

# DIAGNOSTICS AT LBNL



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presented by

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**DOE Vehicle Technologies Annual Merit Review Meeting**  
February 26, 2008

**note: This presentation does not contain any proprietary or confidential information**

# PURPOSE OF WORK

- Determine how the composition and structure of battery electrodes and their solid electrolyte interphases (SEIs) change as batteries degrade
- Characterize SEI formation and growth on model electrode surfaces to improve understanding of interfacial phenomena
- Help understand the respective roles of electrode/electrolyte characteristics and cell formation protocols in determining cell stability
- Suggest approaches to stabilize electrodes and their SEIs

# PROJECT CHANGES BASED ON 2006 ATD PROGRAM MERIT REVIEW

**Recommendation:** Translate results into specific mechanisms in order to help build better cells

**Action:** Developed new “artificial degradation” tool to better characterize SEI changes on graphite anodes

**Recommendation:** De-emphasize AFM, emphasize Raman, move from *ex situ* to *in situ*

**Action:** Apply subtractively normalized infrared reflection spectroscopy (SNIFTERS) for *in situ* characterization of electrode surfaces

**Recommendation:** Specify the ideal SEI layer and model the formation process

**Action:** Artificial degradation tool and other studies led to a new surface processing approach to stabilize the anode SEI

## **BARRIERS ADDRESSED**

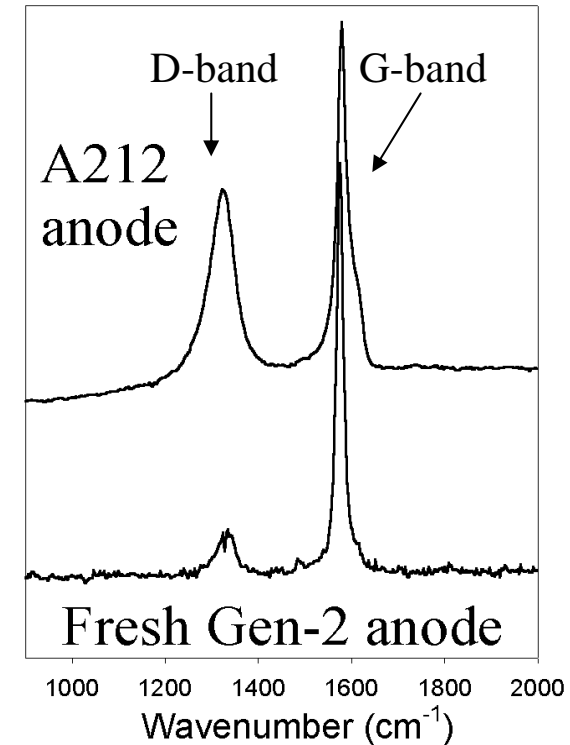
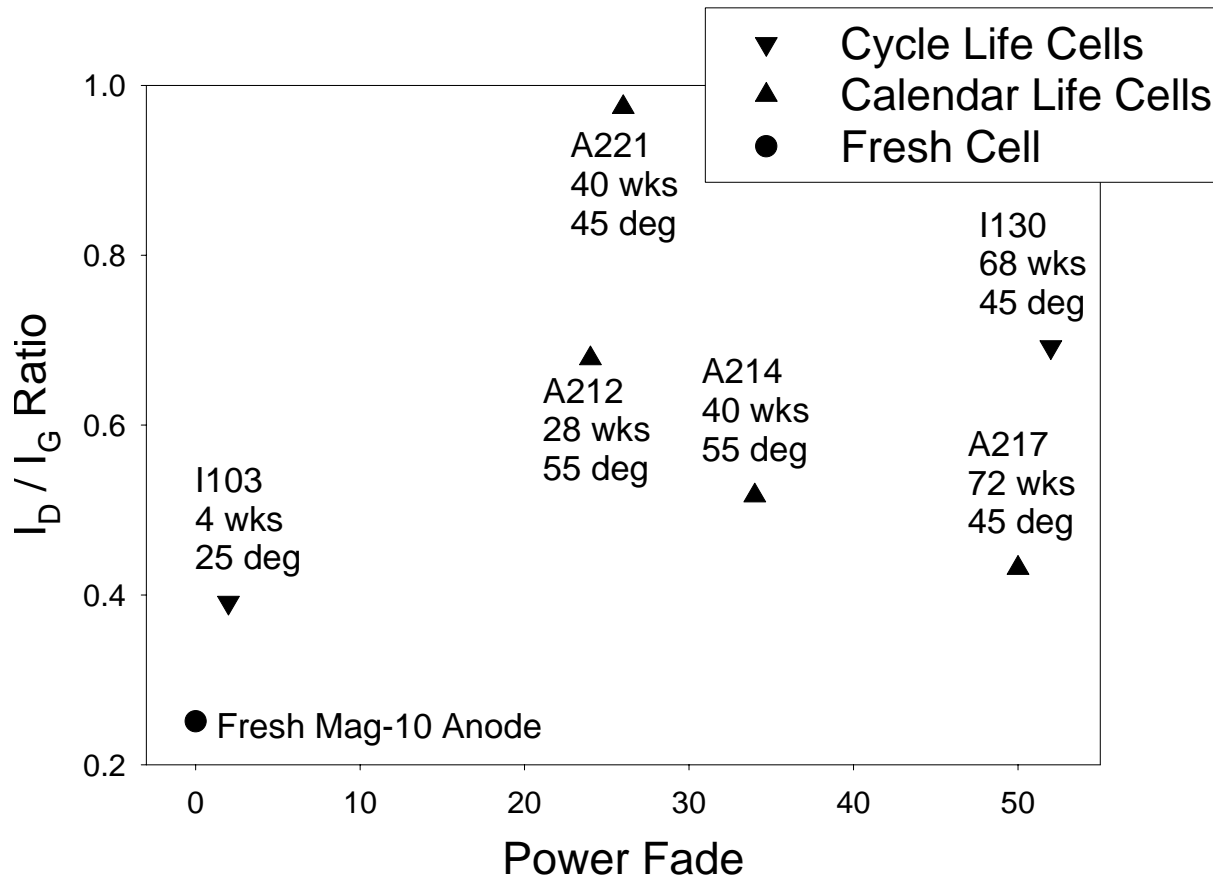
- HEV and PHV battery durability and safety, as well as the need for efficient cell-formation processes, are the major barriers addressed by LBNL diagnostic work.
- The primary LBNL role in the ATD Program is to carry out specific diagnostic evaluations to determine the changes in cell components that 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

Use spectroscopic, microscopic, X-ray, chromatographic, and related techniques to characterize components harvested from:

- Fresh and tested ATD Program cells
- Model thin-film cells
- Special cells used to evaluate electrode formation processes

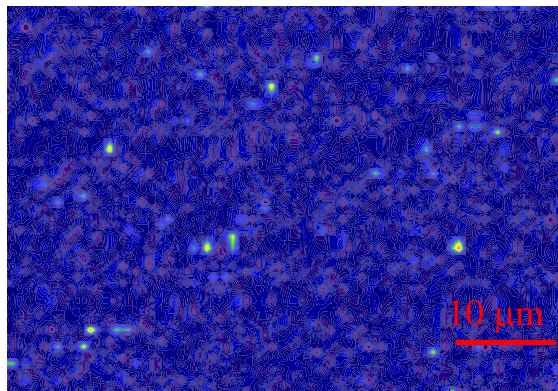
# Raman Spectroscopy of Gen-2 (Mag-10 Graphite) Anodes



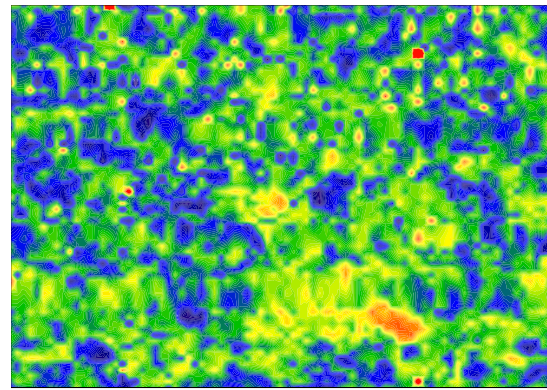
- Anode surface structural disorder was observed in all tested ATD cells.
- This effect appears to occur generally in all graphitic carbons.

*What are the implications for Li-ion cell performance and degradation mechanisms?*

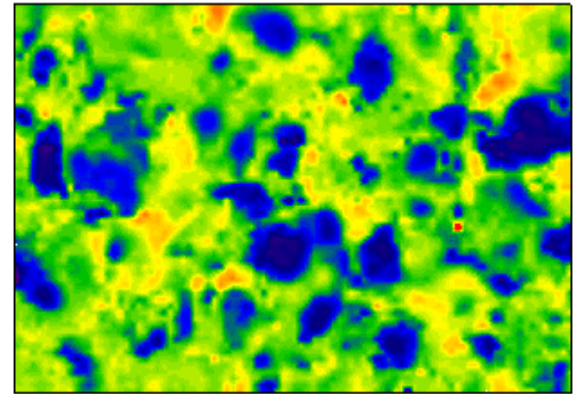
# Raman Images of Anode Surfaces



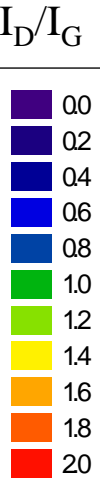
**Fresh Anode** Average  
 $I_D/I_G = 0.25$



**Tested Anode** Average  
 $I_D/I_G = 0.95$



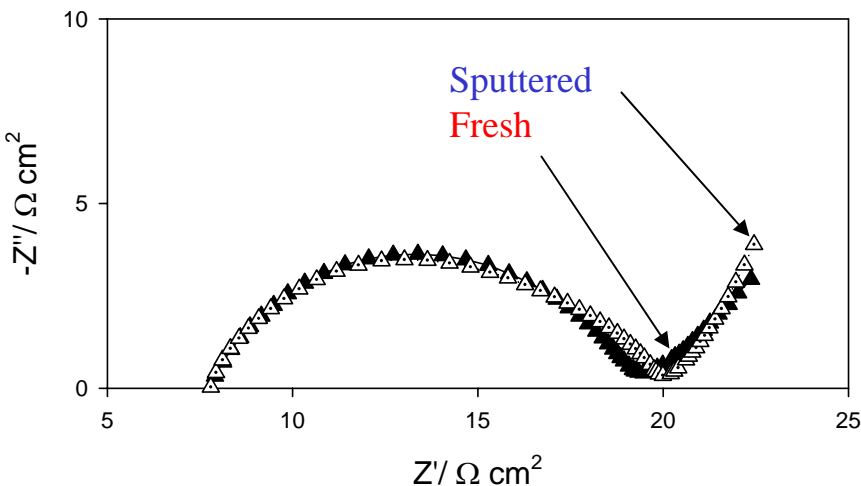
**Sputtered Anode** Average  
 $I_D/I_G = 1.05$



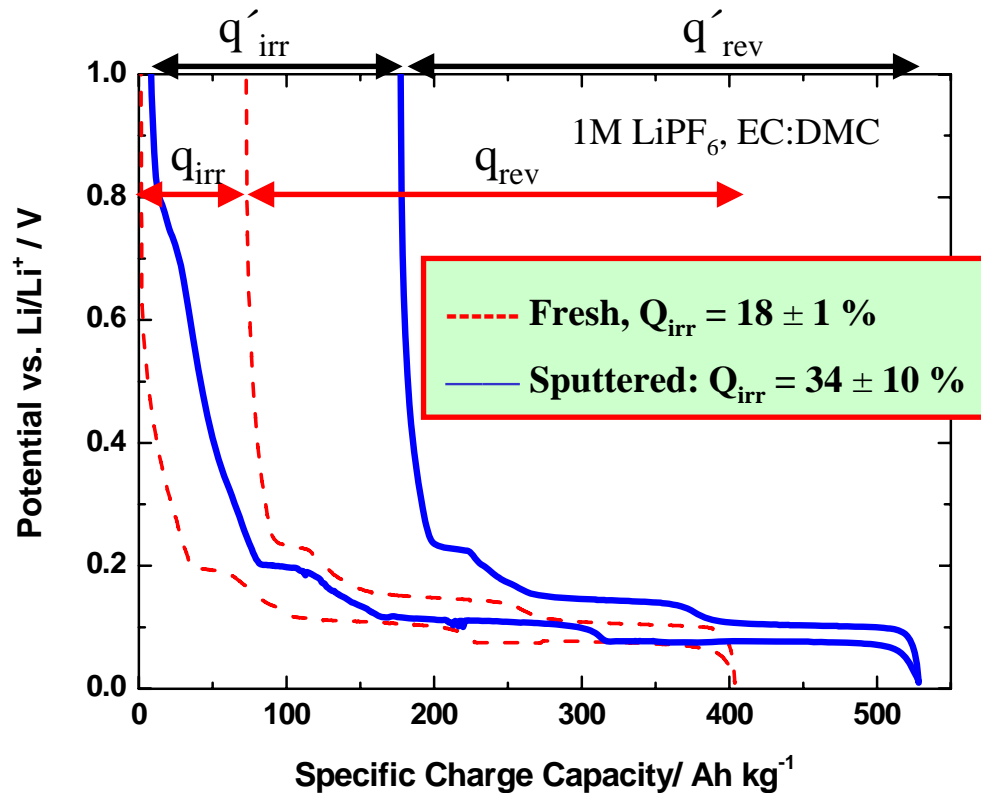
- The extent of structural disorder varies strongly with location.
- Structural disorder was artificially recreated using Ar-ion sputtering.
  - The degree of disorder and its pattern on sputtered electrodes resemble those observed in tested Gen-2 anodes.
  - Anisotropic electronic conductivity of graphite and random distribution of contact resistances within the anode contributed to this effect.
- Comparative diagnostic experiments were carried out to determine the effect of graphite disorder on anode electrochemical behavior.

# Electrochemical Evaluation of Gen-2 Anodes

## AC Impedance Spectra



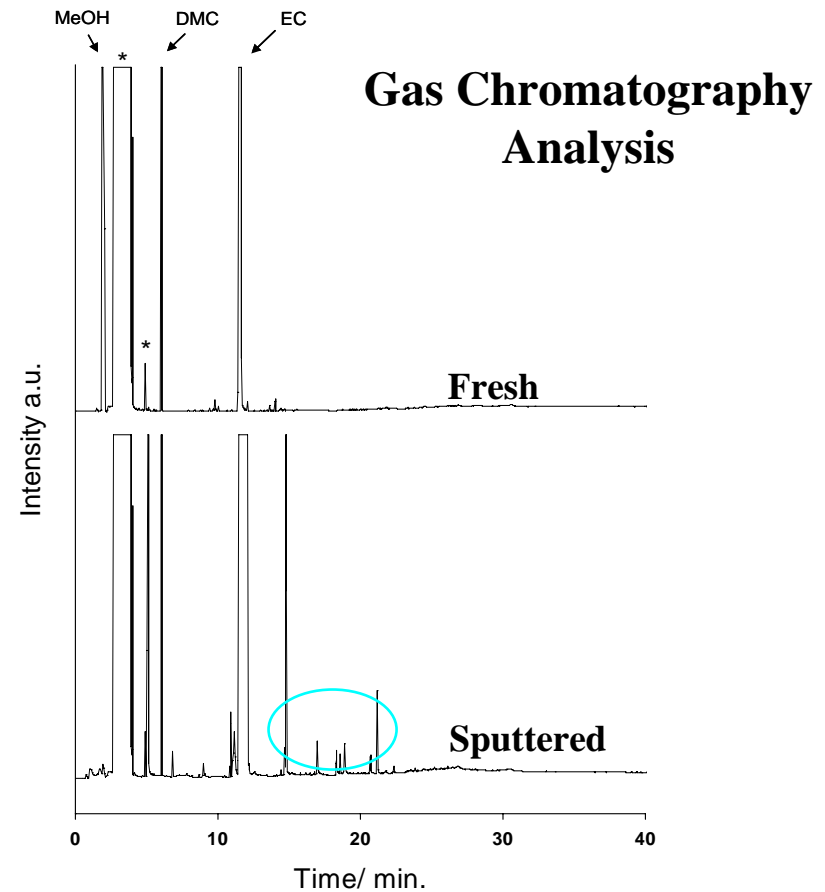
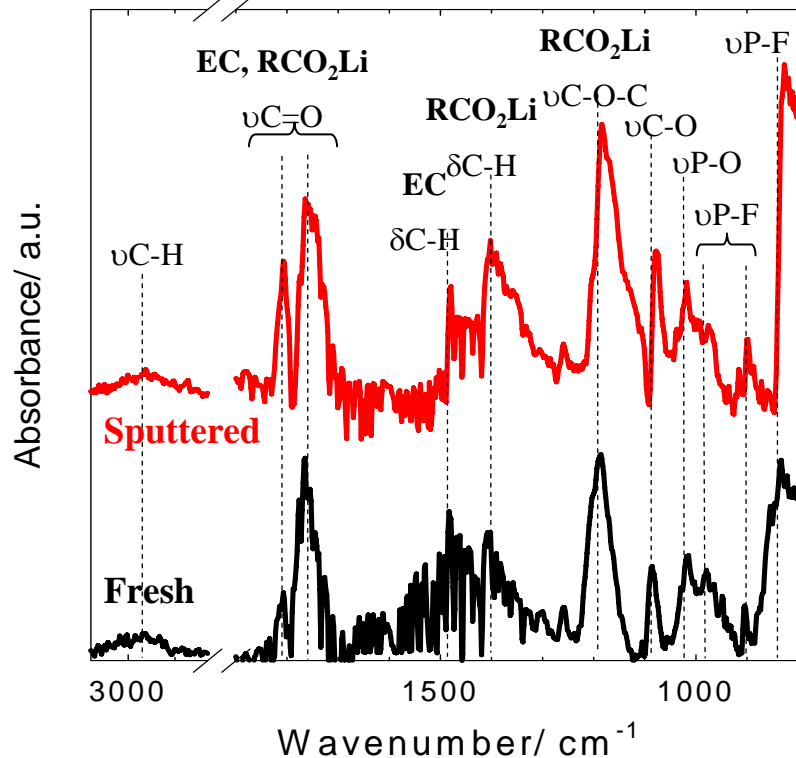
## C/25 Formation Cycle of Mag-10 Anodes



- Induced graphite disorder did not affect the anode  $Q_{\text{rev}}$ .
- Surface structural disorder significantly altered the graphite surface reactivity and almost doubled  $Q_{\text{irrev}}$ .
- The sputtered electrode displays a slightly higher SEI resistance.

# Ex situ Qualitative Analysis of the Gen-2 Anode SEI

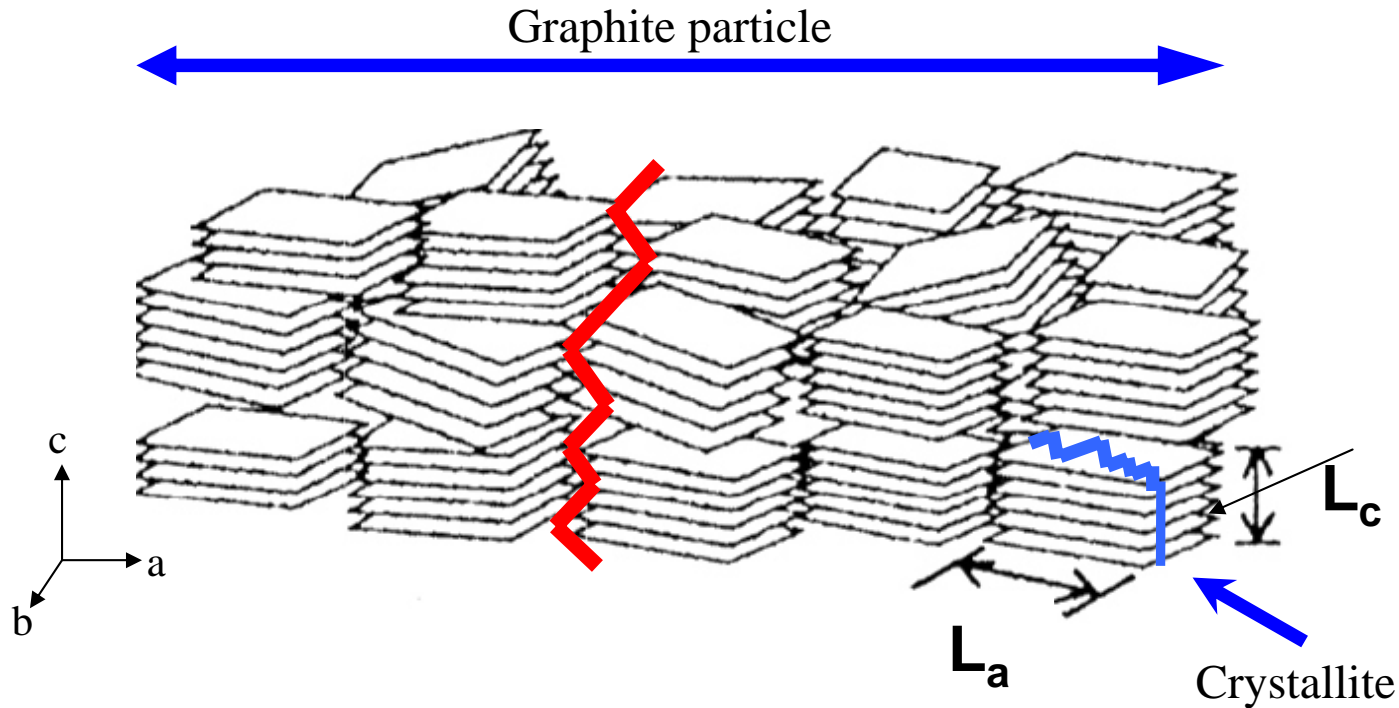
## FTIR Spectra of Mag-10 Anodes



- The SEI on a sputtered anode shows more contribution from inorganic carbonate, phosphate species  $\text{Li}_x\text{PO}_y\text{F}_z$ , and organic alkyl carbonates  $\text{RCO}_2\text{Li}$ .
- FTIR microscopy suggests the formation of a thicker SEI on the sputtered anode.
- GC-MS and GPC analyses indicate the presence of compounds with  $M_w \sim 1600 \text{ gmol}^{-1}$  on the surfaces of sputtered anodes.

# Structural Degradation of Graphite

A single graphite particle consists of many crystallites,  $L_a \sim 40$  nm (Mag-10)



Two types of structural degradation are possible:

1. Particle breakdown – **cracking of the carbon particle**
2. Crystallite fracture – **breaking carbon-carbon bonds**

# Structural Degradation of Graphite - Mechanism

- Graphite particles near the electrode/electrolyte interface exhibit greater structural degradation.
- The structural degradation on the surface is non-uniform at the microscale and varies between particles of graphite.
  - Individual graphite particles may charge/discharge at different rates.
  - Local variations in the electrode/electrolyte interface impedance may occur.
  - Ohmic contact resistances within the composite electrode may be present.
  - Non-uniform SEI layer thickness, composition, and ionic conductivity are likely.
- Local excessive Li concentration gradients near the surface of graphite particles at high charge/discharge rates may surpass their tensile strength limit, and lead to local degradation.

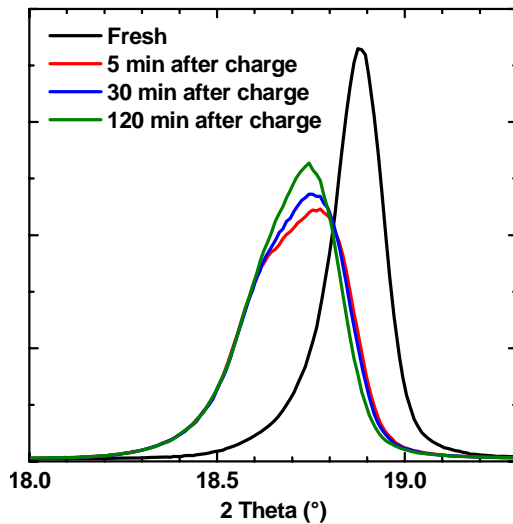
# Implications for Graphite Anodes and Cell Behavior

- Carbon disordering in ATD cells results in a continuous increase of anode surface reactivity vs. the electrolyte.
- Increasing anode structural disorder during cycling/aging induces slow and continuous changes in the SEI.
- The SEI composition shifts from predominantly organic (in a fresh anode) to a mixed organic-inorganic type in aged anodes.
- SEI reformation in Gen-2 cells shifts the cathode to a higher state of charge, which accelerates cathode degradation.

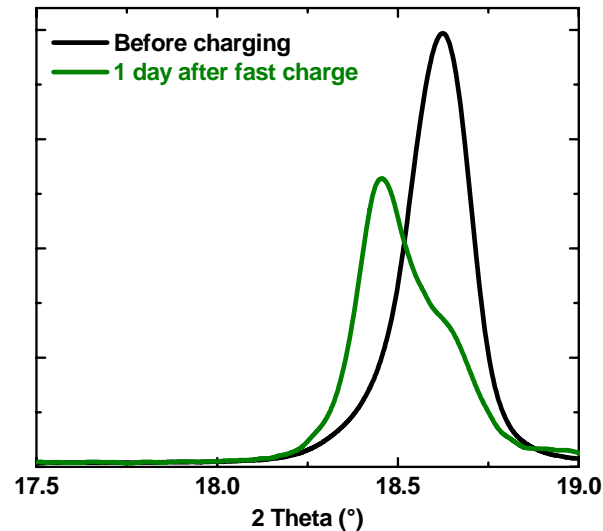
Preventing/inhibiting surface structural damage in graphite and/or rapid passivation of active sites can help stabilize the SEI layer and thereby slow anode and cell degradation.

# No Particle Isolation in Formatted Gen-3 Cathodes

XRD patterns recorded after rapid charging reveal inhomogeneous charge distribution in degraded or defective electrodes.

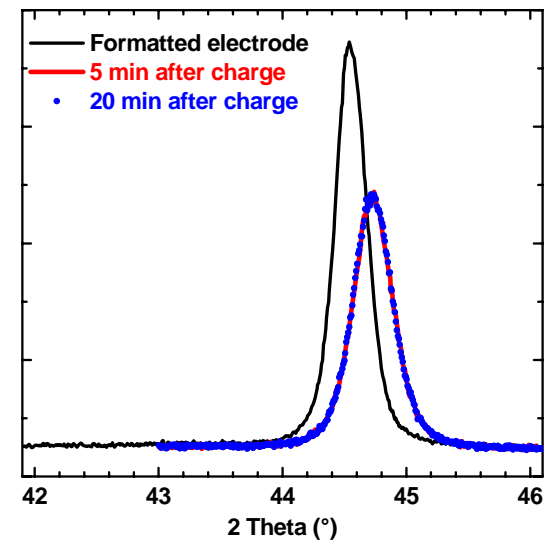


Fresh Gen-2 Cathode  
Small inhomogeneity



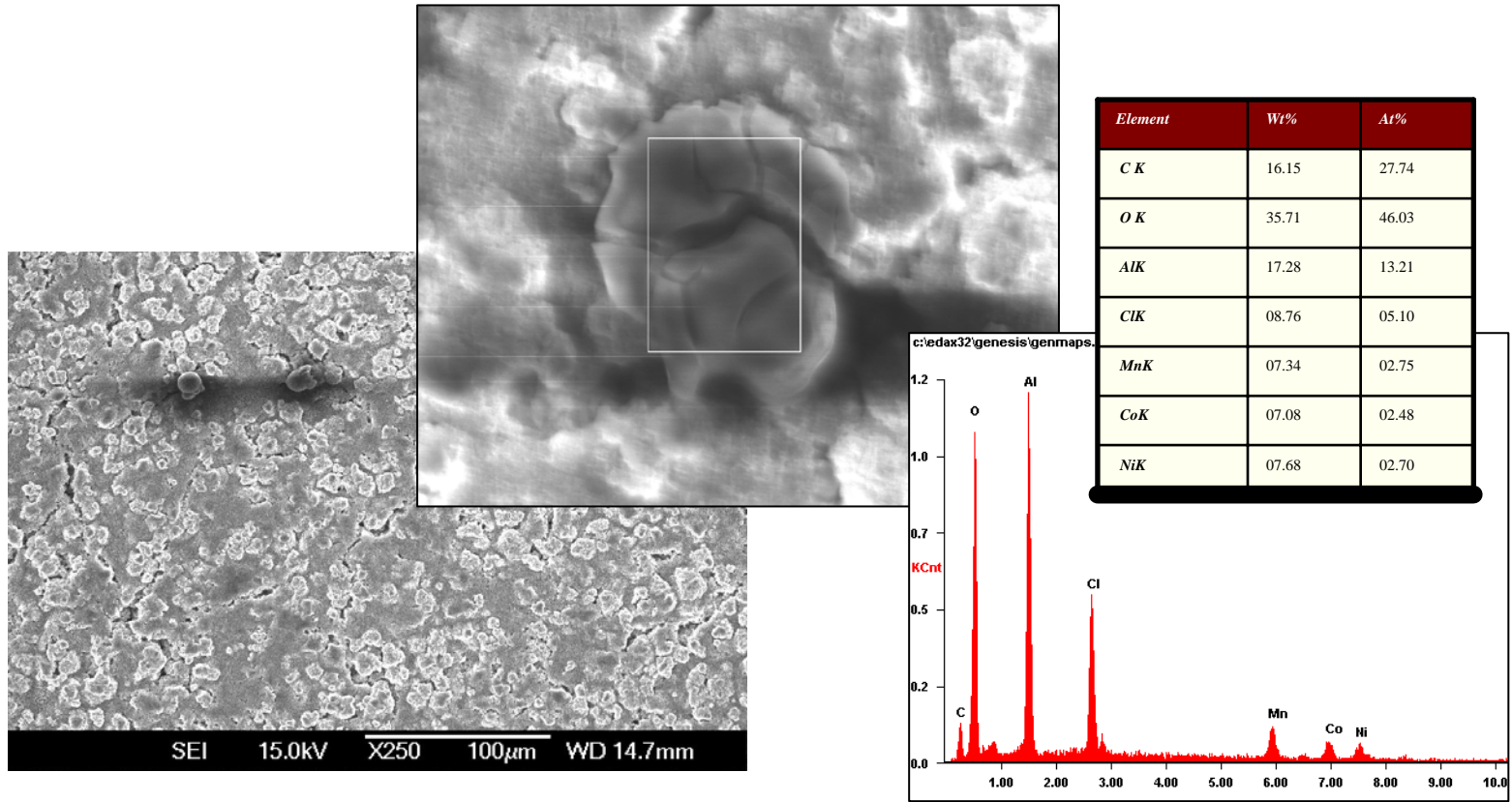
High Power Fade  
Gen-2 Cathode

Severe disconnection of about  
30% of electrode



Fresh Gen-3 Cathode (Vendor D)  
High-quality electrode

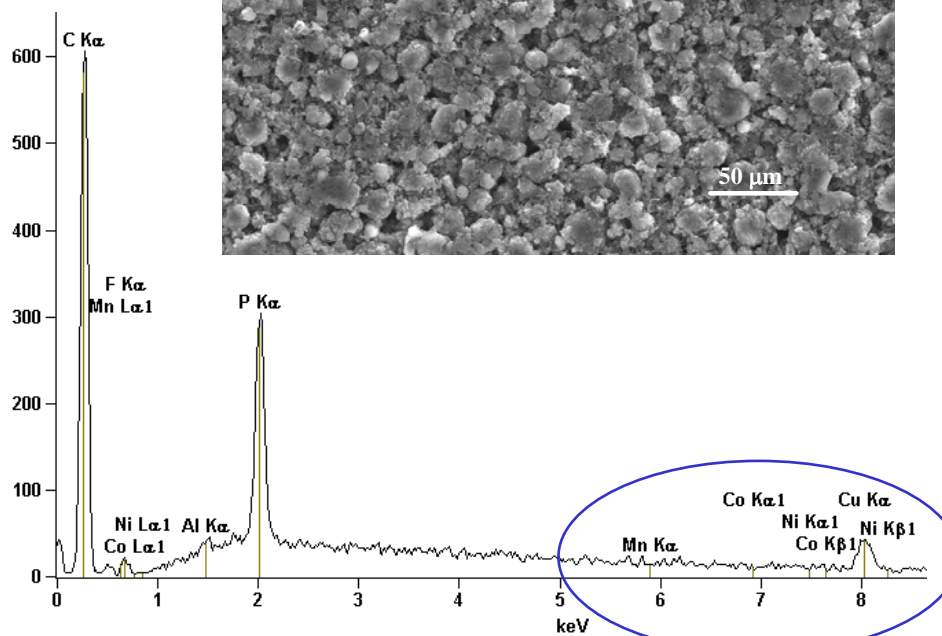
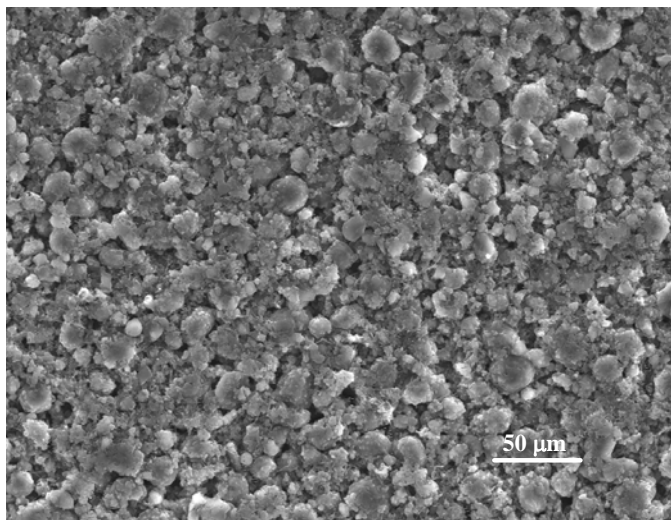
# SEM/EDX of Gen-3 Cathode (Vendor D) After 20 Cycles



- Transition metal composition stable
- Small number of anomalous formations
- Al and Cl present in these, not found elsewhere in sample

# SEM/EDX of Gen-3 Anode From Aged Pouch Cell

Cell DAP10 (with Vendor D electrodes) supplied by D. Abraham, ANL



- Aged at 3.72V and 55°C for 100 days
- Cell impedance rise ~ 40%
- No structural changes observed in either electrode
- No Ni/Co/Mn detected in anode by EDX
- No changes in Ni/Co/Mn ratios in cathode from this cell

Labels show locations of peaks  
Only Cu in this region (current collector)

# TECHNOLOGY TRANSFER

- Goals are to:
  - Understand the factors that can enhance the stability of SEIs without increasing electrode interfacial impedances
  - Determine the mechanisms that lead to particle isolation and other potential causes of cell power and capacity fade
- Meeting the above goals will help:
  - Identify specific ways (surface processing, *etc.*) to increase SEI stability
  - Indicate pathways (additives, electrode designs, *etc.*) to improved electrode performance and life

# FUTURE WORK

- Post-test diagnostic evaluations of components obtained from ATD cells to identify causes of power and capacity fade
  - Characterize changes that occur in electrode structure, morphology, composition, and particle isolation during cell formation, aging, and cycling
  - Emphasis on interfacial phenomena
- Develop a new spectro-electrochemical cell for *in situ* infrared measurements to investigate interfacial processes.
  - SNIFTERS to differentiate spectra from the electrode surface and the electrolyte
  - *In situ* studies of surface processes at model electrodes (collaboration with D. Abraham, ANL)
- Explore how the anode SEI can be modified by a nm-thick CVD coating of Sn
  - Evaluate the effect of such a surface treatment and the role of specific cell-formation protocols on the anode SEI stability

# SUMMARY

- ***Supporting research for improved batteries:***
  - Detailed characterization of electrode composition, structure, and SEIs
  - Identification of new surface processing method to enhance SEI stability
- ***Approach:*** spectroscopic, microscopic, X-ray, chromatographic, and related techniques to characterize cell components
- ***Accomplishments:*** Provided key information on anode SEI characteristics, and demonstrated important differences between Gen-2 and Gen-3 cathodes
- ***Technology Transfer:*** Used advanced spectroscopic techniques and novel artificial degradation method to suggest pathways for improved SEIs
- ***Plans:***
  - Post-test diagnostic evaluations of components obtained from ATD cells
  - SNIFTERS for *in situ* characterization of interfacial processes
  - Evaluate a new surface treatment and the role of specific cell-formation protocols on the stability of the anode SEI

# PUBLICATIONS AND PRESENTATIONS SINCE 2006 REVIEW MEETING

- M. Kerlau and R. Kostecki, “Interfacial Impedance Study of Li-ion Composite Cathodes during Aging at Elevated Temperatures”, *J. Electrochem. Soc.*, **153**, A1644 (2006)
- M. Kerlau, M. Marcinek, V. Srinivasan, and R. Kostecki, "Studies of Local Degradation Phenomena in Composite Cathodes for Lithium-Ion Batteries", *Electrochimica Acta*, **52**, 5422 (2007)
- L.J. Hardwick, M. Marcinek, L. Beer, J.B. Kerr, and R. Kostecki, “An Investigation of the Effect of Graphite Degradation on the Irreversible Capacity in Lithium-ion Cells,” *J. Electrochem. Soc.*, submitted (2007)

# ACKNOWLEDGEMENTS

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ATD Program participants

DOE/EERE Office of Vehicle Technologies

\* New LBNL post-doctoral fellow who will join this project in March 2008