ELECTROCHEMISTRY DIAGNOSTICS OF BASELINE AND NEW MATERIALS

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

Budget

- FY 2010 diagnostics/materials funding $600K
- FY 2011 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 program 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

- Report progress on reduction of contact resistance growth in high-voltage cathodes
- Attend review meetings and present diagnostic results obtained in collaboration with ABRT Program participants

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

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 FY11)

TECHNICAL ACCOMPLISHMENTS

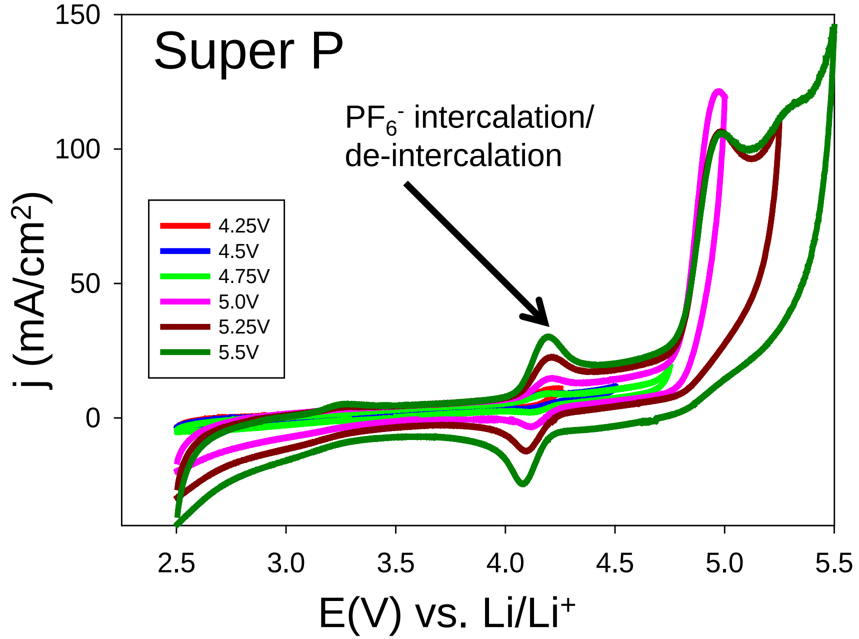
- Completed electrochemical characterization study of common carbon black additives at anodic potentials
- Determined interfacial instability of carbon black in composite high-voltage cathodes
- Elucidated the mechanism of carbon black structural degradation
- Identified an approach to carbon black additive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

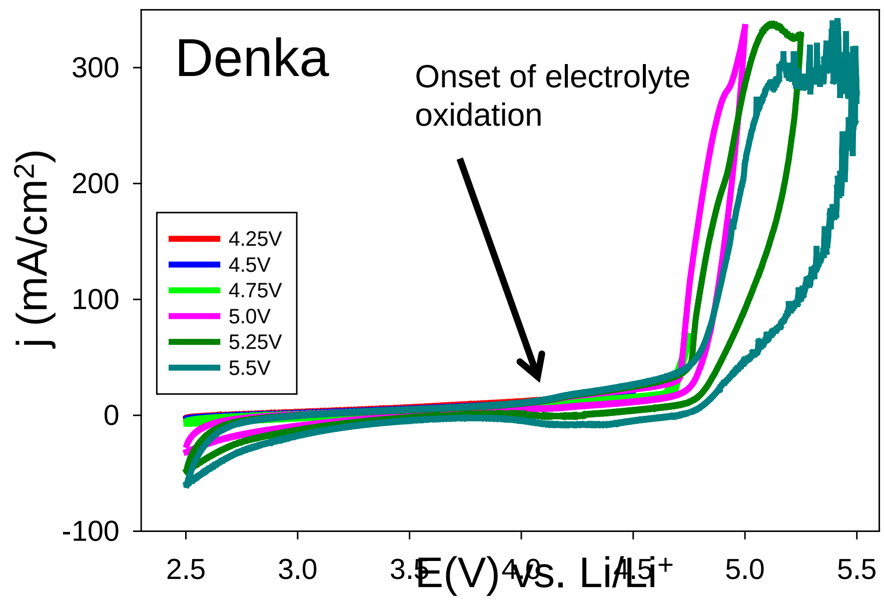
Electrochemical Activity of Carbon Additives

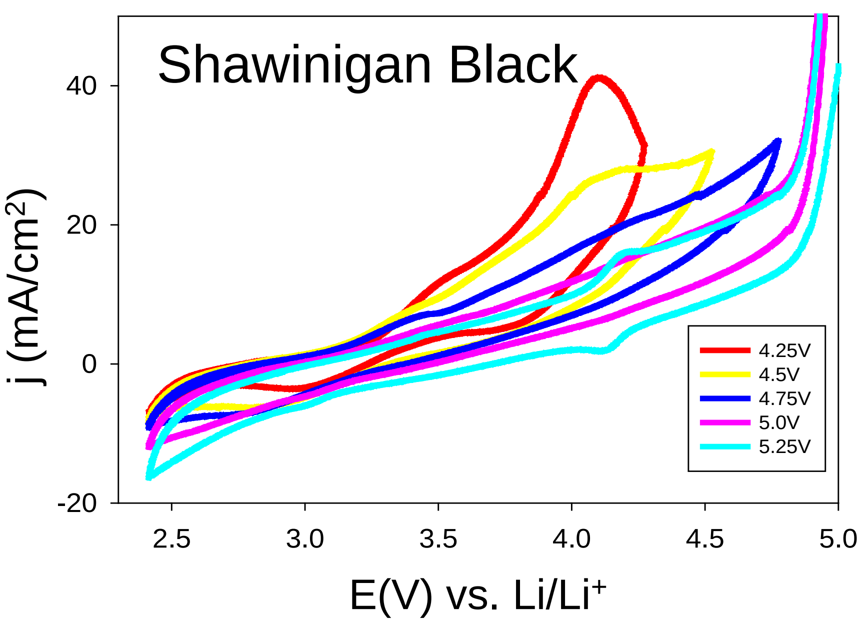
- Three types of carbon black were tested:
  1. Shawinigan Black: produced by continuous thermal decomposition of acetylene (surface area 75-80 m^2/g)
  2. Denka: produced by continuous thermal decomposition of acetylene (surface area 65-68 m^2/g)
  3. Super P: produced by partial oxidation of petrochemical precursors (surface area 62 m^2/g)

- Electrode composition: 90% carbon, 10% PVdF, Al current collector
- Prior to electrochemical testing the electrodes were processed at either 120^{o}C under vacuum for >12 hours or 900^{o}C under a flow of Ar/H_2 for >12 hours
- Carbon black electrodes were tested in three-electrode cells with Li-metal reference and counter electrodes; 1.2 M $LiPF_6$ EC/EMC (3:7)

Electrochemical Activity of Carbon Additives

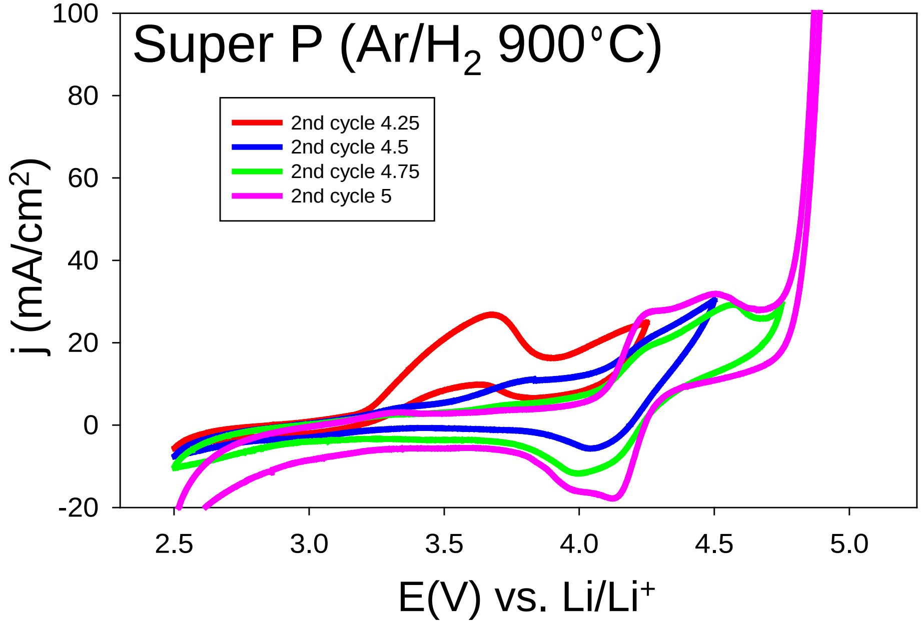


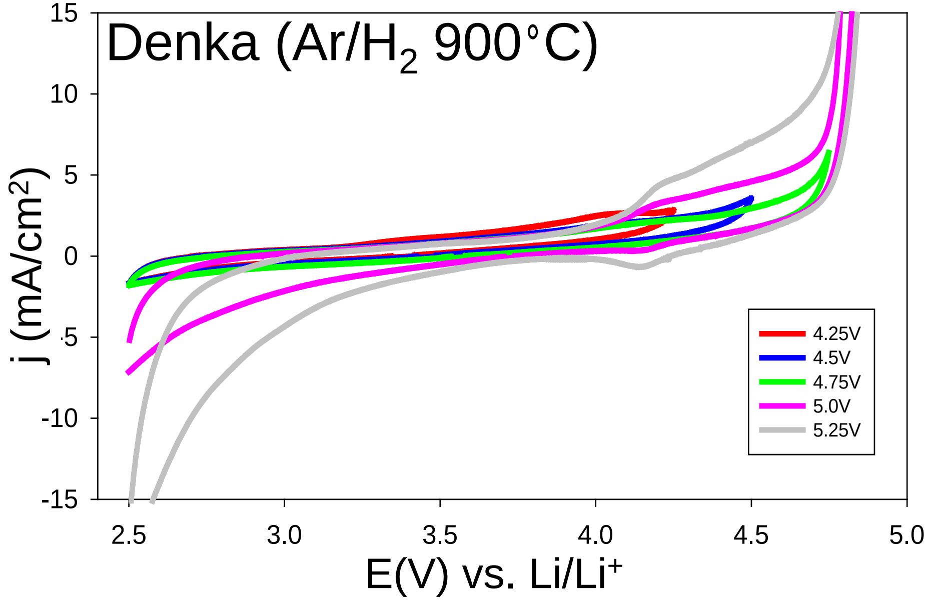


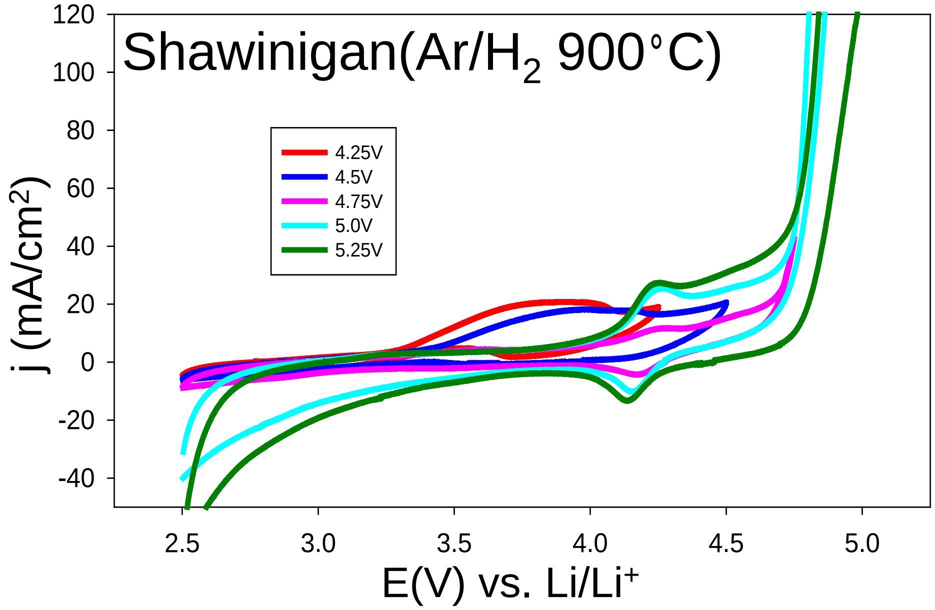


- PF_6^- intercalation at ~4.1 V *vs*. Li/Li$^+$ leads to degradation of sp^2-carbons
  Seel et al. J. Electrochem. Soc. ***147****, 892 (2000)*
- Electrolyte oxidation on carbon black additives limits the use of high-voltage cathode materials

Electrochemical Activity of Carbon Additives





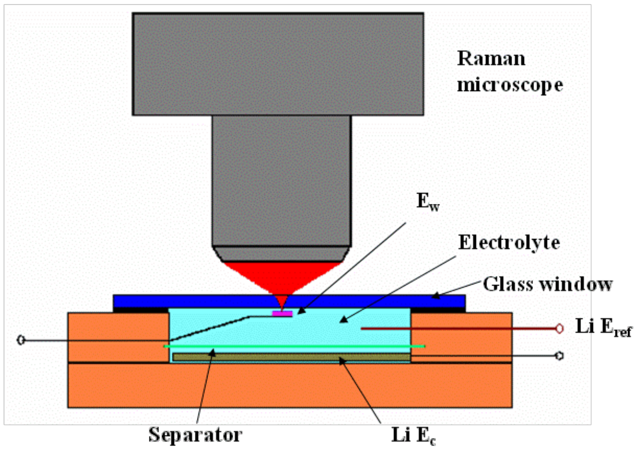


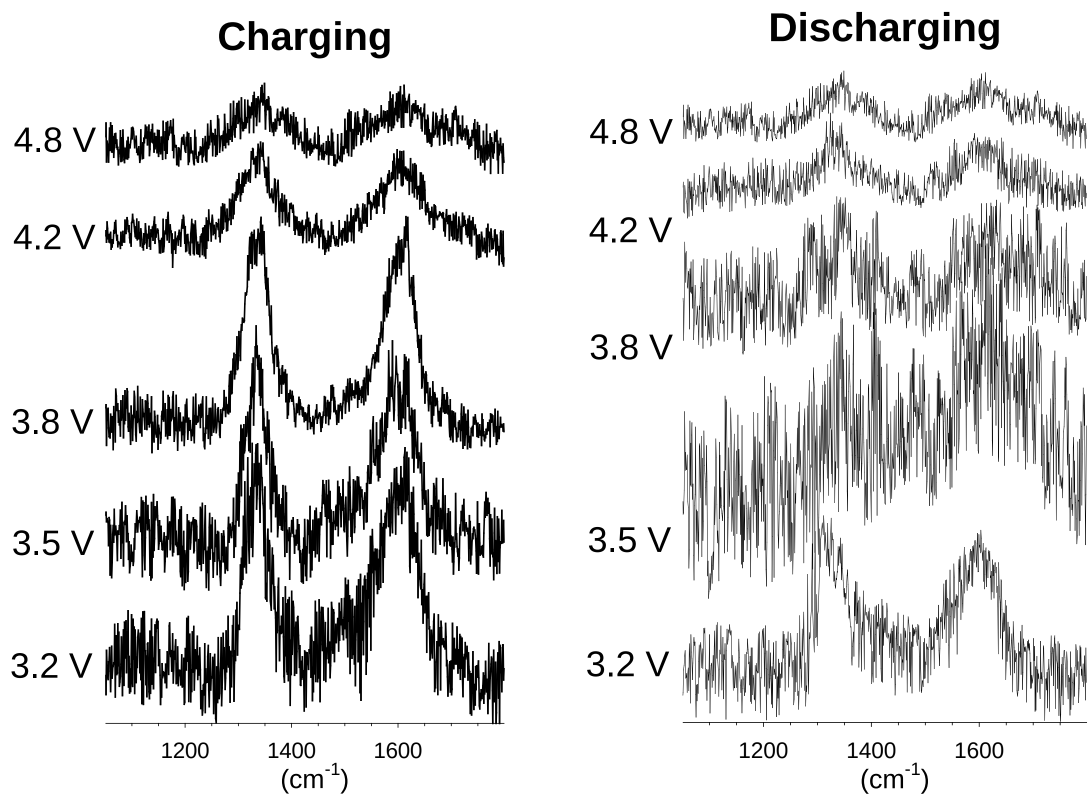
- Heat treatment at 900°C under Ar/H_2 reduced oxygenated surface groups at the carbon surface
- Peaks related to PF_6^- intercalation and electrolyte oxidation are still observed

PF_6^- Intercalation into Graphitic Carbons

In situ Raman Microscopy of Carbon Black Electrodes

In situ MicroRaman Experimental Setup





- Intensity of carbon D and G bands decreases at U>3.8 V
- The carbon black spectrum can be partially restored at U<3.5 V

Surface Treatment of Carbon Black Additives

1. Synthesize carbon black under controlled conditions

   - Pyrolysis of a Kapton polymer layer at 1000ºC to form a binder-free thin-film carbon black electrode

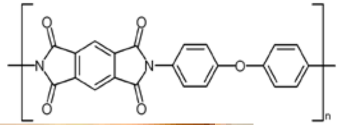
   - Test electrochemical properties of the electrode at high potentials in 1.2 M $LiPF_6$ EC/EMC (3:7)

2. Develop a surface treatment method to reduce the surface electrocatalytic activity of the carbon black material

3. Determine the origin of carbon instability toward lithium battery electrolytes at high potentials

Surface Treatment of Carbon Black Additives

Kapton polymer



Amorphous carbon

Pyrolysis

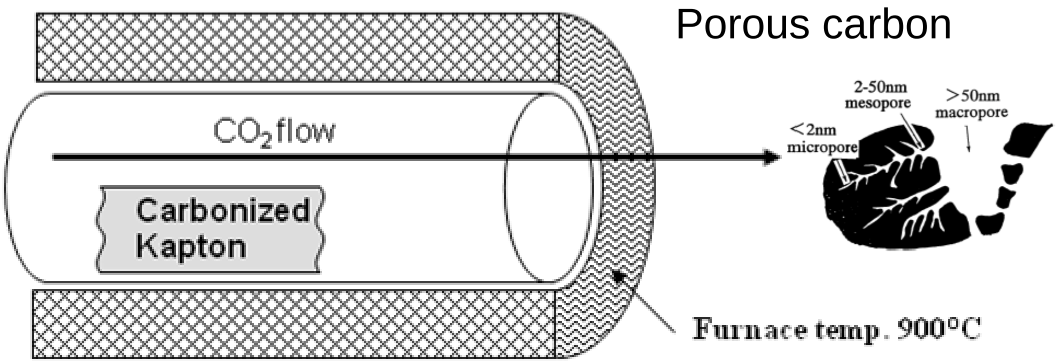
1000°C, Ar

The resulting material is a conductive sp^2-carbon material, >100 S/cm

Pollak *et al.* J. Phys. Chem. B. **110**, 7443 (2006)

Activation

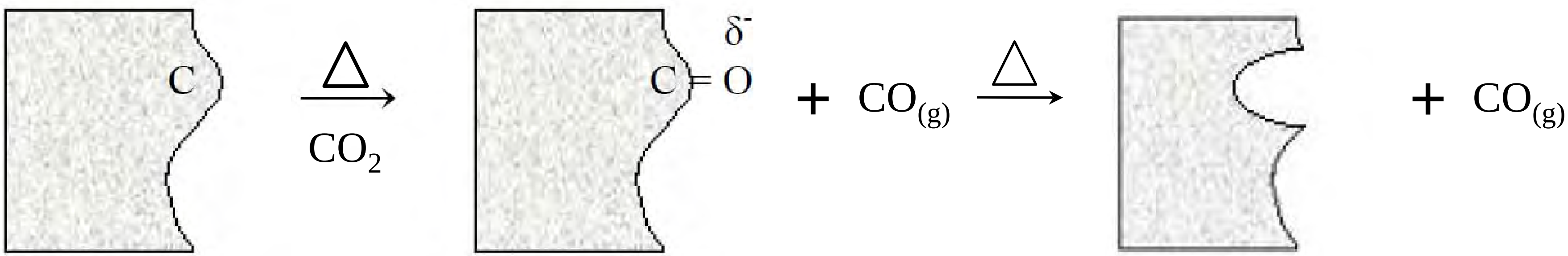
Porous carbon



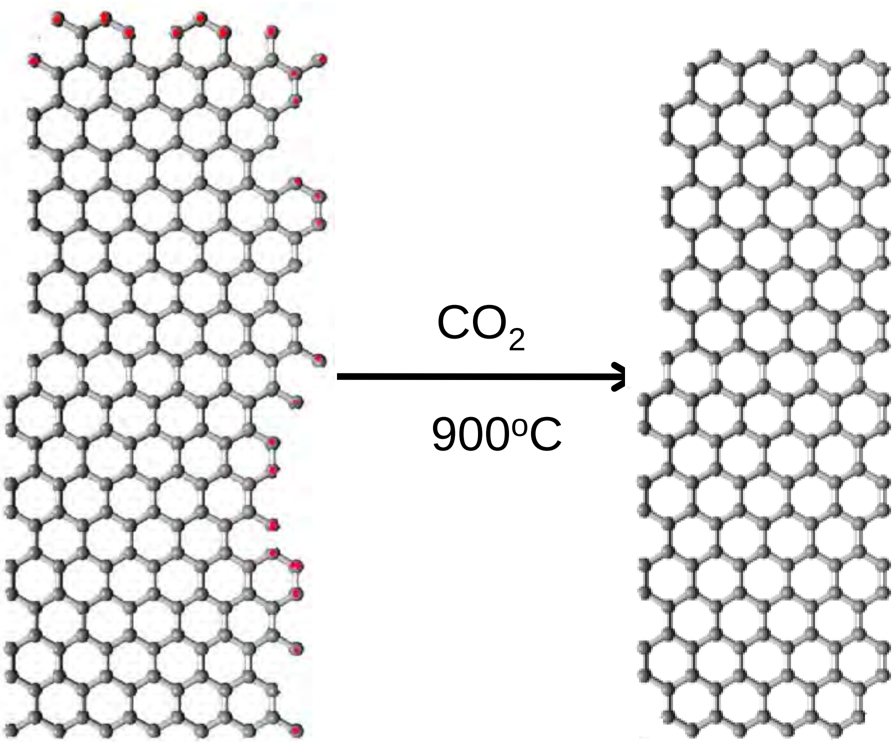
- At elevated temperatures CO_2 acts as a mild oxidizer
- The carbon surface is oxidized and pores are formed
- The conductivity of the porous carbon is ~50 S/cm

Surface Treatment of Carbon Black Additives

Formation of Porous Morphology



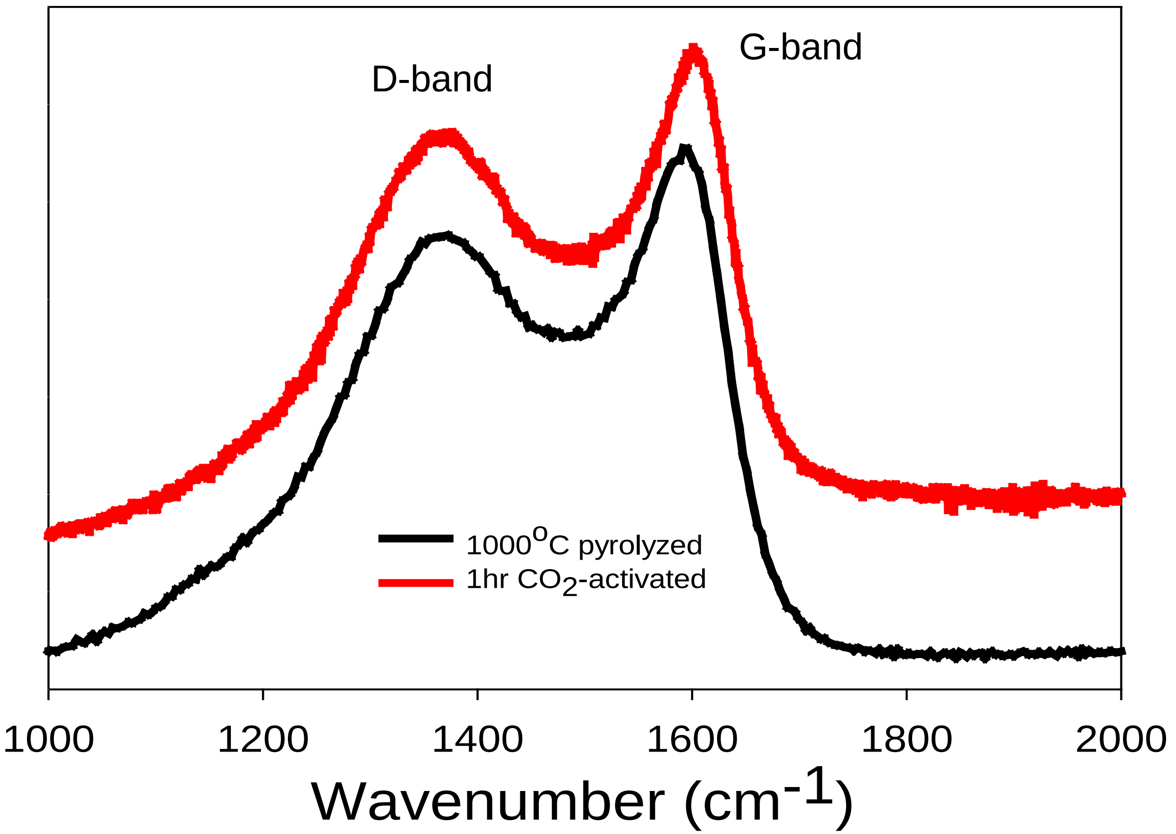
Surface Structure Modification



- 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

Surface Treatment of Carbon Black Additives

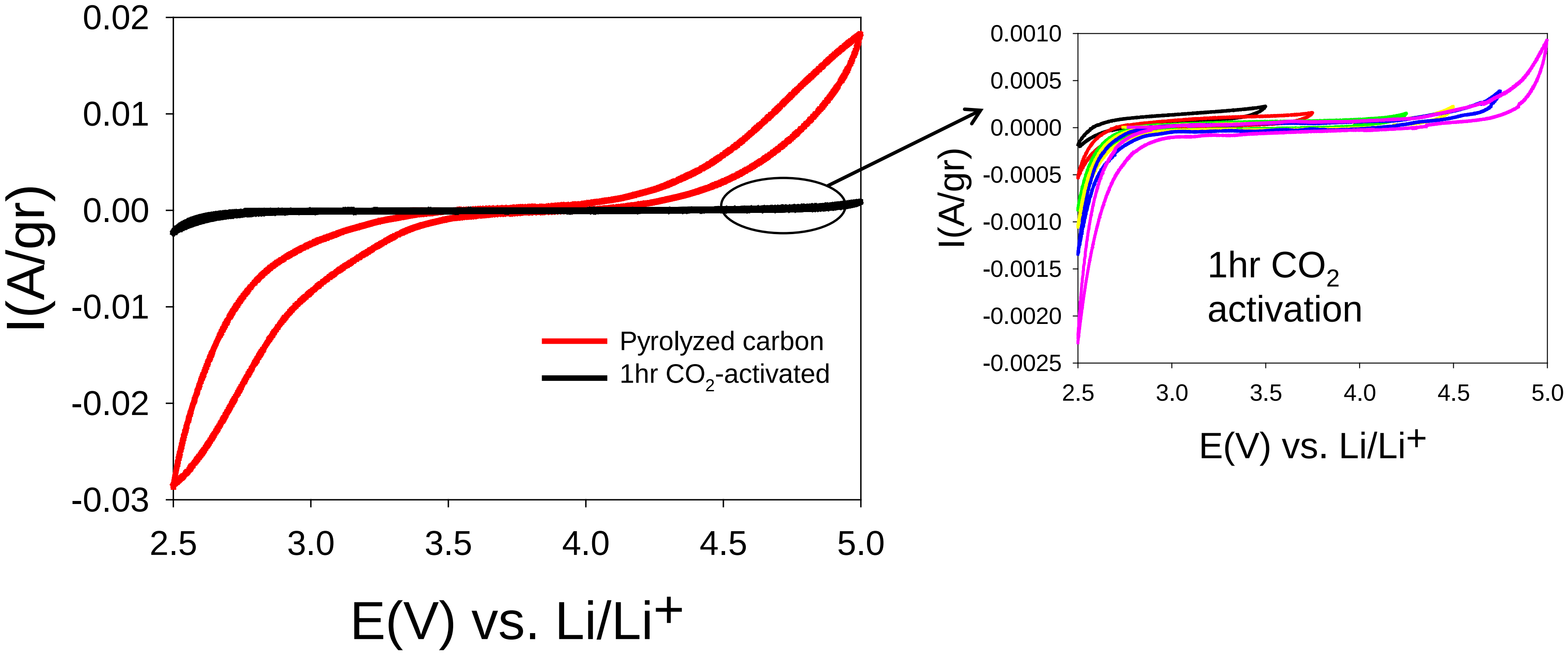
Raman Structural Analysis



- A blue shift of the Raman G band of the activated carbon sample is observed
- Contributions from the D'-band at 1610 cm^{-1} may indicate formation of smaller graphene domains upon CO_2-activation

Electrochemical Activity of Carbon Additives

The Effect of Surface Treatment of Carbon Black Additives



- BET surface area of the CO_2-activated carbon (535 m^2/g) is two orders of magnitude higher than the pyrolyzed carbon.
- Note the low oxidation current of the 1hr activated carbon
- The relatively low graphitization level of this carbon inhibits PF_6^- intercalation

*Isono et al., Carbon, **42**, 1799 (2004)*

Electrochemical Activity of Carbon Additives

The Effect of Surface Treatment of Carbon Black Additives

- Low-temperature (1000°C) carbonization produces amorphous carbon which does not allow PF_6^- intercalation
- The CO_2 activation process inhibits electrolyte oxidation at the carbon surface by several possible mechanisms:
  - Formation of oxygen surface groups (carbonyl, carboxyl, hydroxyl, *etc.*), which prevent electrolyte oxidation
  - Formation of a highly developed porous structure with a low concentration of high-electronic-density carbon edge atoms

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

SUMMARY

- ***Supporting research for improved lithium-ion batteries:***
  - Electrolyte oxidation and PF_6^- intercalation in standard carbon black additives prevents the implementation of high-voltage cathodes
    - ✓ Pyrolysis of organic precursors at relatively low temperatures (1000°C) leads to the formation of amorphous carbon, which does not allow PF_6^- intercalation
    - ✓ CO_2-activation at elevated temperatures (900°C) leads to more than two orders of magnitude higher carbon surface area
    - ✓ High-surface-area carbon electrode shows increased stability toward electrolyte oxidation
  - ***Approach:***
  - Advanced synthetic and characterization techniques to determine factors that affect the interfacial stability of carbon additives
  - Development of new surface-processing methods to increase interfacial electrode stability
- ***Accomplishments:***
  - Identified a candidate processing technique to produce carbon additives for high-voltage cathodes
- ***Plans:***
  - Continue studies of ABRT cell components and electrode/electrolyte interface stabilization in collaboration with ABRT Program partners