

### Electrochemical Degradation of Carbon in Composite Cathodes for Li-ion Cells

Robert Kostecki, Soon-Ki Jeong, Jinglei Lei, Xiangyun Song, Vera Zhuang, Kathryn Striebel, Frank McLarnon

*Environmental Energy Technologies Division  
Lawrence Berkeley National Laboratory  
University of California, Berkeley, CA 94720, USA*

Carbon additives are commonly used to enhance electronic conductivity in composite cathodes for Li-ion batteries. The observed carbon retreat in the composite  $\text{LiAl}_{0.05}\text{Ni}_{0.8}\text{Co}_{0.15}\text{O}_2$  cathodes can lead to significant degradation of cathode power and energy [1]. The objective of this work is to carry out in-depth diagnostic studies of the mechanism of carbon retreat in composite cathodes and determine its impact on cathode electrochemical performance upon cycling and storage in  $\text{LiPF}_6$ -EC-EMC electrolyte at elevated temperatures.

Electrochemical anion intercalation into graphite has been studied for more than two decades [2]. Examples of carbon electrode used as the cathode in a lithium-ion cell have been also demonstrated [3]. The anion intercalation into graphite occurs at relatively high potentials ( $>4.4\text{V}$ ) and it is usually accompanied by electrolyte decomposition. However, there is no published data on electrochemical behavior of amorphous carbons toward anion intercalation.

To investigate the mechanism of carbon retreat or rearrangement in composite cathodes, thin film carbon black electrodes were prepared. An Al current collector was coated with  $20\ \mu\text{m}$  thick layer of 90% Shawignian black and 10% PVDF. The electrodes were stored or cycled vs. Li-metal in 1.2 M  $\text{LiPF}_6$  EC/EMC (3:7) at room temperature and at  $57^\circ\text{C}$ . Cyclic voltammograms of Al current collector and carbon coated Al (Figure 1) reveal that carbon electrodes exhibit significant electrochemical activity at potentials, at which composite cathodes usually operate in Li-ion batteries. A substantial anodic current above 3.8 V and a cathodic current below 2.9 V are observed, especially at elevated temperatures. The electrochemical response from carbon electrode changes continuously during prolonged cycling. The current tends to increase during initial cycles but then starts to decrease steadily and almost disappears completely at the end of cycling.

Raman microscopy analysis of carbon black electrodes cycled at elevated temperatures showed that the structure and electronic properties of carbon undergo severe changes upon cycling in  $\text{LiPF}_6$  containing electrolytes. Raman D and G carbon bands display significant broadening, which reflects structural disorder induced into the carbon structure. SEM images of cycled carbon black electrodes show substantial changes in surface morphology and carbon particle size. Interestingly, carbon electrodes just stored in the electrolyte show no change compared to the fresh electrode.

Reversible  $\text{PF}_6^-$  anion intercalation-deintercalation into carbon, carbon surface oxidation-reduction and electrolyte decomposition are likely processes responsible for the observed carbon degradation. As the matter of fact, one of the technological applications of the anion intercalation into graphite has been its use in preparing exfoliated graphite microparticles [4]. The observed structural degradation of carbon conductive additive in the composite cathodes can

have severe implications on the lifetime and electrochemical performance of composite cathodes.

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### References

1. R. Kostecki and F. McLarnon, *Electrochem. and Solid State Lett.*, in press.
2. A. Jobert, Ph. Touzain and L. Bonnetain, *Carbon*, **19**, 193 (1981).
3. R.T. Carlin, H.C. De Long, J. Fuller, and P.C. Trulove, *J. Electrochem. Soc.*, **141**, L73 (1994)
4. *Carbon-Carbon Materials and Composites*, J. Buckley and D. Edie, Editors, Noyes Publications, Park Ridge, NJ (1993).

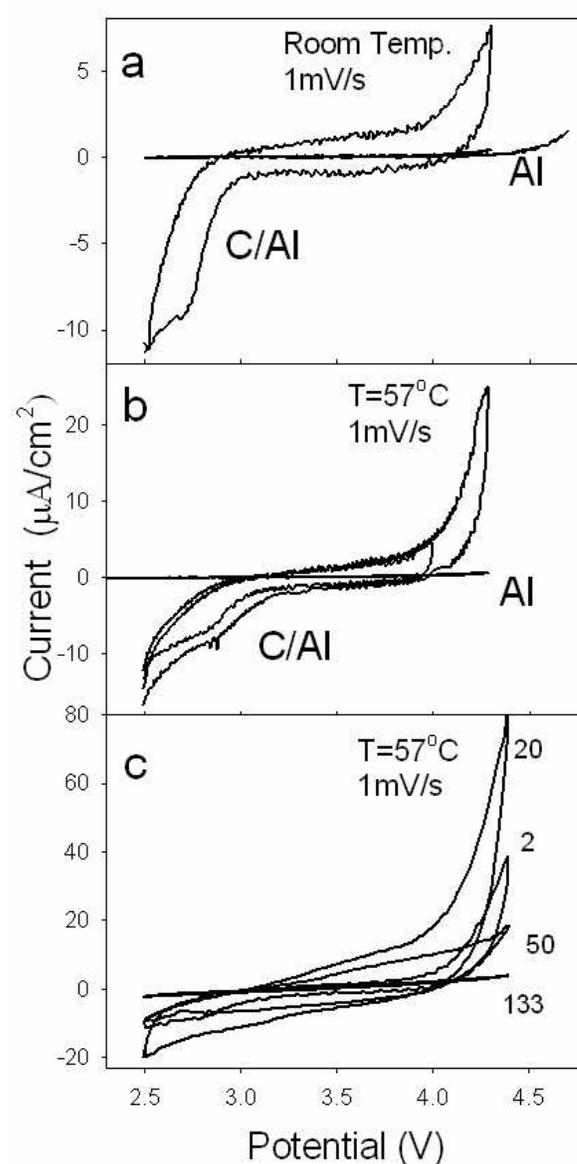


Figure 1. Cyclic voltammograms of Al current collector and carbon coated Al in EC:EMC (3:7), 1.2M  $\text{LiPF}_6$  at: room temperature a),  $57^\circ\text{C}$  b). Selected scans from the prolonged cycling of carbon electrode.