

Electrochemistry Diagnostics of Baseline and New Materials

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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), Battaglia (testing BATT materials), and KostECKI/Richardson (materials)

Budget

- FY 2011 diagnostics/materials funding \$600K
- FY 2012 diagnostics/materials funding \$600K

Barriers addressed

- High energy batteries – poor calendar/cycle lifetimes
- Irreversible capacity losses during formatting and cycling

Partners

- ANL, BNL, INL and SNL
- Dan Abraham is the ABRT Program diagnostic lead
- Venkat Srinivasan (LBNL) is the LBNL electrochemistry lead

Objectives

Task 1.1

- Enable increased cell specific energy by addressing the impact of high potentials on carbons in the cathode
 - Identify physico-chemical changes of carbon additives when subjected to high potentials and suggest approaches to improved carbon stability
 - Investigate surface treatment regimens to reduce side reactions

Task 2.4

- Determine the key factors that contribute to the degradation mechanism in the PHEV test cells and individual cell components
- Characterize SEI formation on model electrode surfaces to improve understanding of key interfacial phenomena in PHEV cells

MILESTONES

Task 1.1

- Determine interfacial degradation mechanism CBs in high-voltage cathodes (July 2012). Synthesize a new type of CB with improved interfacial properties (September 2012).

Task 2.4

- Attend review meetings and present diagnostic results obtained in collaboration with ABRT Program participants.

Barriers Addressed

- HEV and PHEV 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 provides tested cells for characterization at LBNL
- ANL and BNL provide detailed structural, chemical, electrochemical and thermal-stability information for cell materials
- All participating laboratories periodically share results and plans
- Treated/improved materials were provided to cell-building groups to investigate their properties in industrial-close framework

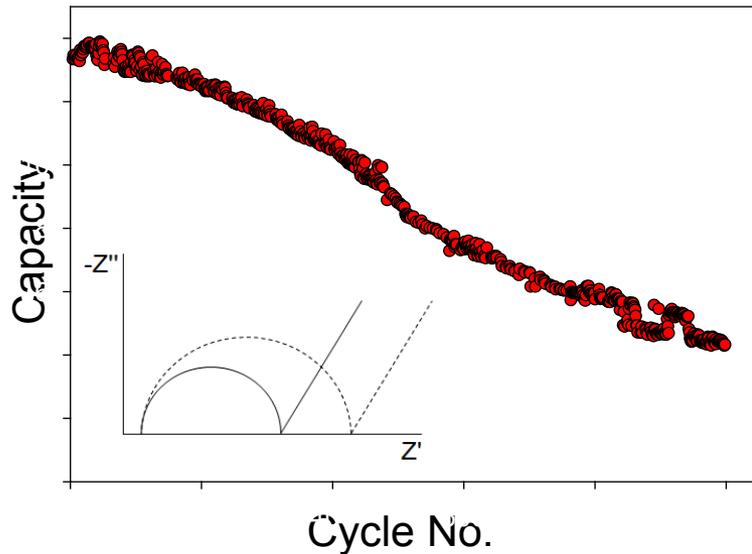
Approach

- Strategies to minimize irreversible capacity losses
 - Determine the mechanisms for carbon damage and migration at high potentials
 - Investigate mitigating treatments, additives and procedures
- Diagnostic evaluation of ABRT Program lithium-ion cell chemistries
 - Carry out post-test diagnostic evaluation of components from ABRT test cells and model cells (no test cells have been sent to LBNL in FY2011 and 2012)

Technical Accomplishments

1. Completed electrochemical characterization study of common carbon black additives at anodic potentials
2. Determined interfacial instability of carbon black in composite high-voltage cathodes
3. Elucidated the mechanism of carbon black structural degradation
4. Identified an approach to carbon black additive stabilization

Li-ion Cells – Modes of Failure



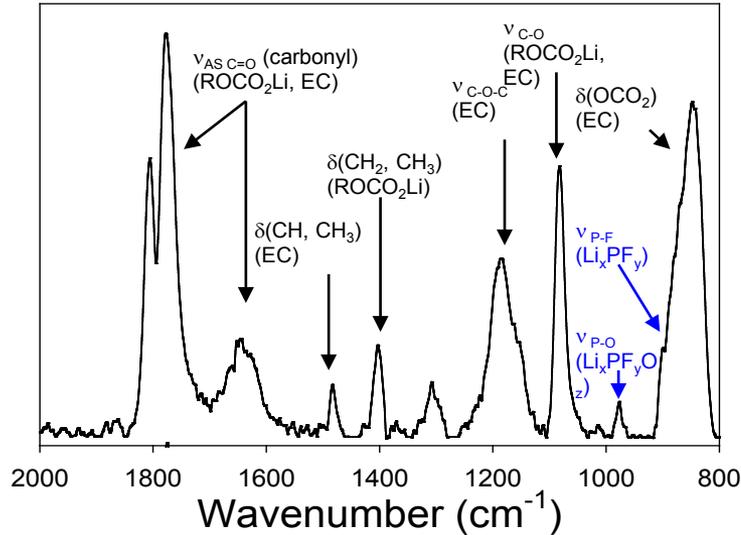
- *Thermodynamically unstable*
- *Significant part of the cell capacity loss can be attributed to shift in cell lithium inventory*
- *Active material loss and poor utilization are also responsible for irreversible capacity losses*

- Capacity loss in lithium-ion batteries affects the cell's specific capacity and leads to eventual cell failure. J. Vetter et al. *J. Power Sources*, 147, 269 2005.
- “Reversible” capacity loss due to balanced and imbalanced side reactions lead to cell self-discharge and/or changes of cyclable lithium
 - cell recharge, cycling beyond normal operating limits, or appropriate lithium sources and sinks may help rebalance the cell.
- “Irreversible” capacity loss is associated with the loss of active electrode material. It is always accompanied by cell impedance rise. J.Christensen, J.Newman, *J. Electrochem.Soc.*,152, A818 (2005)

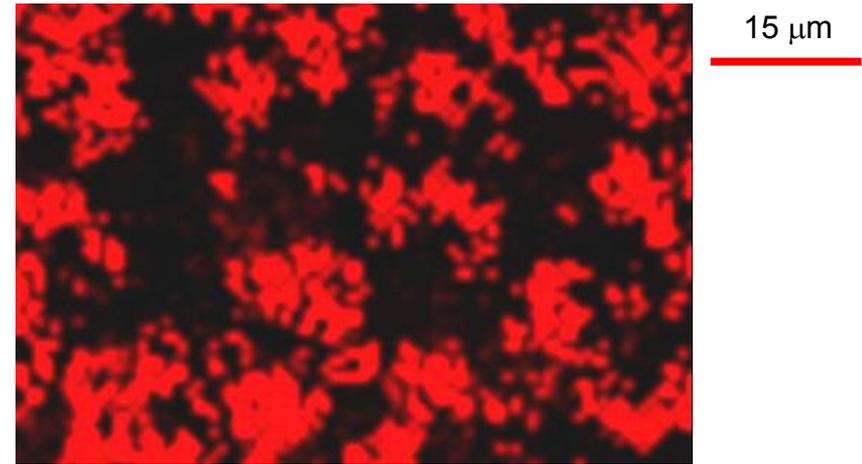
What is the origin and mechanism of these “irreversible” processes that determine cycle- and calendar-life of Li-ion cells?

Fluorescence Imaging of Baseline Electrodes

FTIR of LMNC Composite Cathode



Fluorescence Image of LMNC Composite Cathode

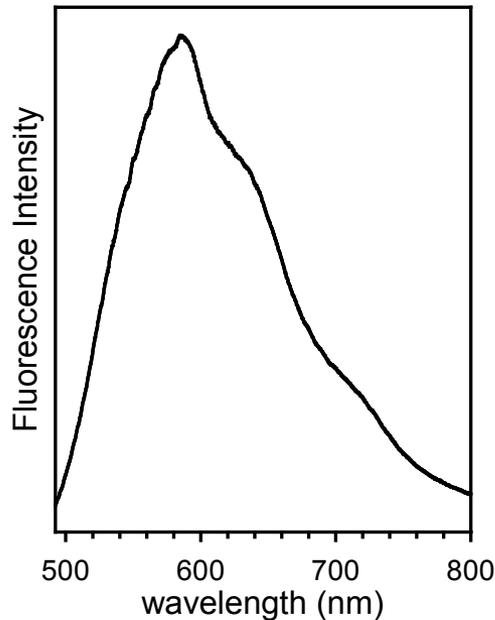


- All components (passive and active) from tested Li-ion cells exhibit strong fluorescence
- Surface of composite cathodes exhibits a non-uniform fluorescence pattern
- FTIR spectra reveal the presence of solvent residues (EC), organic and inorganic electrolyte decomposition products
 - $LiPF_6$ decomposition may yield non-stoichiometric $Li_xPF_yO_z$ compounds
 - Decomposition of organic carbonate solvents gives rise to lithium alkoxide-based products

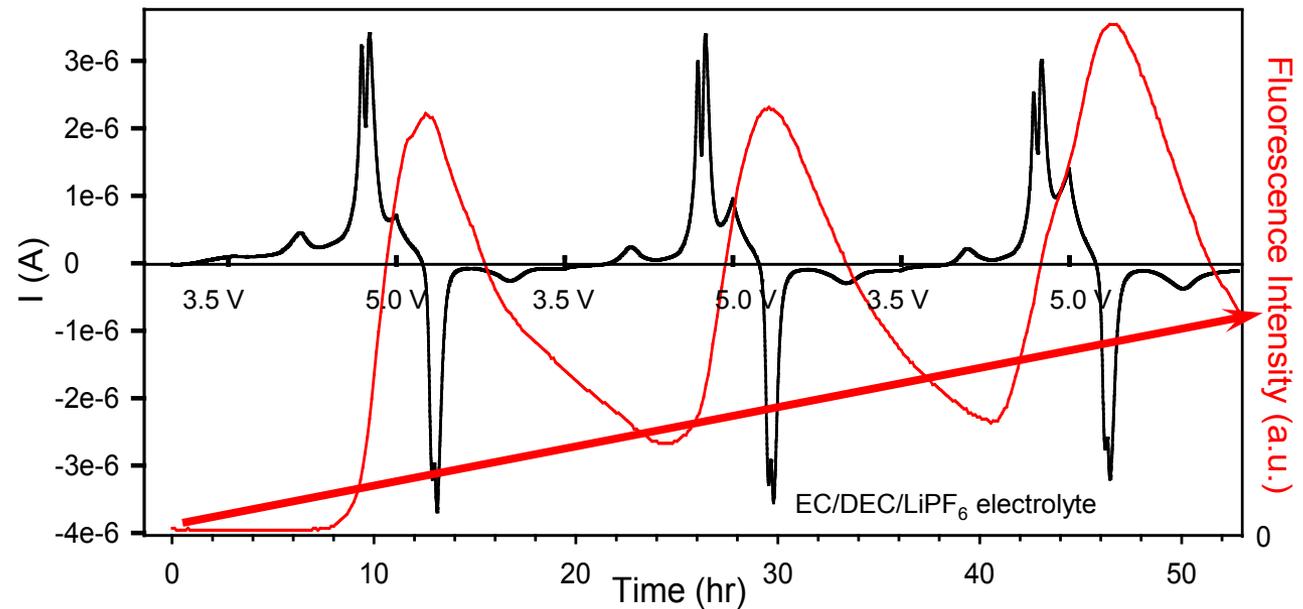
In Situ Fluorescence Spectroscopy of $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ Single Particle Electrode

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 $\lambda = 488 \text{ nm}$)



***In situ* Fluorescence Spectroscopy**



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

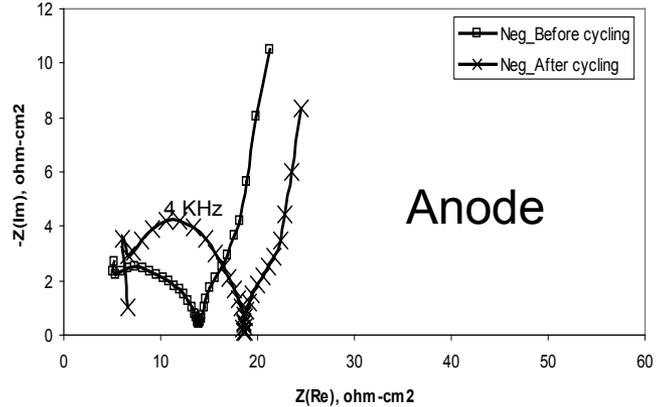
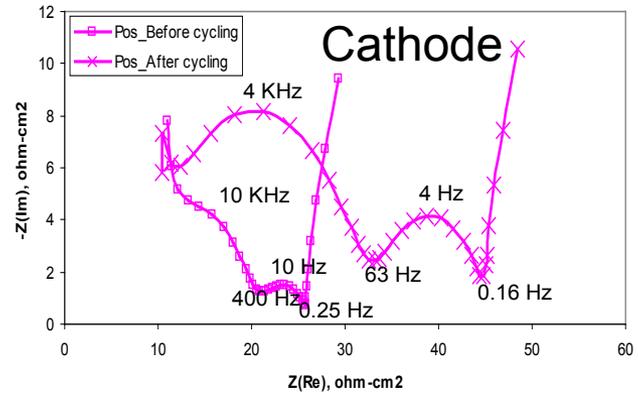
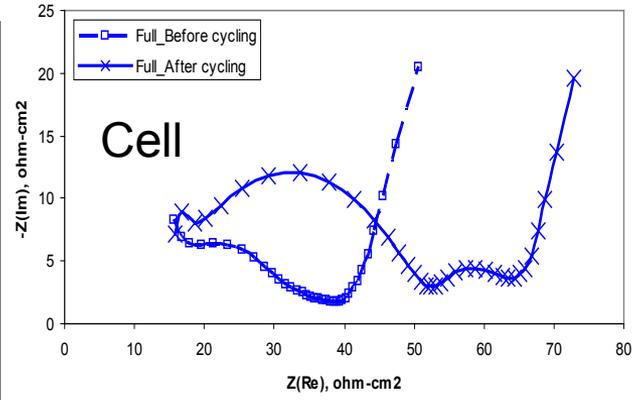
Impedance Spectroscopy of ABR Baseline Cells

Positive Electrode:	Negative Electrode:
86 %wt Toda-HE-5050 NMC	89.8 %wt ConocoPhillips: CGP-A12 graphite
8%wt Solvay 5130 PVDF binder	6%wt KF-9300 Kureha PVDF binder
4%wt Timcal SFG-6 graphite	4 %wt Timcal Super P
2 %wt Timcal Super P	0.17 %wt Oxalic Acid
6.9 mg/cm ² active-material loading density	5.7 mg/cm ² active-material loading density
37.1% electrode porosity	26% electrode porosity
35-μm-thick coating	40-μm-thick coating
15-μm-thick Al current collector	10-μm-thick Cu current collector

Toda HE5050 = $\text{Li}_{1.2}\text{Ni}_{0.15}\text{Mn}_{0.55}\text{Co}_{0.1}\text{O}_2$ electrolyte EC:DEC 1:2 1.2M LiPF_6

EIS spectra, 30 C, 100 kHz-0.01Hz, data after 100 cycles between 2.5 – 4.4V at 30 C (Test data provided by ANL)

- Cycling at 30 C results in increase in high- and mid- frequency sections of impedance plots
- Degradation of the positive electrode is mainly responsible for the observed impedance rise



Degradation Mechanism of Composite Electrodes

Electronic backbone
(carbon additive and
active material)

Initial Stages

Current
Collector

Active material
primary particles

Ionic Phase

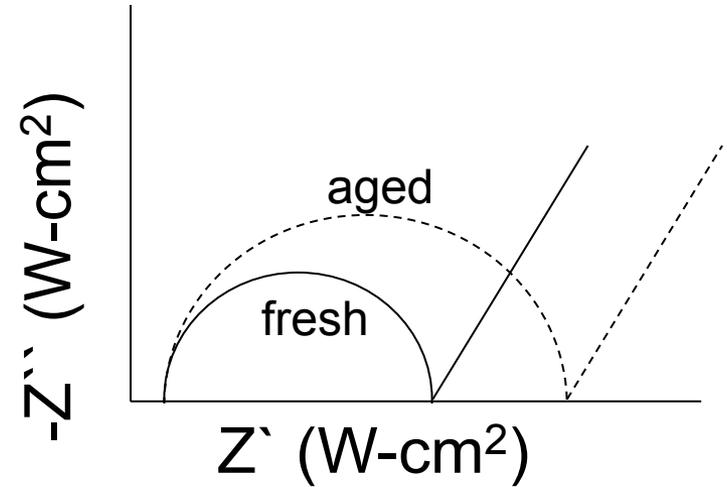
Electrolyte

After Cycling/Aging

Contact
resistance

Contact Resistance
in Composite Electrode

$$C_{res} = \frac{\rho_{carbon} + \rho_{act.mat.}}{4na} + \frac{\rho_{film}}{A}$$



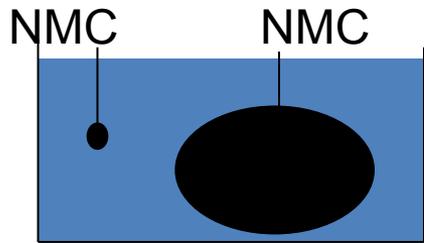
Contact resistance between active material and electrode conductive matrix is responsible for this effect

- Surface film formation
- Mechanical separation

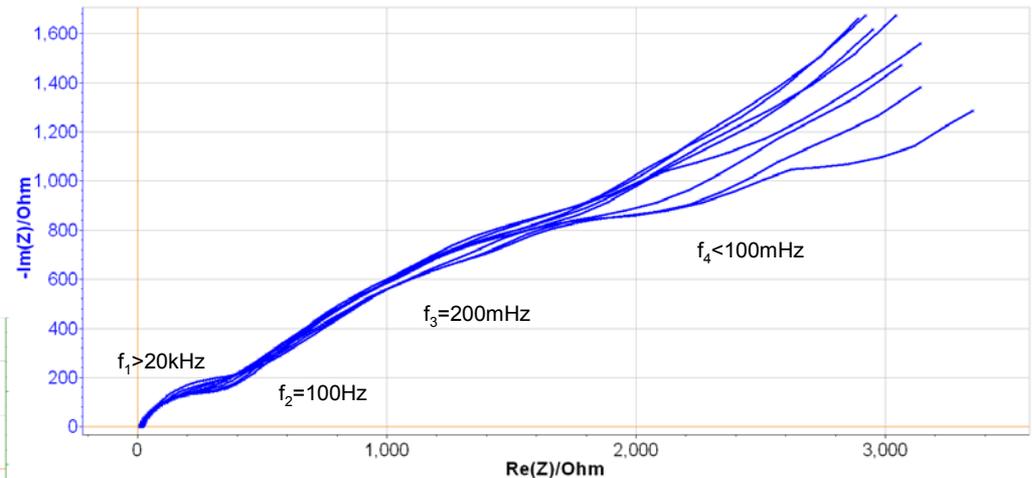
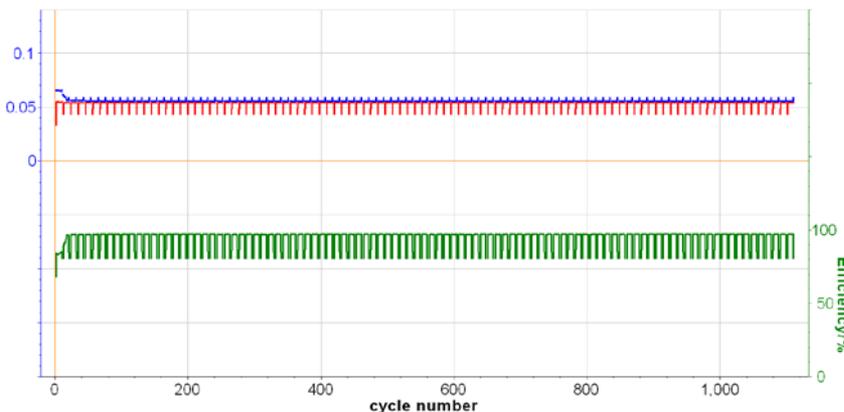
Is the impedance growth on NMC and graphite electrode interrelated i.e., do soluble electrolyte decomposition products from graphite and NMC composite electrodes contribute to cell impedance build-up?

I. The effect of chemical cross-talk in Li-ion baseline cells was studied in model NMC symmetric cells

Small NMC electrode was cycled against oversized partially charged NMC counter electrode for 1200 cycles; small electrode impedance was monitored continuously



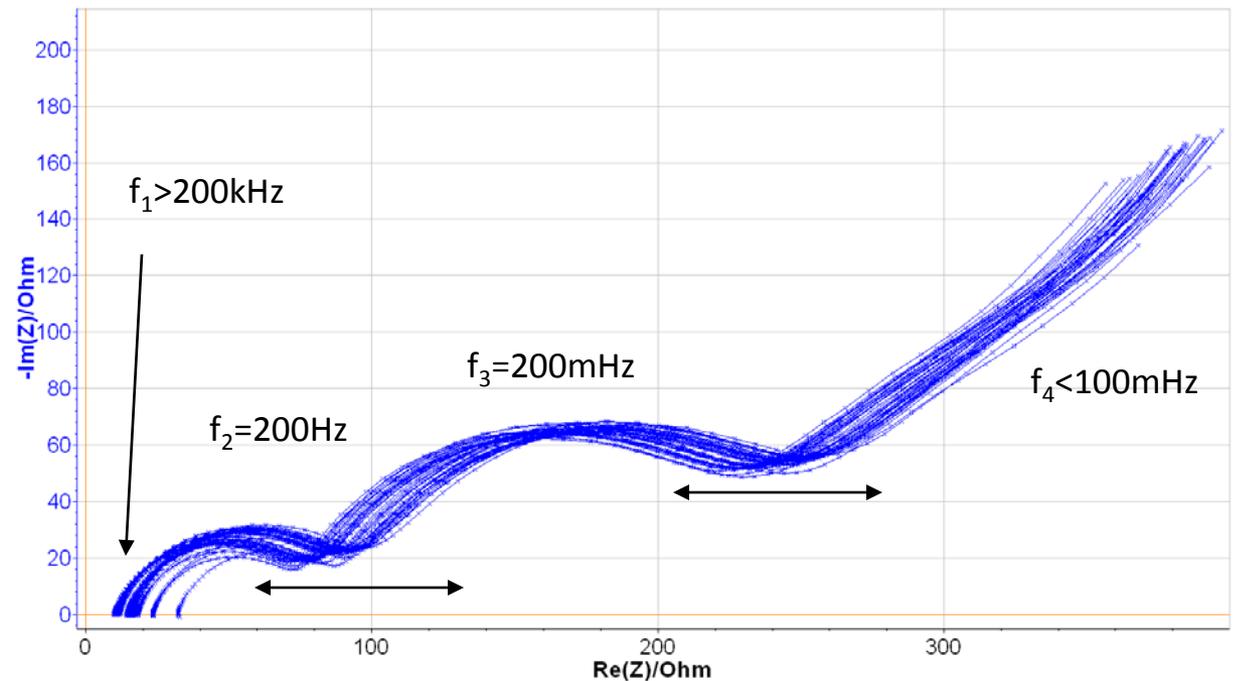
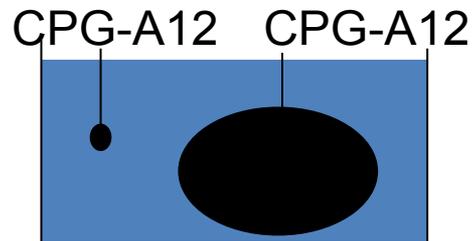
— Q charge vs. cycle number # — Q discharge vs. cycle number — Efficiency vs. cycle number



The charge-discharge capacity and impedance of cycled NMC electrode has not changed substantially after 1200 cycles

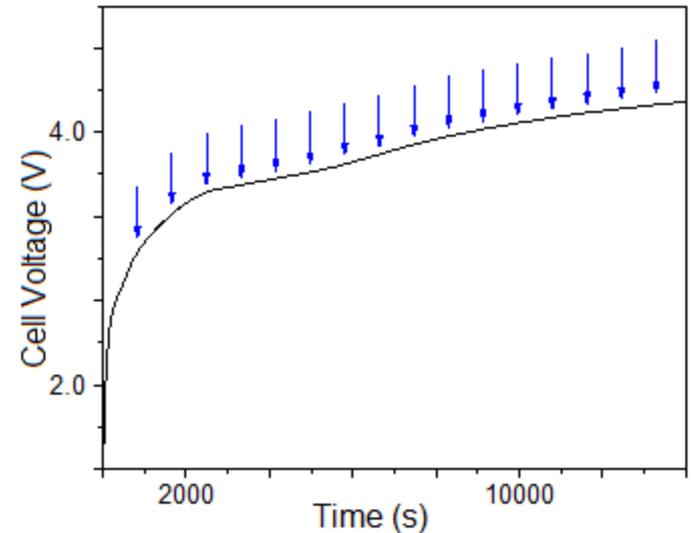
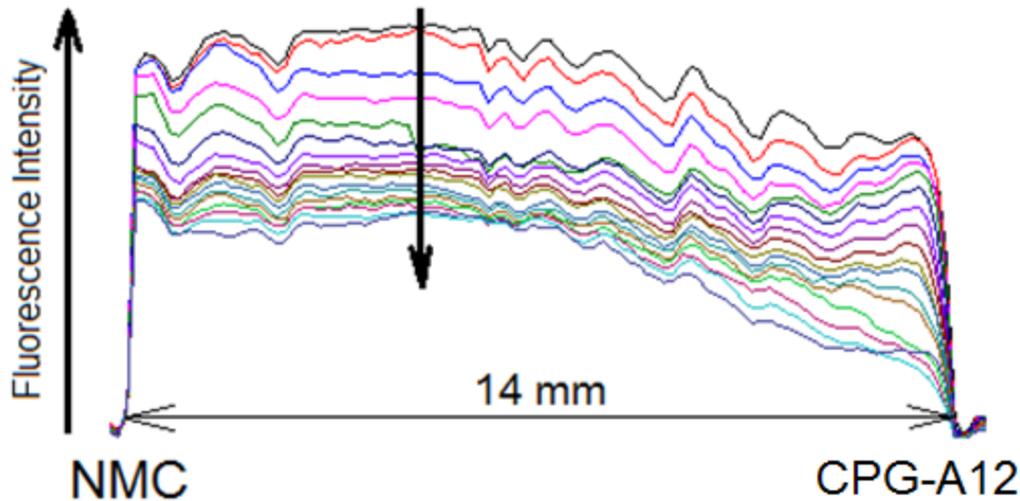
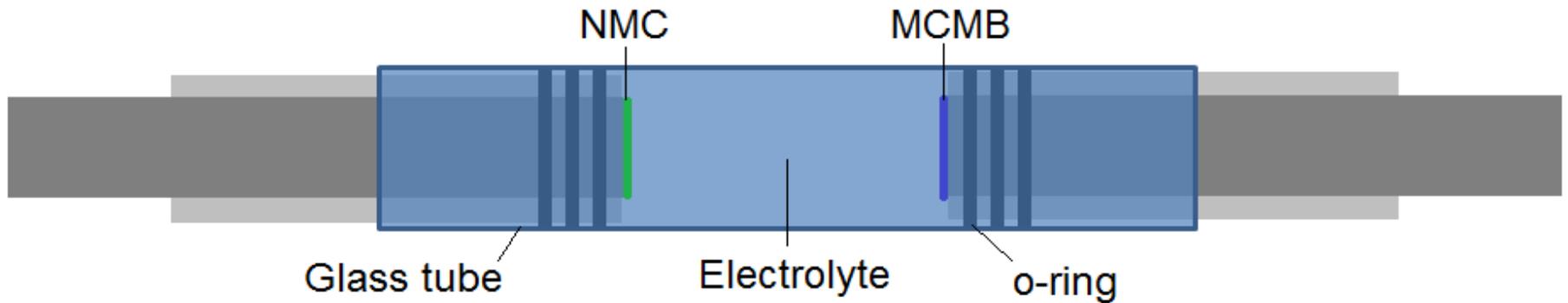
II. The effect of chemical cross-talk in Li-ion baseline cells was studied in model CPG-A12 graphite symmetric cells

Small CPG-A12 electrode was cycled against oversized pre-charged CPG-A12 counter electrode for 420 cycles; small electrode impedance was monitored continuously



The charge-discharge capacity and impedance of cycled CPG-A12 electrode have not changed substantially after 420 cycles either

In Situ Fluorescence Studies of Chemical Cross-Talk in Model Li-ion Cell

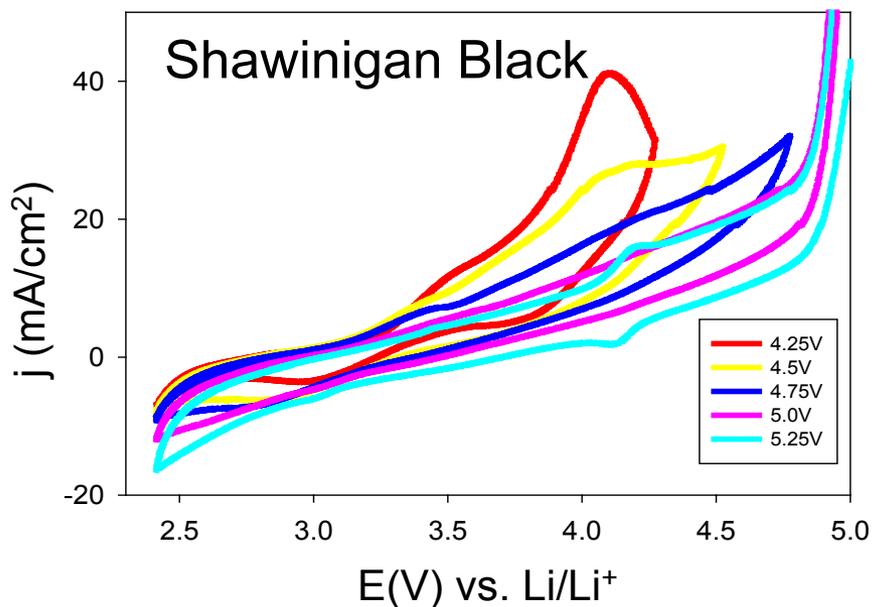
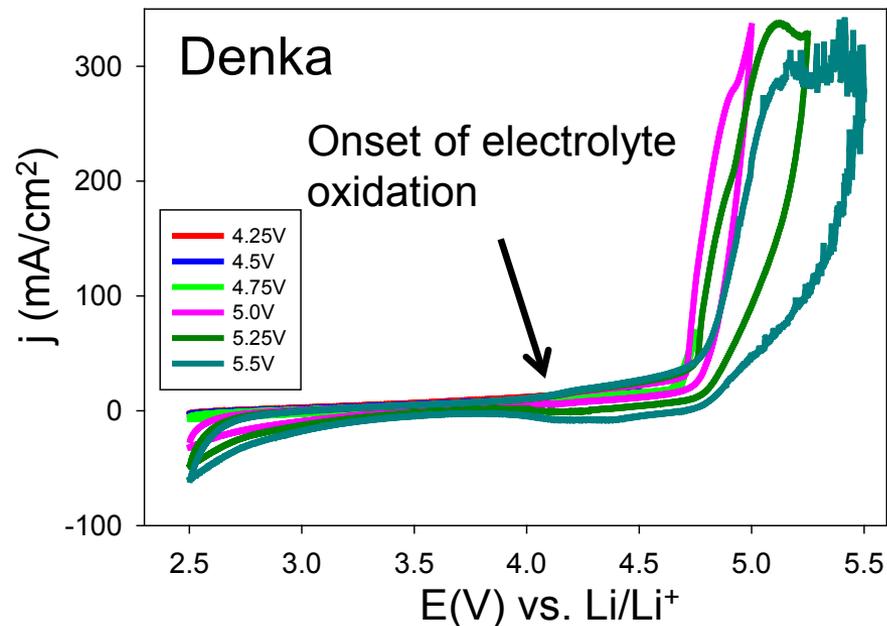
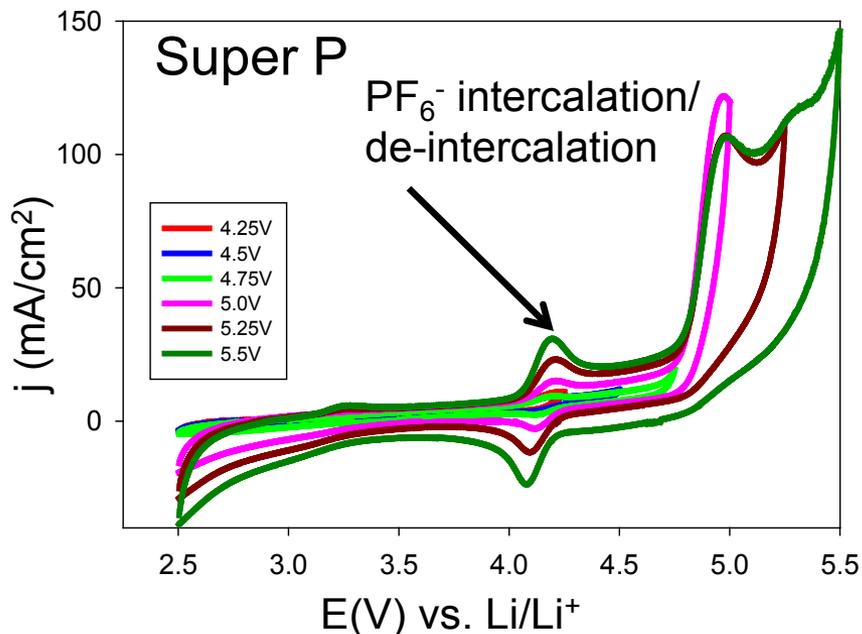


Fluorescent species are produced at the cathode and consumed at the anode during cycling

Summary I

- The gradual impedance growth in baseline cells upon cycling is not observed in symmetric cells with NMC or CPG-A12 electrodes
- Fluorescent species that are generated homogeneously in the electrolyte and on the cathode at high potentials likely contribute to the cell impedance rise
 - Chemical cross-talk between cathode and anode was observed *in situ* via fluorescence intensity variations
 - Composition of the SEI layer on the anode is most likely affected by the reduction products of fluorescence compounds
 - Unbalanced side reactions on the cathode and anode contribute to the Li inventory shift in baseline cells

Electrochemical Activity of CB Additives

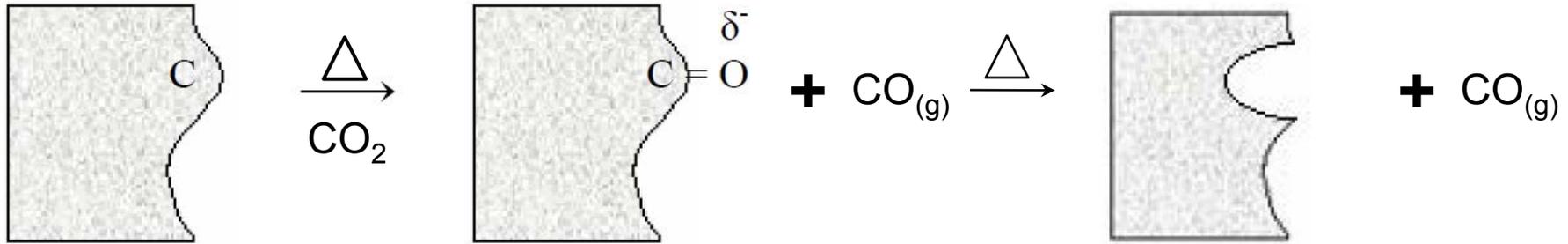


- PF₆⁻ intercalation at ~4.1 V vs. Li/Li⁺ leads to degradation of sp²-carbons
Seel et al. J. Electrochem. Soc. 147, 892 (2000)
- Electrolyte oxidation on carbon black additives limits the use of high-voltage cathode materials

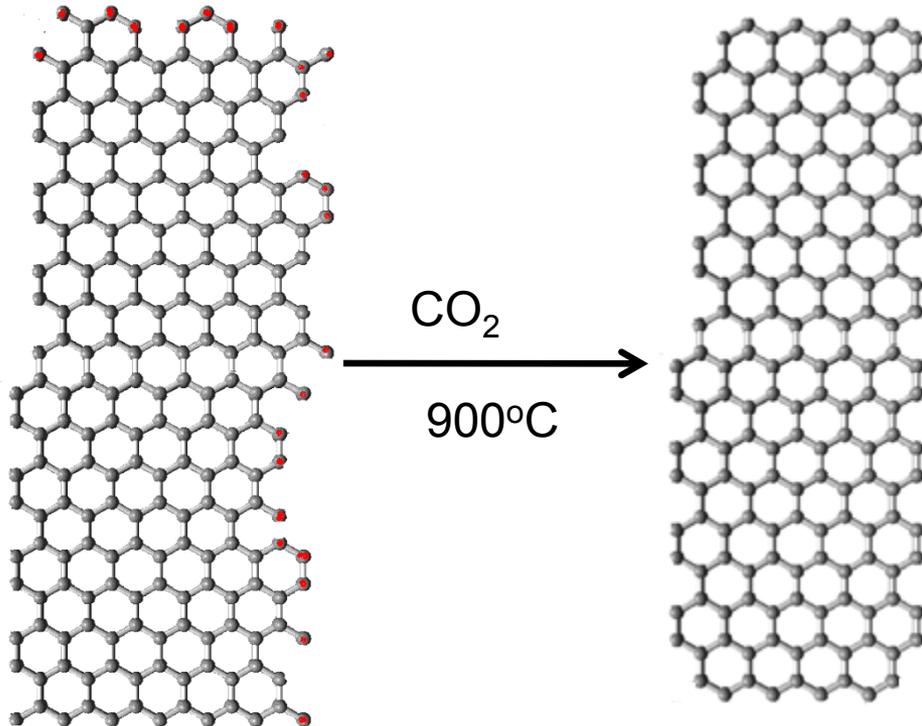
Electrode composition: 90% carbon, 10% PVdF,
1.2 M LiPF₆ EC/EMC (3:7) electrolyte

Surface Treatment of CB Additives

Formation of Porous Morphology



Surface Structure Modification

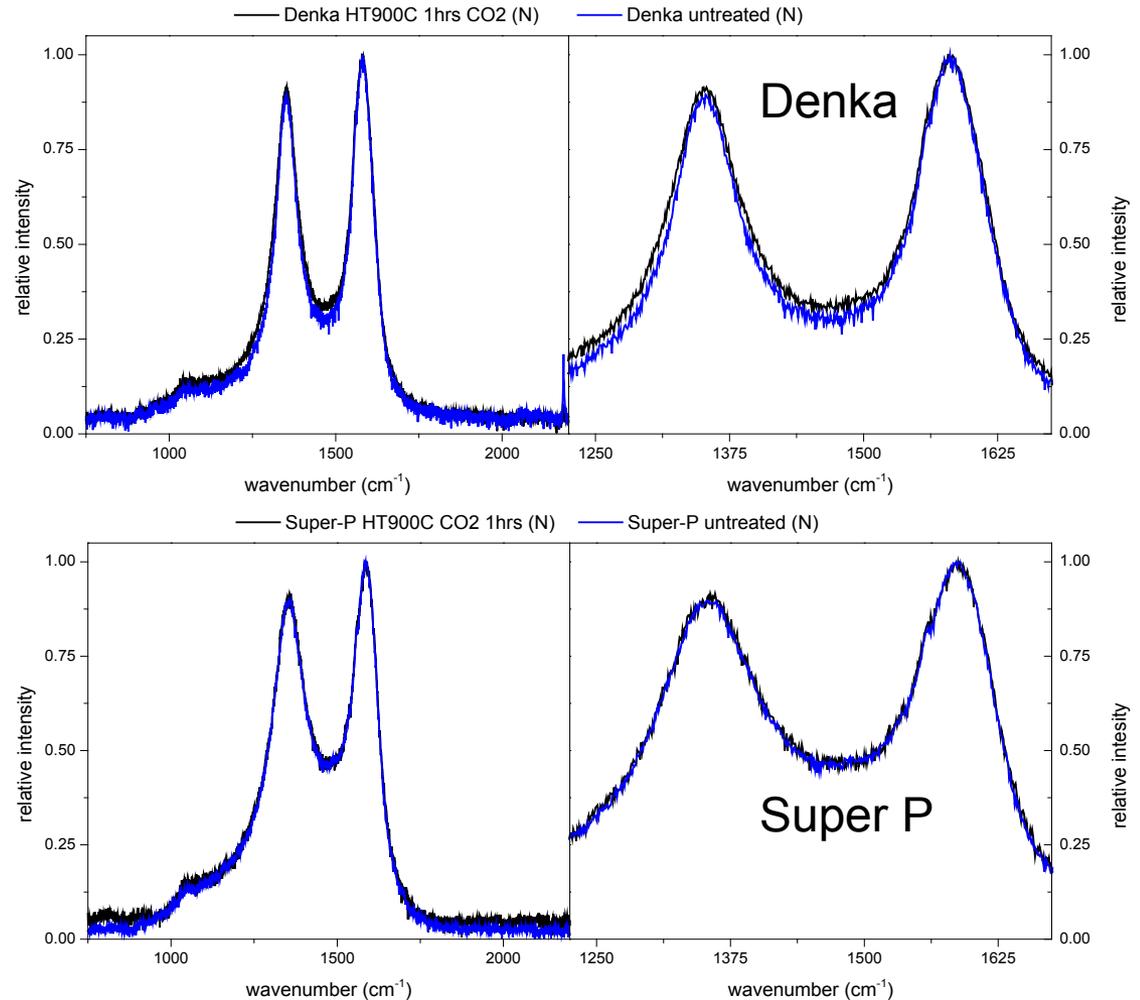
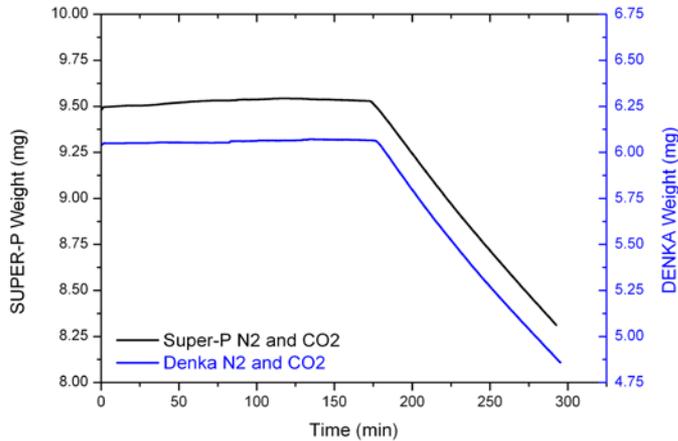


- Electronic states of graphite ribbons depend on the edge shapes
- CO_2 and carbon synproportionation reaction tends to remove carbon edge atoms with high electronic density
- Electronic states of edge carbon atoms determine electrocatalytic activity of carbon vs. organic electrolytes

CO₂ Surface HT Treatment of CB Additives

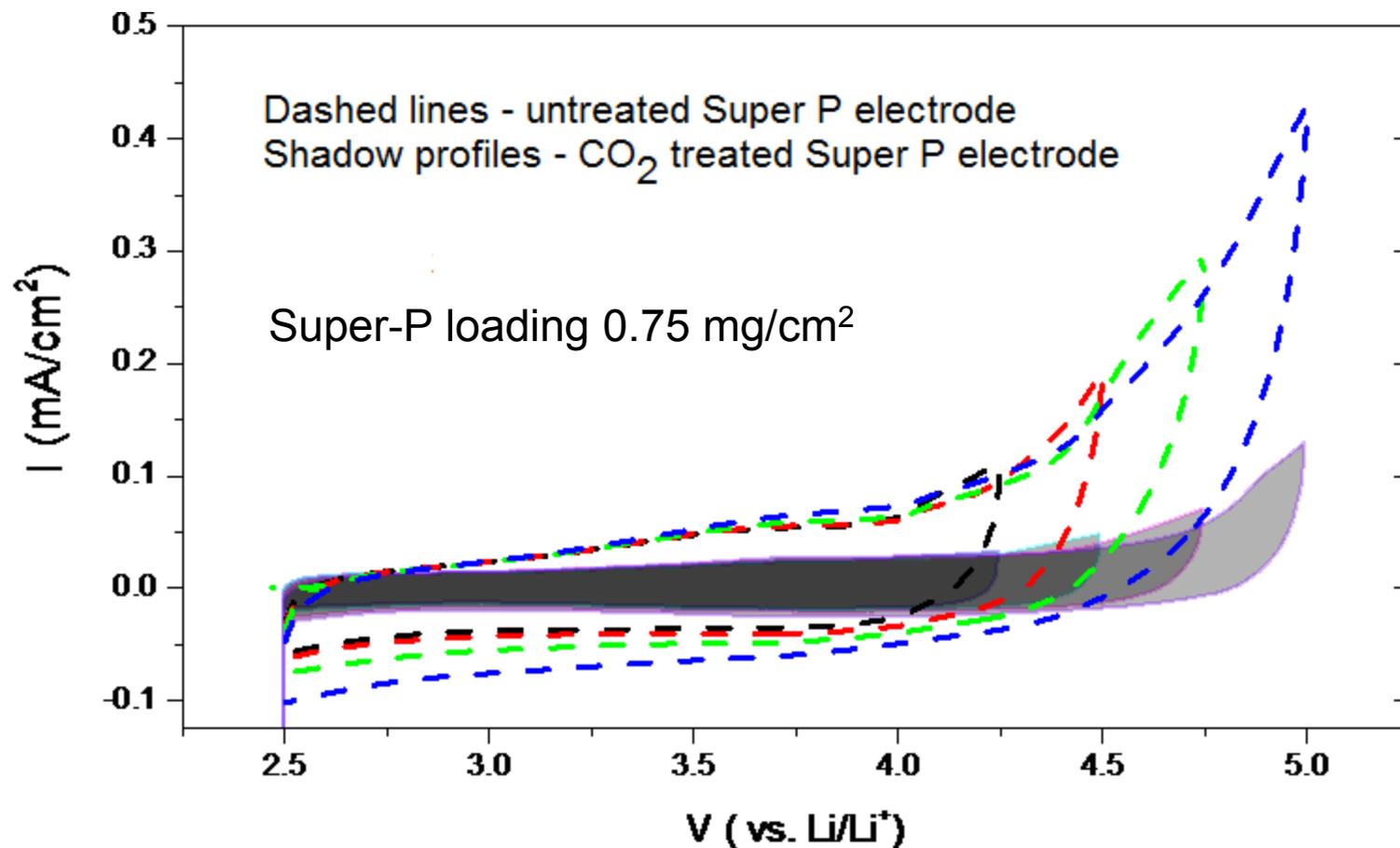
Raman Spectroscopy

TG Analysis



- Various CB additives show very similar reactivity toward CO₂ at 900°C
- CO₂ surface treatment at 900°C has no visible effect on the bulk structure of commercial carbon black additives

Electrochemical Activity of Modified CB Additives



- Higher onset potential for electrolyte decomposition for the CO₂ surface-treated carbon black electrode
- Lower electrolyte reduction current at comparable mass loading and similar surface area

Summary II

- PF_6^- intercalation in carbon black additives and electrolyte oxidation on carbon black additive limit the use of high-voltage cathode materials
- The HT CO_2 activation of commercial carbon black additives process effectively suppresses unwanted side reactions in organic carbonate electrolytes
 - Removal of oxygen surface groups (carbonyl, carboxyl, hydroxyl, *etc.*), which may promote electrolyte oxidation
 - CO_2 and carbon synproportionation reaction tends to remove carbon edge atoms with high electronic density

Planned Future Work

- Continue studies of degradation modes of high-voltage cathodes
 - Continue search for remedies that decrease irreversible capacity losses and improve coulombic efficiency during cycling
 - Reduce the irreversible charge required to form surface 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