ELECTROCHEMISTRY DIAGNOSTICS AT LBNL

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presented by

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OVERVIEW

Timeline

- LBNL participated in the ATD Program since its inception in 1999
- ABRT Program began October 2008

Budget

- Total budget since ATD Program inception $4900K
- FY08 funding $300K
- FY09 funding $600K
- FY10 funding TBD

Barriers Addressed

- Inadequate Li-ion battery energy, durability and safety for PHEV 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 Lithium Battery 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

- **Minimization of Irreversible Capacity Losses**
  - Synthesis and diagnostic evaluation of novel C/Me composites
  - Investigation of reactive impurities in anodes

MILESTONES

- **Completed work on ATD Program cells in FY 2008**
  - Detailed characterization of Gen-2 and Gen-3 electrode composition, structure, and SEIs
  - Provided key information on anode SEI characteristics, and demonstrated important differences between Gen-2 and Gen-3 cathodes
  - Identified new surface processing method to enhance SEI stability

- **Initiated new ABRT Program task in FY 2009**
  - Evaluation and development of new approaches to minimize first-cycle electrode capacity losses

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 battery power fade, capacity fade, and/or catastrophic failure.
- LBNL also seeks to identify the electrode and electrolyte processes that are significantly influenced by various cell-formation protocols.

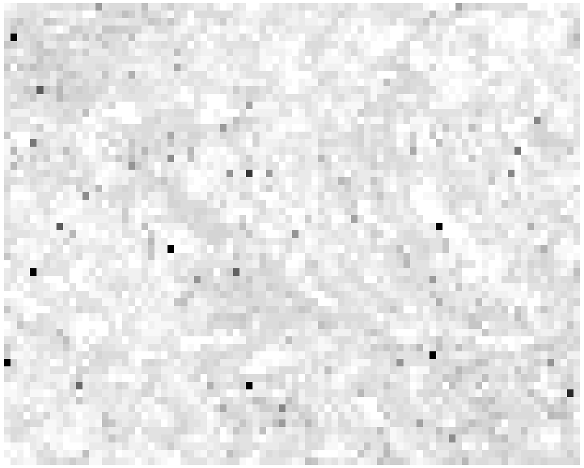
APPROACH

- **Strategies to minimize irreversible capacity losses**
  - Synthesis and diagnostic evaluation of C/Me composites
  - Investigation of reactive impurities in anodes

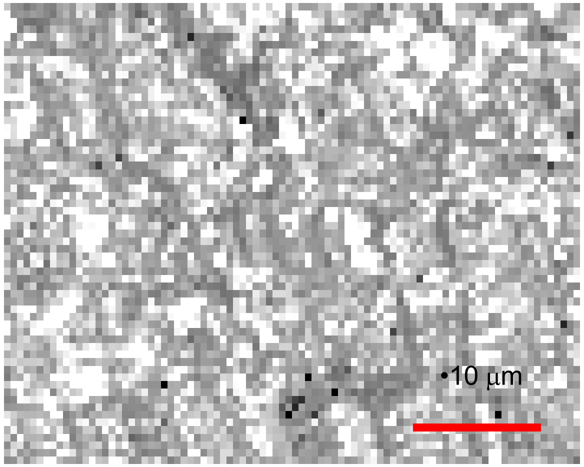
- **Diagnostic evaluation of ABRT Program lithium-ion battery chemistries**
  - Carry out post-mortem diagnostic evaluations of components from ABRT test cells and model thin-film cells
    - ✓ Spectroscopic, microscopic, X-ray, chromatographic, and related techniques
  - Understand factors that can enhance the stability of SEI layers
  - Establish and investigate degradation mechanisms of PHEV cells

GRAPHITE ANODE SURFACE STRUCTURE

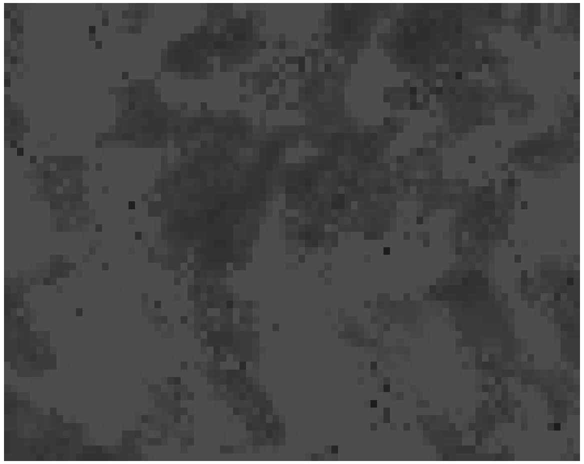
D/G Band Intensity Ratio Mapping



Fresh Mag-10 anode

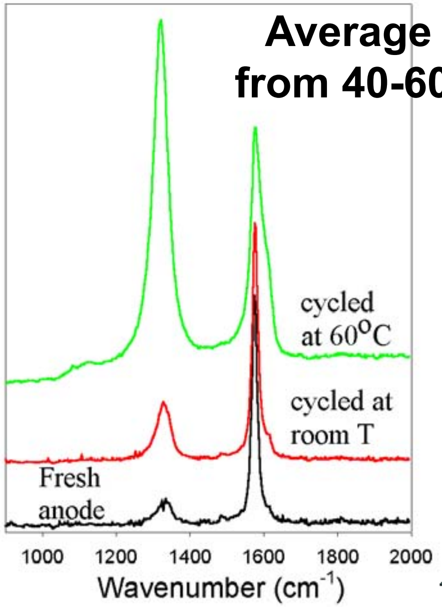


480 cycles, RT, 33% Q_{rev} loss



140 cycles, 60˚C, 65% Q_{rev} loss

- Structure of graphite in the anode breaks down slowly upon cycling at relatively high rates
- Substantial surface disorder was observed in the anode cycled at 60^{o}C
- Continuous change of anode surface reactivity *vs*. the electrolyte can be expected



Average spectra from 40-60 µm area

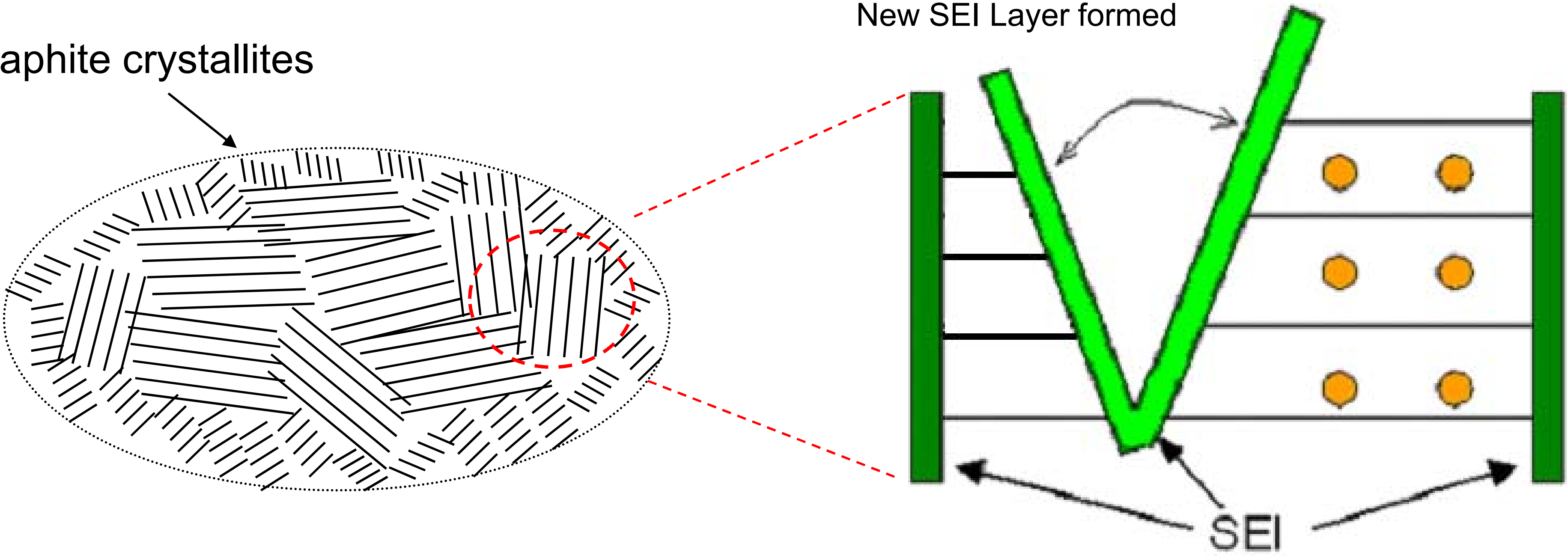
DIAGNOSTICS OF GRAPHITIC ANODES

Summary of Work Completed in FY 2008

- The surface of the graphite anode undergoes gradual structural degradation upon cycling.
- 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 determines the properties of the SEI layer. S. K. Jeong et al., *J. Power Sources (*2003), P. Novák *et al.*, *J. Power Sources, (2007)*

What are the possible implications for Li-ion cell electrochemical performance and degradation mechanism?

DISORERING OF GRAPHITIC ANODES DURING CELL CYCLING



Fresh graphite edges exposed to the electrolyte

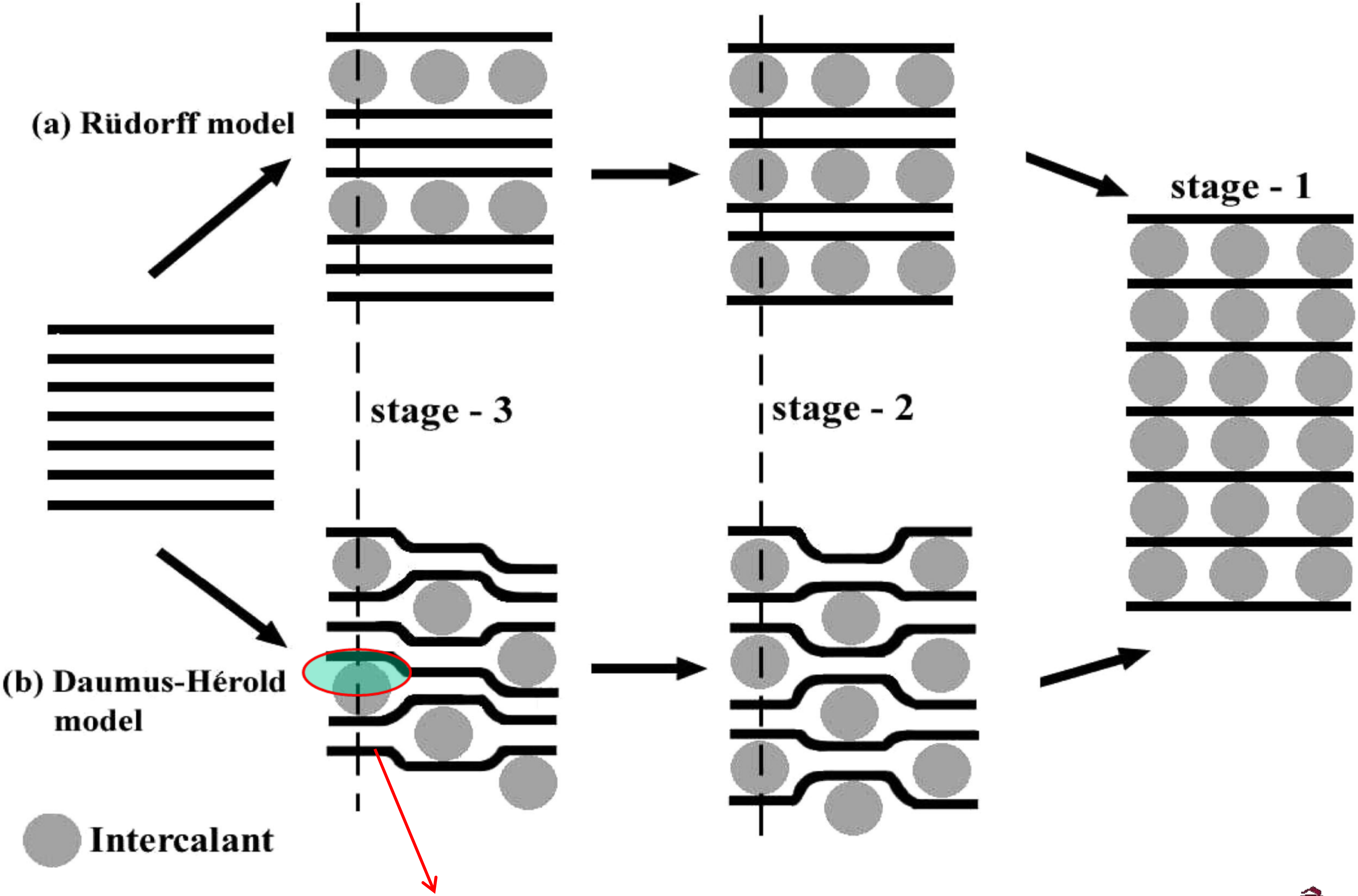
New SEI Layer formed

Graphite crystallites

SEI

- High Li$^+$ concentration gradients upon charging/discharging may cause the surface crystallites to breakdown
- What magnitude of force is needed to achieve this?

MODELS OF INTERCALATION INTO GRAPHITE



~10% local expansion upon Li+ intercalation

DIAGNOSTICS OF CYCLED ANODES

Mag-10/1M $LiPF_6$, EC:DMC/Li cells were cycled 200 times at 25°C between various potential limits at the C/5 rate

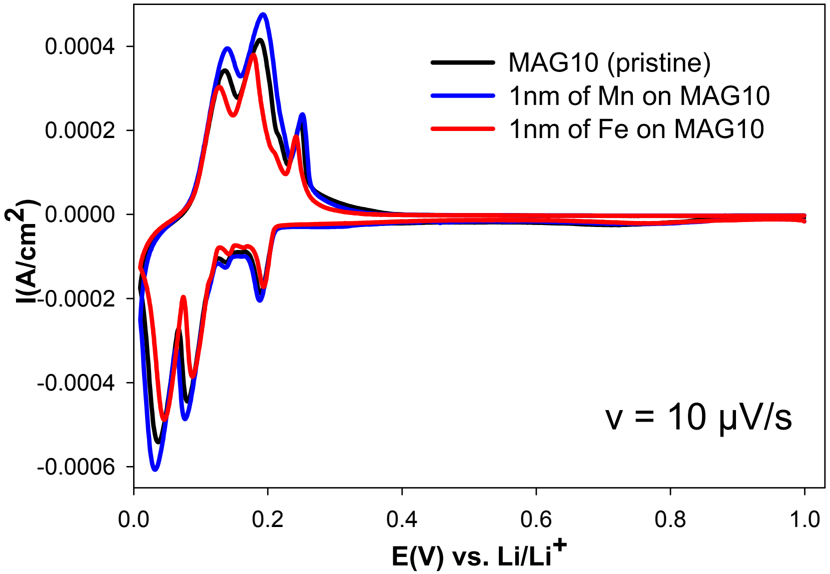
Electrode	Cycling Potential Range	Li_xC_6 limits	I_d/I_g
Fresh	**-**	**$x=0$**	**0.25 ± 0.03**
Anode 1	**1.0 <-> 0.18 V**	**$0 \leq x < 0.05$**	**0.61 ± 0.04**
Anode 2	**0.23 <-> 0.098 V**	**$0.1 < x < 0.5$**	**0.58 ± 0.03**
Anode 3	**0.15 <-> 0.005 V**	**$0.5 < x \leq 1$**	**0.45 ± 0.06**

- The initial phase of lithium intercalation into graphite (*ca*. $Li_{0.05}C_6$) is responsible for most of the structural damage
- Avoid complete de-lithiation of graphite to minimize graphite disordering!

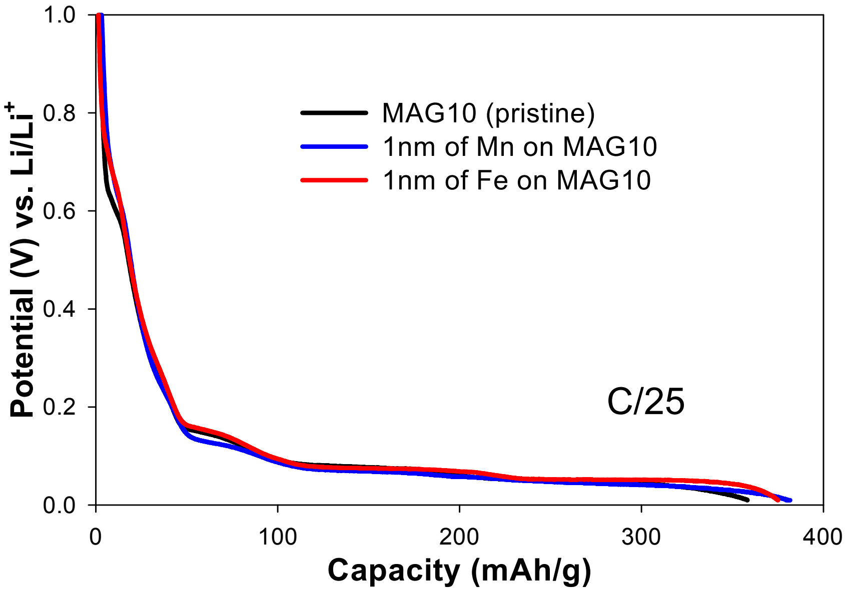
DEGRADATION OF GRAPHITIC ANODES

Effects of Fe, Mn, Co, and Ni Surface Poisoning

1 nm films of Mn and Fe were deposited onto MAG10 composite anodes



Cyclic Voltammetry

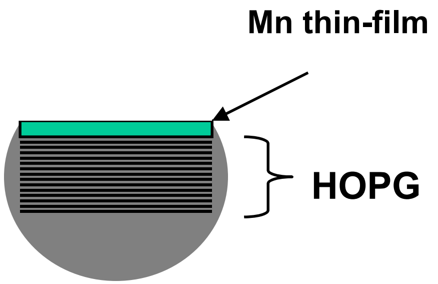


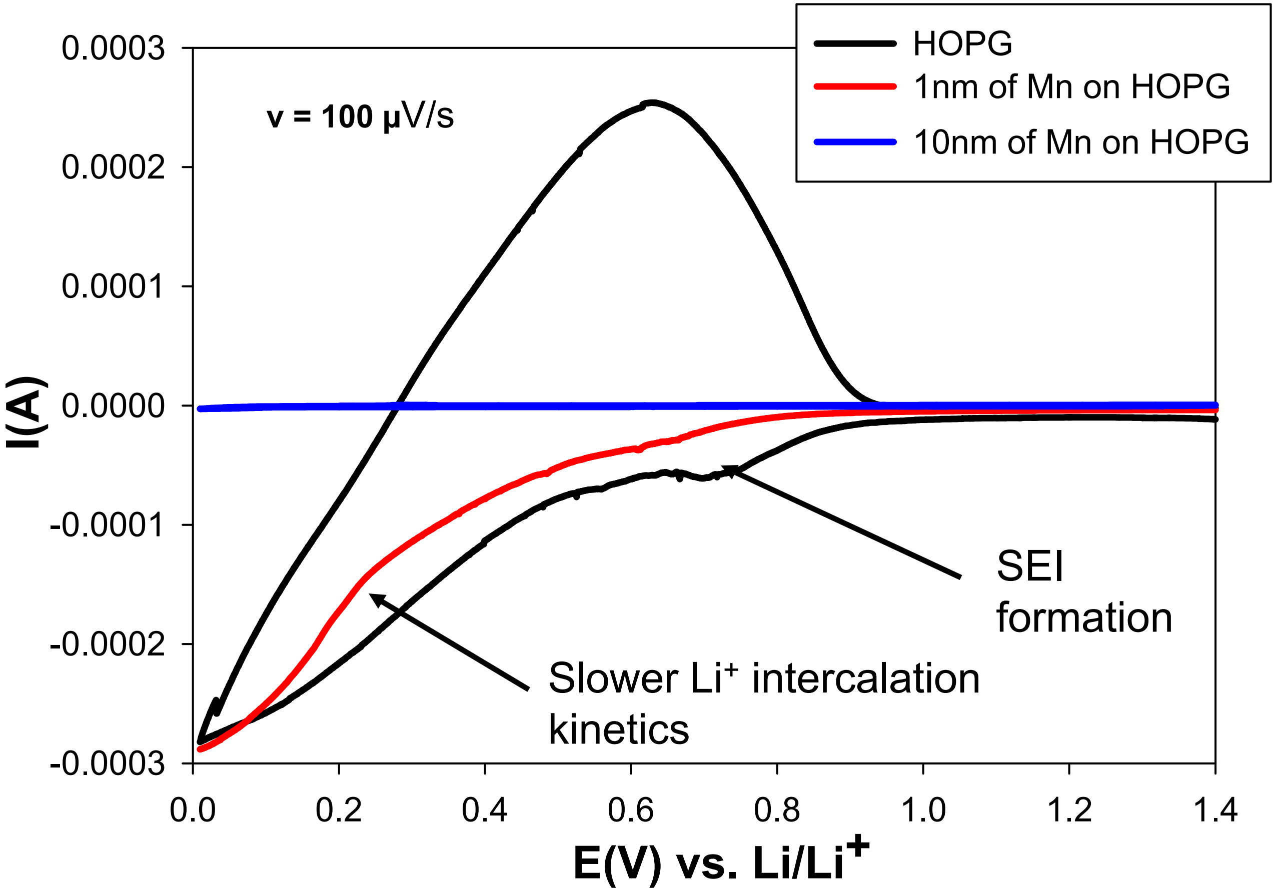
Galvanostatic Charge

- Thick layers (~50 nm) of Ni, Co, Mn on graphite accelerate degradation of graphitic composite anodes.
- 1 nm layers of Fe or Mn on composite MAG-10 anodes affect slightly the kinetics of SEI layer formation and Li^+ intercalation/deintercalation.
- Fe, Mn thin films covered only a small fraction of the total graphite surface area in the composite electrode.

MANANGANESE POISONING OF HOPG

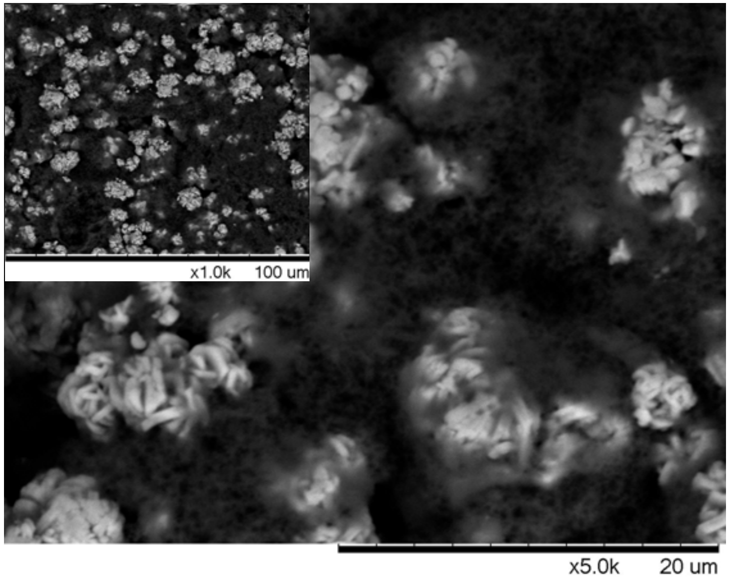
HOPG Basal Plane Electrode

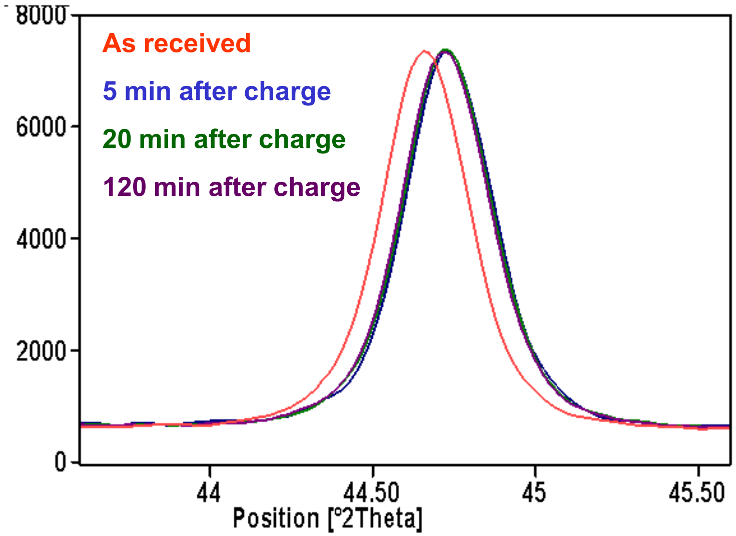




- Mn thin film (1 nm) on the HOPG basal plane affects the electrochemical response of graphite in 1M $LiPF_6$, EC:DEC electrolyte.
  - Formation of the SEI at 0.8V is suppressed.
  - Kinetics of lithium intercalation at low potentials are inhibited.
- A thicker (10 nm) Mn layer completely blocks the HOPG surface.

GEN-3 CATHODE DIAGNOSTICS





Cell G3A.60L45.I105.23.64.54.G.T

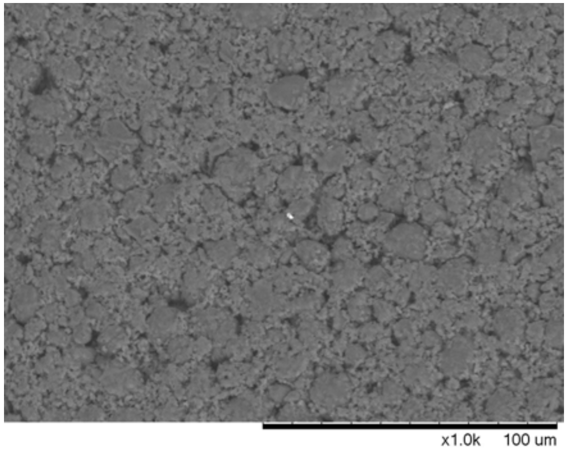
- Cycle Life tested at 45°C
- 20% capacity fade and 54% power fade @ 64 weeks
- Received Dec 2008, cell ID #A-05

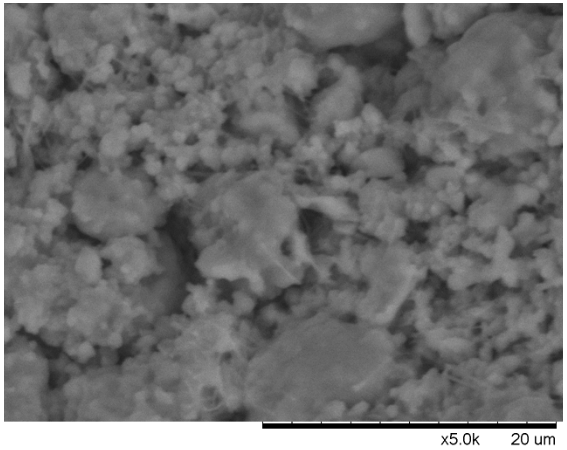
Results

- C/25 capacity after disassembly was 100% of initial (1.29 mAh/cm^2)
- No evidence for particle isolation by XRD after rapid charging
- Active material morphology and composition like new

GEN-3 ANODE DIAGNOSTICS

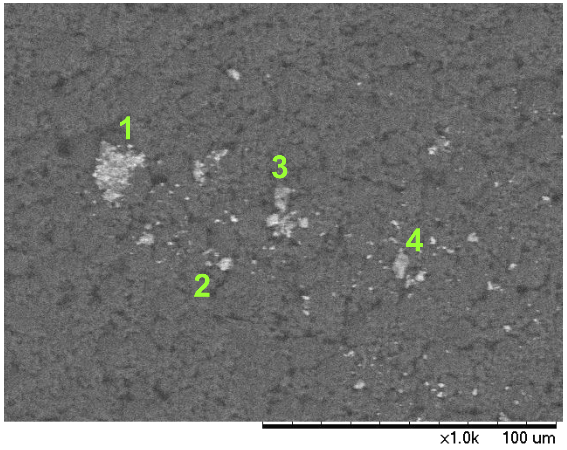
Cell G3A.60L45.I105.23.64.54.G.T





Results

- No visible damage
- No transition metals in most areas
- Very small number of small deposits with variable metal ratios
- Most likely fade mechanisms:
  - Loss of available lithium
  - Electrolyte starvation (separator was dry upon opening the cell)



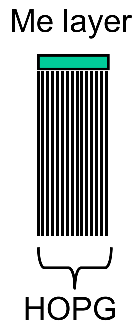
EDX Metals Analysis

Deposit	Mn	Ni	Co
1	47.5	35.2	17.3
2	-	-	100
3	100	-	-
4	78.5	21.5	-

FUTURE WORK

- **Studies of SEI layer formation/stabilization**
    - Continue studies of the effect of surface poisoning by transition metals on anode processes and cell performance
    - Conduct spectroelectrochemical experiments on the edge planes of model HOPG electrodes
- **Diagnostics of ABRT Program cell components**
    - Examine electrode composition, structure, and surface films
    - Compare degradation mechanisms in ATD *vs.* ABRT cells
- **Overcharge Protection**
    - Develop a reliable, inexpensive, self-actuating mechanism for overcharge protection in Li-ion batteries for PHEVs
- **Material Scale-up**
    - Carry out property-consistent scale-up of promising new materials developed in the Batteries for Advanced Transportation Technologies (BATT) Program and test the materials according to PHEV protocols

Edge Plane Electrode



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.
    - ✓ Complete delithiation of graphitic anodes accelerates structural disordering and must be avoided in order to extend Li-ion cell lifetimes.
  - Diagnostic analyses showed little electrode degradation of a Gen-3 cell with significant capacity and power loss.
    - ✓ 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 cell components
  - Development of new surface-processing methods
- ***Accomplishments:***
  - Completed systematic study of graphite anode structural degradation in FY 08, and extended study in FY 09 to identify approach to anode stabilization
  - Identified likely fade mechanisms in Gen-3 cells
- ***Plans:***
  - Continue studies of cell components and anode SEI stabilization
  - Initiate new work on cell overcharge protection and BATT Program materials scale up.