Electrochemistry Diagnostics of Baseline and New Materials

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Project ID # ES033

Overview

Timeline

- LBNL carried out diagnostics in the ATD Program since its 1999 inception
- ABRT Program began October 2008
- LBNL role expandend beyond diagnostics in FY 2009: Chen & Richardson (overcharge protection), Battaglia (testing BATT materials), and Kostecki/Richardson (materials)
- Project will be terminated in 09-2013

Budget

- FY 2012 diagnostics/materials funding $600K
- FY 2013 diagnostics/materials funding $600K

Barriers adressed

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

Partners

- ANL, BNL, INL
- Dan Abraham is the ABRT Program diagnostic lead
- Venkat Srinivasan (LBNL) is the LBNL electrochemistry lead
- Electrode manufacturing co-op with Vincent Battaglia, LBNL and Bryant Polzin, ANL

Objectives

Task 1.1

- Increase specific energy on the cell level by addressing the impact of elevated potentials on carbon blacks
  - Explore structural and chemical changes of carbon black additives utilized at elevated potentials and investigate attempts to reduce side reactions occurring
  - Explore surface modification methods to improve stability of carbon blacks additives in high-energy Li-ion systems

Task 2.4

- Study degradation mechanism(s) in the PHEV test cells and at the system and cell components level
- Investigate the mechanism of chemical cross-talk between electrodes and its implication for electrochemical performance and lifetime of high-energy Li-ion systems

Milestones

Task 1.1

- Develop new electrochemically stable carbon black additives for high-voltage composite electrodes. (July 2013 – on track)

Task 2.4

- Determine the mechanism of chemical cross-talk in high-energy Li-ion systems and evaluate its impact on the cell performance (September 2013 – on track)
- 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 efficent 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
- New improved materials are transferred for evaluation in full battery configuration in ABR Program cell development & testing facilities (Battaglia, LBNL; Polzin, ANL)

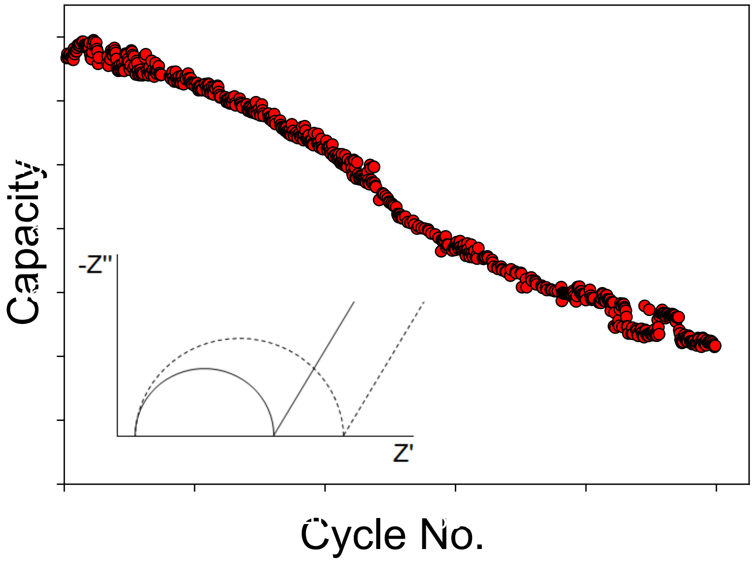
Approach

- Strategies to minimize irreversible capacity losses
  - Determine the mechanism of carbon additive degradation and migration at high potentials and in high voltage composite electrodes
  - Improve carbon black stability at high potentials via surface treatment
- 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 FY2012 and FY2013)

Technical Accomplishments

1. Improved carbon black additive was synthesized and tested in selected composite high-voltage positive electrodes. Enhanced lifetime and reversibility of modified electrodes have been demonstrated.
   - Invention disclosure/patent application filled by LBNL.
   - LBNL Technology Transfer grant obtained to commercialize the technology
2. The mechanism of chemical cross-talk in high-energy Li-ion cells has been determined and possible implications for cell electrochemical performance evaluated

Li-ion Cells – Modes of Failure

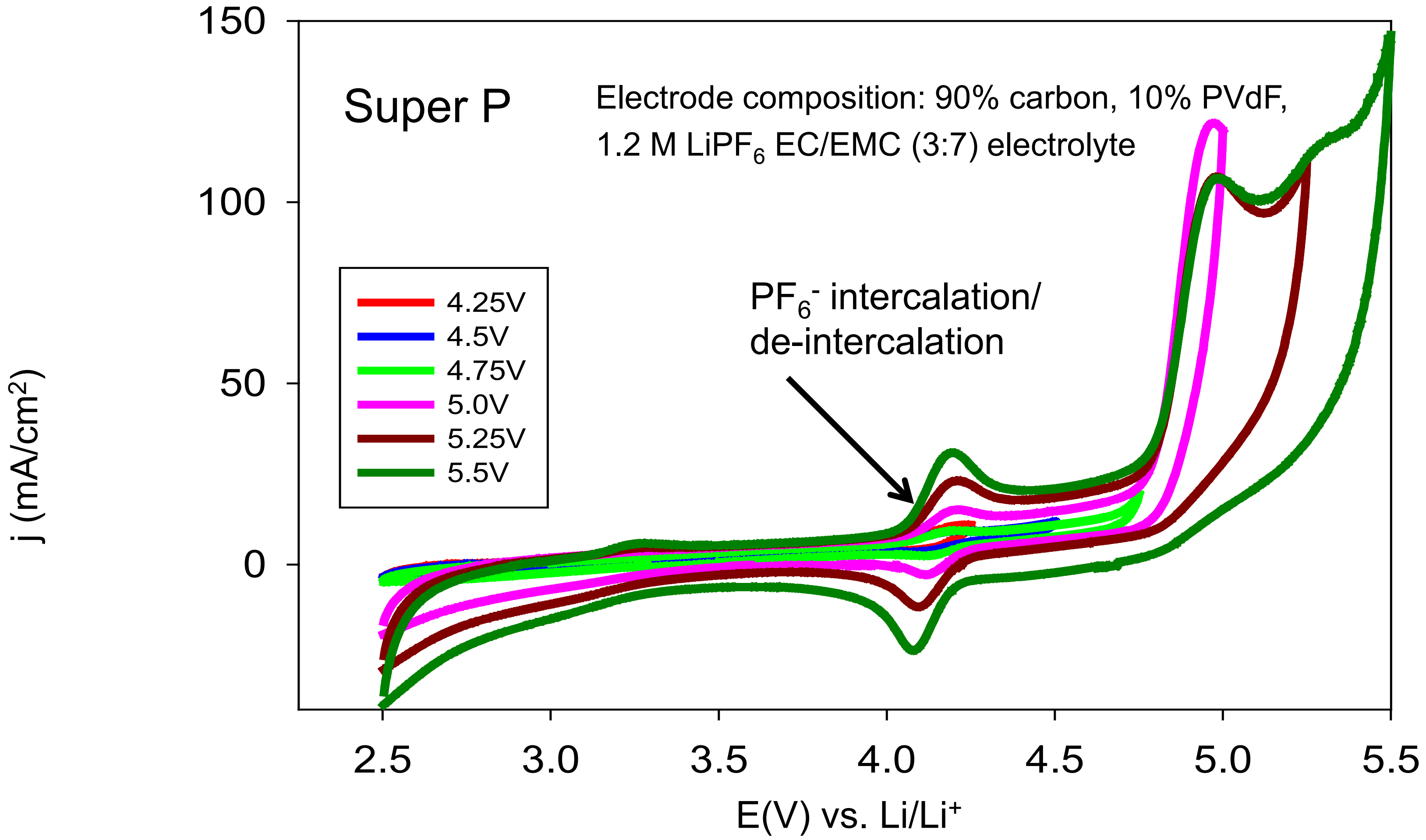


- *Thermodynamically unstable*
- *Significant part of the cell capacity loss can be attributed to shift in cell lithium inventory*
- *Active material loss and poor utilization are also responsible for irreversible capacity losses*

- 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?

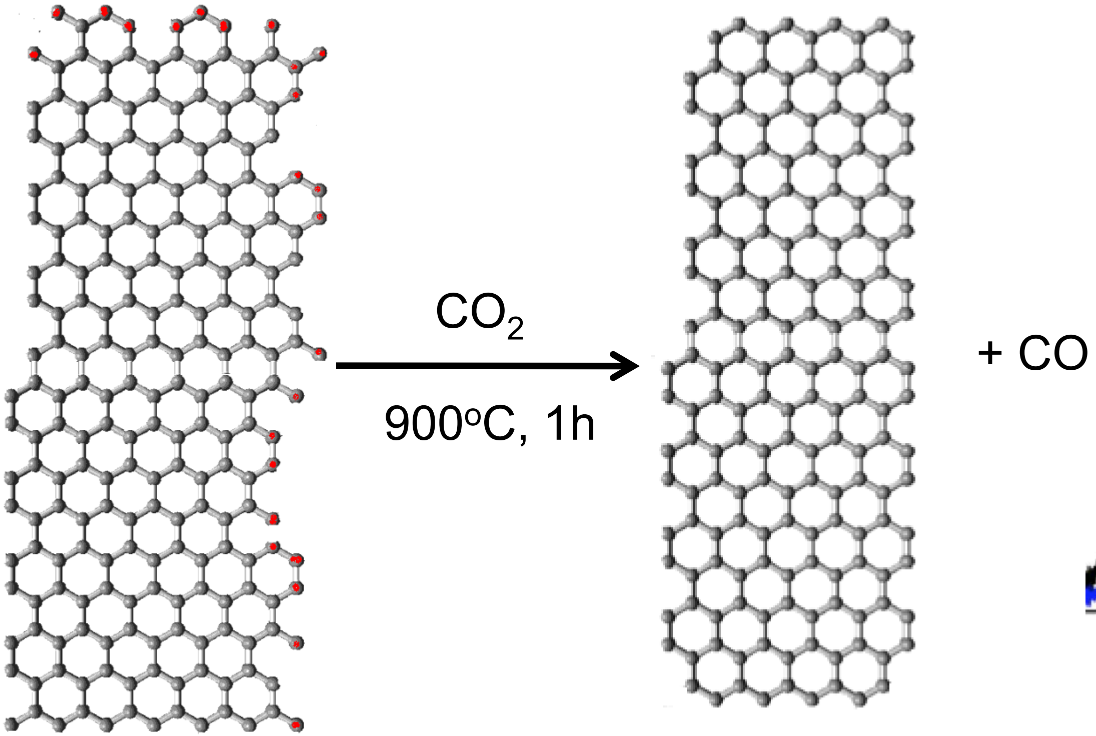
Electrochemical Activity of CB Additives



- PF$_6^-$ intercalation at ~4.1 V *vs.* Li/Li$^+$ leads to degradation of sp^2-carbons *Seel et al. J. Electrochem. Soc.* ***147****, 892 (2000)*
- Electrolyte oxidation on carbon black additives contributes to coulombic inefficiency of limits the use of high-voltage cathode materials

Surface Treatment of CB Additives

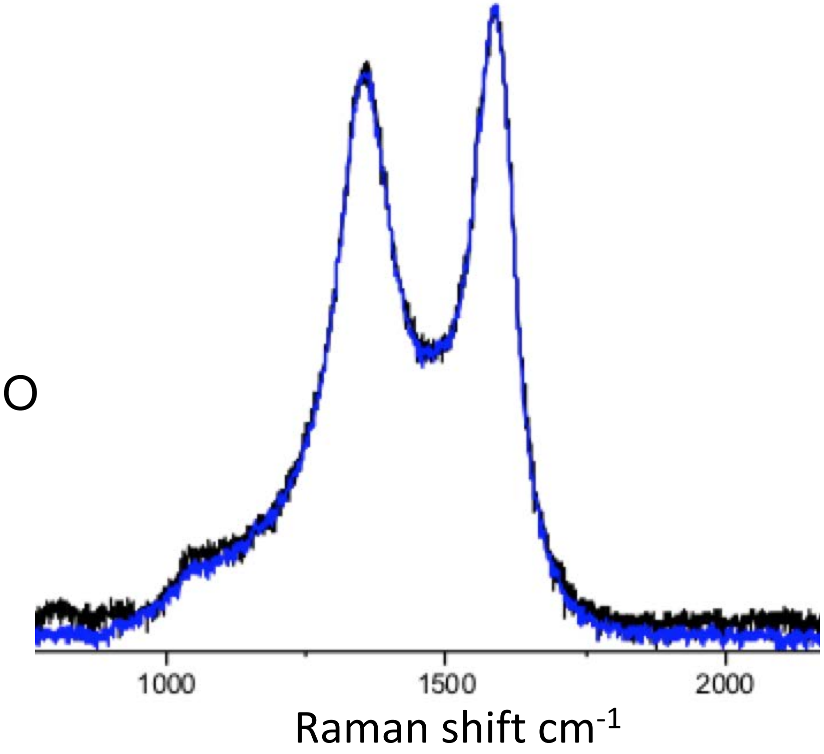
CB Structure and Morphology Studies



CO_2

900°C, 1h

+ CO

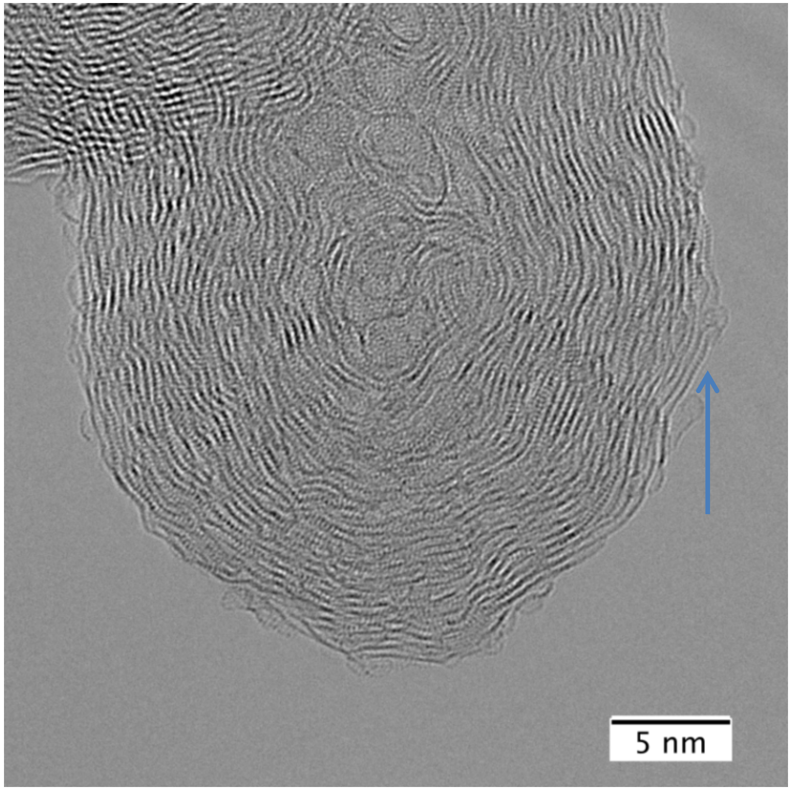


- Electronic states of graphite ribbons depend on the edge shapes
- Electronic states of edge carbon atoms determine electrocatalytic activity of carbon *vs*. organic electrolytes
- Heat-treatment leads to synproportionation reaction of carbon edge atoms and CO_2 whereas bulk structure remains unaffected

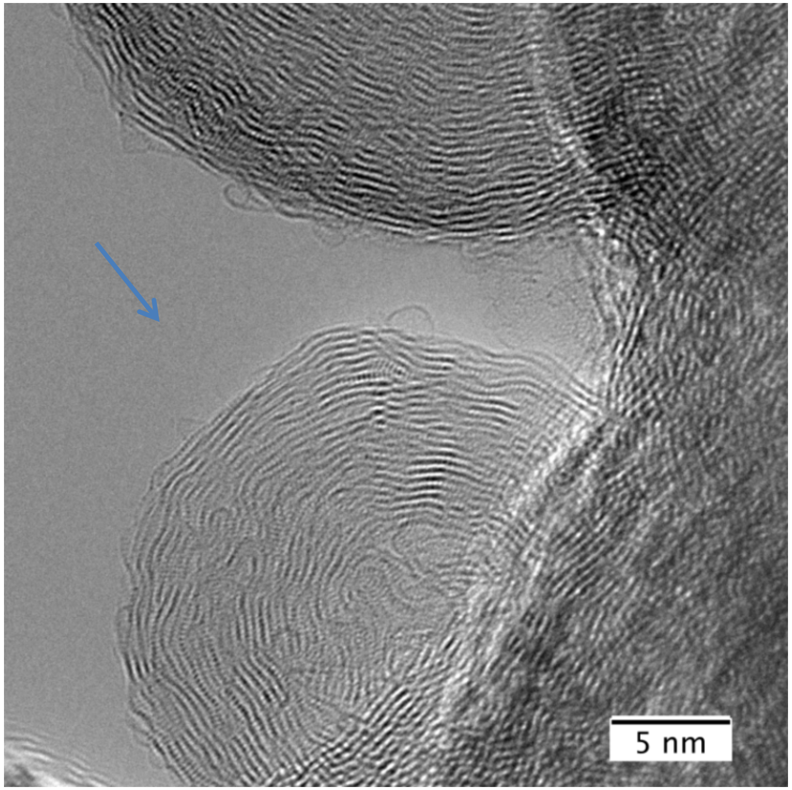
Surface Treatment of CB Additives

CB Structure and Morphology Studies

Pristine



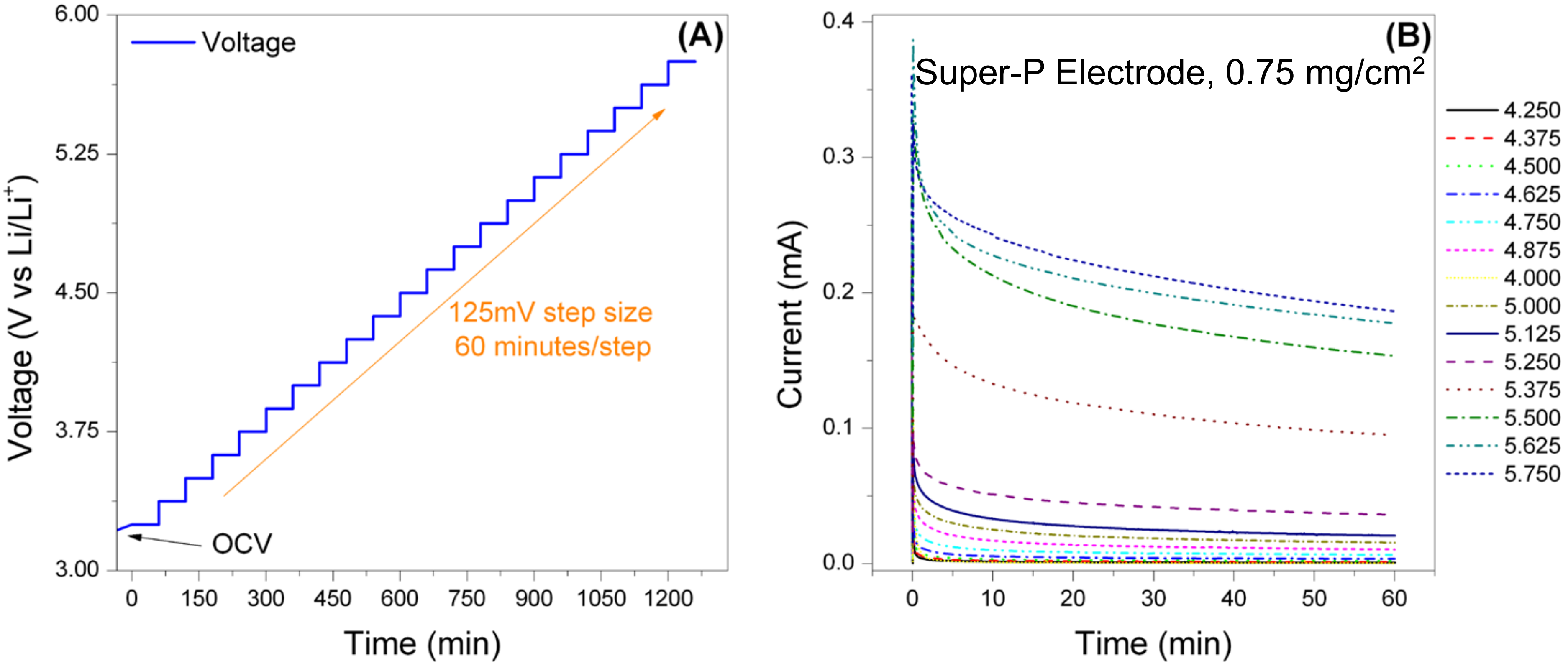
Heat treated



- Heat-treatment removes carbon edge atoms and CO_2 whereas bulk structure remains unaffected
- Prolonged HT leads to excessive surface carbon etching and surface area increase
- HT/CO_2 processing needs to be optimized for commercial carbon black additives

Electrochemical Activity of CB Additives

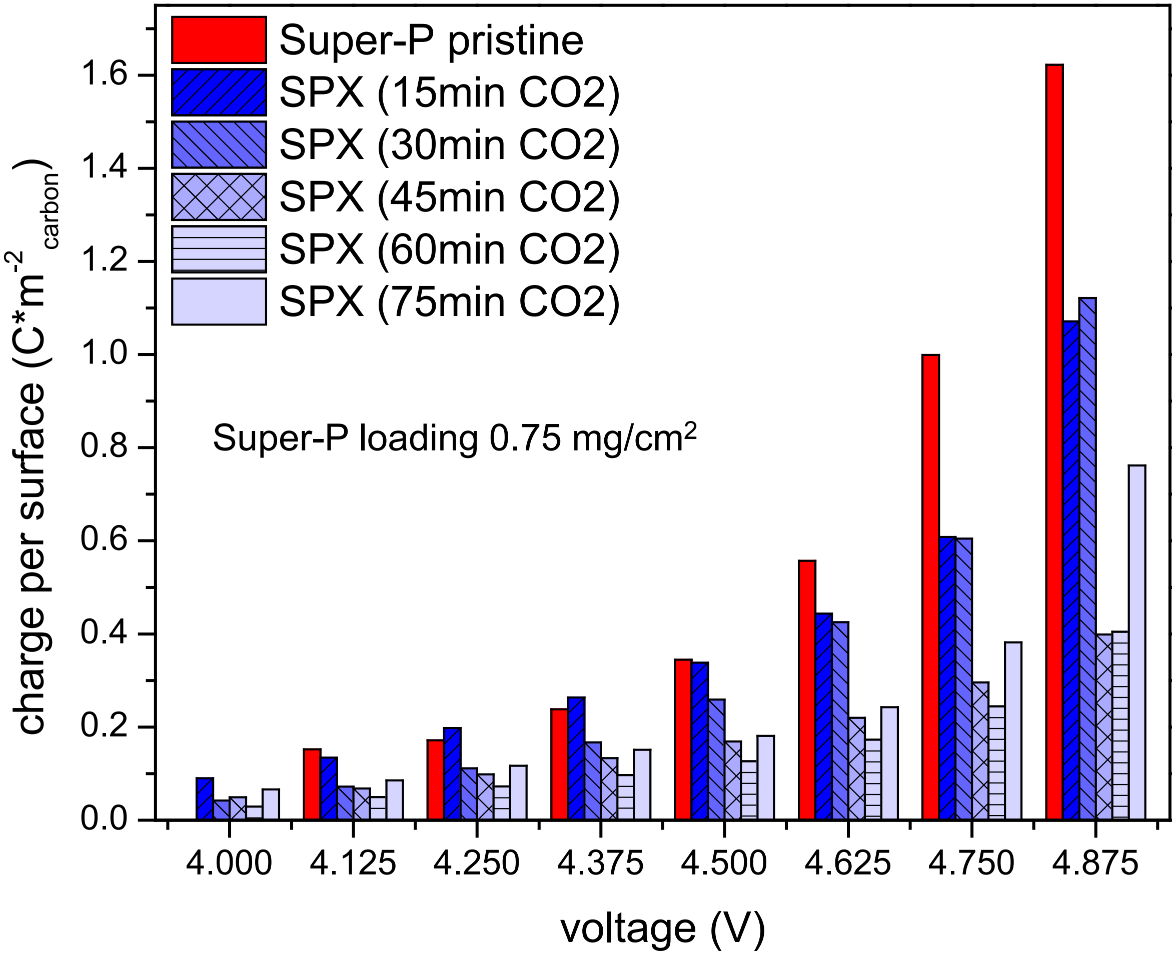
Potentiometric Measurements



Continuous electrolyte oxidation on carbon black additives at high potentials contributes to columbic inefficiency of composite positive electrodes and lithium inventory shift in high-voltage Li-ion cells

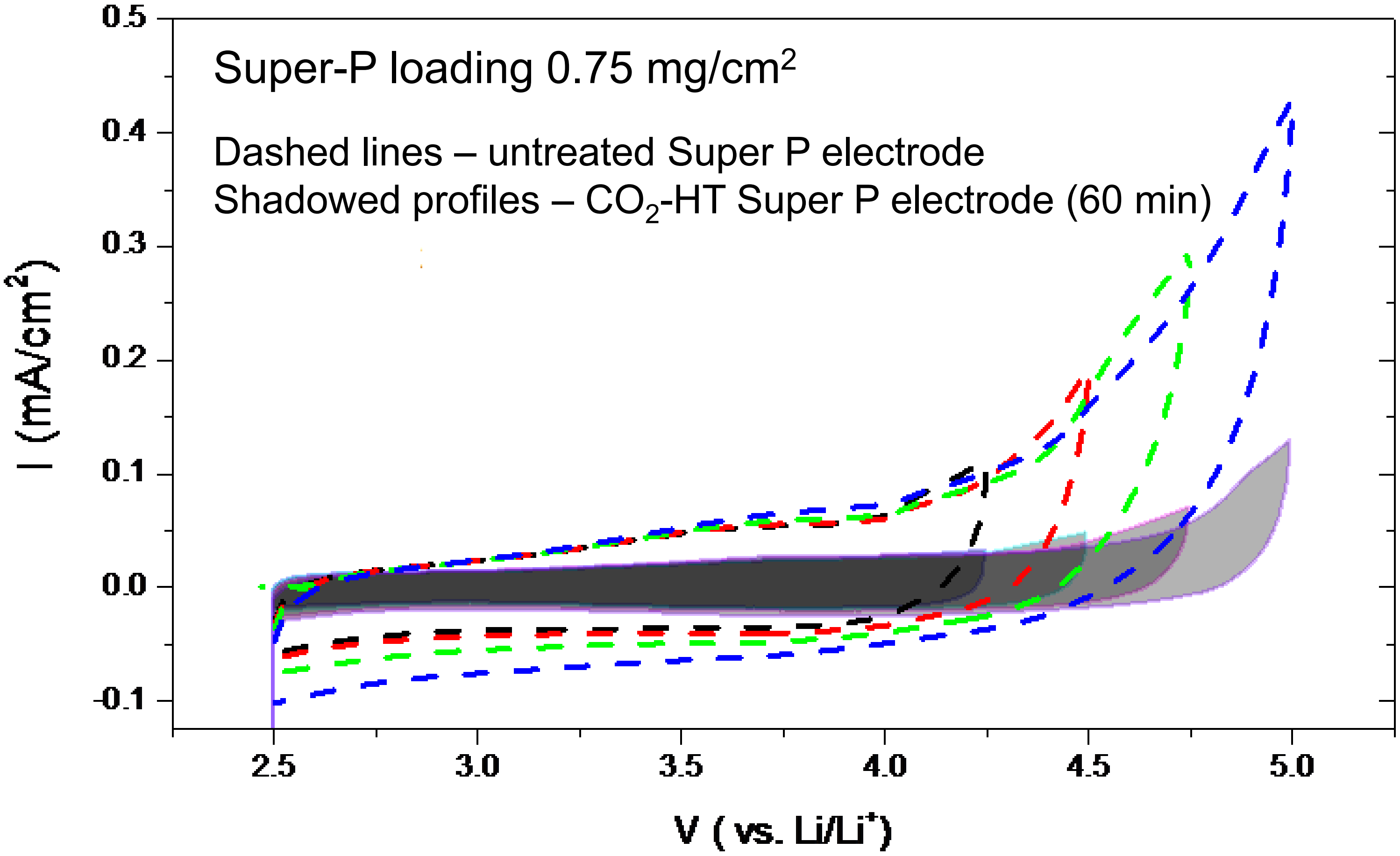
Electrochemical Activity of CB Additives

Effect of CO_2 HT Processing Time



CO_2 heat-treatment at 900°C for 45 min < t_{HT} < 60 min suppresses electrochemical activity of Super P additive most effectively

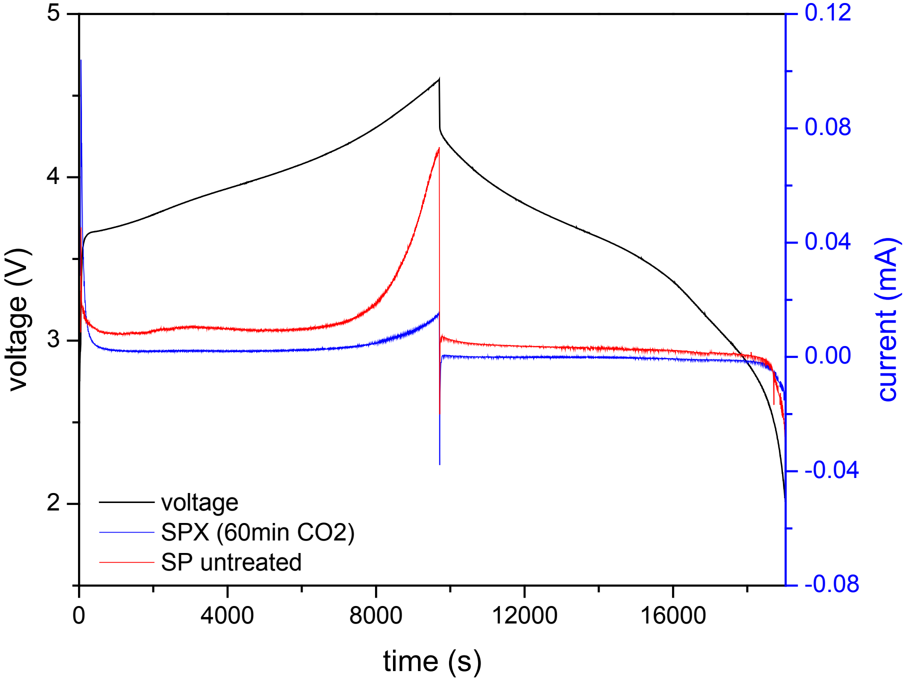
Electrochemical Activity of Modified CB Additives



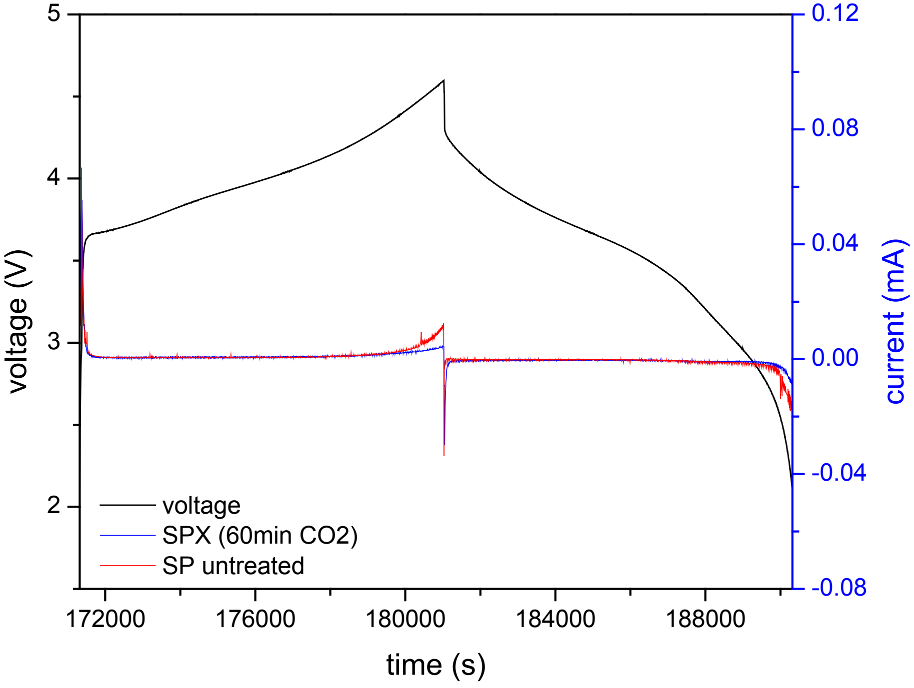
- Higher onset potential for electrolyte decomposition for the CO_2 surface-treated carbon black electrode
- Lower electrolyte reduction current at comparable mass loading and similar surface area

The Effect of CB Additive on Electrochemical Performance of Composite Electrodes

50th cycle charge-discharge profile of a full cell Toda-HE5050 ($Li_{1.2}Ni_{0.15}Co_{0.1}Mn_{0.55}O_2$) vs. graphite) was reproduced extrapolated into numerous potentiostatic steps. This potential profile was applied to the CB electrode to evaluate its current contribution

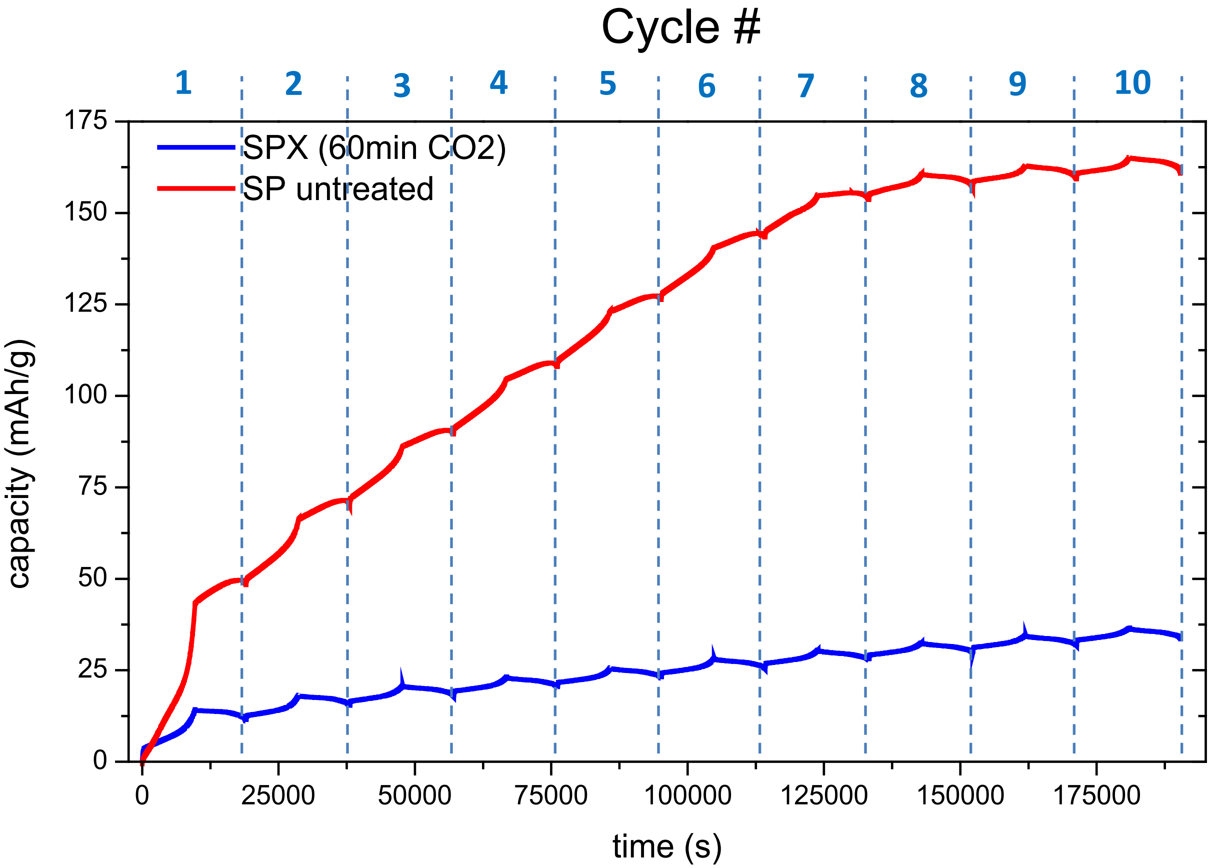


1st cycle



10th cycle

The Effect of CB Additive on Electrochemical Performance of Composite Positive Electrodes



untreated/CO_2-treated

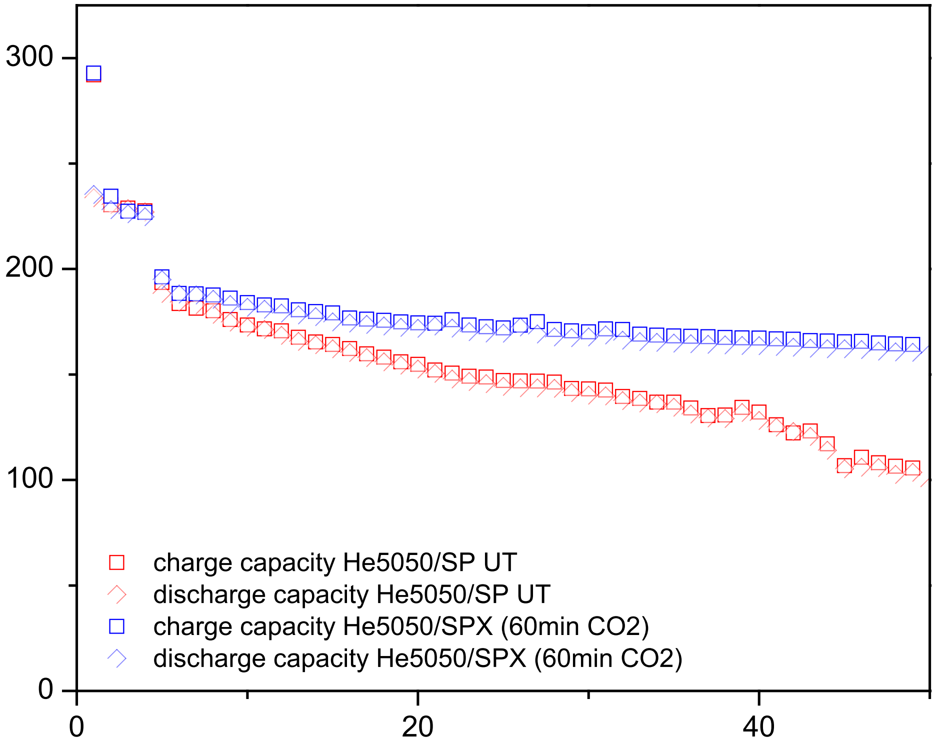
Super P electrode

- 2.5 to 4.65 V
- 1M $LiPF_6$, EC:DEC

- After 10 cycles the charge consumed in irreversible electrolyte oxidation reactions at carbon black additive corresponds to 2.7% of the overall capacity of a Li-ion cell
- CO_2 HT helps reduce impact of the unwanted side reactions to 0.3 %

Modified Carbon Black Additives for Improved High-Energy Composite Cathodes

Collaboration with V. Battaglia (LBNL) and Bryant Polzin, ANL



Electrode composition

- 88% $Li_{1.2}Ni_{0.15}Co_{0.10}Mn_{0.55}O_2$ (Toda He 5050)
- 8% PVdF (KF-1100, Kureha Co. Ltd)
- 4% Super-P Li pristine/CO_2-treated

Mass loading

9.35 mg/cm^2 for treated
8.32 mg/cm^2 for pristine
7.44 mg/cm^2 for ABR baseline (SAFT)

Cycling

4xC/12 and 50xC/3 (210 mAh/g)

Composite cathodes with modified carbon black additive display superior cycling performance and better capacity retention than baseline electrodes

Patent application submitted; received LBNL Tech Transfer grant to commercialize the technology – work is ongoing

Summary I

- Evaluated electrochemical behavior of carbon black additives in composite positive Li-ion electrode
- The HT CO_2 activation of commercial carbon black additives process effectively suppresses unwanted side reactions in organic carbonate electrolytes
- Carbon black as conductive additive in the cathode is responsible for 2.7% of the capacity loss in ABR baseline cells during the first 10 cycles
- CO_2 heat treatment reduces such irreversible losses to 0.3%
- Preliminary tests of CB-modified Toda He 5050 composite electrodes in full Li-ion cells demonstrated **extended lifetime and a higher reversibility**

Impedance Spectroscopy of ABR Baseline Cells

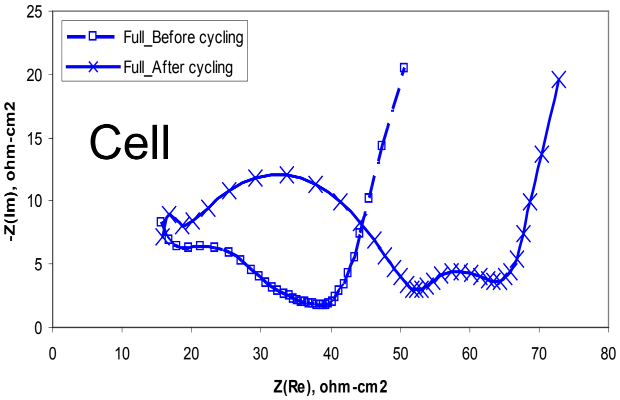
Positive Electrode:	**Negative Electrode:**
86 %wt Toda-HE-5050 NMC	89.8 %wt ConocoPhillips: CGP-A12 graphite
8%wt Solvay® 5130 PVDF binder	6%wt KF-9300 Kureha PVDF binder
4%wt Timcal® SFG-6 graphite	4 %wt Timcal Super P®
2 %wt Timcal Super P®	0.17 %wt Oxalic Acid
6.9 mg/cm² active-material loading density	5.7 mg/cm² 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

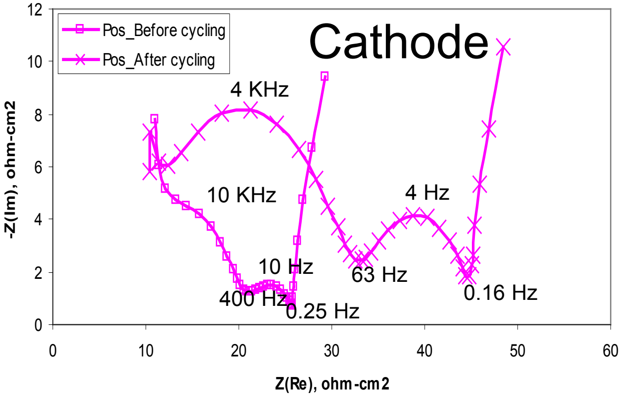
Toda HE5050 = $Li_{1.2}Ni_{0.15}Mn_{0.55}Co_{0.1}O_2$

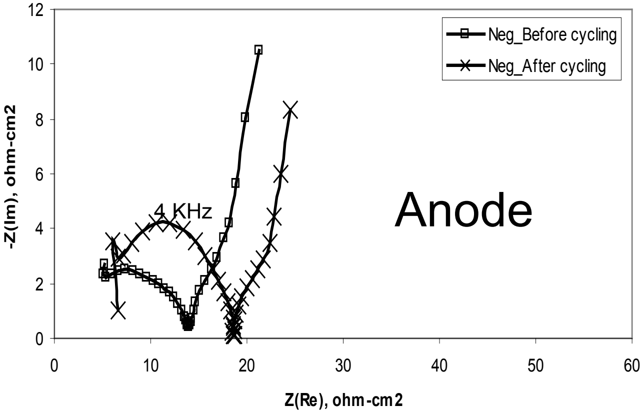
electrolyte EC:DEC 1:2 1.2M $LiPF_6$

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

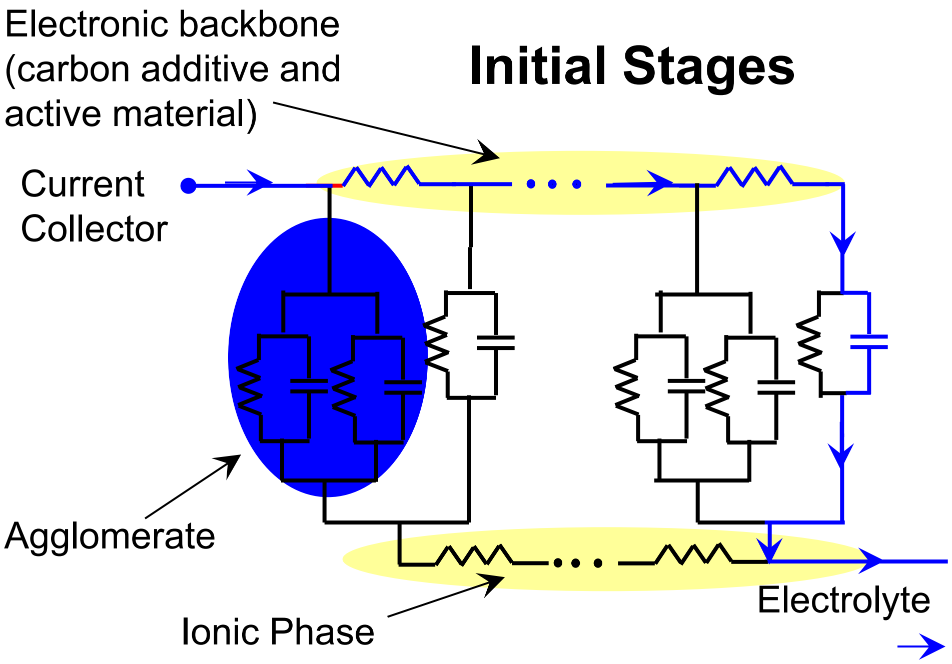






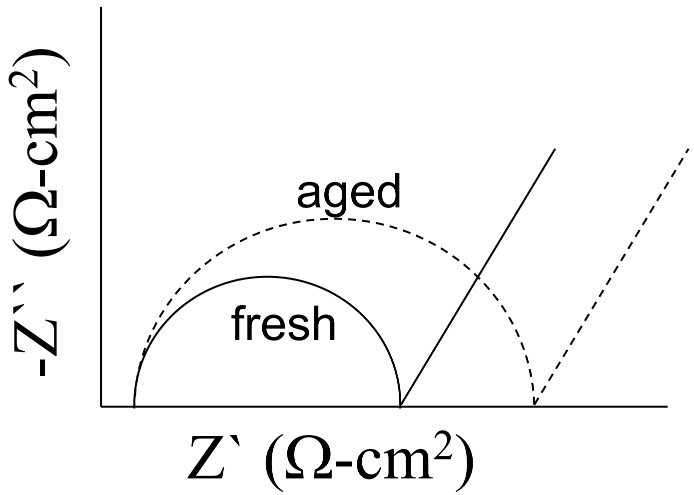
Theoretical Model for Composite Electrodes

Initial Stages

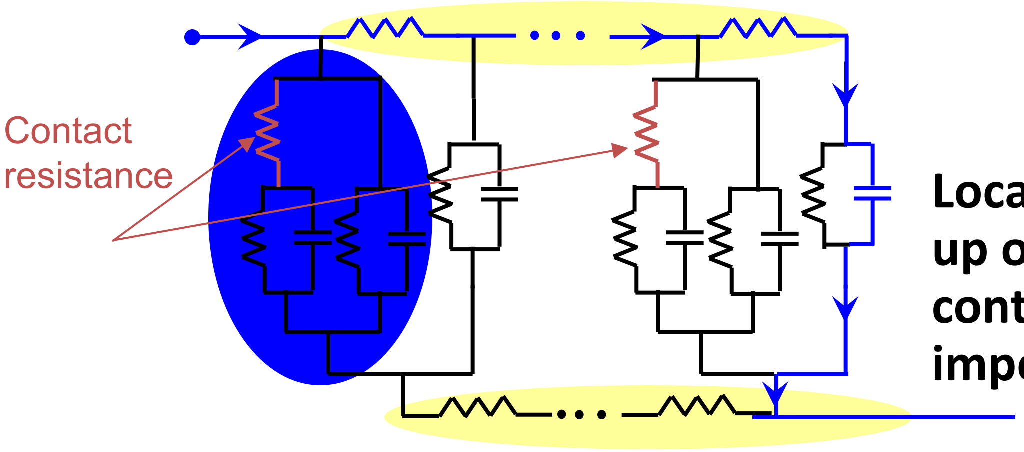


Contact Resistance
within Composite Electrode

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



After Cycling/Aging



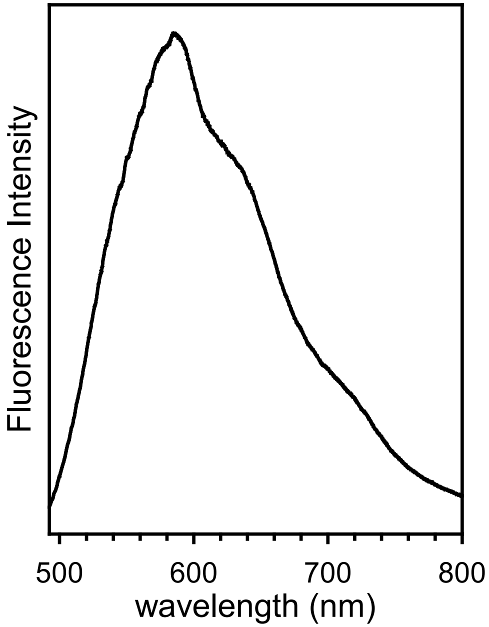
Local processes are responsible for build up of ionic and electronic barriers which contribute to composite electrode impedance rise

Fluorescence Spectroscopy of $LiNi_{0.5}Mn_{1.5}O_4$ Single Particle

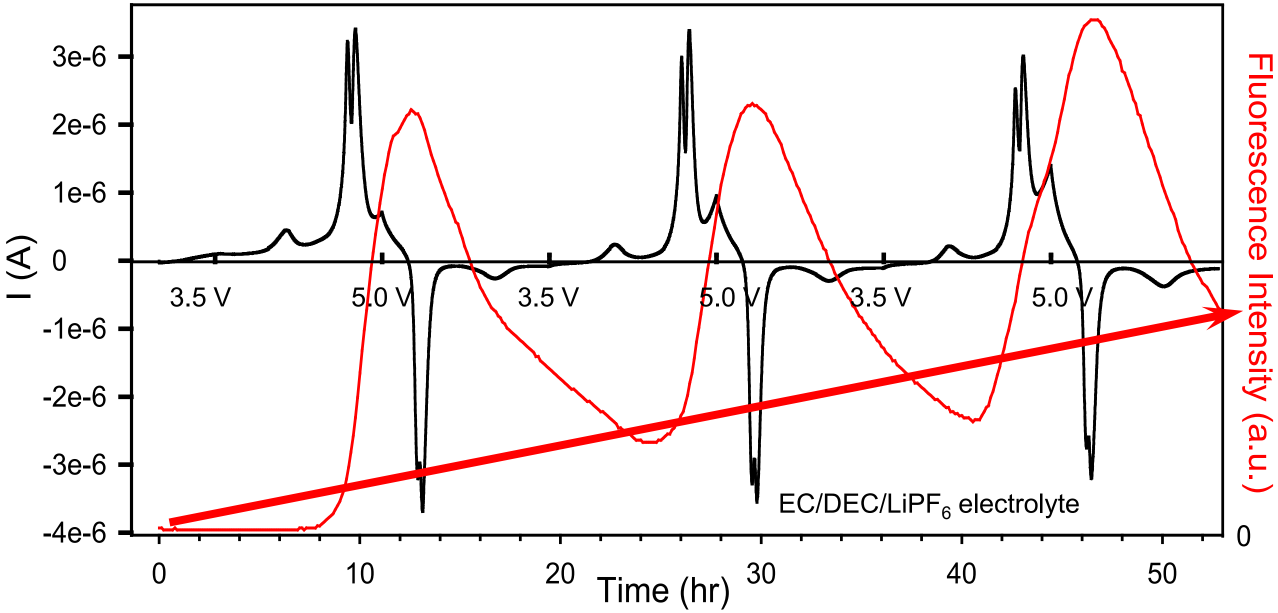
Strong fluorescence is a common phenomenon observed *in situ* and *ex situ* in cycled high-voltage cathodes. It originates from inorganic species that form during electrolyte decomposition. Fluorescence spectroscopy can be used to probe the composition and dynamics of surface film (re)formation during charge/discharge cycling

Fluorescence spectrum

(Excitation λ = 488 nm)



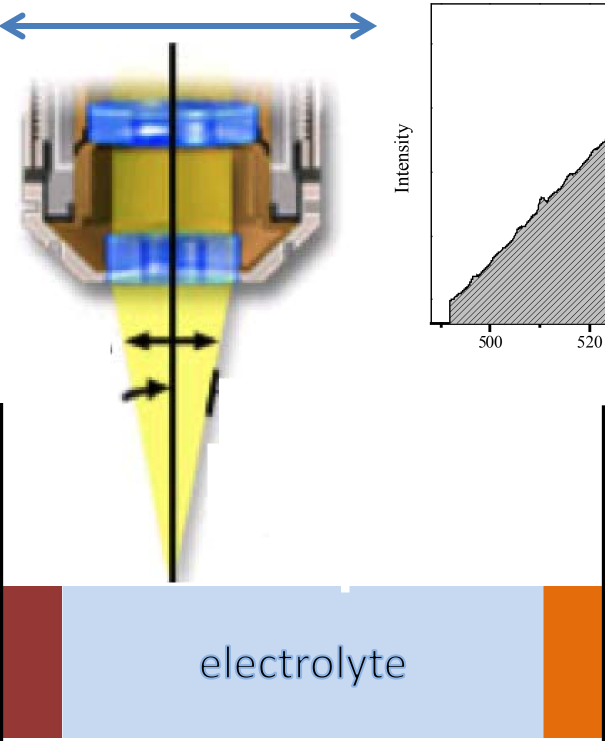
***In situ* Fluorescence Spectroscopy**

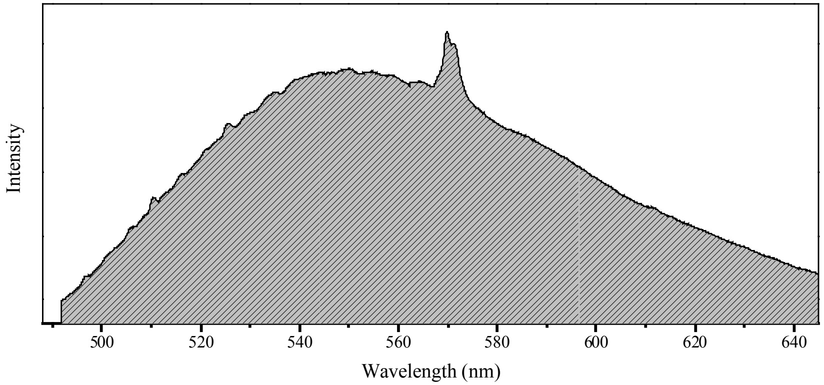


- Electrolyte oxidation products form on the surface of LNMO during charging and slowly disappear from the electrode surface during discharge
- The inorganic fluorescent decomposition products tend to accumulate on the surface of LNMO during cycling

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

Raman microscope probe scans across the electrolyte gap between the cathode and anode. Fluorescence intensity is measured *in situ* as a function of cell voltage.





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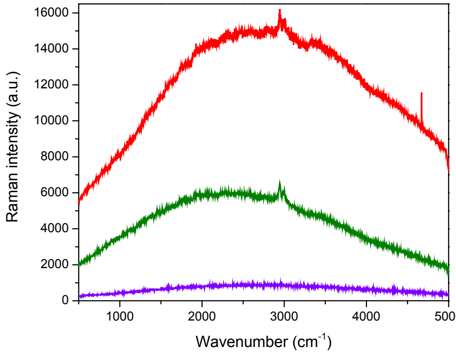
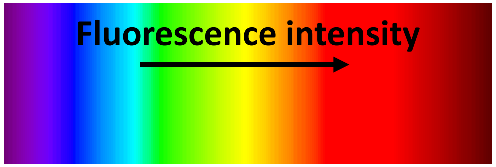
8%wt Solvay 5130 PVDF binder
4%wt Timcal SFG-6 graphite
2 %wt Timcal Super P
6.9 mg/cm^2 active-material loading density
37.1% electrode porosity
35-µm-thick coating
15-µm-thick Al current collector

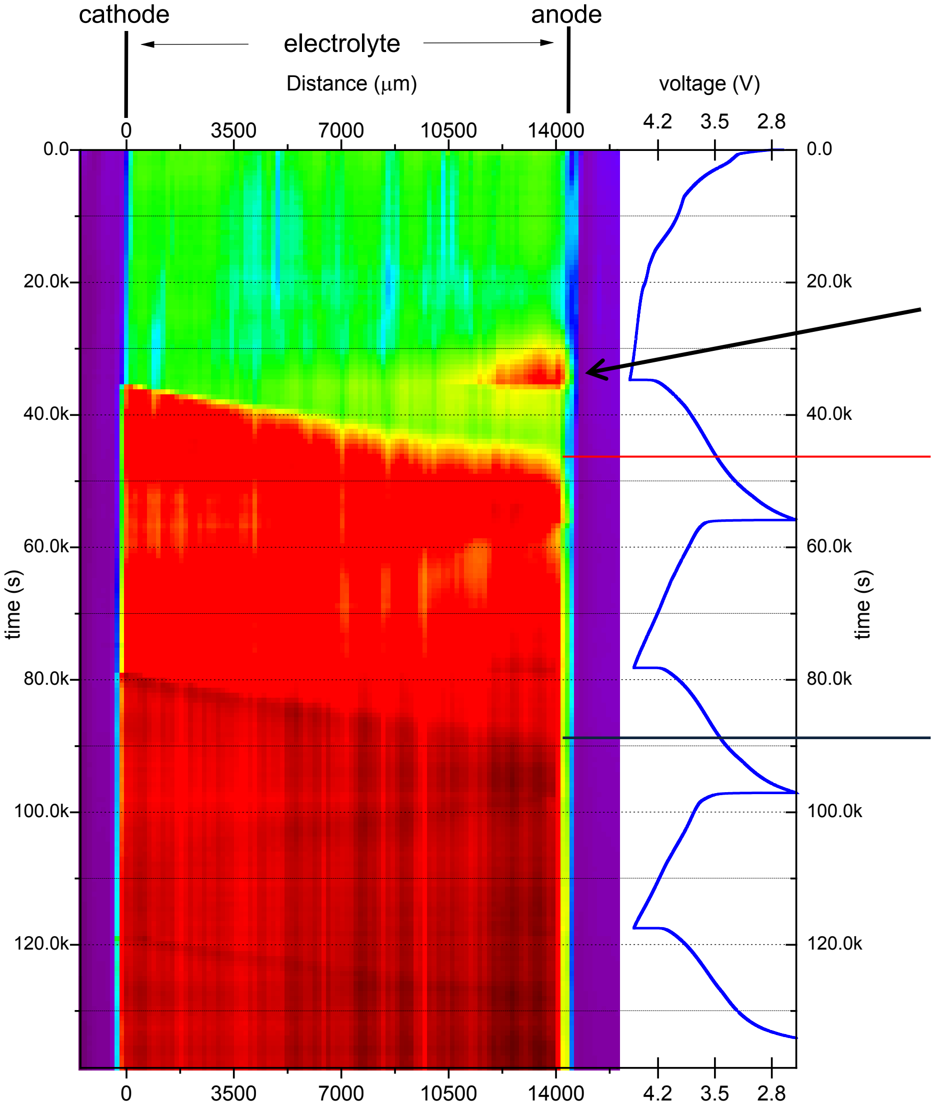
Negative Electrode:
89.8 %wt ConocoPhillips: CGP-A12 graphite
6%wt KF-9300 Kureha PVDF binder
4 %wt Timcal Super P
0.17 %wt Oxalic Acid
5.7 mg/cm^2 active-material loading density
26% electrode porosity
40-µm-thick coating
10-µm-thick Cu current collector

Interfacial reactions products contribute to the electrolyte fluorescence background which changes upon cell polarization

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





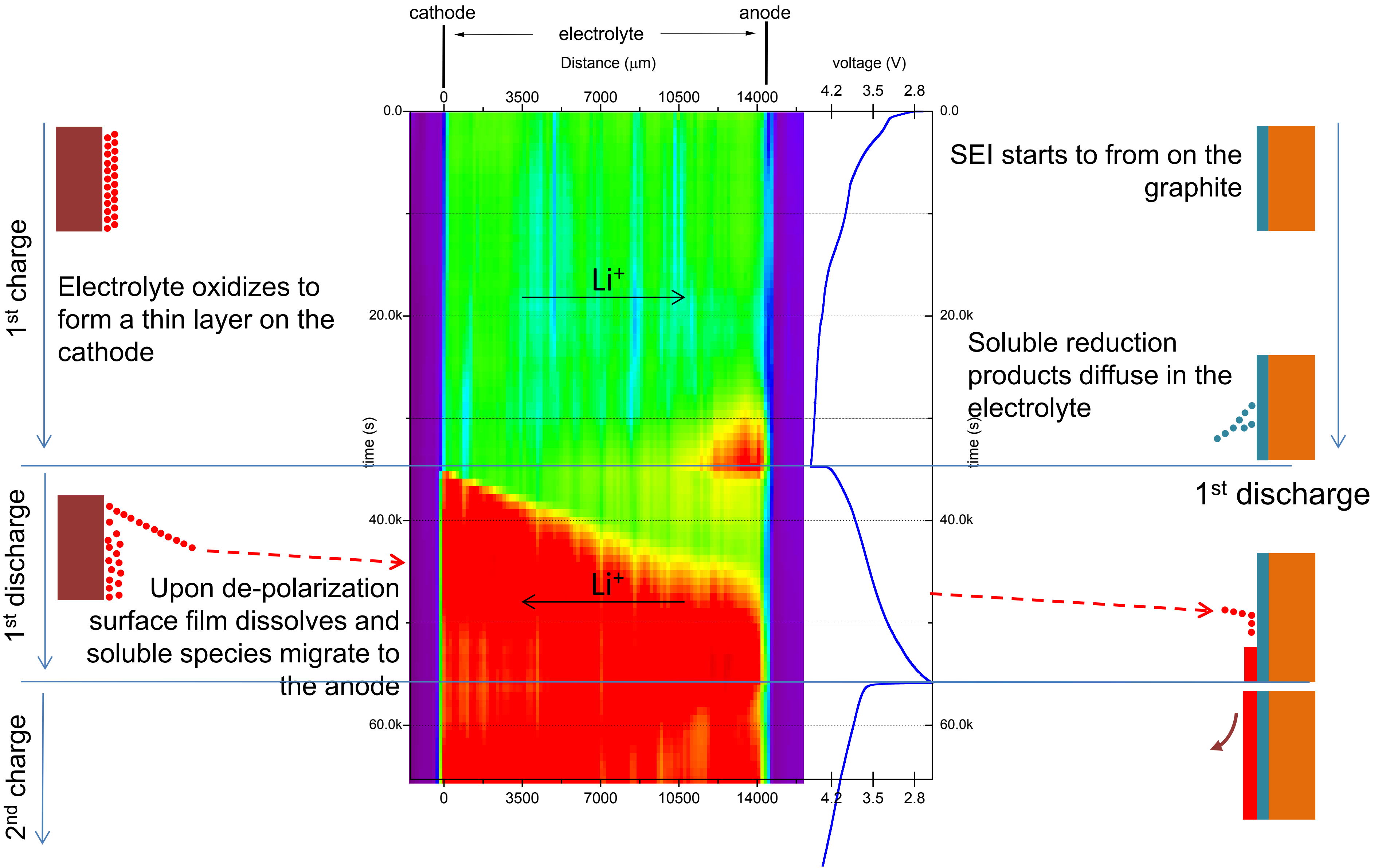


SEI formation on the graphite

Products formed on the cathode migrate to the anode

Similar process repeats itself in 2nd cycle

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



1st charge

Electrolyte oxidizes to form a thin layer on the cathode

SEI starts to from on the graphite

Soluble reduction products diffuse in the electrolyte

1st discharge

1st discharge

Upon de-polarization surface film dissolves and soluble species migrate to the anode

2nd charge

Summary II

- Inorganic and organic fluorescent electrolyte decomposition products form at the cathode and anode
  - Phase transformation in the lithium-rich NMC leads to formation of soluble fluorescent species, which diffuse toward the anode and interfere with the anode (SEI Mn poisoning?)
  - Mn and/or Ni dissolution is the root cause of fluorescence compounds formation on positive electrode
- Insoluble electrolyte decomposition products form electronic and ionic barriers in composite cathodes
  - These species contribute to the impedance rise in Li-ion cells
- Electrolyte additives, surface coatings could be effective strategies to reduce surface reactivity of high-voltage cathodes

Future Work

- Work directly with industrial partners and ANL/LBNL cell manufacturing/testing facilities on development of high-energy Li-ion systems
- Carry out post-test characterization of components from ABRT model cells
- Continue studies of degradation modes of high-voltage systems. Extend diagnostic studies to LMR-LMO
- Continue search for remedies that decrease irreversible capacity losses and stabilize material during long-term cycling
    - Reduce irreversible charge losses from surface reactions
    - Investigate pretreatment regimens to reduce side reactions
    - Understand factors that can enhance the stability of SEI layers

Planned Future Work

(ABR program is re-competed FY 2014)

- Continuation of migration studies and the influence of this migration on the internal resistance
  - Identify the two species, originating from (a) cathode and (b) the SEI formation at the anode
    - Determine their influence on the cell performance
- Submit a proposal with Eniva in the re-competition of the ABR program to upscale and further exploit the carbon black treatment, especially considering commercial cells
  - Investigate graphite (as component of the ABR baseline electrode) at elevated potential
- Investigate the surface treated carbon black in combination with different cathode materials, e.g. NMC and LMNO (funded by received Technology Transfer grant from LBNL)