~80% completed
4. Carry out preliminary near-field measurements of SEI layers on Si, Sn anodes and high voltage cathodes (September, 2011)
   - Work in progress ~20% completed
5. Characterize surface phenomena in high-voltage composite cathode (September, 2011)
   - Work in progress ~60% completed

Interfacial and Bulk Processes in High-Voltage Cathodes

Approach

- Apply *in situ* and *ex situ* Raman microscopy, FTIR spectroscopy, and standard electrochemical techniques to probe and characterize chemical, structural and interfacial changes in $LiMnPO_4$ and $LiNi_{0.5}Mn_{1.5}O_4$ during charge/discharge
  - Perform *ex situ* FTIR-transmission and *in situ* FTIR-ATR measurements on composite cathodes
  - Design and construct a new spectro-electrochemical cell for *in situ* Raman microscopy measurements

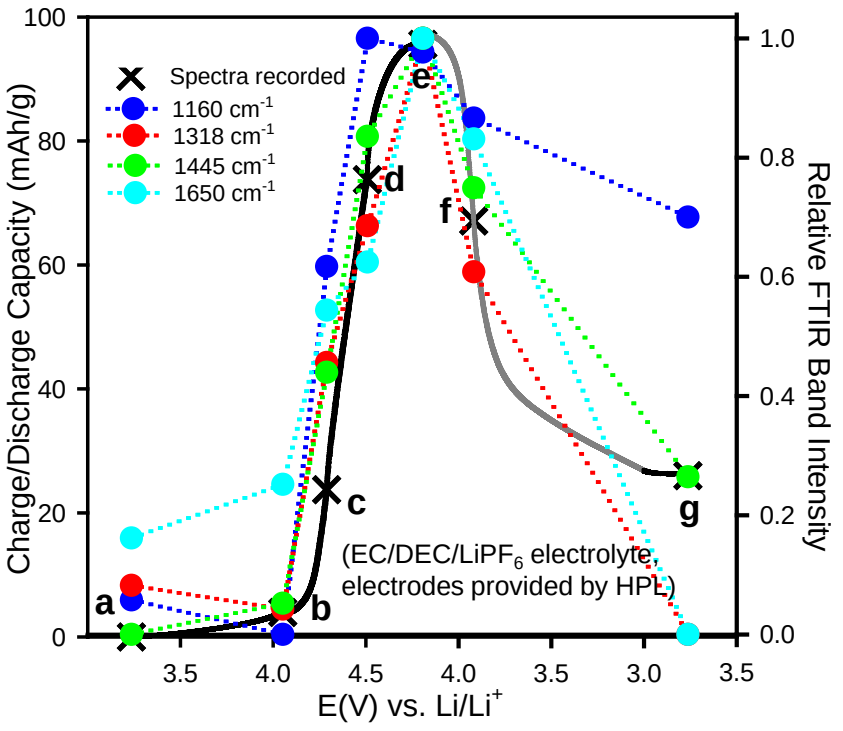
Accomplishments

- Characterization of the interfacial phenomena of a $LiMnPO_4$ composite cathode was completed
  - Charge/discharge of $LiMnPO_4$ composite cathode produce an unstable surface layer
  - Composition of the film changes continuously during cycling. Inorganic electrolyte oxidation products tend to gradually accumulate on the electrode surface
- Preliminary *in situ* and *ex situ* studies of $LiNi_{0.5}Mn_{1.5}O_4$ surface reactivity were carried out
  - $LiNi_{0.5}Mn_{1.5}O_4$ exhibits surface instability in EC/DEC/$LIPF_6$ electrolyte

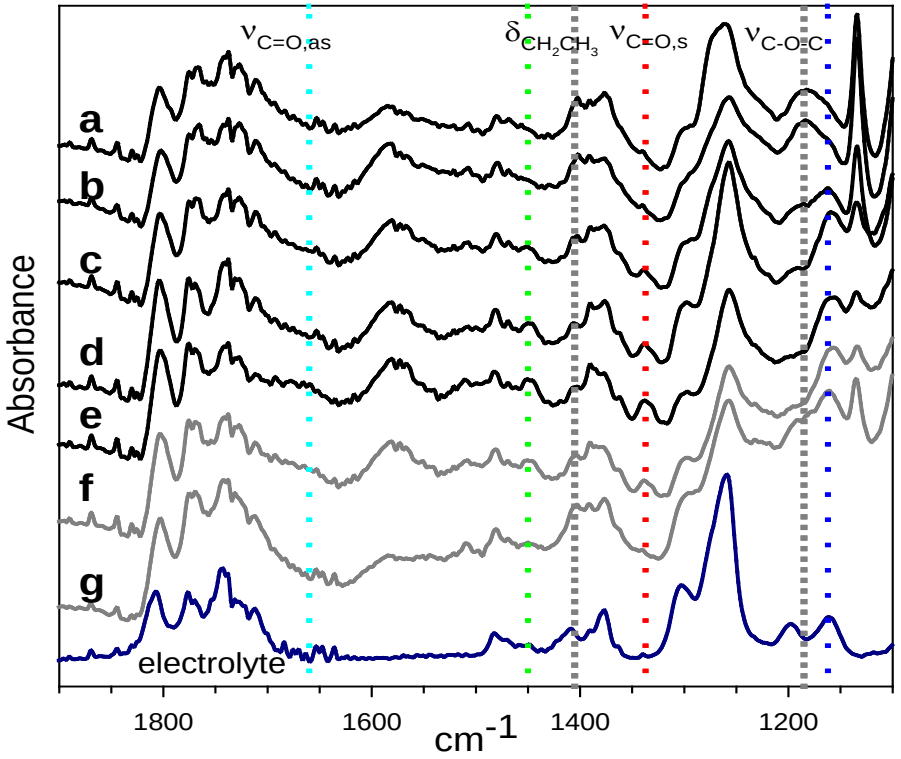
Collaboration with "BATT Ni/Mn Spinel" Task Group

In situ FTIR-ATR of $LiMnPO_4$ Composite Cathodes

FTIR Band Intensity vs. SOC



In situ FTIR-ATR spectra

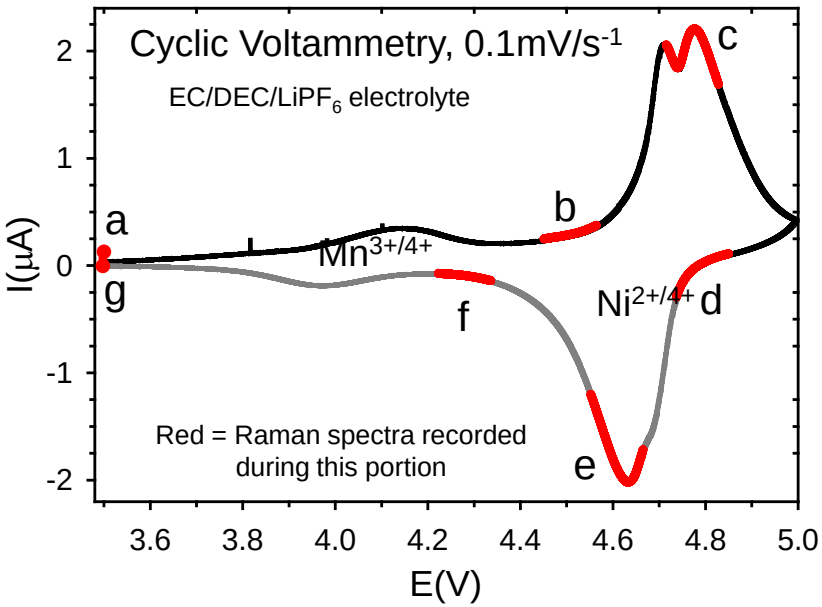


- Bands at 1650 cm^{-1} ($\nu_{C=O}$), 1445 cm^{-1} ($\delta_{CH_2CH_3}$), 1318 cm^{-1} ($\nu_{C=O}$) and 1160 cm^{-1} (ν_{C-O-C}) which are characteristic for lithium alkyl carbonates appear on FTIR spectra during charging
- Peaks intensity tend to increase during charge and decrease during discharge
- Non-uniform peak intensity variation during charge-discharge may indicate changes in film composition

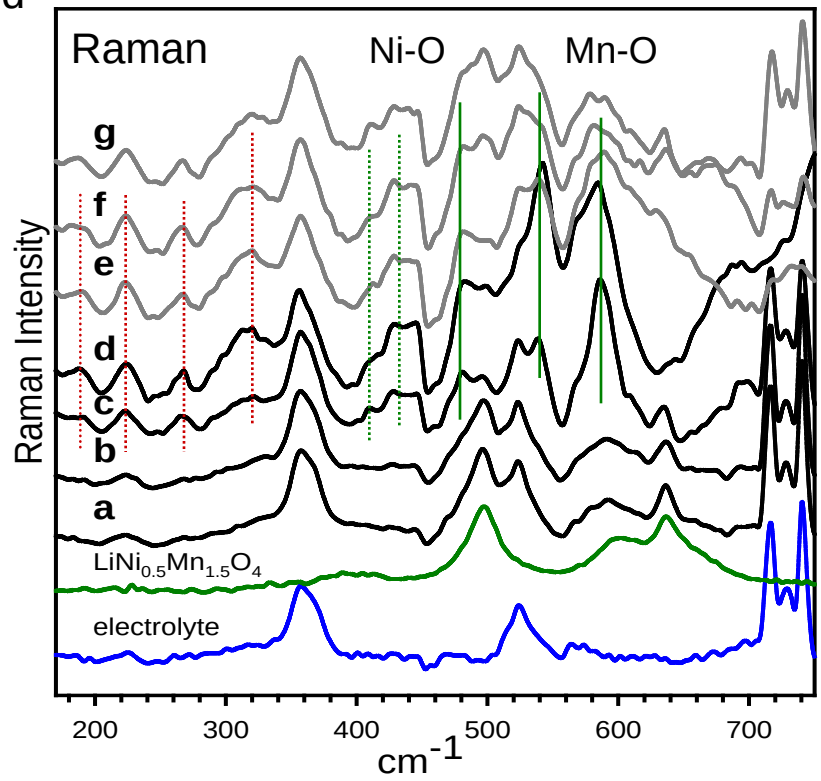
Electrolyte decomposition products do not form a stable layer on the surface of $LiMnPO_4$ composite cathode

In Situ Raman Microscopy of $LiNi_{0.5}Mn_{1.5}O_4$ Single Particle Electrode

The electrode consists of LNMO particles pressed into Al current collector (LMNO powder sample provided by J. Cabana). No carbon, no binder used



Presence of $Mn^{3+/4+}$ redox in sample consistent with findings of excess Mn in spinel sample (J. Cabana)



- New Raman bands (180-340 cm^{-1} and 400-460 cm^{-1}) emerge upon first charge
- Ni^{4+}-O, Mn^{4+}-O symmetric stretch vibrations rise and fall during charge and discharge. Delithiated phase is still present after discharge, possible loss electronic contact
- Intensity variation of v_{PF_6} at 740 cm^{-1} may indicate surface reactions that involve PF_6^- anions

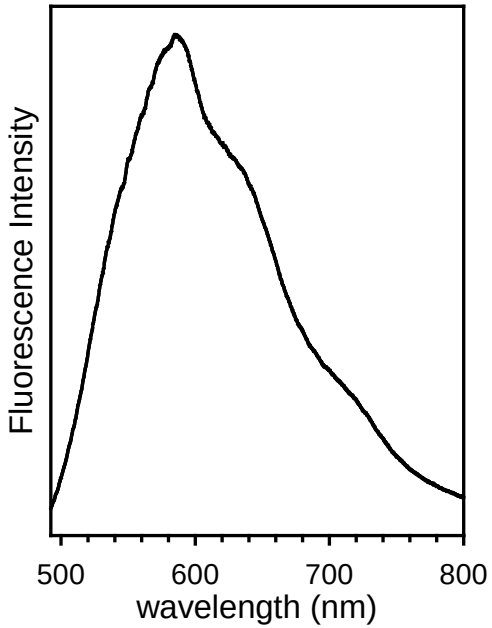
Direct spectroscopic evidence of structural changes in LNMO and surface film formation during charge/discharge cycles

In Situ Fluorescence Spectroscopy of $LiNi_{0.5}Mn_{1.5}O_4$ Single Particle Electrode

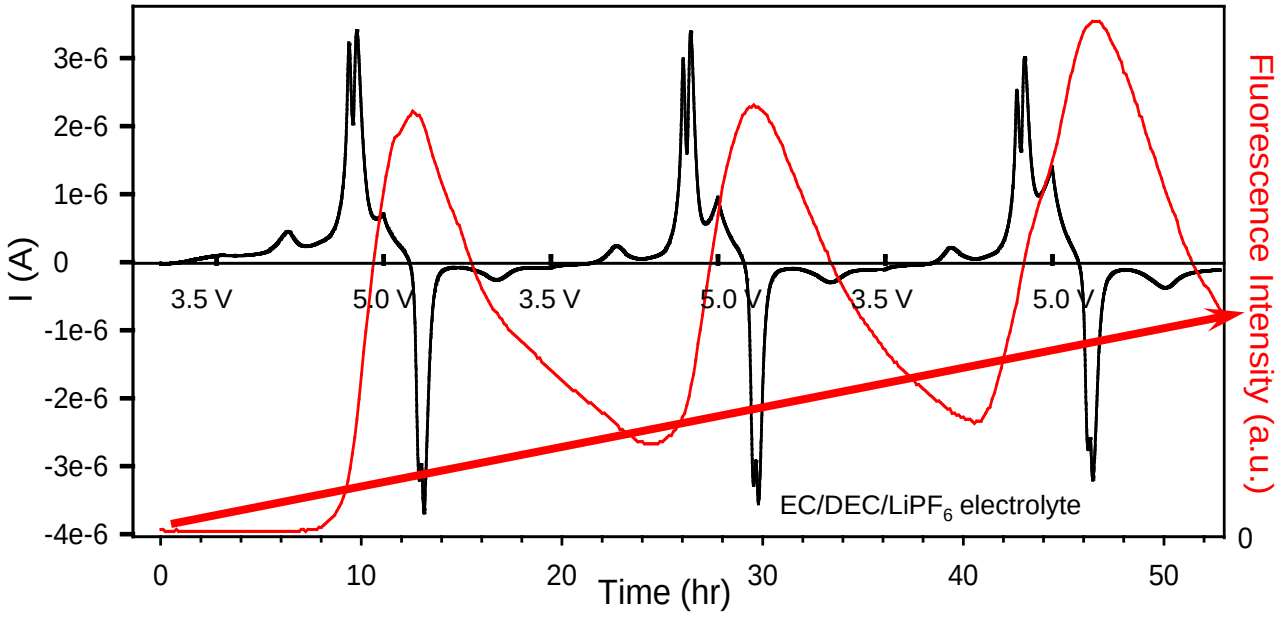
Strong fluorescence is a common phenomenon observed *in situ* and *ex situ* in cycled high-voltage cathodes. It originates from inorganic species that form during electrolyte decomposition. Fluorescence spectroscopy can be used to probe the composition and dynamics of surface film (re)formation during charge/discharge cycling

Fluorescence spectrum

(Excitation λ = 488 nm)



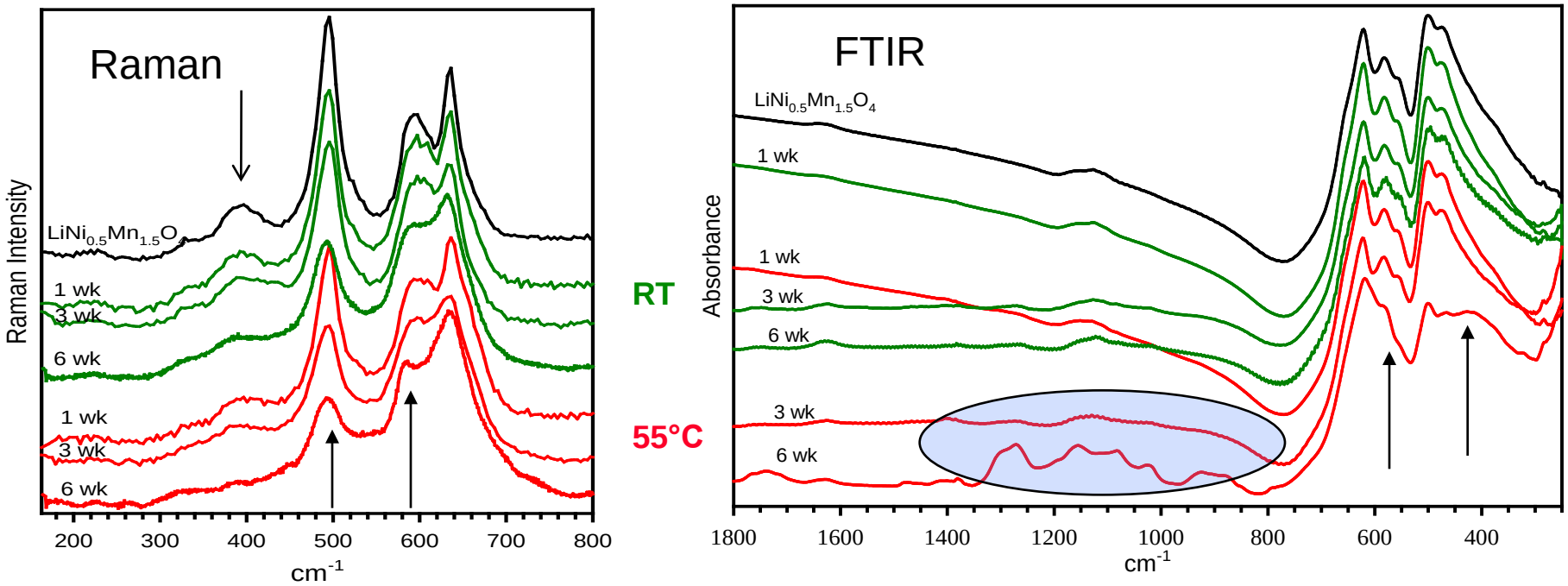
***In situ* Fluorescence Spectroscopy**



- Nonstoichiometric halophosphates $Li_xPO_yF_z$ form on the surface of LNMO during charging and slowly disappear from the electrode surface during discharge
- The inorganic fluorescent decomposition products tend to accumulate on the surface of LNMO during cycling

Long-Term Aging of $LiNi_{0.5}Mn_{1.5}O_4$ in EC/DEC/$LiPF_6$

LNMO powder was stored in EC/DEC/$LiPF_6$ at room temperature and 55°C for several weeks



- Raman and FTIR v_{Mn-O} and v_{Ni-O} vibrations peak intensity changes indicate Ni depletion and Mn^{3+} surface enrichment upon aging
- Evidence of electrolyte decomposition and surface film formation
- Elevated temperature accelerates structural changes within LNMO and promotes surface film formation

Similar tests for fully charged Ni-Mn spinel are ongoing

Summary I

- $LiMnPO_4$ composite cathode is unstable vs. $LiPF_6$, organic carbonate electrolytes
  - Electrolyte decomposition products do not form a stable layer on the surface of $LiMnPO_4$ composite cathode
  - Surface film forms at the exposed Li_xMnPO_4 active material. No surface film was detected on carbon black additive
- *In situ* Raman and fluorescence spectra of $LiNi_{0.5}Ni_{1.5}O_4$ single particle cathodes reveal a surface film rich in $Li_xPO_yF_z$ products
  - Composition and thickness of the film vary significantly during charge/discharge cycles
  - Large portion of electrolyte decomposition products diffuse away from the surface in the electrolyte – possible cross-talk with the anode SEI
- Prolonged exposure of $LiNi_{0.5}Mn_{1.5}O_4$ to EC/DEC/$LiPF_6$ leads to surface Ni^{3+} depletion, Mn^{3+} enrichment, and surface film formation of electrolyte decomposition products

Surface and interfacial instability of $LiMnPO_4$ and $LiNi_{0.5}Ni_{1.5}O_4$ likely precludes this material from achieving commercial viability without developing better routes for stabilizing the active material bulk and surface structure

Basic Studies of Interfacial Behavior of Sn

Approach

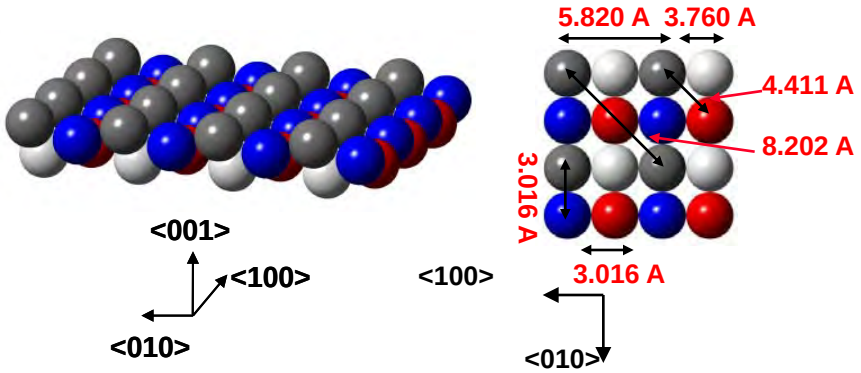
- Apply *in situ* and *ex situ* Raman and FTIR spectroscopy, spectroscopic ellipsometry, AFM, SEM, HRTEM, and standard electrochemical techniques to detect and characterize interfacial processes at intermetallic anodes
- Use model single crystal electrodes to determine the mechanism and kinetics of detrimental processes associated with large irreversible capacity of polycrystalline Sn
- Determine implications of the basic interfacial phenomena for long–term electrochemical performance of intermetallic anodes in high-energy Li^+-systems

Accomplishments

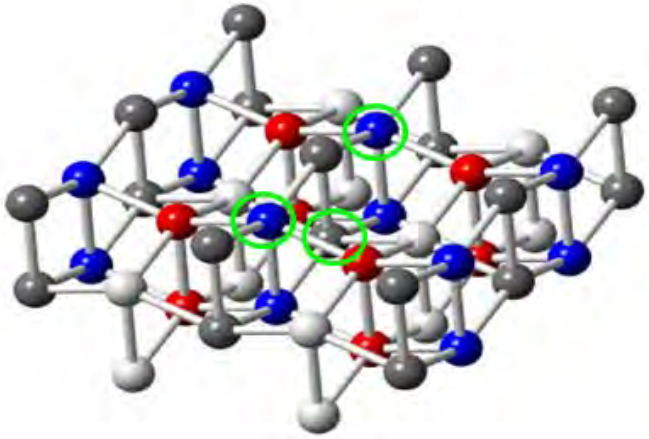
- Fundamental study of interfacial properties at Sn electrode was completed
  - *In situ* study revealed that an effective SEI layer never forms on polycrystalline Sn in EC-DEC $LiPF_6$ electrolytes mainly due to high reactivity of (001) Sn surface orientation
  - The mechanism of interfacial reactions at Sn (001) and (100) electrode surface orientations was determined and characterized
- Effective strategies to suppress unwanted surface reactions on Sn electrodes were proposed

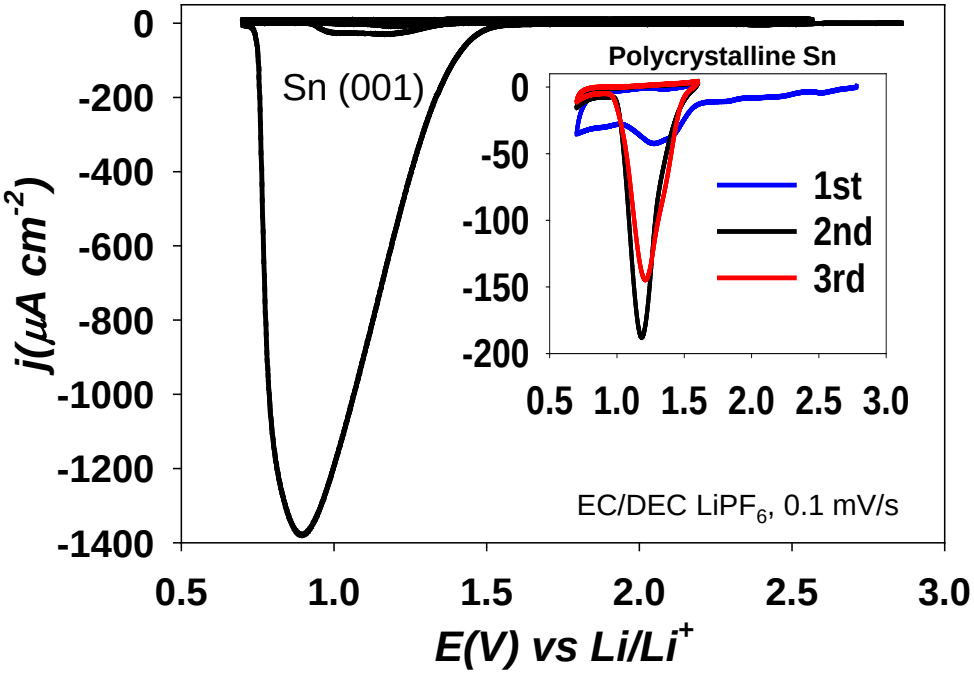
Collaboration with BATT Task Group "SEI on Alloys"

Basic Studies of Interfacial Behavior of Sn (001) Single Crystal Electrode



Surface atoms occupy four distinct planes that consist of Sn atoms with coordination number “3” or “5”



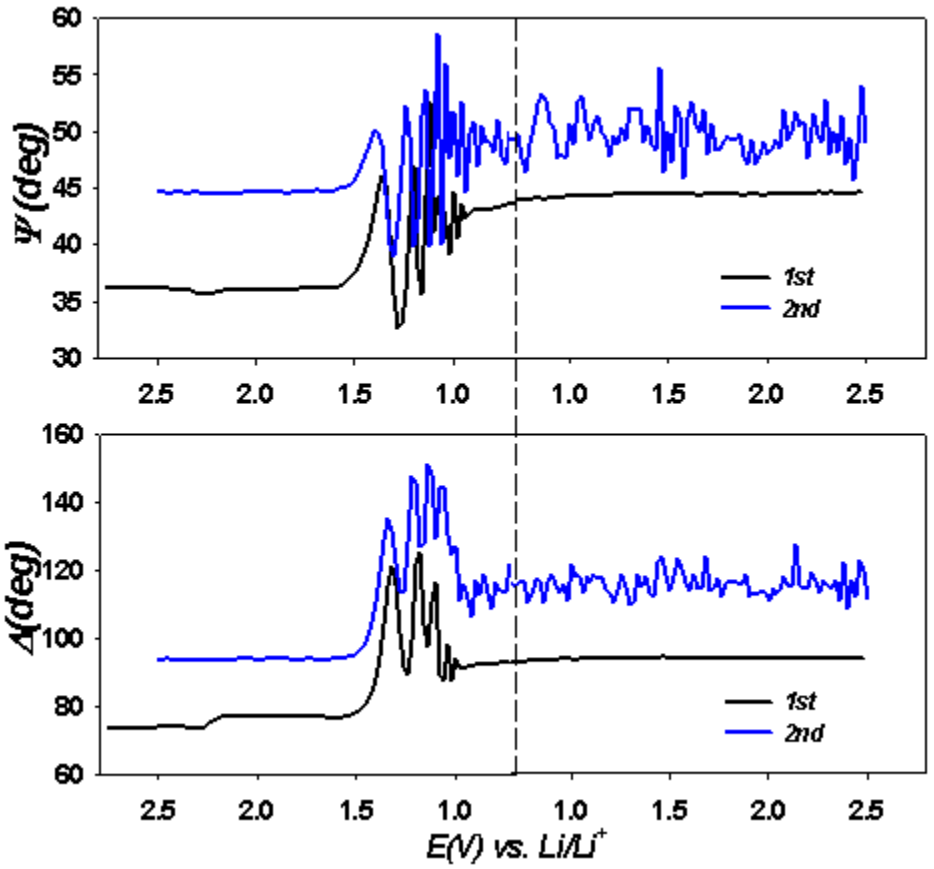


- Sn (001) electrode exhibits a significant surface activity toward EC/DEC/$LiPF_6$ electrolyte
- Electrolyte reduction yields non-passivating products that dissolve in the electrolyte

Highly reactive Sn (001) surface may account for the poor SEI layer and large irreversible capacity observed on polycrystalline Sn

In situ Spectroscopic Ellipsometry of Sn (001) Single Crystal Electrode

Ellipsometric parameters (Δ,Ψ)

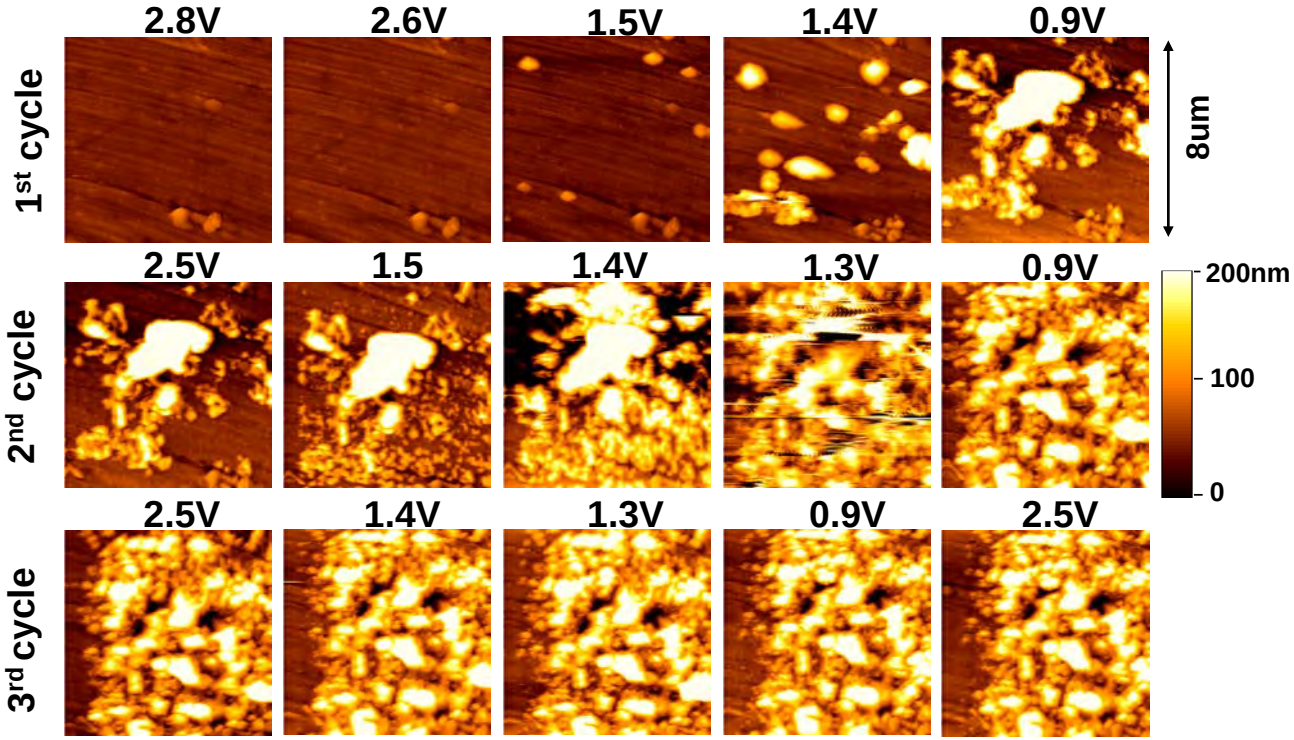


CV cycles of Sn (001) electrode in EC:DEC, 1M $LiPF_6$, 0.1 mV/s

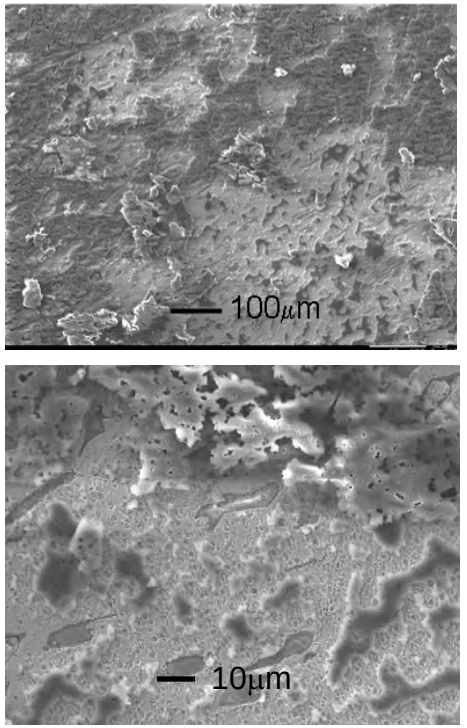
- Early stages of SEI formation at 2.3 V
- Significant changes of Δ and Ψ at 1.5 V correspond to rapid growth of a surface film
- Strong oscillations of Δ and Ψ at <1.3 V are due to poor stability of the SEI layer and formation of soluble compounds that dissolve in the electrolyte
- Continuous reformation of SEI upon cycling gradually shifts Δ and Ψ to higher values
- Formation of a rough and absorbing surface layer causes loss of the optical signal during 2nd cycle

Effective SEI layer never forms at the surface the Sn (001) electrode. Continuous reformation of the SEI layer is very similar to the behavior of polycrystalline Sn

In situ AFM of Sn (001) Single Crystal Electrode

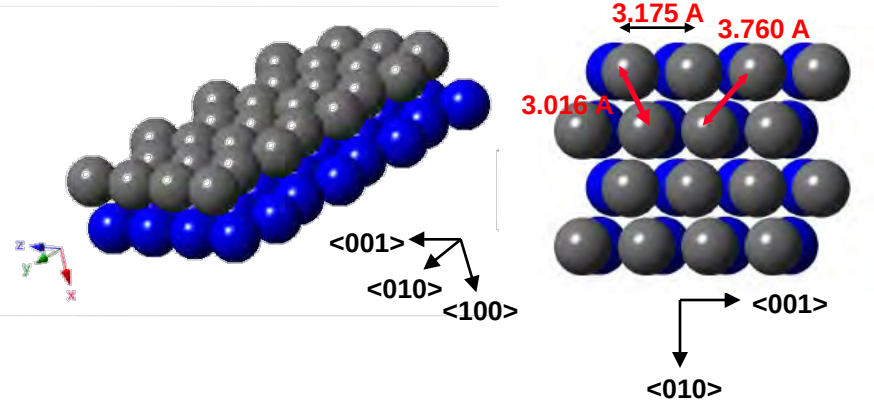


SEM images

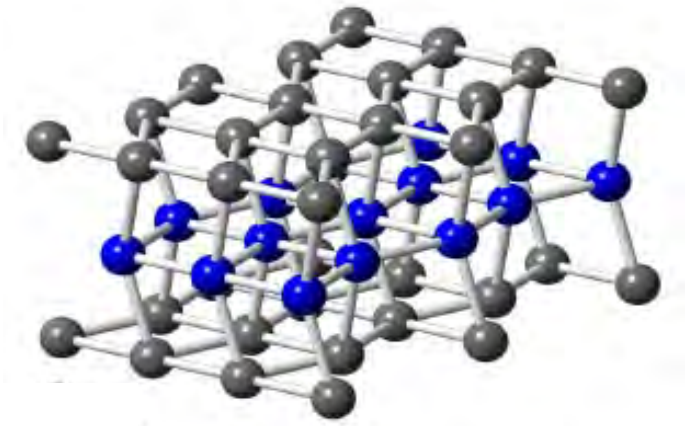


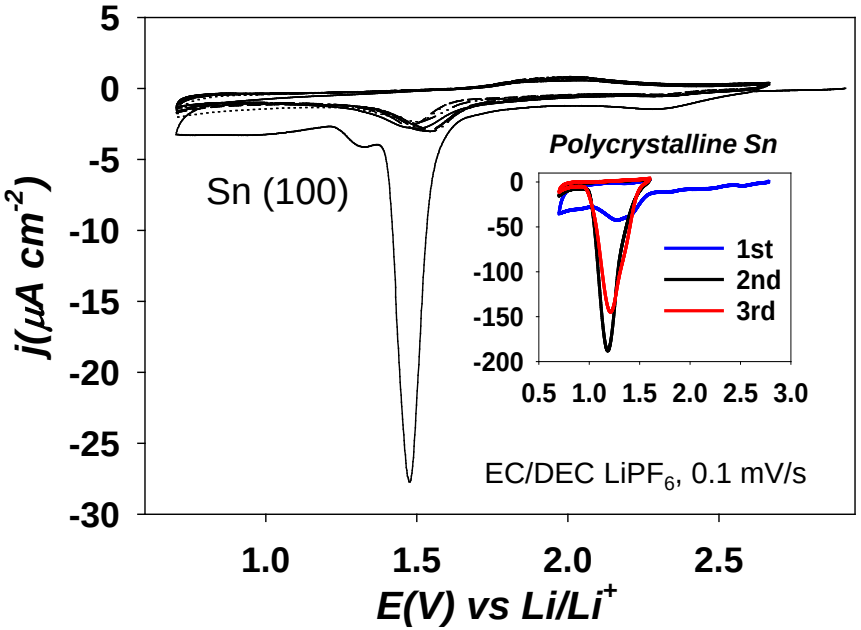
- *In situ* AFM images of the Sn (001) electrode reveal non-uniform, rough film that consists of predominantly inorganic products of electrolyte reduction
  - A very thin SEI (<10 nm) develops at U > 2 V
  - Large clusters (200-400 nm) of electrode reduction products form at U < 1.5 V
  - The film undergoes a continuous reformation during cycling. Some electrode surface areas remain uncovered by SEI after 3 cycles

Fundamental Study of Interfacial Properties at Sn Single crystal (100)



Surface atoms are densely packed and occupy a single plane that consist of Sn atoms with coordination number “5”



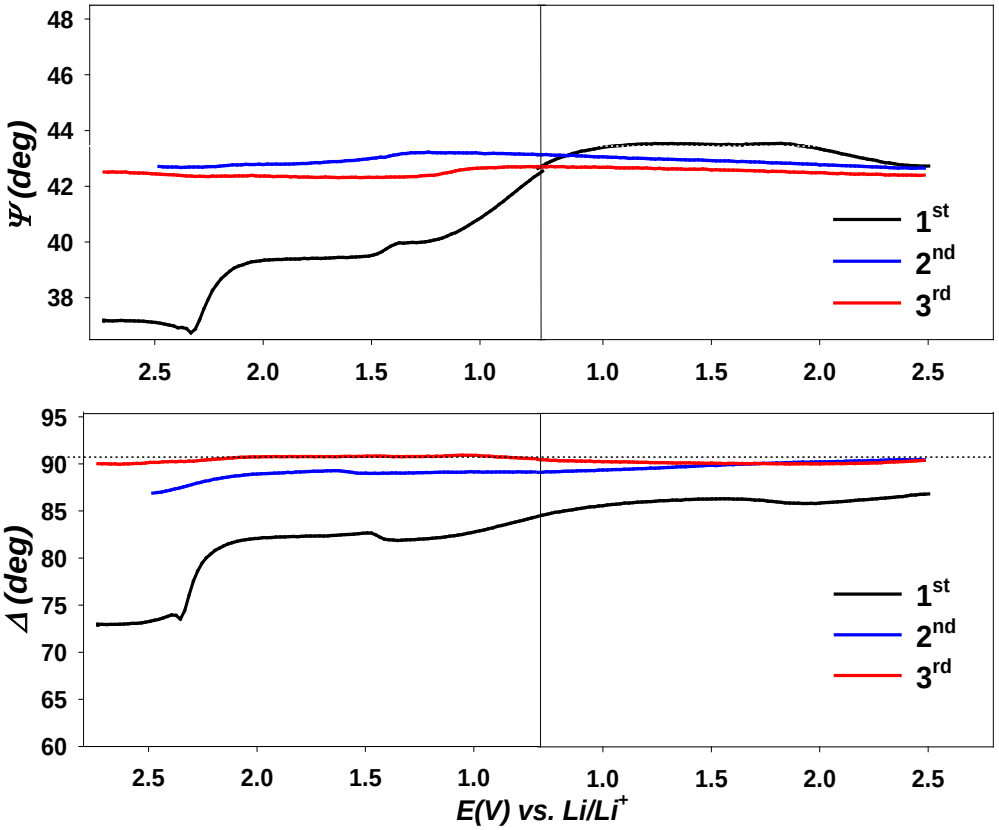


- Sn (100) electrode exhibits a moderate surface activity toward EC/DEC/$LiPF_6$ electrolyte
- Electrolyte reduction processes yield insoluble products that form a stable SEI layer

The mechanism of interfacial processes on Sn (100) electrode is noticeably different from Sn (001) and polycrystalline tin

In situ Spectroscopic Ellipsometry of Sn (100) Single Crystal Electrode

Ellipsometric parameters (Δ,Ψ)

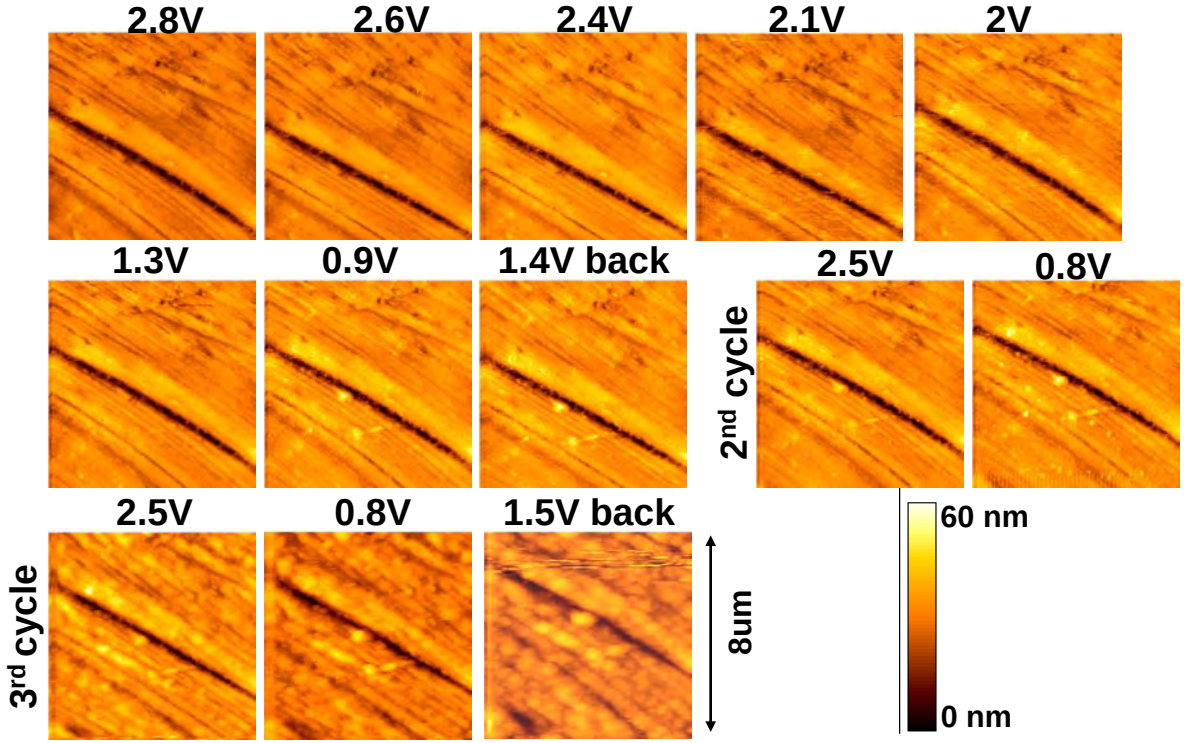


CV cycles of Sn (001) electrode in EC:DEC, 1M $LiPF_6$, 0.1 mV/s

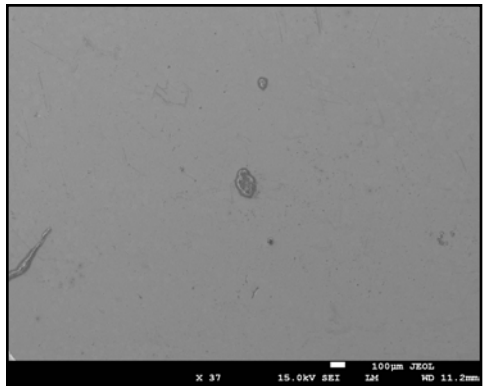
- Early stages of SEI formation at 2.3 V
- Small changes of Δ and Ψ at U < 1.5 V indicate slow growth of a surface film
- Negligible changes of Δ and Ψ were observed during 1st reverse scan and the following cycles
- The thickness and composition of the SEI tend to remain constant after 1st cycle

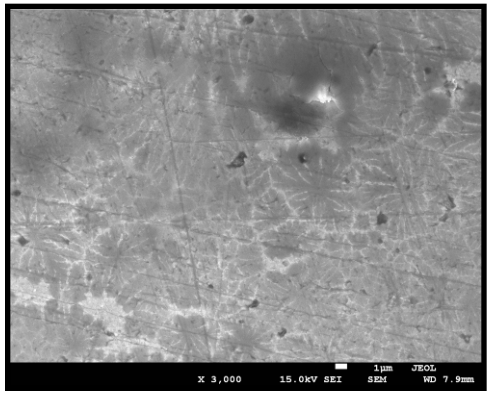
Sn (100) electrode produces very thin but effective SEI layer after one CV cycle

In situ AFM of Sn (100) Single Crystal Electrode



SEM images

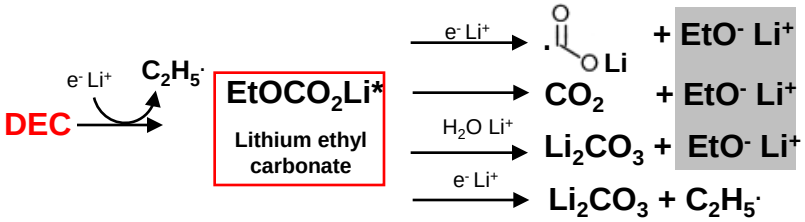




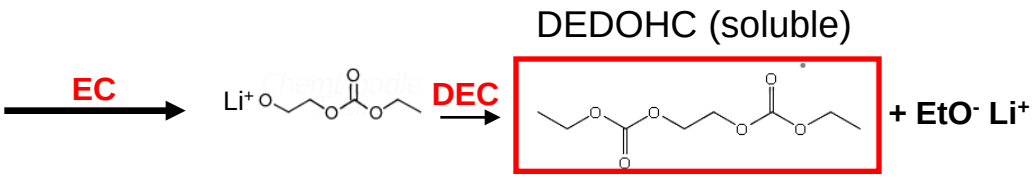
- *In situ* AFM images of the Sn (100) electrode reveal a uniform thin film
  - A thin SEI (<10 nm) grows on Sn (100) at U > 2 V, similar to the film observed on Sn (001) (100 nm SEI layer was detected on polycrystalline Sn)
  - The SEI grows gradually at U < 1.3 V and during the following two CV cycles to reach 60 nm
  - The film is very uniform and consists of densely packed nanoparticles of electrolyte decomposition products

The Mechanism of Interfacial Reactions at Sn Electrode

Electrochemical reduction of DEC

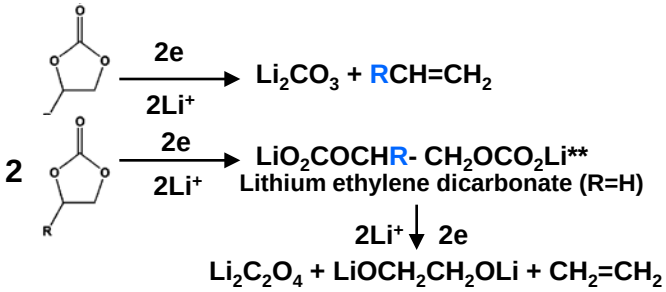


*Zhuang, *Electrochem. Solid State Letters* **2006**, *9*, A64



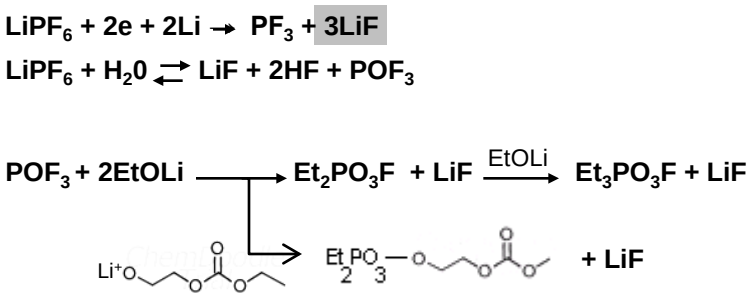
G. Gachot et al, *Journal of Power Sources* **2008,** *178*, 409-421

Electrochemical reduction of EC



** Zhuang, *J. Phys Chem B* **2005**, *109*, 17567

Reduction and decomposition of $LiPF_6$



- Electrochemical reduction of DEC most likely occurs on Sn (001) surface whereas reduction of EC is promoted on Sn (100)
  - Li_2CO_3, CO_2 additives suppress formation of EtOLi and soluble DEDOHC compounds
  - Electroreduction of DEC/$LiPF_6$ electrolyte on Sn produces good SEI layer. Excellent interfacial behavior was also observed in EC/Gyme/$LiPF_6$
  - LiF additive tends to suppress PF_6^- decomposition

Summary II

- Fundamental study of interfacial processes on Sn electrode was completed
- *In situ* studies revealed that the nature and kinetics of interfacial processes strongly dependent on the electrode surface structure and electrolyte composition
  - Stable surface film never forms on Sn (001) in EC/DEC/$LiPF_6$ electrolyte. The electrocatalytic behavior of Sn (001) surface possibly accounts for large irreversible charge losses observed for polycrystalline Sn anode
  - Effective SEI layer forms on Sn crystal domains (100)
  - Electrochemical reduction of DEC most likely occurs on Sn (001) surface whereas reduction of EC is promoted on Sn (100)
- Sn interface instability in organic carbonate electrolytes can be remedied by careful optimization of Sn electrode surface design, 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.

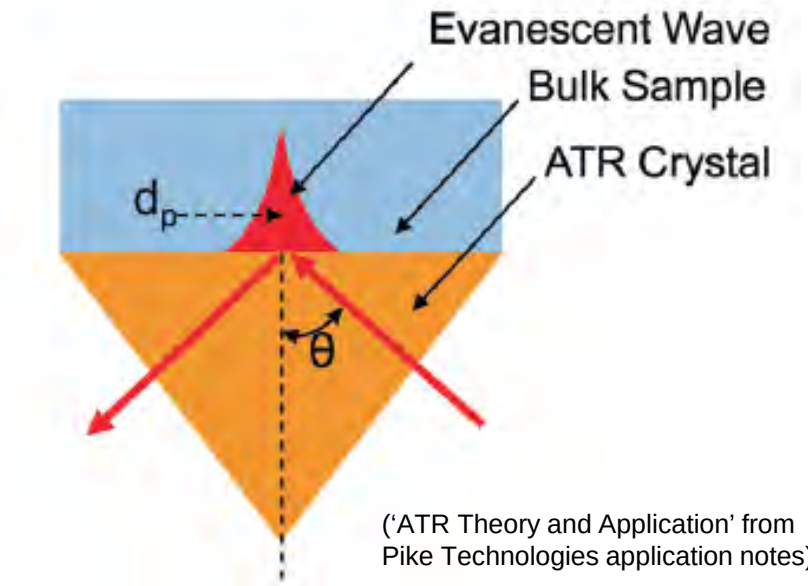
Future Work

1. 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 Task Group "SEI on Alloys“ and industrial partners (3M) to investigate the effect of material structure, morphology 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
2. Diagnostic evaluation of detrimental phenomena in high-voltage (>4.3 V) 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
   - Collaborate with BATT Task Group “Ni/Mn Spinel“ and industrial partners (HQ, Dow Chemical) to investigate detrimental processes that impede commercialization of new cathode materials
3. Develop and introduce new *in situ* instrumental techniques and experimental methodologies to study mass and charge transfer processes in Li-ion systems
   - Improve sensitivity, selectivity and achieve sub-wavelength spatial resolution in optical microscopy/spectroscopy
   - Acquire, adapt and introduce near-field technques to our diagnostic effort

Technical Back-up Slides

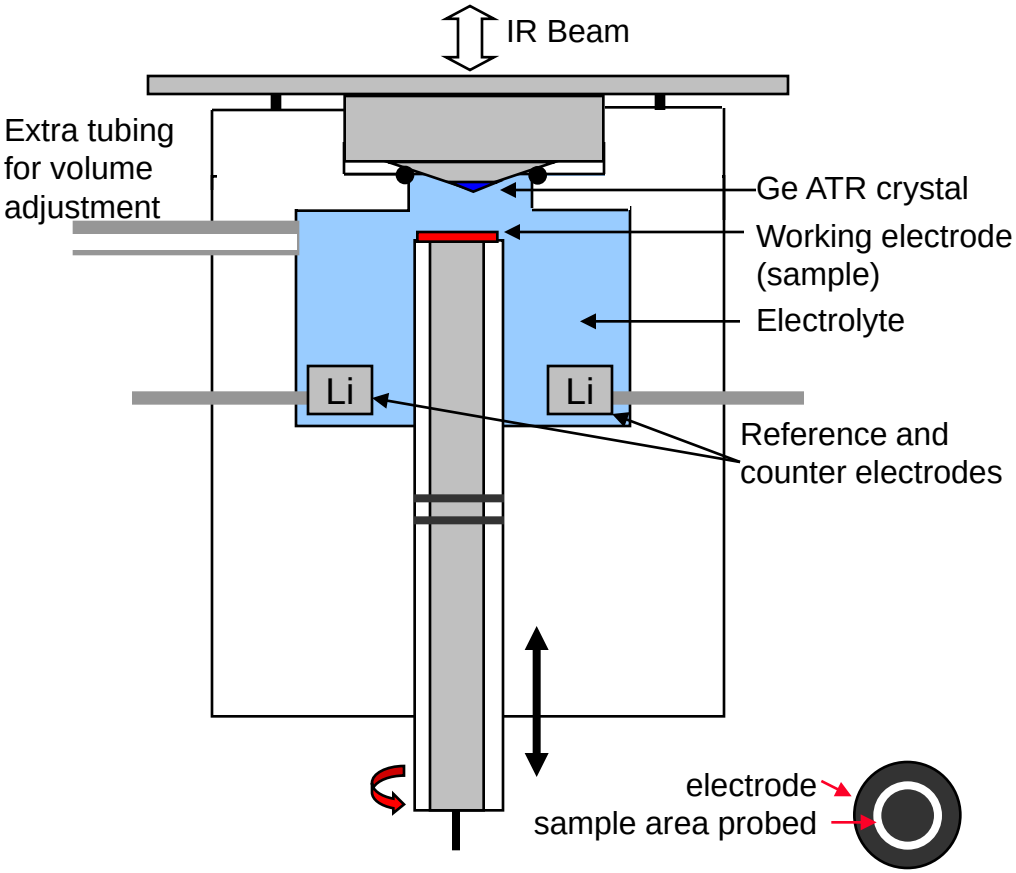
In situ FTIR-ATR Spectro-Electrochemical Cell

Attenuated Total Reflectance



('ATR Theory and Application' from Pike Technologies application notes)

Cell for *in situ* studies

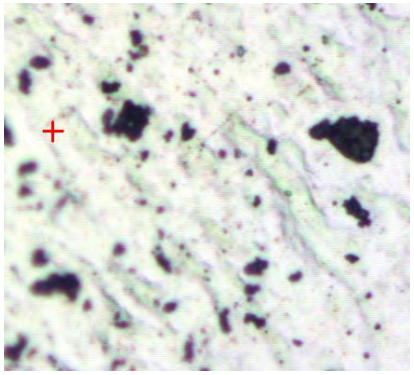


- Approach mechanism (not shown) to control distance between the Ge ATR crystal and sample, and probing location
- ATR sample penetration depth ~ 1 μm

In Situ Raman Microscopy - Single Particle Electrode Experimental Setup

- A solution of dispersed $LiNi_{0.5}Mn_{1.5}O_4$ particles was drop-cast onto an Al foil current collector
- The bottom of the Al current collector was glued to the working electrode of the cell with conductive epoxy and sealed at the edges
- The cell with Li-foil reference and counter electrodes was, filled with 1 M $LiPF_6$, EC/DEC 1/2 electrolyte in the glove box
- A CV was recorded at 0.1 mV/s between 3.5 V and 5.0 V. Average Raman spectra were collected from the 3 x 6 um particle area

$LiNi_{0.5}Mn_{1.5}O_4$ powder pressed on Al-foil

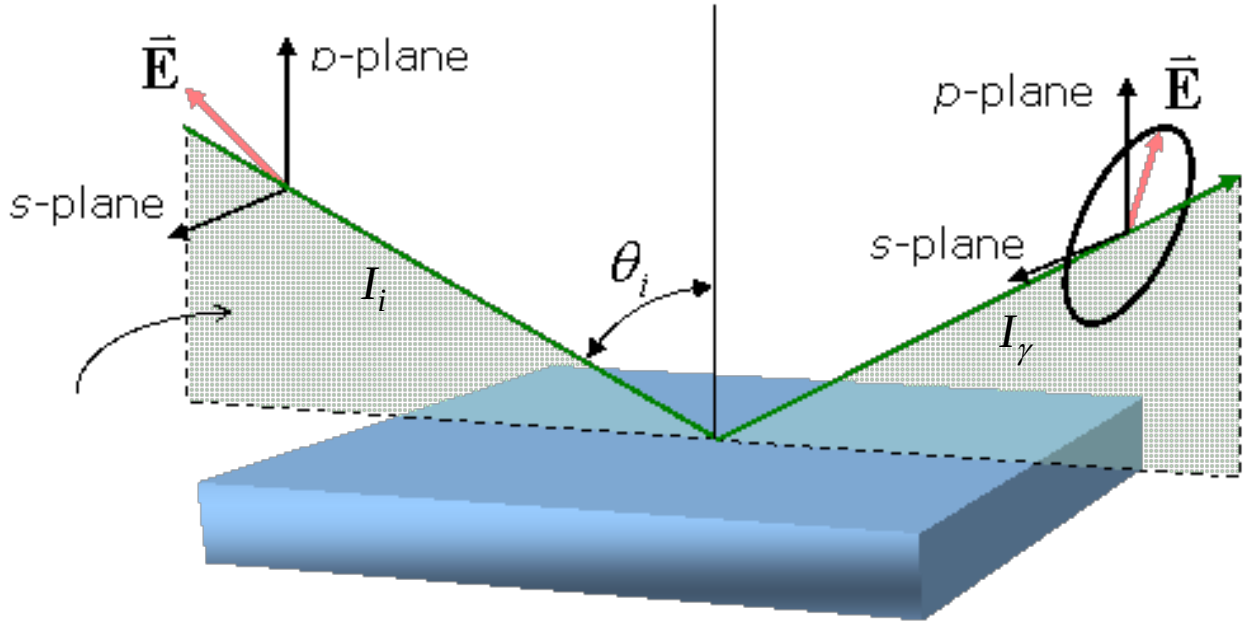


In situ spectro-electrochemical Raman cell

In situ Spectroscopic Ellipsometry

$$R = \frac{I_r}{I_i}$$

$$\tan(\Psi)e^{i\Delta} = \frac{R_p}{R_s}$$



Ellipsometry measures the change in polarization state of light reflected from the surface of a sample. The measured Δ and Ψ 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.