

Electrochemical Activity of Carbon Blacks in LiPF₆-based Organic Electrolytes

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Composite electrodes in lithium-ion cells typically consist of an active material, conductive carbon additive(s), and a binder. Surface reactions, structural degradation and carbon additive distribution changes may alter the electronic properties of the conductive carbon matrix and lead to the loss of electrochemical performance of composite electrodes [1, 2]. In fact, carbon black (CB) additives constitute 80-98% of the composite electrode surface area, but very little is known about their electrochemical activity and possible contribution to the electrode and system operation and degradation mechanism.

The electrochemical intercalation of anions into carbons has not been studied as extensively as the cation intercalation, and the majority of these studies focused on graphite and graphitic carbons. Electrochemical behavior of carbon black (CB) additives in 1M LiPF₆ EC/DEC (3:7 vol.) electrolyte within the operation potential range of positive electrodes in Li-ion cells was investigated.

All types of carbon black additives appear to be electrochemically active toward LiPF₆-based organic carbonate electrolytes at potentials at which most Li-ion positive electrodes operate (>4 V). The mechanism of these interfacial processes on CB electrodes and their implications for electrochemical performance of high-voltage Li-ion electrodes during long-term cycling is evaluated.

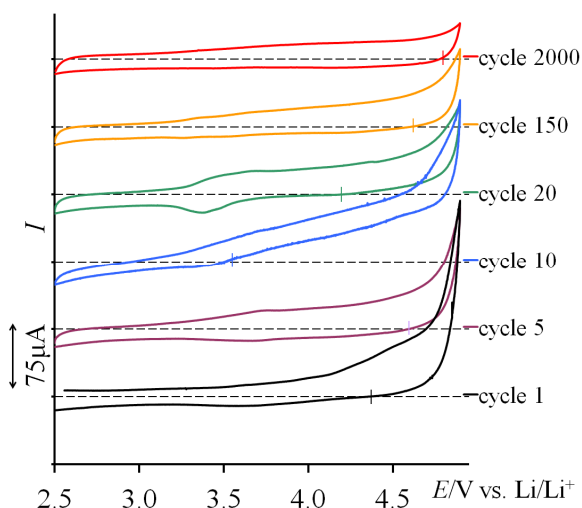


Figure 1: Cyclic voltammograms of Shawinigan Black composite electrode in 1M LiPF₆ EC/DEC 3:7 (vol.) electrolyte. Scan rate: 1 mV/s, Li metal counter electrode

PF₆⁻ anion intercalation into different types of carbon blacks was observed in 1M LiPF₆ EC/DEC (3:7 vol.) electrolyte. The PF₆⁻ intercalation into CB occurs at potentials significantly lower than for PF₆⁻ intercalation in graphite (~4.5 V) [3], which is assigned to larger d₀₀₂ spacing in CB than in graphite. *In situ* X-ray diffraction,

Raman spectroscopy, and *ex situ* scanning electron microscopy and FTIR spectroscopy showed that this process is not fully reversible and constitutes the main cause of morphological and structural changes of carbon material, leading to possible changes in its structure, morphology and electronic properties. It is the main cause of carbon particles decrepitation and gradual loss of material from the composite electrodes.

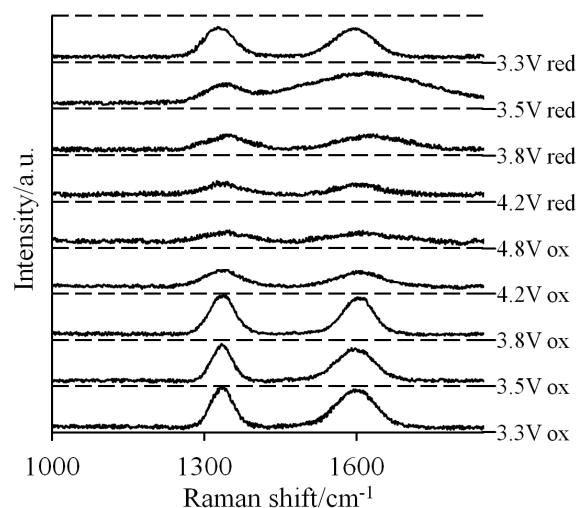


Figure 2: *In situ* Raman spectra of the Shawinigan Black electrode during the first CV scan between 2.5 and 4.9 V at 1 mV/s.

The spectro-electrochemical investigations also reveal electrolyte oxidation processes on carbon black at high electrochemical potentials. Electrolyte degradation products precipitate at the surface of carbon black, and contribute to the buildup of ionic and electronic barriers within the electrode. It leads to impedance rise of composite electrodes (decrease of carbon electronic conductivity and increase of contact resistance between carbon and active material). The observed electrochemical activity of carbon blacks in organic electrolytes at high potentials contributes to the gradual loss of power and charge capacity in Li-ion electrodes operating at high potentials.

The structural properties and distribution of carbon conductive additives for high voltage positive electrodes must be carefully optimized and matched to expected cycling potential range and electrolyte chemistry in order to provide reliable long-term electrochemical performance and safe operation

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