



Interfacial Processes – Diagnostics

Robert Kostecki

Lawrence Berkeley National Laboratory

Berkeley, California 94720

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Overview



Timeline

- PI participated in the BATT Program since 1999
- Task #1 started on Oct. 30, 2007 completed on Sept. 30, 2008
- Task #2 started on April 1, 2008 70% completed

Barriers Addressed

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

Budget

- FY10 funding TBD
- FY09 funding \$520K
- FY08 funding \$485K
- FY07 funding \$320K
- FY06 funding \$305K

Partners

- ANL, HQ, LBNL, SUNY, UP, and UU (BATT Task Group "SEI on Alloys")
- M. Doeff, LBNL (BATT Task Group "Phosphates - LiMnPO_4 ")
- John Newman (LBNL/UCB) is the program lead

Project Objectives



- ❑ Establish direct correlations between BATT baseline electrodes surface chemistry, interfacial phenomena morphology, topology, and degradation mechanisms
- ❑ Evaluate and improve the capacity and cycle life of intermetallic anodes
 - 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
 - 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
 - Provide remedies to interface instability e.g., new alloys and/or structures, electrolyte additives, co-deposition of other metals etc.

Milestones



1. Preliminary results of the Li transport study in the Devanathan-Stachurski cell (04-2008)
 - Accomplished on time. Novel experimental methodology developed and applied to study of Li diffusion in graphitic carbons
2. Evaluate surface phenomena on Sn anodes and their impact on the electrochemical behavior of the electrode. (08-2008)
 - Accomplished on time. Preliminary *in situ* AFM studies completed
3. Preliminary results of ellipsometric and optical spectroscopy studies of the SEI formation on Sn anodes (09-2009)
 - Work in progress ~70% completed
4. Evaluate surface and bulk phenomena in LiMnPO_4 cathodes (07-2009)
 - Work in progress ~50% completed

Study of Lithium Diffusion in Graphitic Carbons



Approach

- Design and use an electrochemical cell of the Devanathan-Stachurski type to study mass and charge transfer mechanism in graphite
- Develop a time-dependent mass transport model to validate the observed experimental behavior and determine Li transport parameters in graphite
- Apply *in situ* and *ex situ* Raman and FTIR spectroscopy, spectroscopic ellipsometry, AFM, SEM, HRTEM, and electrochemical techniques to detect and characterize surface processes in graphite anodes

Accomplishments

- Two different mechanisms of Li diffusion in graphite were revealed and quantified
- New nano- and micro-designs of high performance carbonaceous materials were proposed

Study of Lithium Diffusion in Graphitic Carbons



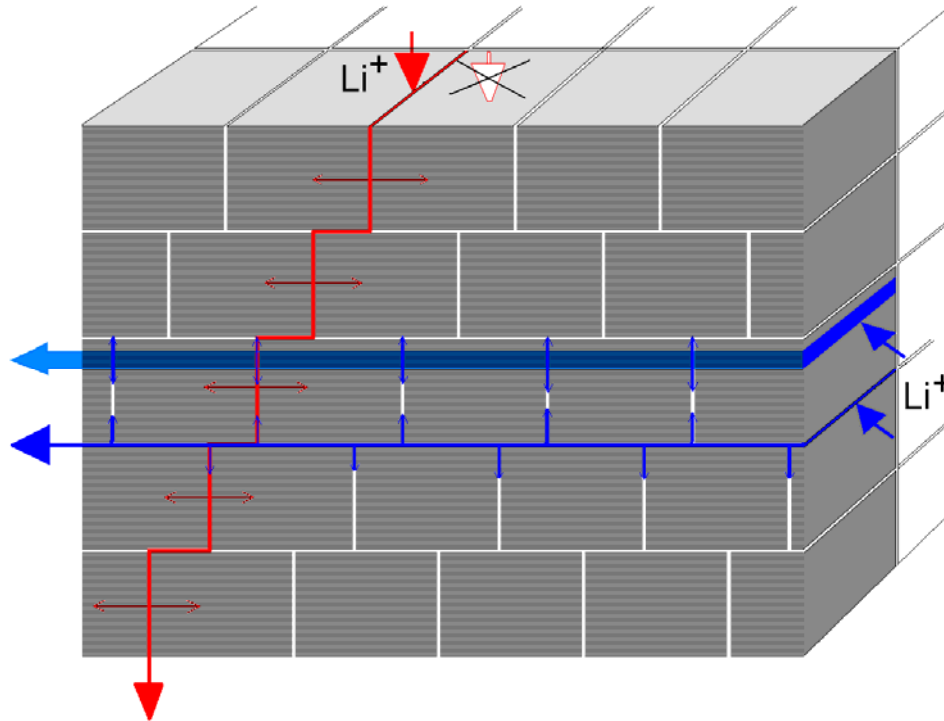
Reported lithium diffusion coefficients in graphite vary from 10^{-6} to 10^{-14} cm^2s^{-1}

Type of Graphite	D_{Li} ($\text{cm}^2 \text{s}^{-1}$)	Technique	Reference
Natural Graphite	$10^{-7} - 10^{-9}$	EIS	Takami et al. <i>J Electrochem Soc</i> (1995)
Artificial Graphite	$10^{-7.5} - 10^{-9.4}$	EIS	Takami et al. <i>J Electrochem Soc</i> (1995)
Graphite powder	$10^{-12} - 9.3 \times 10^{-14}$	PITT, EIS	Yu et al. <i>J Electrochem Soc</i> (1999)
MCMB	$10^{-6} - 10^{-10}$	EIS	Umeda et al. <i>Electrochim Acta</i> (2001)
Natural Graphite	$10^{-10} - 10^{-11}$	CV	Shim et al. <i>J Power Sources</i> (2004)
HOPG	$10^{-11} - 10^{-12}$	EIS	NuLi et al. <i>J Phys Chem Sol</i> (2006)

What causes this disparity of results?

Study of Lithium Diffusion in Graphitic Carbons

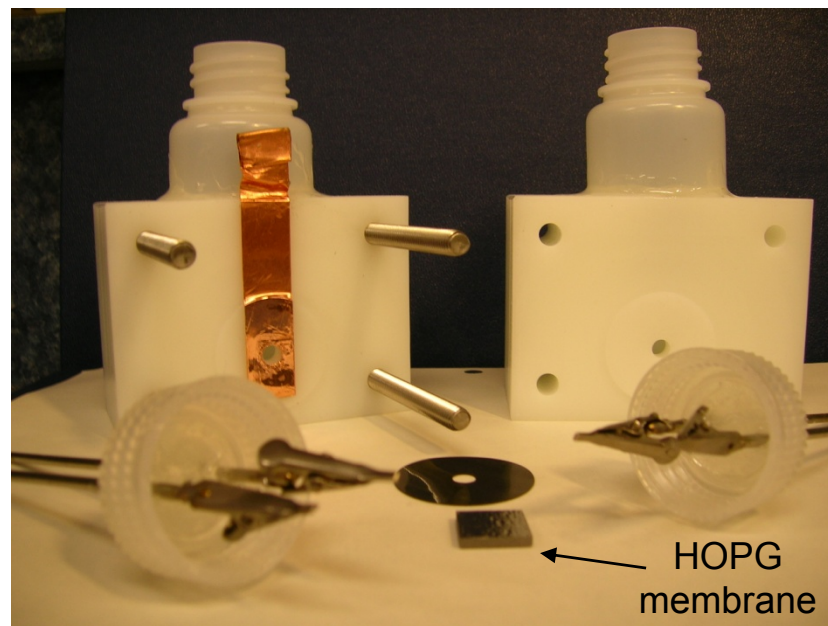
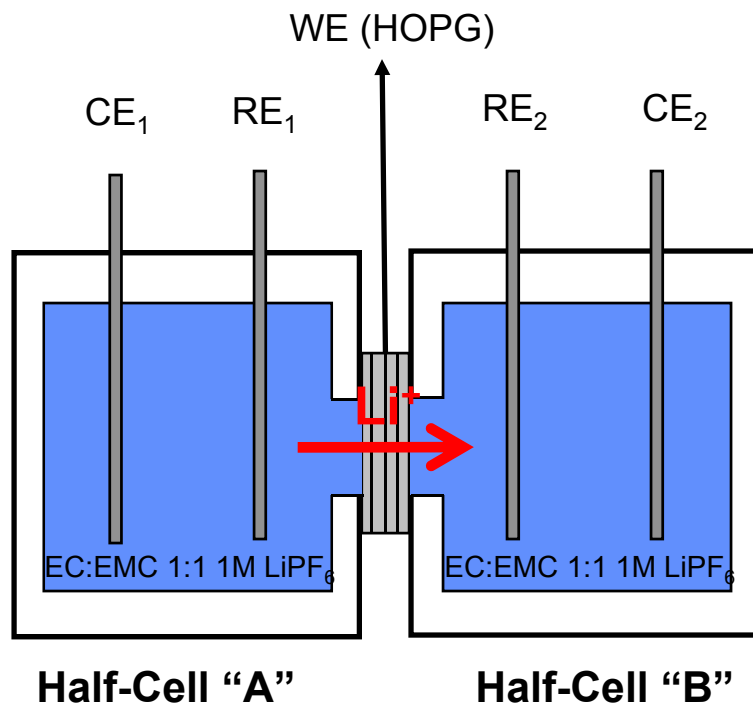
HOPG is an agglomerate of perfectly aligned graphene blocks
XRD data indicate ~300 - 400 nm domains with relatively small aspect ratio



- Li diffusion in graphite can occur along graphene domain boundaries and between graphene planes
- What is the rate-controlling mechanism of Li diffusion in polycrystalline graphite?

Study of Lithium Diffusion in Graphitic Carbons

Devanathan-Stachurski Cell for Studies of Li Diffusion in HOPG



Half-Cell A - Li intercalation, HOPG is polarized at constant $U = 5 \text{ mV vs. Li/Li}^+$ or $i = -25 \mu\text{Acm}^{-2}$

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

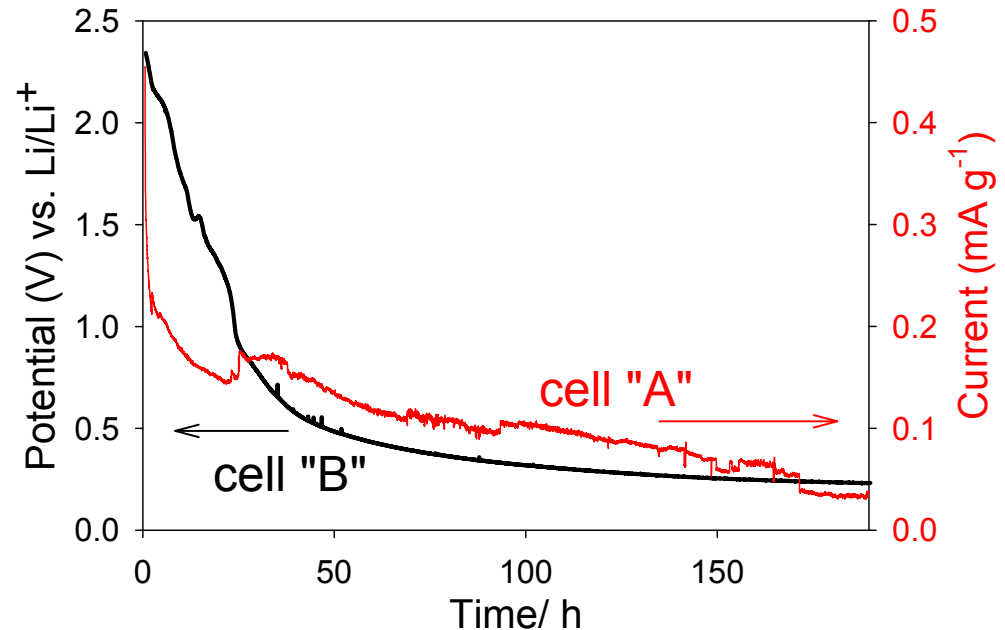
Study of Lithium Diffusion in Graphitic Carbons



Cell A - $U = 5 \text{ mV}$ vs. Li/Li^+

Cell B - OCP vs. Li/Li^+

Membrane - $90 \mu\text{m}$ HOPG



The model of Li intercalation and transport in HOPG is similar to a Langmuir adsorption isotherm and can be mathematically described as:

$$\left[1 + \frac{C_C k_{\text{eq}}}{(1 + k_{\text{eq}} C_{\text{Li}^+})^2} \right] \frac{\partial C_{\text{Li}^+}}{\partial t} = \frac{\partial}{\partial x} \left[D_{\text{Li}^+} \frac{\partial C_{\text{Li}^+}}{\partial x} \right] \quad k_{\text{eq}} - \text{rate constant of Li intercalation/deintercalation}$$

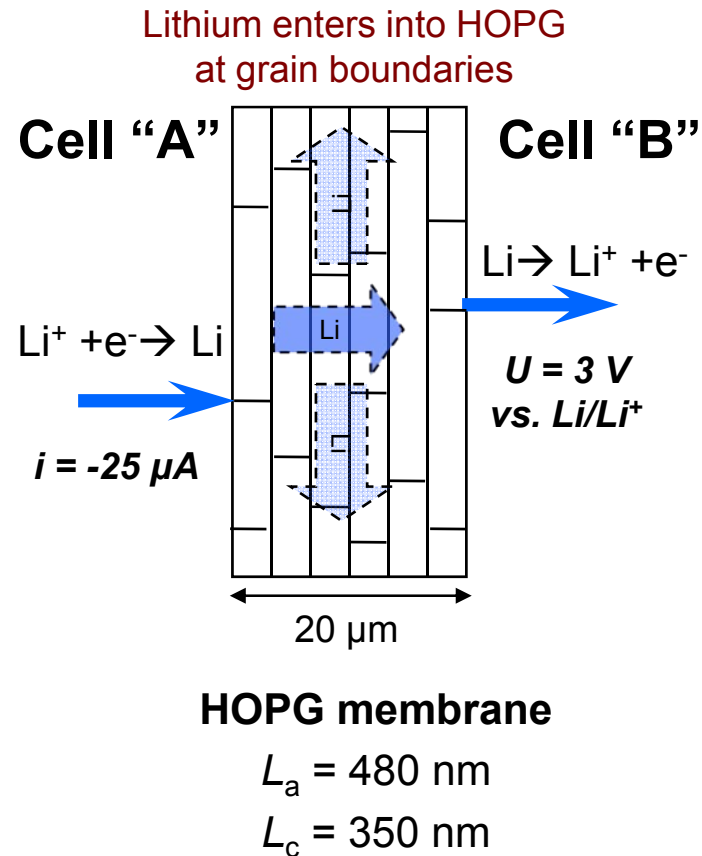
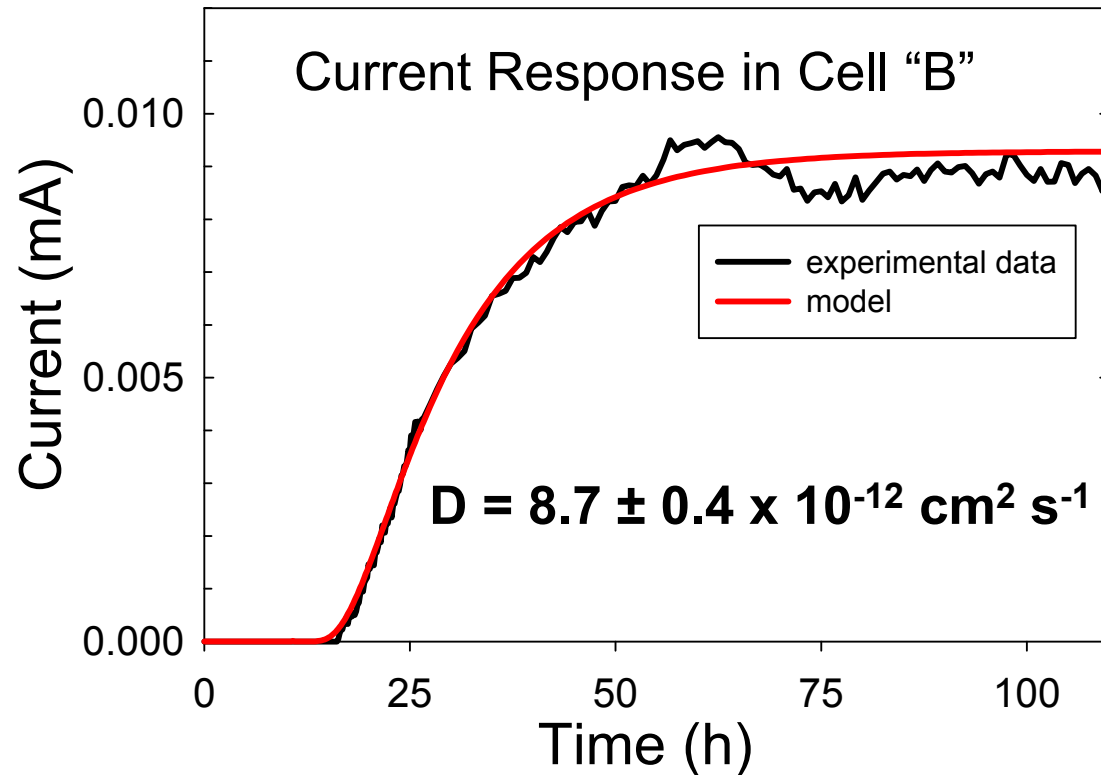
$$i(t) = n_e F A D_{\text{Li}^+} \left. \frac{\partial C_{\text{Li}}}{\partial x} \right|_{x=L}$$

$$C_{\text{Li}} = 0 \text{ for } 0 \leq x \leq L \text{ and } t = 0$$

$$C_{\text{Li}} = 0 \text{ for } x = L \text{ and } t \geq 0$$

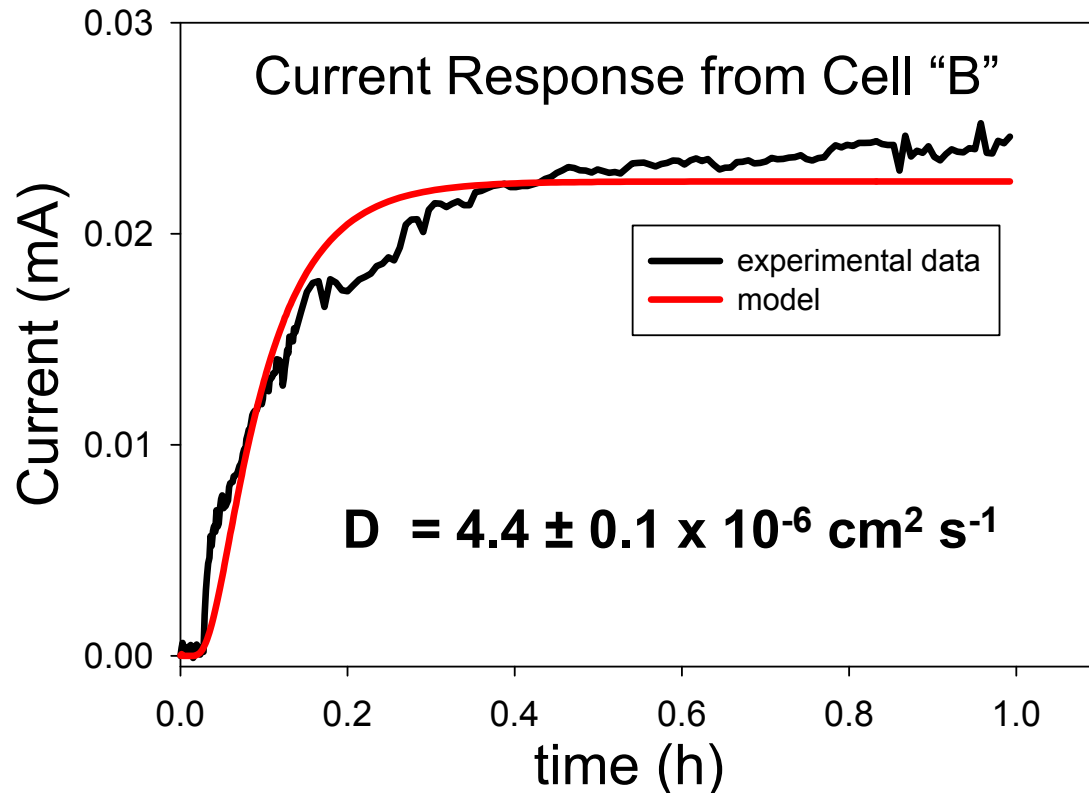
Collaboration with V. Srinivasan

Li Diffusion in HOPG - Experiment I

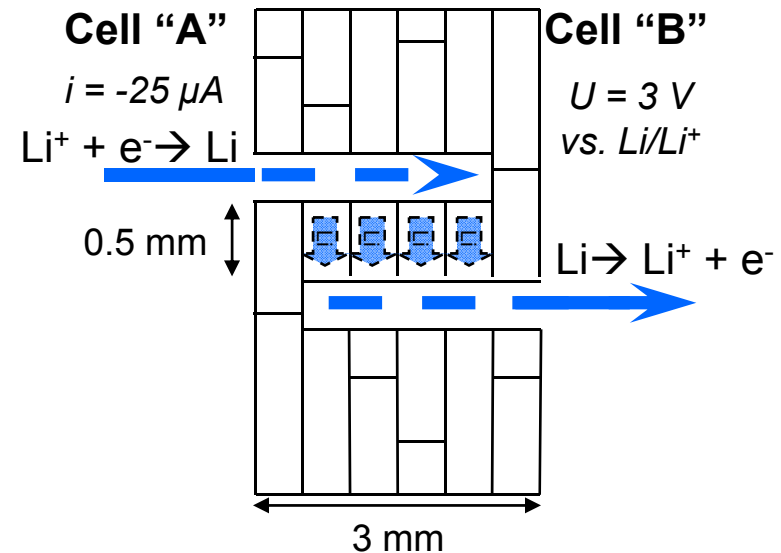


- Only 36 % of all Li that entered in the HOPG membrane in cell "A" reappeared on the other side of the membrane in cell "B"
- Li diffusion between graphene planes is most likely responsible for the "missing Li"

Li Diffusion in HOPG – Experiment II



Lithium enters into HOPG
at interplanar sites and grain boundaries



HOPG membrane

two partial \varnothing 1 mm holes, 0.5 mm apart

$L_a = 300 \text{ nm}$

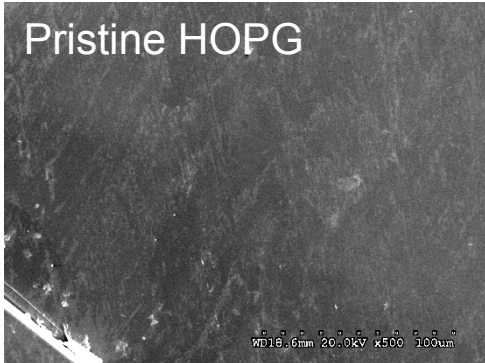
$L_c = 200 \text{ nm}$

- Almost 100 % current efficiency between red-ox reactions in cells "A" and "B"
- Li diffusion between graphene planes is much faster than Li transport along the boundaries of graphene domains

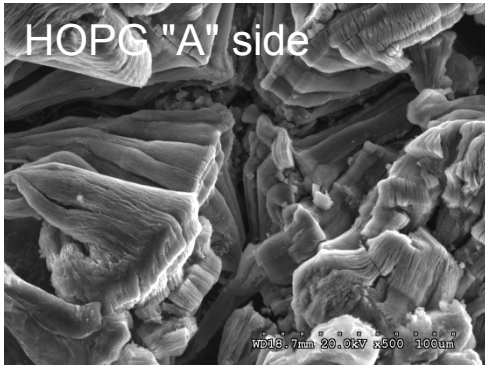
Surface Analysis of HOPG Membranes

SEM Images

Pristine HOPG



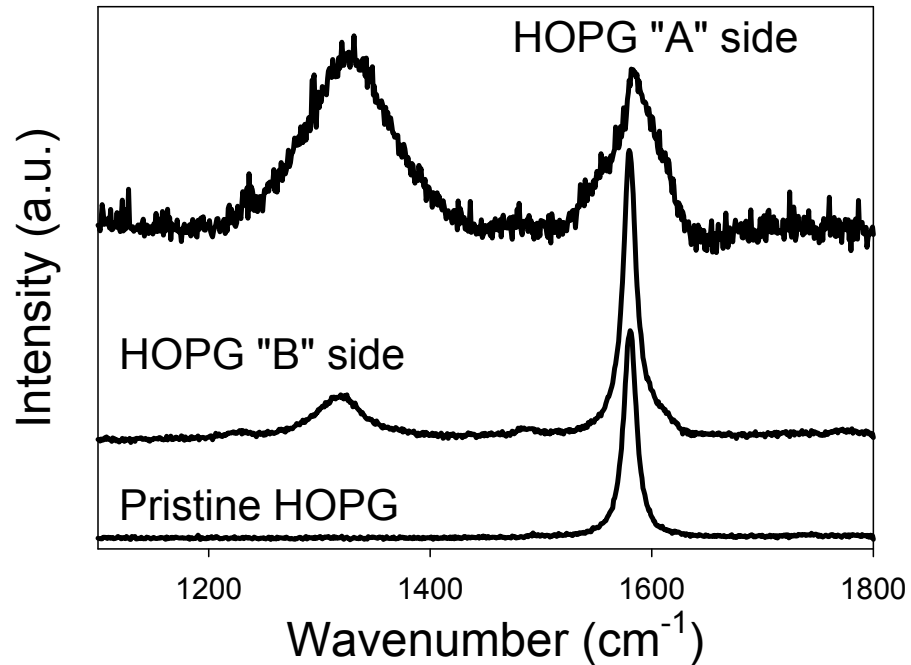
HOPG "A" side



HOPG "B" side



Raman Spectra

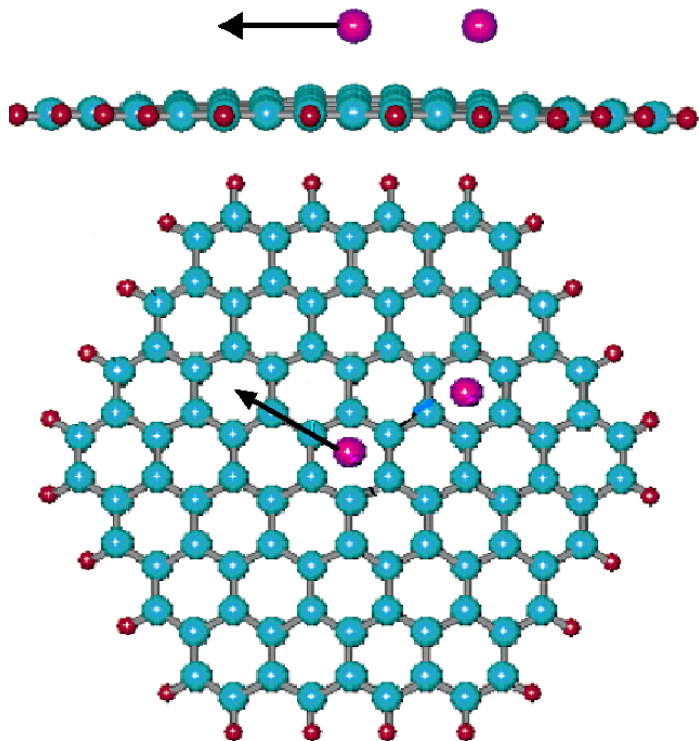


- Substantial morphology change and structural damage occur at the surface of the HOPG membrane in cell "A"
 - Evidence of break-up of crystallites and exfoliation
 - Strong "disorder" D-band in the Raman spectrum
- Slight surface degradation on the "exit" side of the membrane
- Diluted stage 4 and 3 graphite intercalation compounds (GIC) observed on both sides

Diffusion Dynamics of Li on Carbon



DFT studies of the interactions between Li^+ and hydrogen terminated C-cluster



Most of electrons with high energy are predominantly localized on the surface active edge sites

Li transport in carbons is highly anisotropic

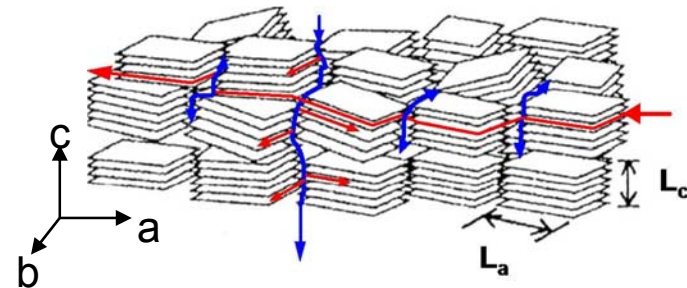
Li atoms tend to diffuse toward the edge sites where they are preferentially bound

J. Phys. Chem. B, 2006, 110, 20445

- Li diffusion coefficient in the direction of graphene plane $D = 7.6 \times 10^{-8} \text{ cm}^2\text{s}^{-1}$ for HOPG and $3.99 \times 10^{-9} \text{ cm}^2\text{s}^{-1}$ for amorphous carbon (Li couples with a phonon mode of graphite cluster and moves faster)
- Binding energy of a single Li atom 1.598 eV decreases to 0.934 eV in the presence of another Li atom

Summary I

- ❑ Li diffusion between graphene layers is several orders of magnitude faster than diffusion along graphene domains boundaries
- ❑ Rate of lithium diffusion in polycrystalline graphite strongly depends on the orientation of graphene domains
- ❑ Morphology and topology of graphite is highly anisotropic and varies depending on the fabrication process. The microstructure determine the kinetic behavior of graphite toward Li intercalation



Careful micro- and nano-design and advanced manufacturing methods of carbonaceous materials may significantly 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
- Manufacture and use model mirror-finished Sn electrodes to detect and monitor early stages of the SEI formation
- 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

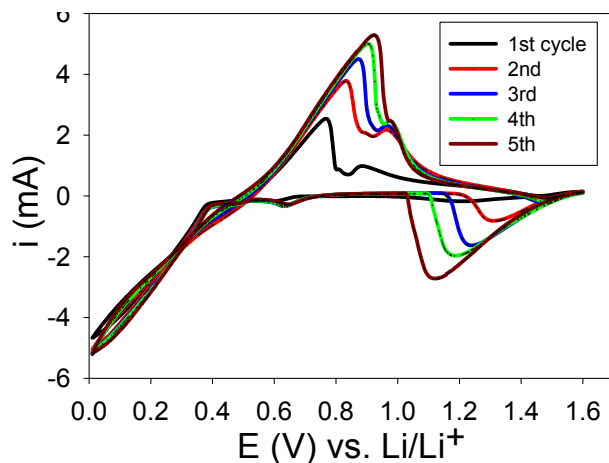
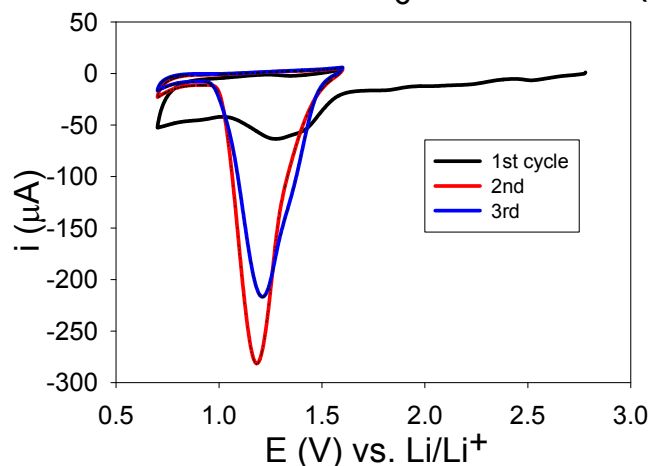
Accomplishments

- Preliminary assessment of interfacial processes on Sn electrode was completed
 - *In situ* studies revealed that an effective SEI layer never forms on Sn in EC-based electrolytes
- Effective strategies to suppress unwanted surface reactions on Sn electrodes were proposed

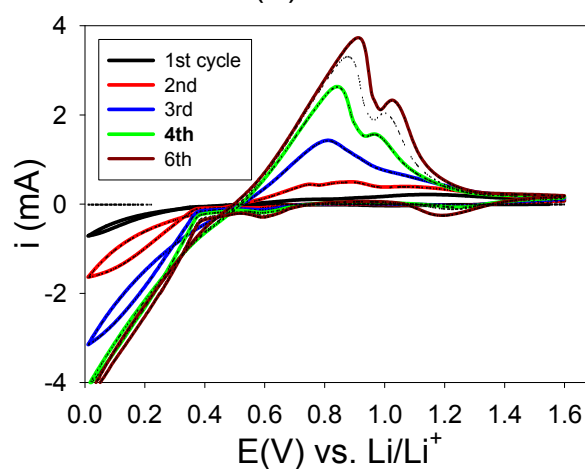
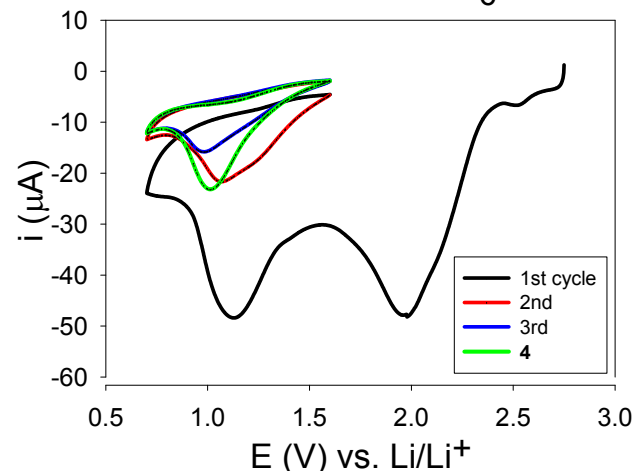
Study of Interfacial Phenomena at Sn Anodes



Sn-foil in 1M LiPF₆, EC:DEC (1:2)

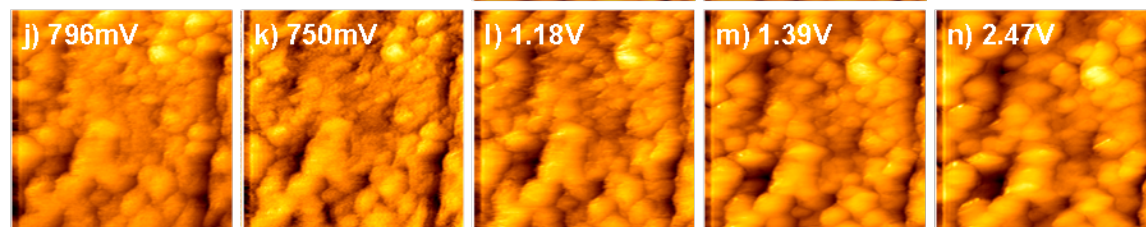
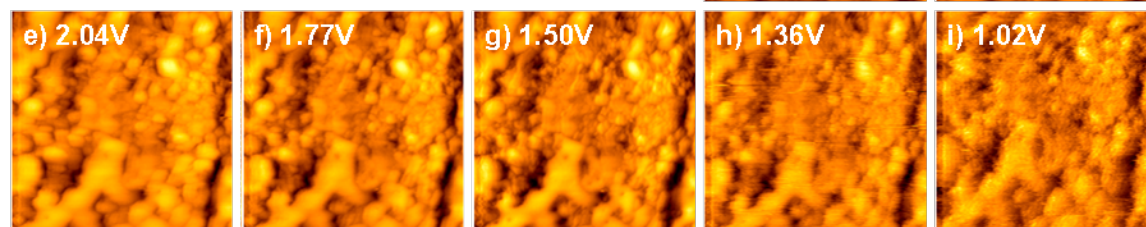
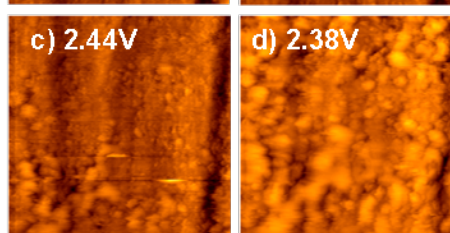
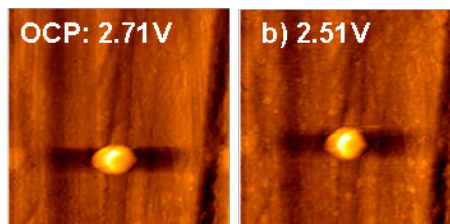
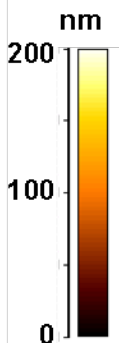
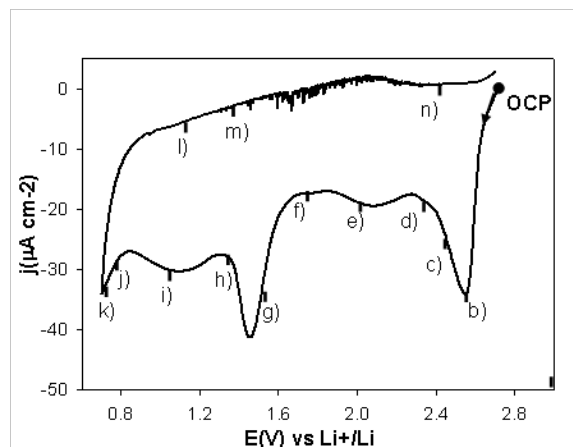


Sn-foil in 1M LiPF₆, PC



- Effective SEI layer never forms at the surface of Sn in EC-based electrolyte
 - Intense irreversible reduction peak at 1.2 V is attributed to the electrolyte decomposition
- Surface reactions are inhibited in PC electrolyte, SEI layer “seals” the surface of Sn

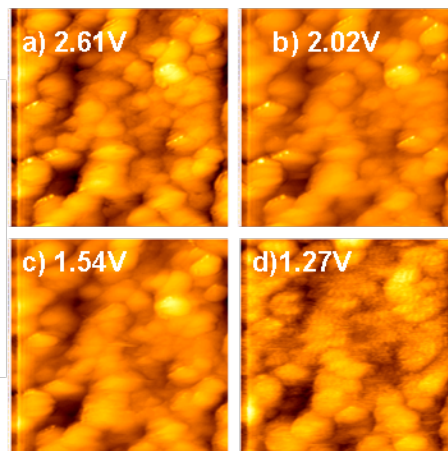
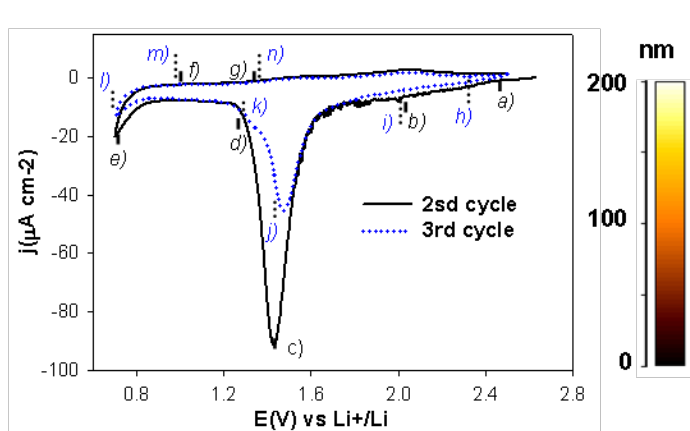
Study of Interfacial Phenomena at Sn Anodes



In situ AFM 8 x 8 μm images of Sn-foil electrode in 1M LiPF_6 , EC:DEC (1:2), $v = 2 \text{ mVs}^{-1}$

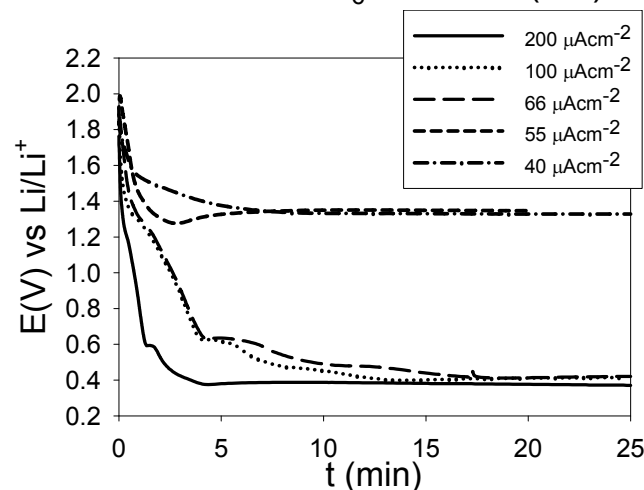
- *In situ* AFM images of the Sn-foil electrode reveal non-uniform, multilayer film that consists of predominantly inorganic products of electrolyte reduction
 - Direct experimental evidence of film formation at potentials $\leq 2.5 \text{ V}$
 - Average thickness of the film ca. 200 nm

Studies of Interfacial Phenomena at Sn Anodes



In situ AFM 8 x 8 μm images of Sn-foil electrode in 1M LiPF₆, EC:DEC (1:2), $v = 2 \text{ mVs}^{-1}$

Chronopotentiometric plots of Sn-foil electrode in LiPF₆ EC:DEC (1:2)



- Morphology of the surface layer continue to evolve with cycling
- The amount of surface deposits does not account for the charge consumed during cathodic scans
- Soluble reduction products diffuse back into the electrolyte

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 Sn in EC-based electrolytes
 - ✓ Soluble products of electrolyte reduction diffuse back into the electrolyte
 - Surface reactions on Sn in PC-based electrolytes are inhibited. Stable SEI layer forms after a few formation cycles
 - Contrary to crystalline tin, amorphous Sn tends to produce a stable SEI layer
 - Unwanted cathodic surface processes can be suppressed by the presence of thin surface coatings of Cu or Ag

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



- **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 electrode materials (V. Srinivasan)
- **Apply *in situ* and *ex situ* instrumental methods 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 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 LiMePO_4 cathodes