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Formation/SEI Studies at Argonne

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February 26, 2008

Presentation at the Office of Vehicle Technologies, 2008 Annual Merit Review Meeting

This presentation does not contain any proprietary or confidential information

Vehicle Technologies Program

Outline

- Purpose of Work
- Barriers
- Approach
- Accomplishments and Technical Progress
- Some Relevant Publications
- Plans for Next Fiscal Year
- Summary

Contributors

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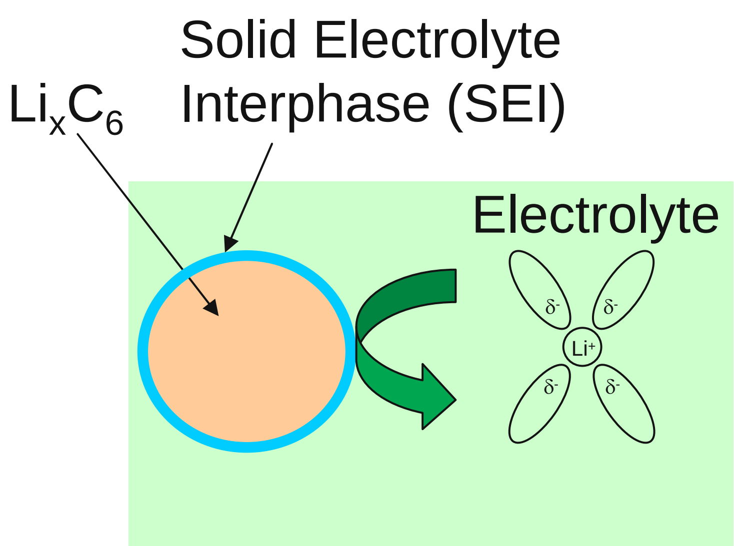
Purpose of Work - Study SEI formed on negative and positive electrodes after initial cycling and determine SEI formation mechanisms

- **Passivation films (SEI layers) form during the initial charge that tend to protect electrode active materials from further reactions with electrolyte components**
  - Nature of these films is key to the stability of the cell chemistry, affecting cell life & safety



Desired SEI Properties

- **Low resistance to Li^+ transport**
- **Thin and pin hole free**
- **Adherent & flexible**
- **Electronically insulating and $t_{Li+} = 1$**
- **Low solubility in the electrolyte**
- **Stable against oxidation or reduction**
- **Produces minimum capacity loss**

Major Technical Barrier

Cell Calendar and Cycle Life

- Enable development of Lithium-ion Batteries that will meet the 15y calendar life goal
- Definition of formation cycling - Initial cycling under a controlled set of conditions that every cell must undergo before it is given/sold to the user
- Appropriate formation cycling protocols can produce “desirable” passivation films, which limit electrode-electrolyte reactions that contribute to performance degradation of lithium-ion cells

Approach

- Multi-institution effort to gain an understanding of relationship between formation conditions, SEI characteristics and electrode performance

Formation Conditions
T, t, UCV, etc. (ANL, INL)

DOEx Study (INL)
Statistical study of formation parameters & their interactions

SEI morphology & composition
(ANL, LBNL, BNL, URI, UIUC)

Electrode Performance
(ANL, INL)
In various electrolyte systems

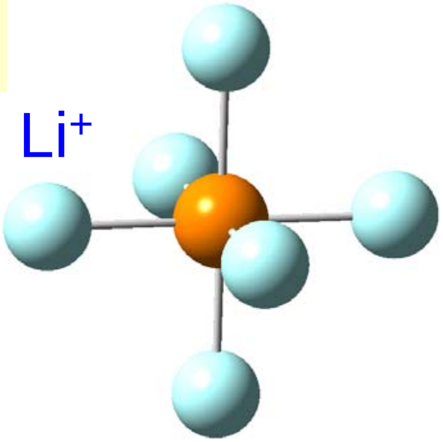
BCF oxide
BF graphite
(ANL, LBNL, UIUC, URI)

Performance Measure/Technical Accomplishments – FY07

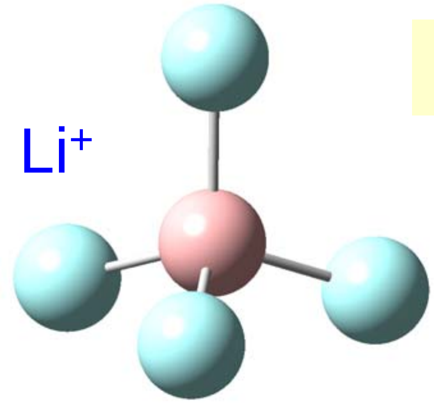
- Initiate electrode SEI studies on composite electrodes
  - Conducted studies in reference electrode cells containing various electrolytes to determine electrode contribution to cell impedance after initial (formation) cycling
    - *Showed that electrolyte salt composition has a significant effect on cell cycling and impedance behavior.*
    - *Observed that the effects of formation cycling are mainly on the negative electrode*
- Determine nature and morphology of electrode surface films and correlate with cell impedance
  - Developed binder- and carbon- free oxide electrodes and binder-free graphite electrodes to examine surface films that result from interaction with the electrolyte
    - *Showed that the electrode surface films formed in $LiPF_6$ and LiF_2OB –based electrolytes are very different.*

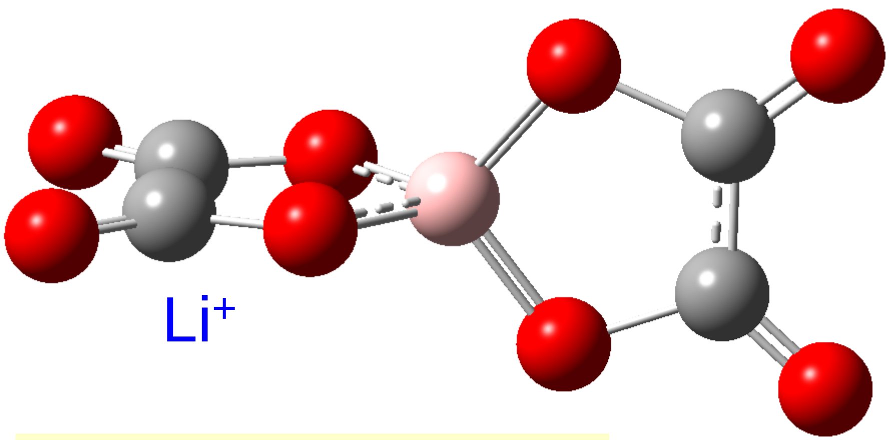
Various Li-salts studied (in 3EC:7EMC by wt. solvent) to determine effects of formation cycling

$LiPF_6$

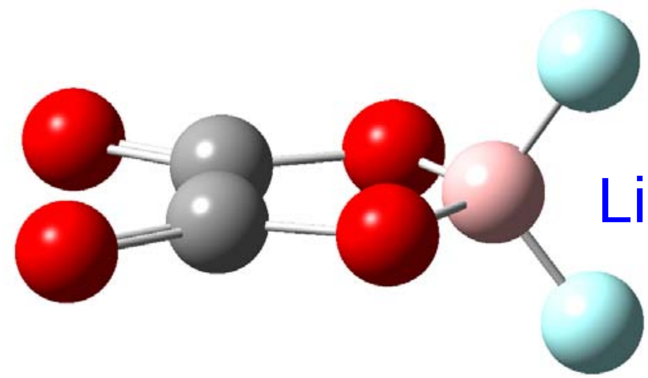


$LiBF_4$



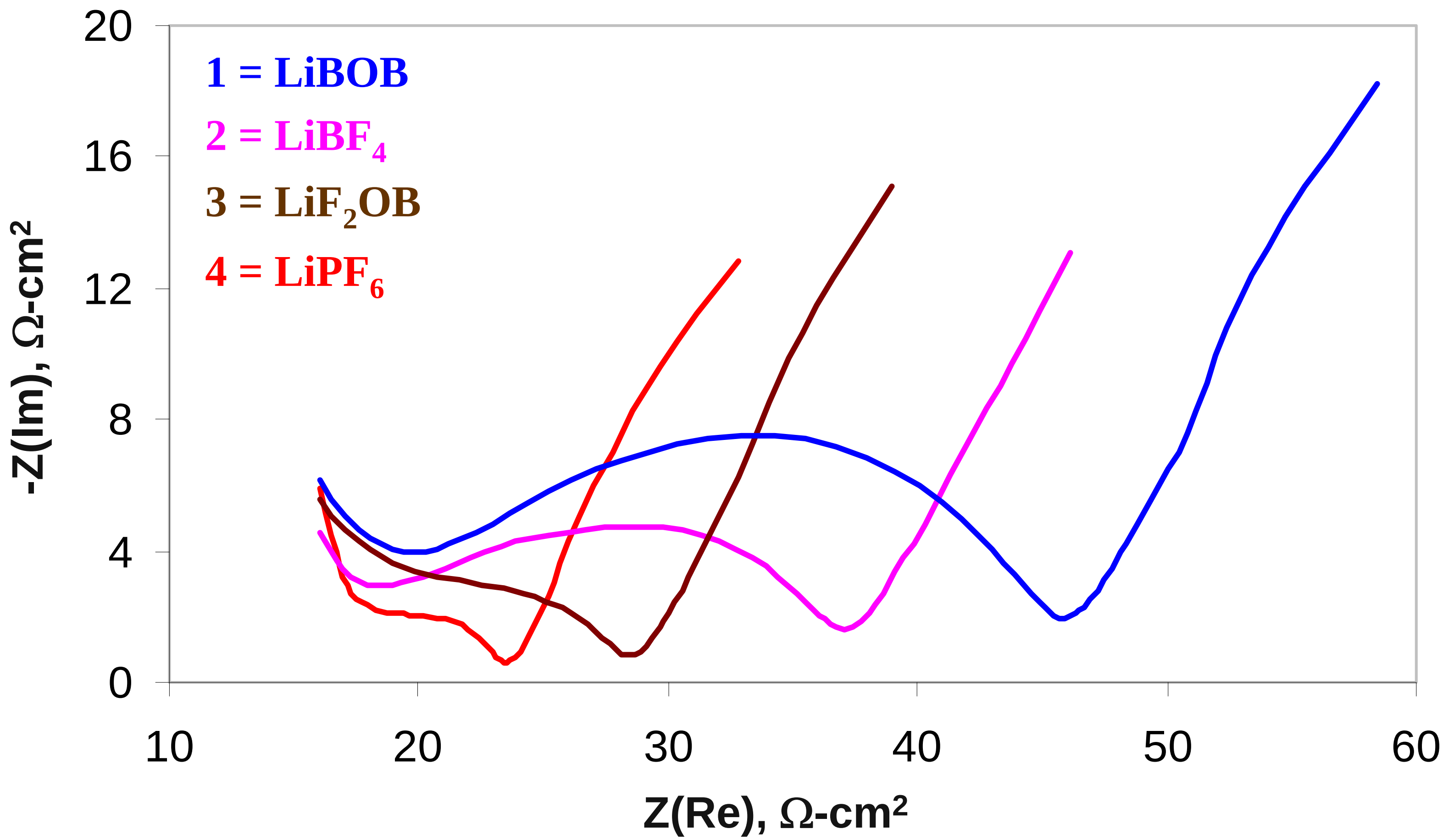


$LiB(C_2O_4)_2$ = LiBOB



$LiF_2B(C_2O_4)$ = LiF_2OB

Full Cell impedance after formation cycling
- data at 30°C, 3.72V, 25 kHz – 0.01 Hz



Full Cell Impedance: LiBOB > $LiBF_4$ > LiF_2OB > $LiPF_6$

Negative electrode impedance (after formation cycling) shows strong dependence on electrolyte composition

Graphite Electrode Impedance

LiBOB > $LiBF_4$ > LiF_2OB > $LiPF_6$

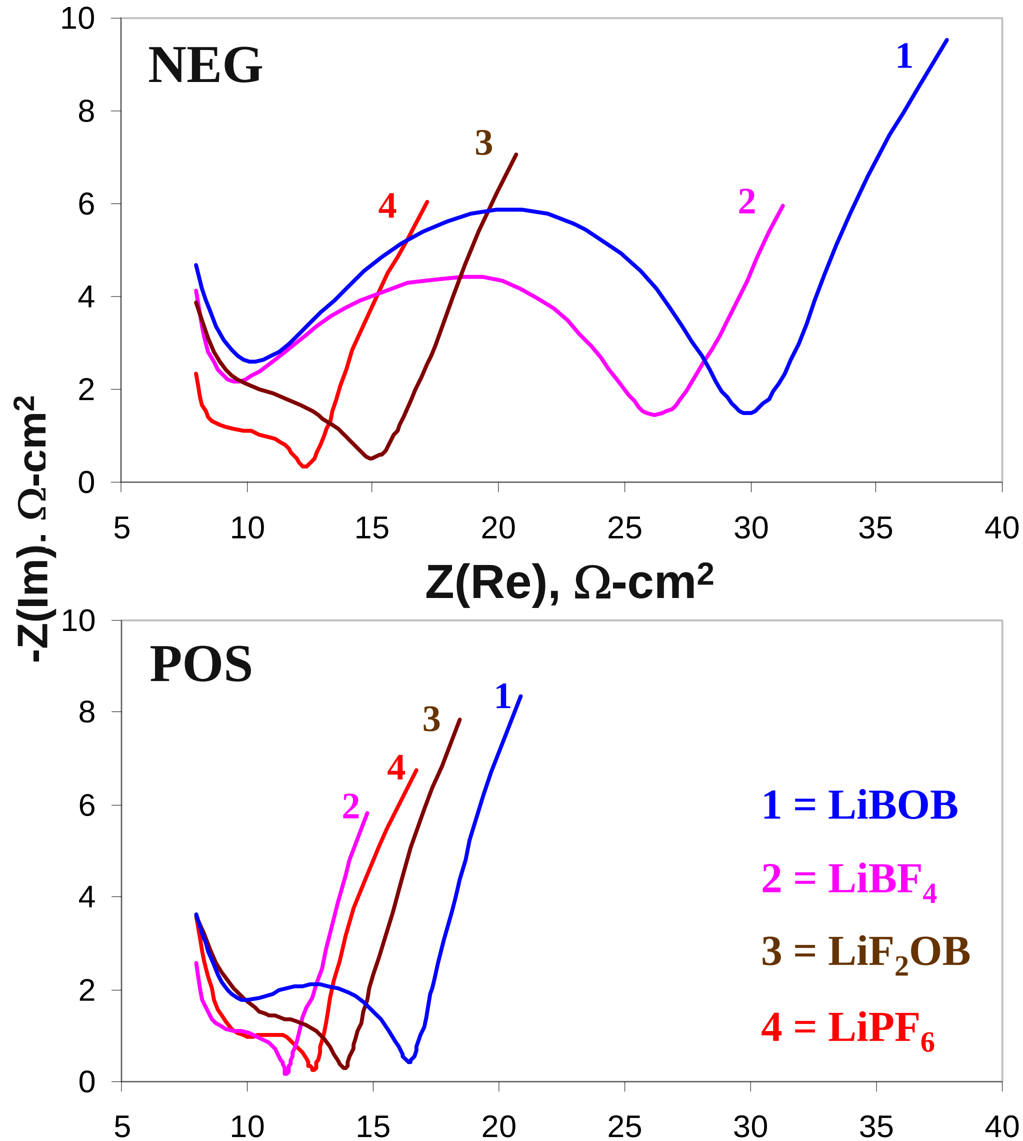
(same trend as FULL data)

Differences arise from variations in SEI morphology and composition

Oxide Electrode Impedance

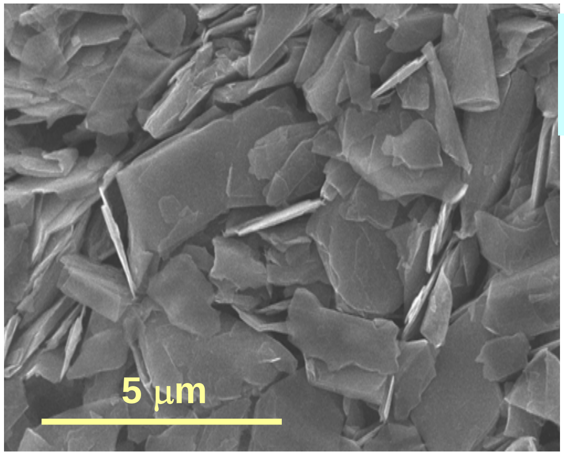
LiBOB > $LiBF_4$ ≈ LiF_2OB ≈ $LiPF_6$

Differences arise from different surface films on oxide particles

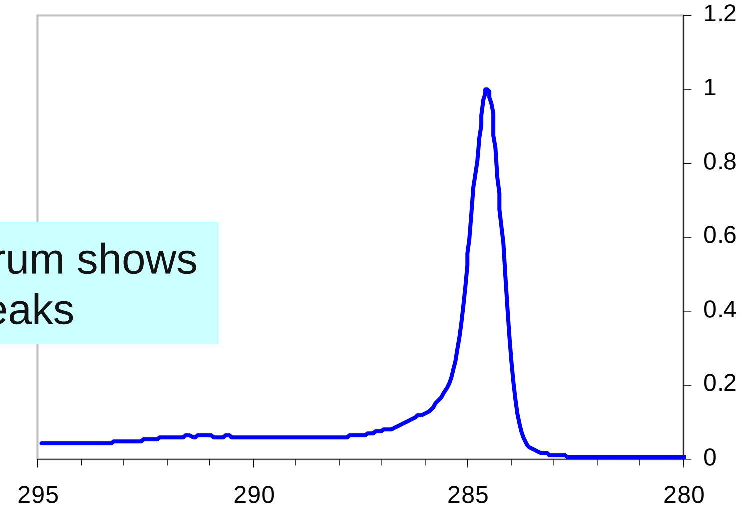


A Binder-Free (BF) electrode has been developed to study SEI films on graphite electrodes -

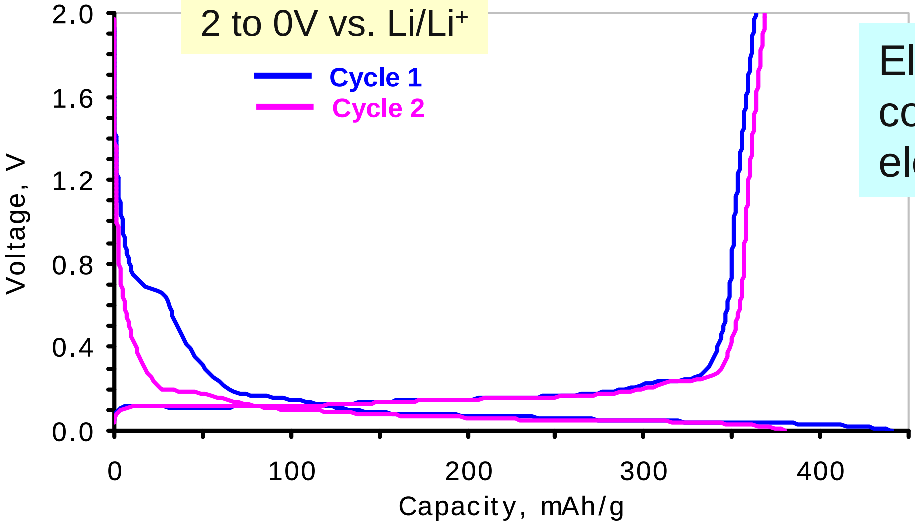
absence of PVdF binder simplifies data interpretation



SEM image showing graphite particles

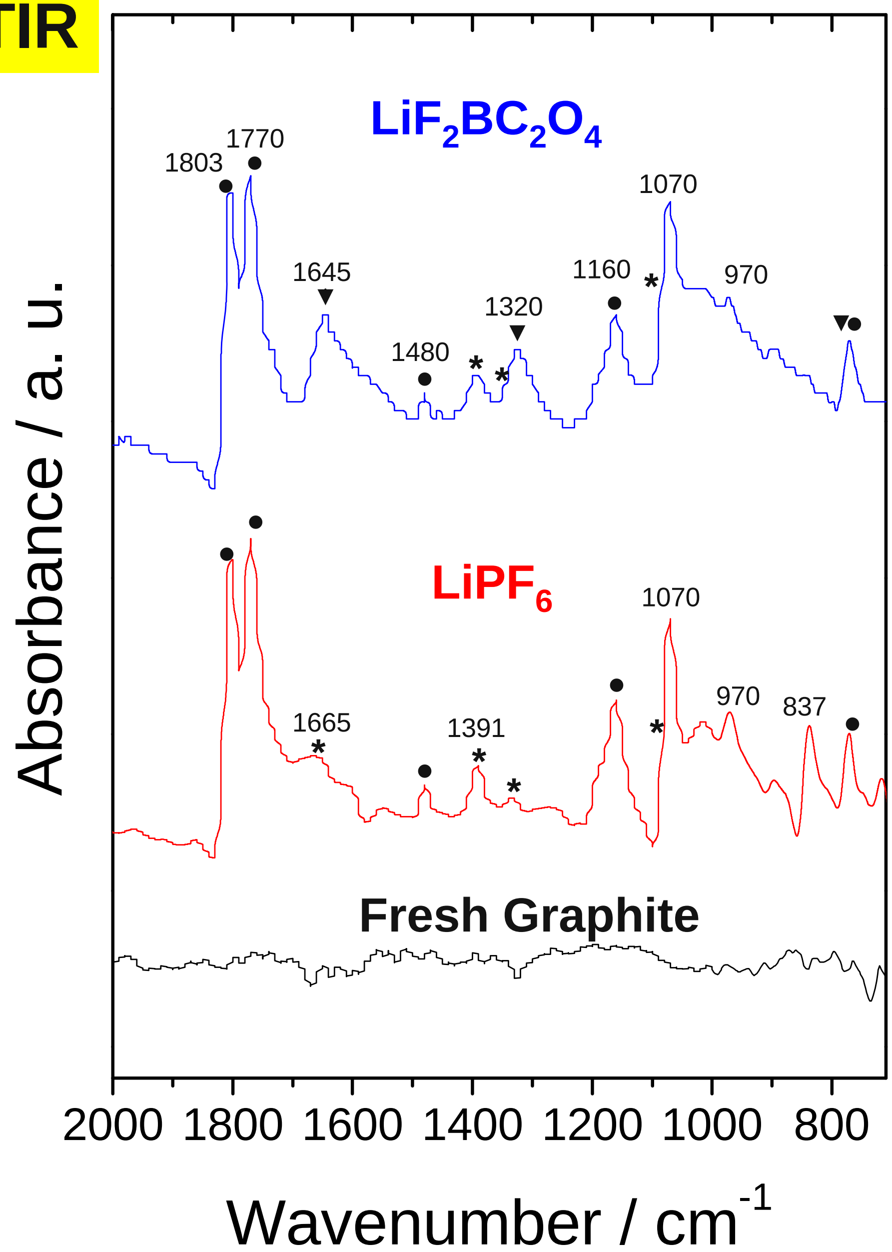


C1s XPS spectrum shows only graphite peaks



Electrode cycling behavior comparable to composite electrode cycling behavior

FTIR



SEI study (samples not rinsed)

In both spectra we see evidence of the following species:

Lithium ethylene dicarbonate (and related species such as lithium methyl carbonate, lithium ethyl carbonate).

Lithium methoxide (and related species, such as lithium ethoxide).

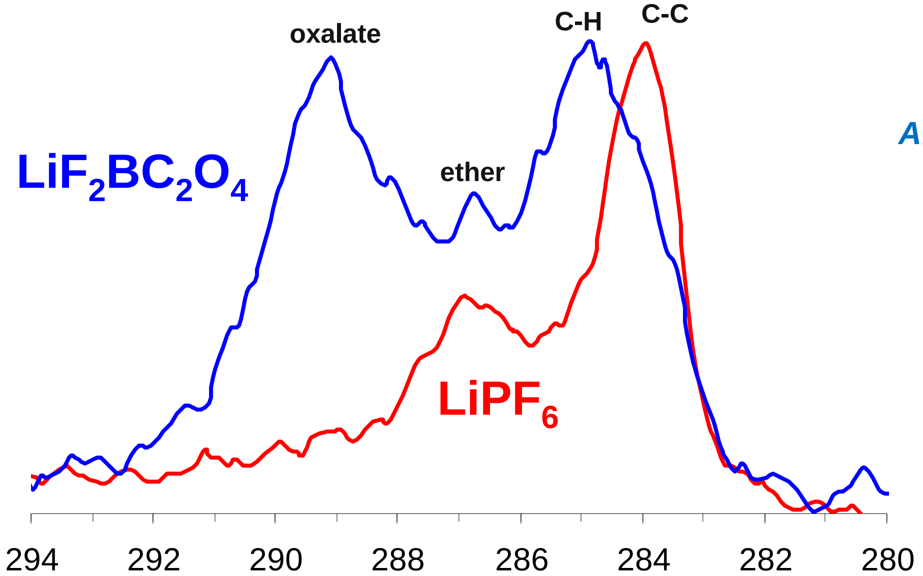
EC residue (or solvated EC:Li)

In the $LiPF_6$ sample, there is evidence of **lithium (alkyl or fluro)phosphates**

In the $LiF_2BC_2O_4$ sample, there is evidence of either lithium oxalate (or **alkyl esters of oxalic acid**)

No evidence of Li_2CO_3 in either sample

Significant differences are observed in the XPS spectra of BF-graphite samples formed in $LiPF_6$ and $LiF_2BC_2O_4$ electrolytes



Samples not rinsed
After 1 complete cycle
(2-0 V vs. Li)

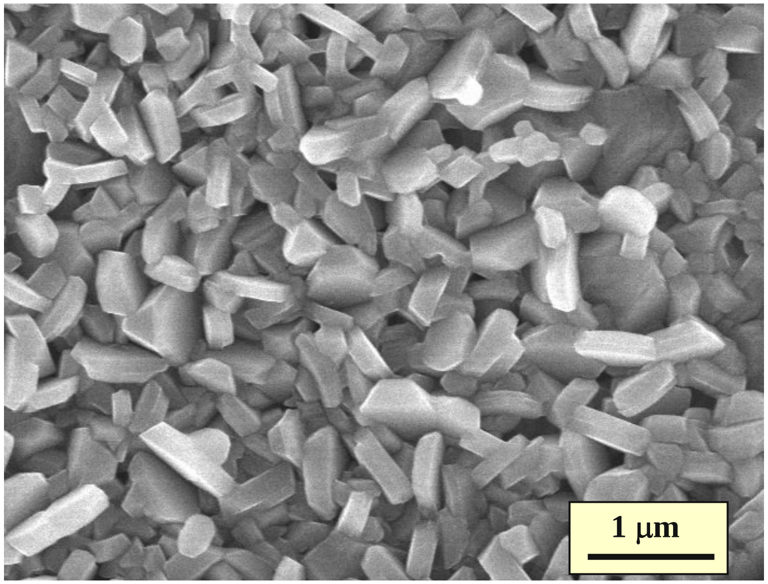
C1s

Our XPS data

- indicate that the SEI layer coverage is more complete on the $LiF_2BC_2O_4$ sample than on the $LiPF_6$ sample
- are consistent with presence of lithium alkyl carbonates ($ROCO_2Li$) and lithium alkoxides (ROLi)
- indicate existence of trigonal borate oligomers on the $LiF_2BC_2O_4$ sample and $Li_xPO_yF_z$ compounds on the $LiPF_6$ sample

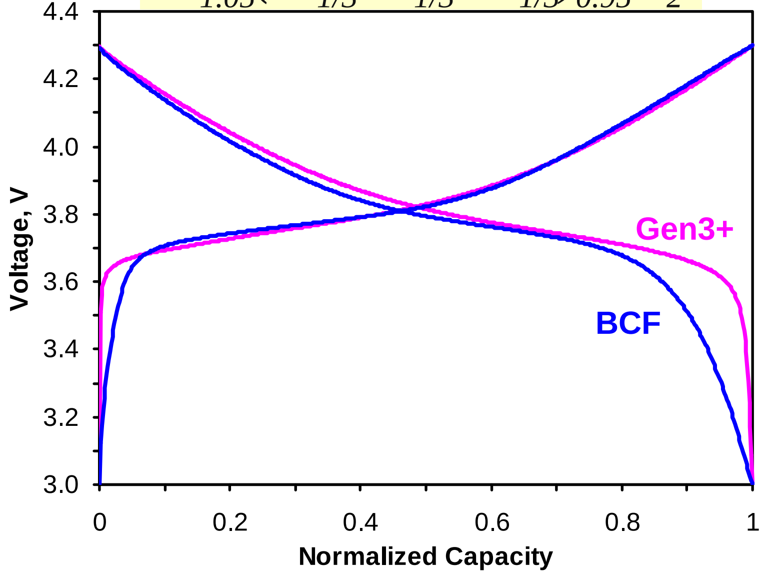
Binder- and Carbon- Free (BCF) oxide electrodes have been developed to study surface films resulting from oxide-electrolyte interactions

$Li_{1.05}(Ni_{1/3}Co_{1/3}Mn_{1/3})_{0.95}O_2$



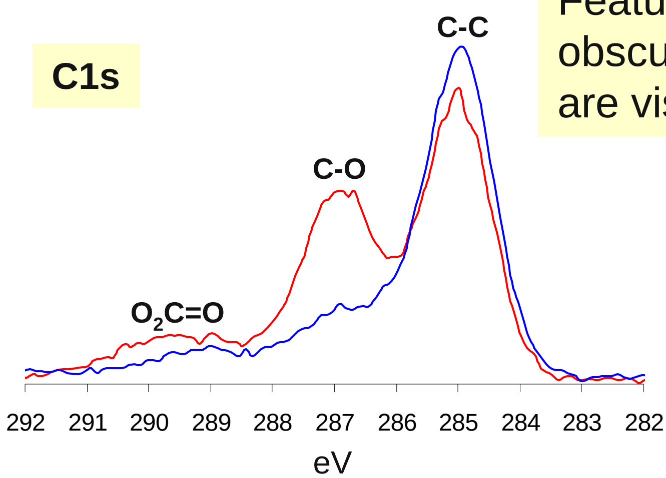
The BCF oxide particle size is similar to that of primary particles in the Gen3 oxide

$Li_{1.05}(Ni_{1/3}Co_{1/3}Mn_{1/3})_{0.95}O_2$



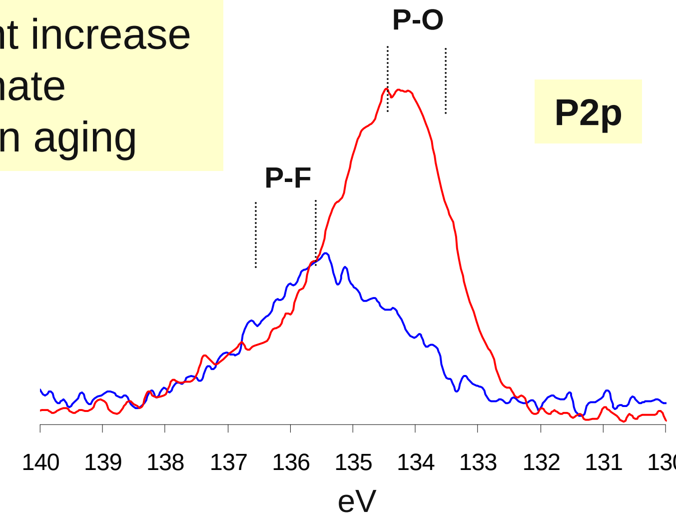
Voltage profiles of BCF oxide electrode and Gen3+ composite electrode are very similar.

XPS spectra (Al Kα X-rays) BCF electrode surface – 55°C aging effect



Features normally obscured by PVdF are visible.

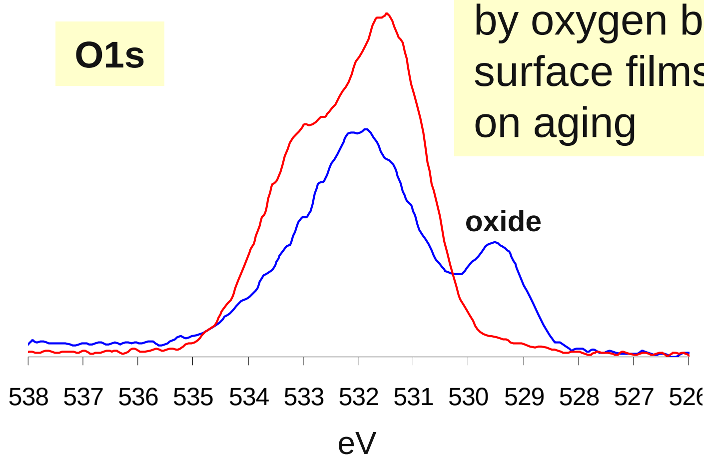
Significant increase in phosphate content on aging



—— before aging

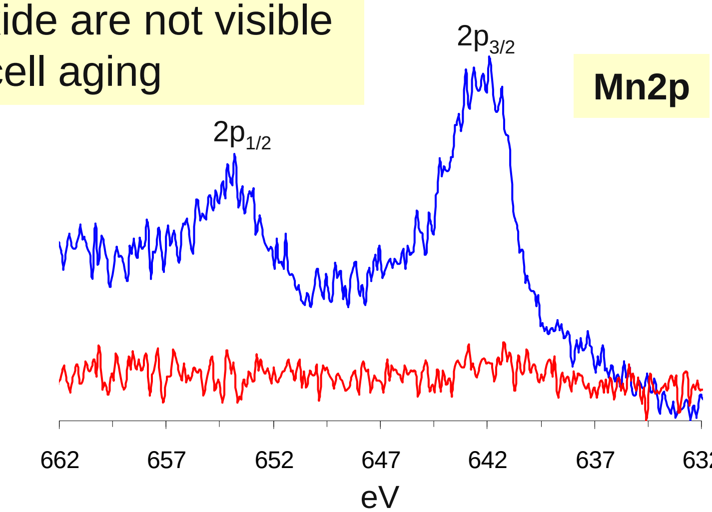
—— after 55° C aging

Samples not washed



Oxide peaks masked by oxygen bearing surface films formed on aging

Mn, Co, Ni peaks from the oxide are not visible after cell aging



Some Relevant Publications

1. D.P. Abraham, M.M. Furczon, S.-H. Kang, D.W. Dees, A.N. Jansen, *Accepted by the Journal of Power Sources (2008)*.
2. S.-H. Kang, W.-S. Yoon, K-W. Nam, X.-Q. Yang, D.P. Abraham, *Accepted by J. Mater. Sci. (2008).*
3. S.-H. Kang, D.P. Abraham, A. Xiao, B.L. Lucht, *J. Power Sources 175 (2008) 526.*
4. S.-H. Kang, D.P. Abraham *J. Power Sources 174 (2007) 1229.*
5. K. Edstrom, M. Herstedt, D.P. Abraham, *Journal of Power Sources 153 (2006) pp. 380-384.*

Activities for Fiscal Year 2008 (and beyond)

- Systematic study of anode SEI formation mechanisms in cells containing various electrolytes
  - *Studies with BF-graphite electrodes*
- Systematic study of positive electrode surface films in cells containing various electrolytes
  - *Studies with BCF Gen3 oxide electrodes*
- Physicochemical diagnostic examination of differences between “super” and “poor” formation conditions
  - *Follow up to INL study on cell formation parameters and “effective” cell formation*

Summary

- Formation of electrode passivation layers can reduce cell performance degradation, which increases cell longevity. Improved life reduces cell lifetime cost making it more attractive for transportation applications.
- Our approach is to develop an understanding of the relationship between formation conditions, SEI characteristics, and electrode performance.
- We've been studying electrode cycling and impedance behavior in various electrolyte systems. We have obtained detailed information on the electrode surface films formed in $LiPF_6$-based electrolytes. We have also developed BCF oxide and BF graphite -electrodes to study electrode surface films formed after initial cycling and aging.
- We have published several articles on formation cycling. Our data have also been presented at several conferences and DOE meetings.
- In the coming year, we will continue our systematic study of surface films formed in various electrolytes with the goal of relating SEI characteristics to electrode performance.