ELECTROCHEMISTRY DIAGNOSTICS AT LBNL

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presented by

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OVERVIEW

Timeline

- LBNL carried out diagnostics in the ATD Program since its 1999 inception
- ABRT Program began October 2008
- LBNL role expanded beyond diagnostics in FY 2009: Chen & Richardson (overcharge protection), and Battaglia (testing of BATT Program materials)

Budget

- FY 2009 diagnostics funding $600K
- FY 2010 diagnostics funding $600K

Barriers Addressed

- Inadequate Li-ion battery energy, durability, and safety for PHEV and EV applications
- High irreversible capacity loss during first cycle

Partners

- ANL, BNL, INL, and SNL
- Dan Abraham is the ABRT Program diagnostic lead
- John Newman (LBNL/UCB) is the Berkeley electrochemistry program lead

OBJECTIVES

- **Diagnostic evaluation of ABRT Program chemistries**
  - Carry out post-test characterization of components from ABRT test cells
  - Understand factors that can enhance the stability of SEI layers
  - Establish and investigate degradation mechanisms of PHEV cells

- **Develop strategies to minimize irreversible cell capacity losses**
  - Fabricate anodes that reduce the charge required to form stable SEI layers
  - Investigate surface treatment regimens to reduce side reactions

MILESTONES

- **Task 1.1: Report progress on reduction of irreversible capacity losses (July 2009)**
  - Identified the origin of a graphite-degradation mode in Li-ion cells
  - Avoiding complete anode delithiation slows the rate and extent of anode structural damage, SEI layer reformation, cell impedance rise, and loss of available lithium

- **Initiated new ABRT Program task in FY 2010: interface stabilization *via* surface functionalization**
  - Chemical grafting of fluorine onto carbon edge sites was employed to weaken C_{edge}-Li^+ bonds, but it did not help stabilize the SEI
  - C_{edge} substitution with surface functional groups (-OH, -OOH, -SH) will be employed to stabilize the graphite/electrolyte interface

BARRIERS ADDRESSED

- HEV and PHV battery durability and safety, as well as the need for efficient cell-formation processes, are the major barriers addressed by LBNL diagnostic work
- The primary LBNL role in the ABRT Program is to carry out specific diagnostic evaluations to determine the changes in cell components that accompany Li-ion cell power fade, capacity fade, and/or failure
- LBNL also seeks to identify electrode and electrolyte processes that are significantly influenced by various cell-formation protocols

PARTNER INTERACTIONS

- ANL and INL provide tested cells for characterization at LBNL
- ANL, BNL, and SNL provide detailed structural, chemical, electrochemical, and thermal-stability information for cell materials
- All participating laboratories periodically share results and plans

APPROACH

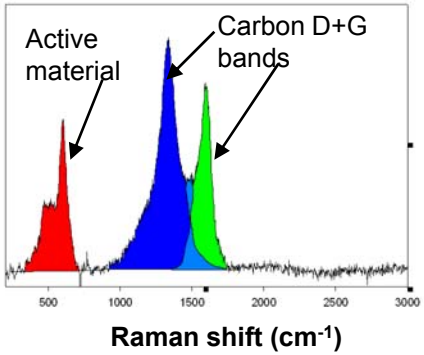
- **Strategies to minimize irreversible capacity losses**
  - Synthesis and diagnostic evaluation of C/Me composites and surface-modified carbons
  - Investigation of reactive impurities in anodes
- **Diagnostic evaluation of ABRT Program lithium-ion cell chemistries**
  - Carry out post-test diagnostic evaluation of components from ABRT test cells and model thin-film cells
    - ✓ Spectroscopic, microscopic, X-ray, chromatographic, and related techniques
  - Understand factors that can enhance the stability of SEI layers
    - ✓ Use results to suggest approaches to stabilize interfaces
  - Establish and investigate degradation mechanisms of PHEV cells

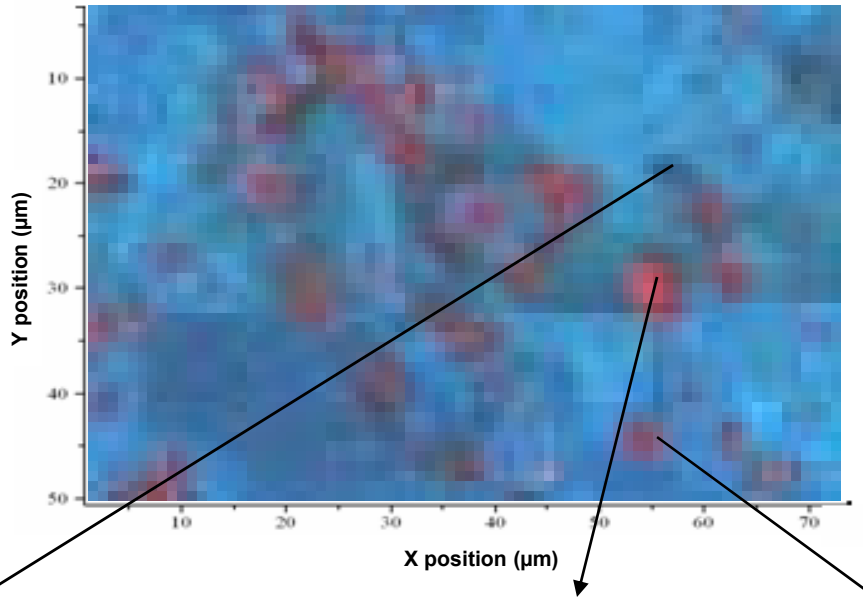
TECHNICAL ACCOMPLISHMENTS

- Completed study of graphite anode structural degradation
- Identified approaches to anode stabilization
- Identified candidate anode and cathode fade mechanisms in Gen-3 cells

DIAGNOSTIC ANALYSIS OF CATHODES

Raman map of discharged
$LiCo_{1/3}Ni_{1/3}Mn_{1/3}O_2$ cathode

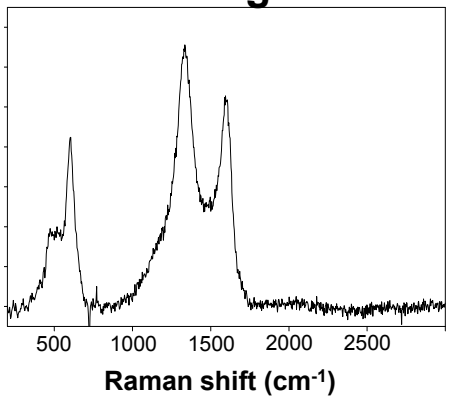




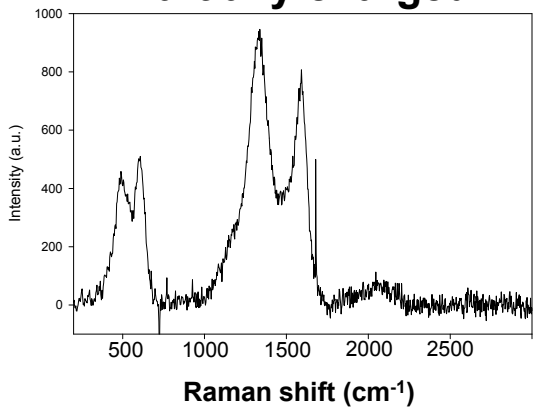
Areas of the discharged cathode remained charged

Particle isolation or electrolyte loss may contribute to cell power & capacity fade

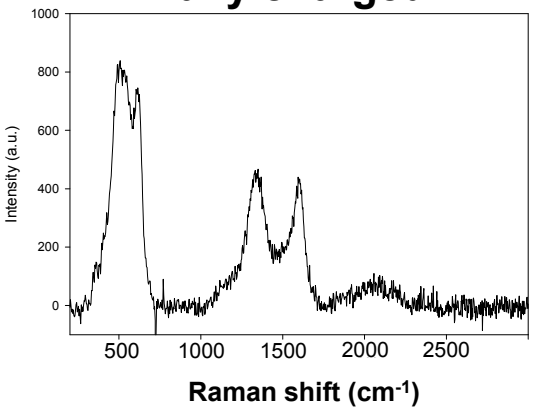
Discharged



Partially charged

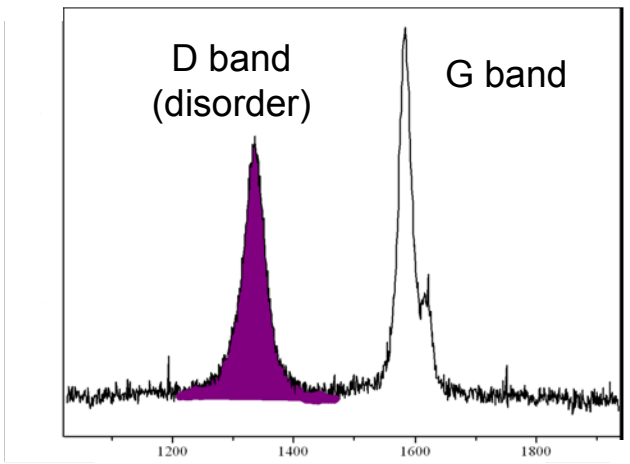


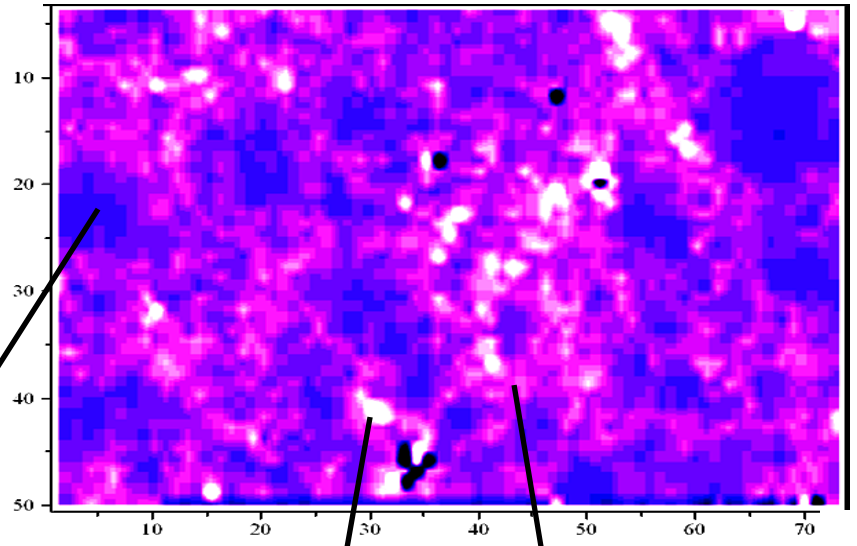
Fully charged



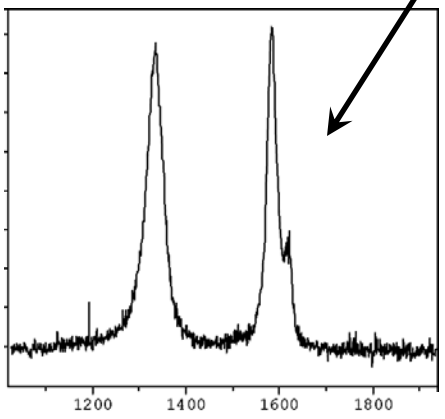
DIAGNOSTIC ANALYSIS OF MCMB ANODE

D/G Band Intensity Ratio Mapping

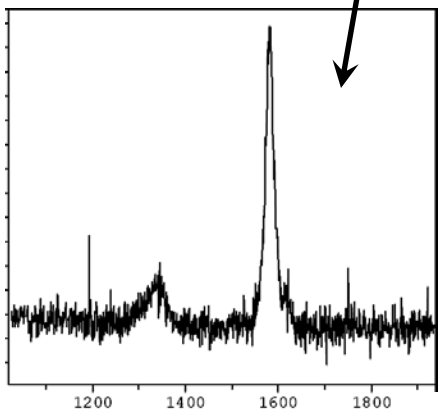




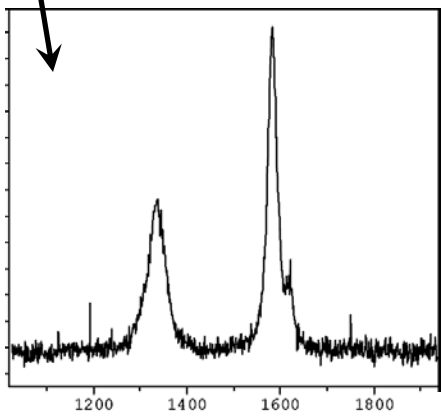
Highly disordered



Not affected



Partly disordered



The graphite surface structure of breaks down slowly upon cycling

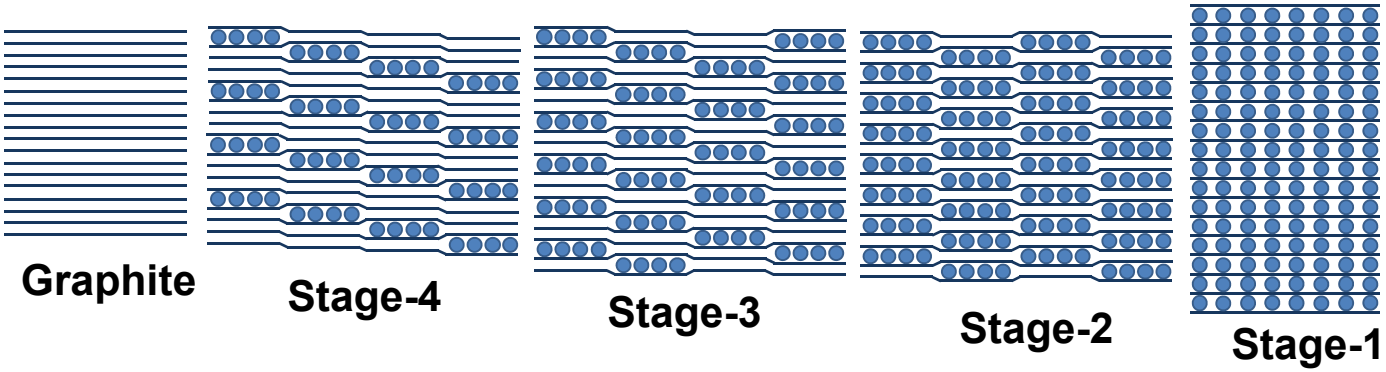
DIAGNOSTICS OF MCMB ANODES

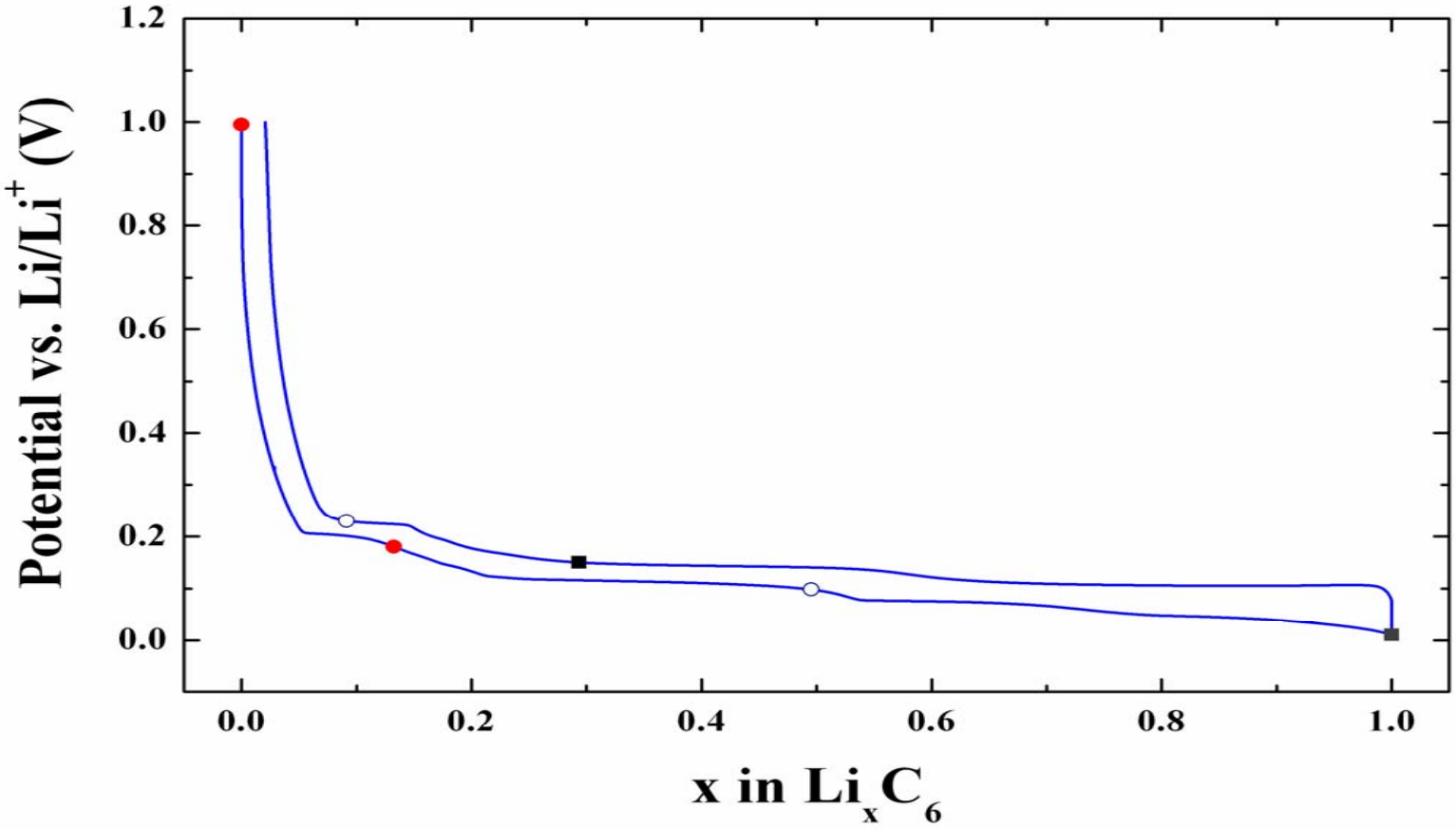
Summary of Work Completed in FY 2009

- The graphite anode surface undergoes gradual structural degradation during cycling
- A continuous change of anode surface reactivity *vs*. the electrolyte can be expected
- This phenomenon has been reported in the literature and appears to occur generally in all graphitic carbons *Kostecki et al., J. Power Sources (2003), Markevich et al., J. Power Sources (2005), Hardwick et al., J. Electrochem. Soc.* (2008)
- The carbon structure and morphology determine the properties of the SEI layer S. K. Jeong et al., *J. Power Sources (*2003), P. Novák *et al*., *J. Power Sources, (2007)*

What is the structural degradation mechanism?
Possible implications for Li-ion cell stability?

CHARGE-DISCHARGE PROFILE OF GRAPHITE ELECTRODES

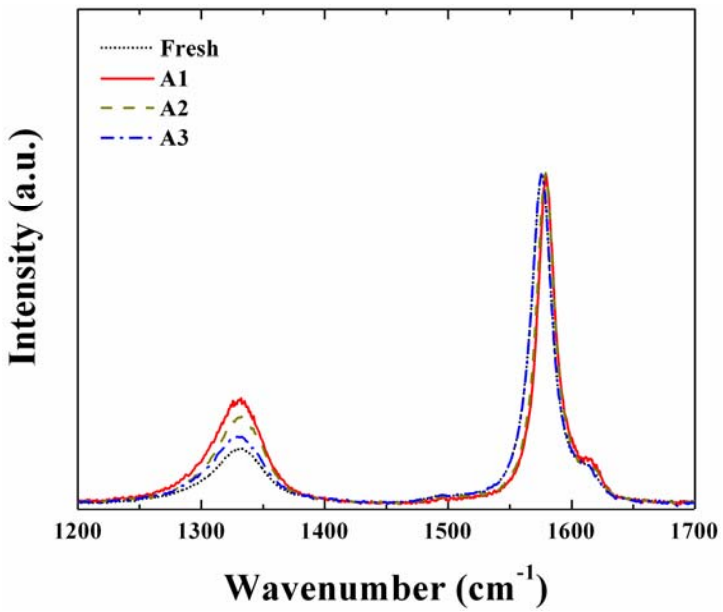




DIAGNOSTICS OF GRAPHITE ANODES

Graphite/1M $LiPF_6$, EC:DMC/Li cells cycled 200 times between various potential limits at C/5 & 25°C

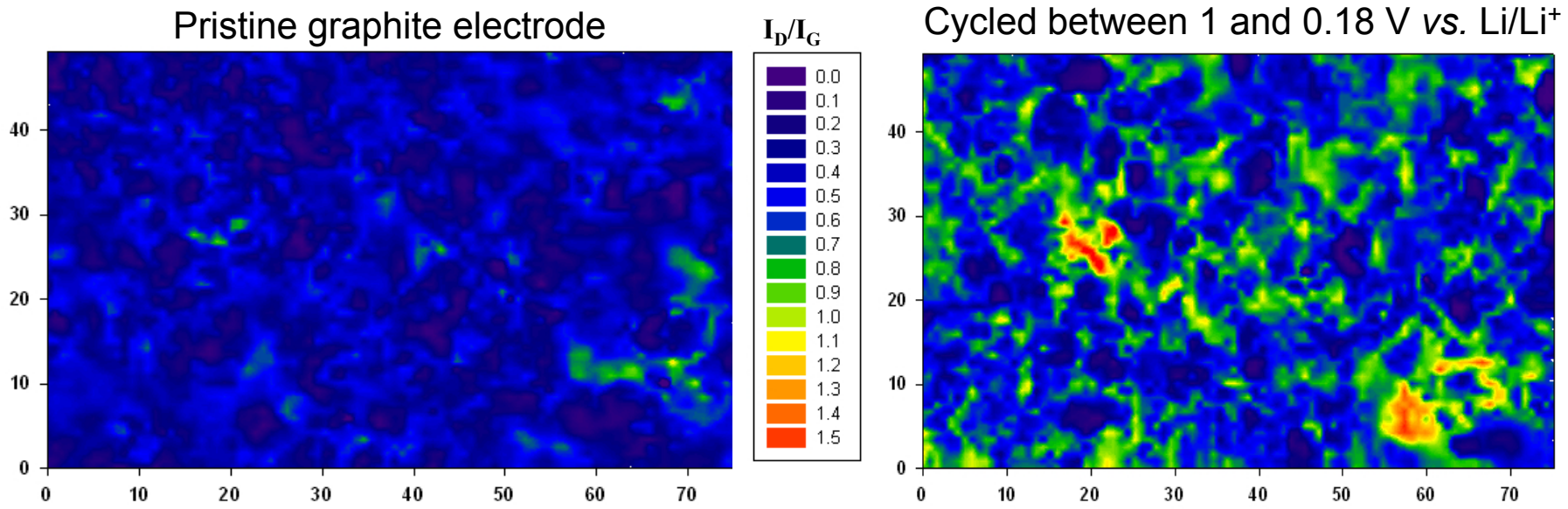
Electrode	Cycling Potential Range	Li_xC_6 limits	I_d/I_g
Fresh	-	x=0	0.25 ± 0.03
Anode 1	1.0 <-> 0.18 V	0≤x<0.05	0.61 ± 0.04
Anode 2	0.23 <-> 0.098 V	0.1<x<0.5	0.58 ± 0.03
Anode 3	0.15 <-> 0.005 V	0.5<x≤1	0.45 ± 0.06



- The initial phase of lithium intercalation into graphite (*ca*. $Li_{0.05}C_6$) is responsible for most of the structural damage
- High Li^+ ion concentration gradients upon charging/discharging may cause the surface crystallites to break down
- Avoid complete delithiation of graphite to minimize graphite disordering!

GRAPHITE ANODE SURFACE STRUCTURE

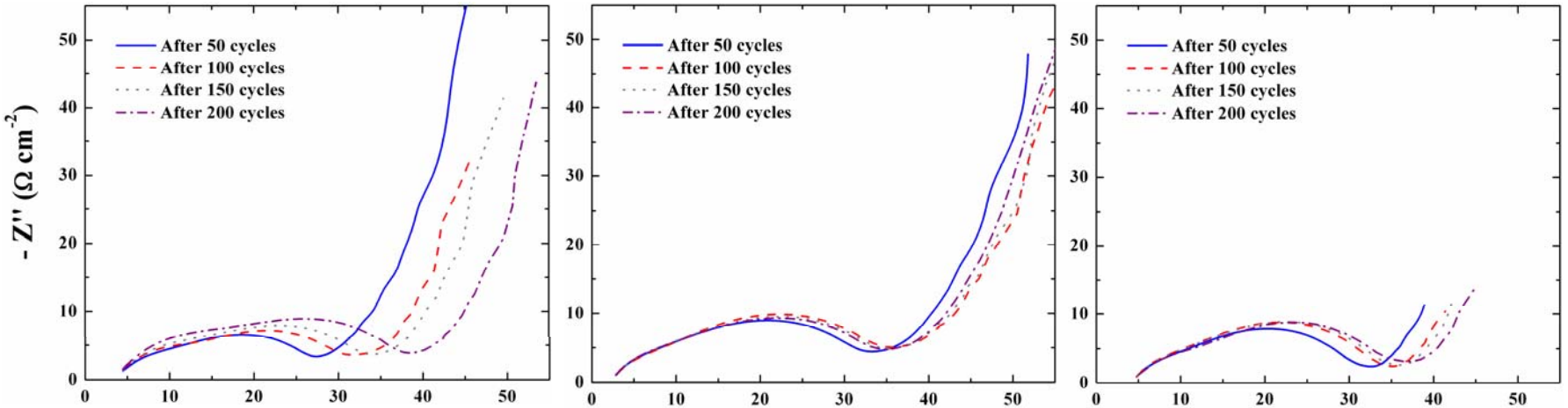
D/G Band Intensity Ratio Mapping



- The fresh anode displays a fairly uniform graphitic structure with some local disorder
- Severe local structural disorder is observed in the cycled anode, with only a few local areas retaining the original graphitic structure
- Graphite structural degradation proceeds in a highly non-uniform manner

ELECTROCHEMICAL IMPEDANCE SPECTRA OF GRAPHITE ANODES

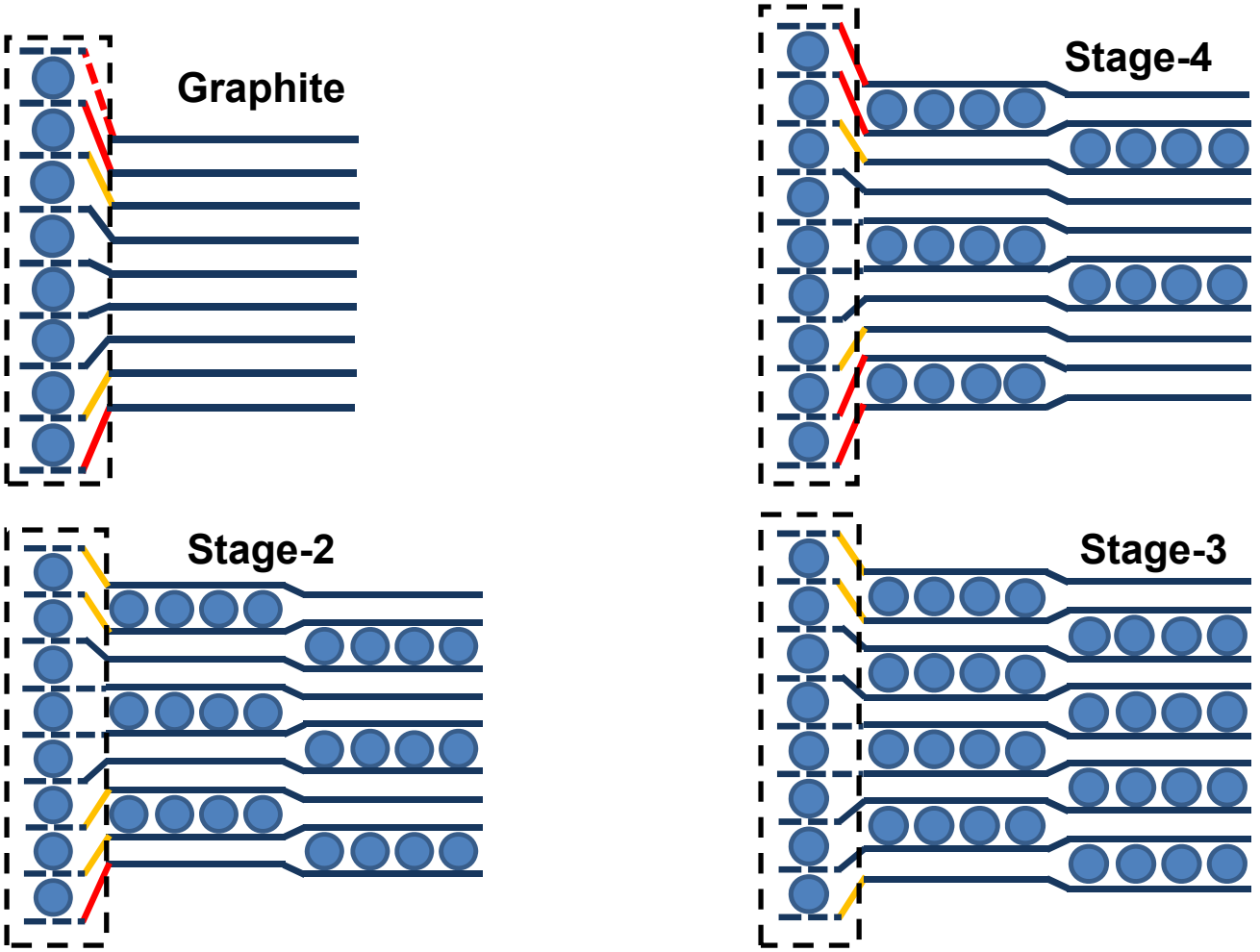
Cycled between 1.0 and 0.18 V Cycled between 0.1 and 0.23 V Cycled between 0.005 and 0.15 V



- All three cells show an increase in the mid-frequency section of the impedance spectra after cycling
- Significant mass-transfer and charge-transfer barriers across the SEI layer build up during cycling
- Greatest impedance increase for the anode cycled from 1.0 to 0.18 V
- Impedance behavior corresponds to the extent of surface carbon disordering observed by the Raman measurements

LITHIUM INTERCALATION INTO GRAPHITE

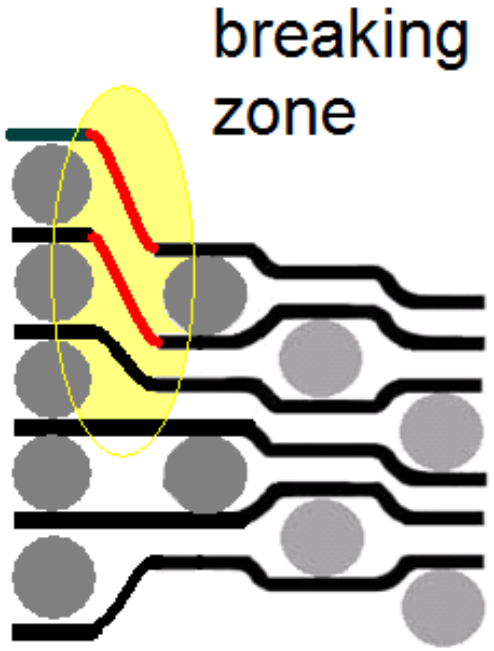
Non-Equilibrium Surface Conditions



Intercalation/deintercalation at high rates may create steep local concentration gradients and induce local stresses in the lattice

GRAPHITE DEGRADATION MECHANISM

- Li^+ ions tend to form stronger bonds with carbon edge atoms than in between graphene layers
- Li^+ surface concentration in graphite during intercalation is always higher than in the bulk
- Li^+ concentration gradient between the fully occupied surface sites and the bulk induces significant local stress
- Li^+ surface-bulk concentration gradients gradually diminish during the formation of Li^+-rich stages 1-3

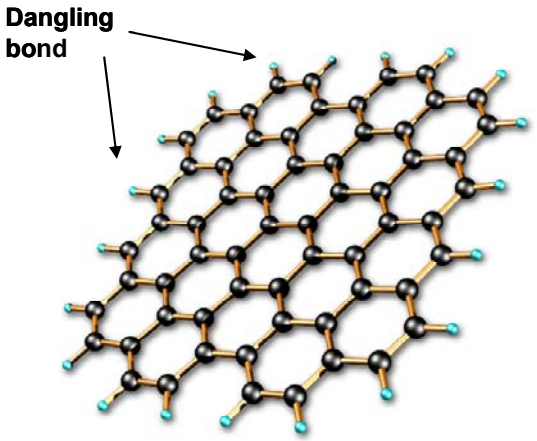


- Preventing/inhibiting surface structural damage and/or rapid passivation of active sites can help stabilize the SEI layer and prevent/minimize anode degradation
- Chemical grafting of carbon edge sites to weaken the strength of C_{edge}-Li^+ bonds can help minimize surface structural disordering

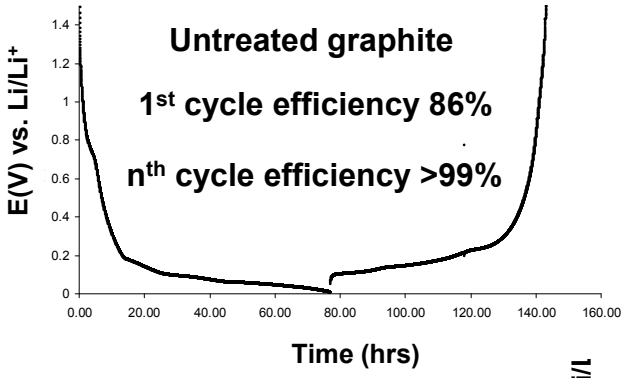
STRATEGIES TO MINIMIZE IRREVERSIBLE CELL CAPACITY LOSSES:

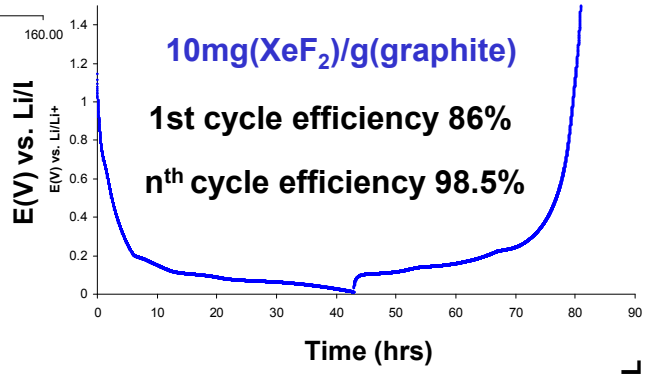
Partial Fluorination of Graphite

- Some irreversible capacity loss results from reaction of Li with dangling bonds and oxo-species (-OH, -OCH, -OCH_3, *etc*.) at graphene plane edges
- Mild fluorination of graphite may passivate the dangling bonds and replace larger edge species with strongly bonded fluoride, thereby reducing Li loss during SEI formation



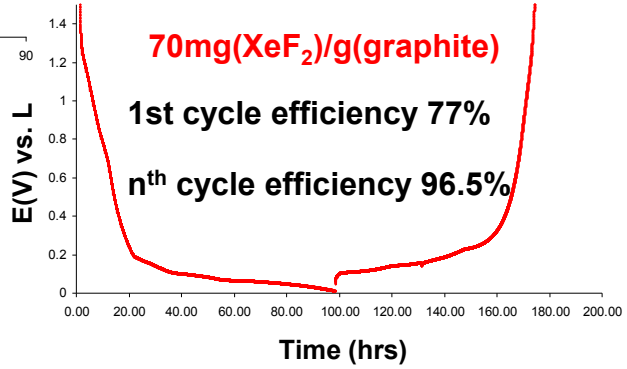
FLUORINATED GRAPHITE CHARGE - DISCHARGE PERFORMANCE





Too much fluorine?

decreased 1st cycle and nth cycle efficiencies



Too little or too much fluorine?

No effect on the 1st cycle efficiency, minor effect on nth cycle efficiency

We will examine alternative treatments to modify pre-formation edges and reduce water content

PLANNED FUTURE WORK

- **Studies of SEI layer formation/stabilization**
  - Continue search for anodes that display smaller irreversible capacity losses and improved coulombic efficiency during cycling
    - ✓ Reduce the irreversible charge required to form stable SEI layers
    - ✓ Investigate pretreatment regimens to reduce side reactions
- **Diagnostics of ABRT Program cell components**
  - Carry out post-test characterization of components from ABRT cells
    - ✓ Examine electrode composition, structure, and surface films
    - ✓ Understand factors that can enhance the stability of SEI layers
  - Establish and investigate degradation mechanisms of PHEV cells
  - Compare degradation mechanisms in ATD *vs*. ABRT cells

SUMMARY

- ***Supporting research for improved lithium-ion batteries:***
  - Carbon disordering increases anode surface reactivity and causes SEI layer reformation, which shifts the cathode to a higher SOC and accelerates cathode degradation
    - ✓ Li^+ concentration gradient between occupied surface sites and bulk induces local stress
    - ✓ Surface-bulk Li^+ concentration gradients diminish during formation of Li^+-rich stages 1-3
    - ✓ Complete delithiation of graphitic anodes accelerates structural disordering and must be avoided to increase Li-ion cell lifetimes
    - ✓ Chemical grafting of fluorine onto graphite edges did not improve anode performance
  - Diagnostic analyses of a Gen-3 cathodes showed degradation characteristics similar to Gen-2 cathodes
    - ✓ Contact resistances between primary particles and conductive carbon matrix, loss of available Li, and/or electrolyte starvation are likely cell fade mechanisms
- ***Approach:***
  - Advanced spectroscopic, microscopic, X-ray, chromatographic, and related techniques to characterize ABRT cell components
  - Development of new surface-processing methods
- ***Accomplishments:***
  - Completed study of graphite anode structural degradation in FY 2009, and in FY 2010 used results of this study to identify approaches to anode stabilization
  - Identified candidate anode and cathode fade mechanisms in Gen-3 cells
- ***Plans:***
  - Continue studies of ABRT cell components and anode SEI stabilization