CAPSULES
notes and applications from Bioanalytical Systems, Inc.
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Electrochemical Impedance Spectroscopy #7 Characterization of Graphite Electrodes as Anodes for Secondary Lithium Batteries

Purpose

Although there is considerable interest in using lithium electrodes as anodes for secondary (rechargeable) batteries, the poor cycling properties and safety problems associated with such batteries has hindered their development. Lithium ion batteries, on the other hand, do not suffer from such disadvantages, and hence much effort has recently been devoted to the development of such batteries.

The anode in lithium ion batteries is generally a carbonaceous material (e.g., graphite), which can intercalate lithium ions. Graphite can intercalate reversibly up to a stoichiometry of LiC_6 at a potential close to that of the Li/Li^+ couple. However, for many electrolytes, cycling of graphite electrodes leads to destruction of the electrodes, due to co-intercalation of solvent molecules. One solvent combination that has been found to be suitable for graphite anodes is ethylene carbonate (EC) and diethyl carbonate (DEC). The aim of this study was to investigate the interfacial processes that occur at graphite anodes in EC-DEC solvent systems.

Reference

The Study of Electrolyte Solutions Based on Ethylene and Diethyl Carbonates for Rechargeable Li Batteries, D. Aurbach, Y. Ein-Eli, B. Markovsky, A. Zaban, S. Luski, Y. Carmeli and H. Yamin, J. Electrochem. Soc. 142 (1995) 2882-2890.

Method

Electrochemical impedance spectroscopy (EIS) is a powerful method for investigating processes occurring at the electrode/electrolyte interface. Since a range of frequencies is used, processes occurring at different rates (e.g., diffusion through a passivating layer and charge transfer at the electrode surface) can be detected within one experiment.

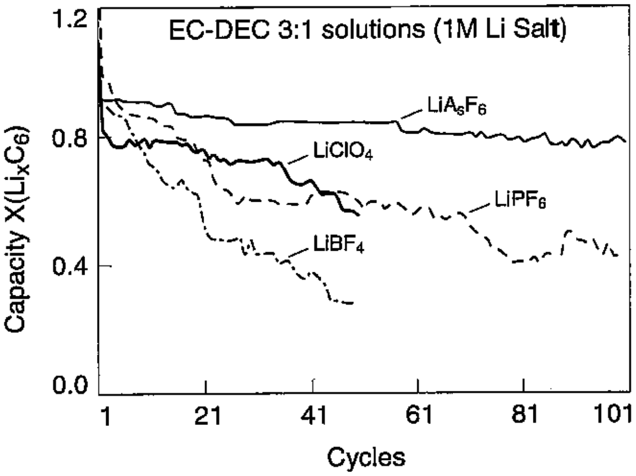

Figure 1. Comparison of the cycle life of graphite electrode in various salts in 1M solution in EC-DEC (3:1 mixture) under argon. Figure adapted from reference.

Results

One method for examining the suitability of graphite anodes for secondary batteries is to measure the capacity of the anodes as a function of the number of cycles. The data for four such experiments is shown in F1. Each of the lines represents the data for a different electrolyte salt. It is evident that capacity is best maintained when using $LiAsF_6$ as the salt. Similar experiments using different proportions of EC and DEC and running the experiments under argon or carbon dioxide showed that the performance increased with increasing EC content and when carbon dioxide was used.

The impedance spectra were also found to depend on the salt. F2 and F3 show the spectra recorded during intercalation and deintercalation, respectively, when using $LiAsF_6$ as the salt. At the open circuit voltage (2.31 V), the spectrum consists of a semi-circle at high frequencies, with a sloping line at lower frequencies. This is consistent with non-active elec-

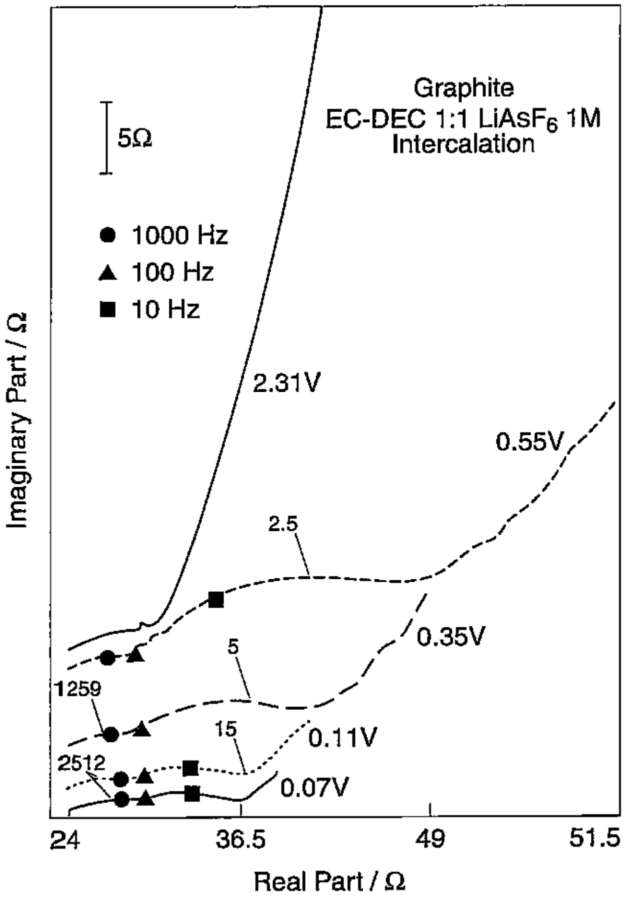

Figure 2. Nyquist plots for a graphite electrode during intercalation in 1M $LiAsF_6$/EC-DEC (1:1 mixture). All potentials measured with reference to Li/Li^+. The spectra are vertically offset. Figure adapted from reference.

trodes covered by surface films (formed by solvent reduction) with the only possible charge transfer reaction being solvent reduction. However, at lower potentials, the spectra exhibit two semi-circles together with a straight line at low frequencies. One of these semi-circles was attributed to migration of lithium ions through a film on the carbon surface, whereas the other was associated with the intercalation process (a combination of charge transfer and the electrode capacitance). The formation of an ionically-conducting surface film permits the intercalation of lithium ions but prevents the co-intercalation of solvent molecules; that is, the electrode is stabilized. It should also be noted that spectra recorded during the deintercalation process are similar to those recorded at similar potentials during the intercalation process; this suggests that the interface is stable during the cycling process.

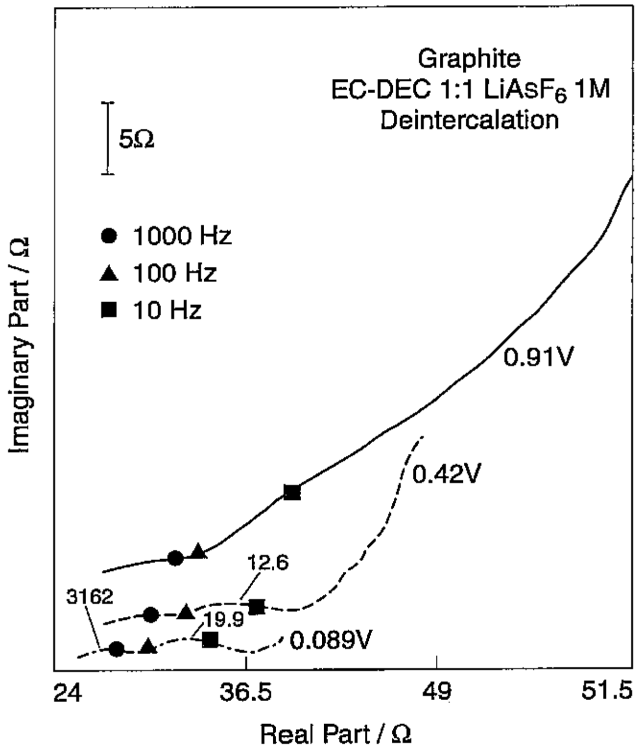

Figure 3. Nyquist plots for a graphite electrode during deintercalation in 1M $LiAsF_6$/EC-DEC (1:1 mixture). All potentials measured with reference to Li/Li^+. The spectra are vertically offset. Figure adapted from reference.

The analogous spectra for experiments using $LiPF_6$ as the salt are shown in F4 and F5. These show a number of differences when compared to the spectra discussed above. There is only one semi-circle in the spectra recorded at low potentials and this is larger than the semi-circles shown in F2 and F3. In addition, the semi-circles of the deintercalation spectra are larger than those for the intercalation. This shows that the interfacial resistance is larger for the $LiPF_6$ system and that the interface is not stable.

These differences can be explained by examining the Fourier transform infrared (FTIR) spectra of the surface films. For both salts, the film initially consists of organic carbonate salts generated by solvent reduction. However, when $LiPF_6$ is used as the salt, these carbonates are partially substituted by LiF and other salt reduction products; the surface film hence becomes more resistive. Analogous substitution does not occur when using LiAsF6 as a salt, which leads to a more stable, less resistive interface.

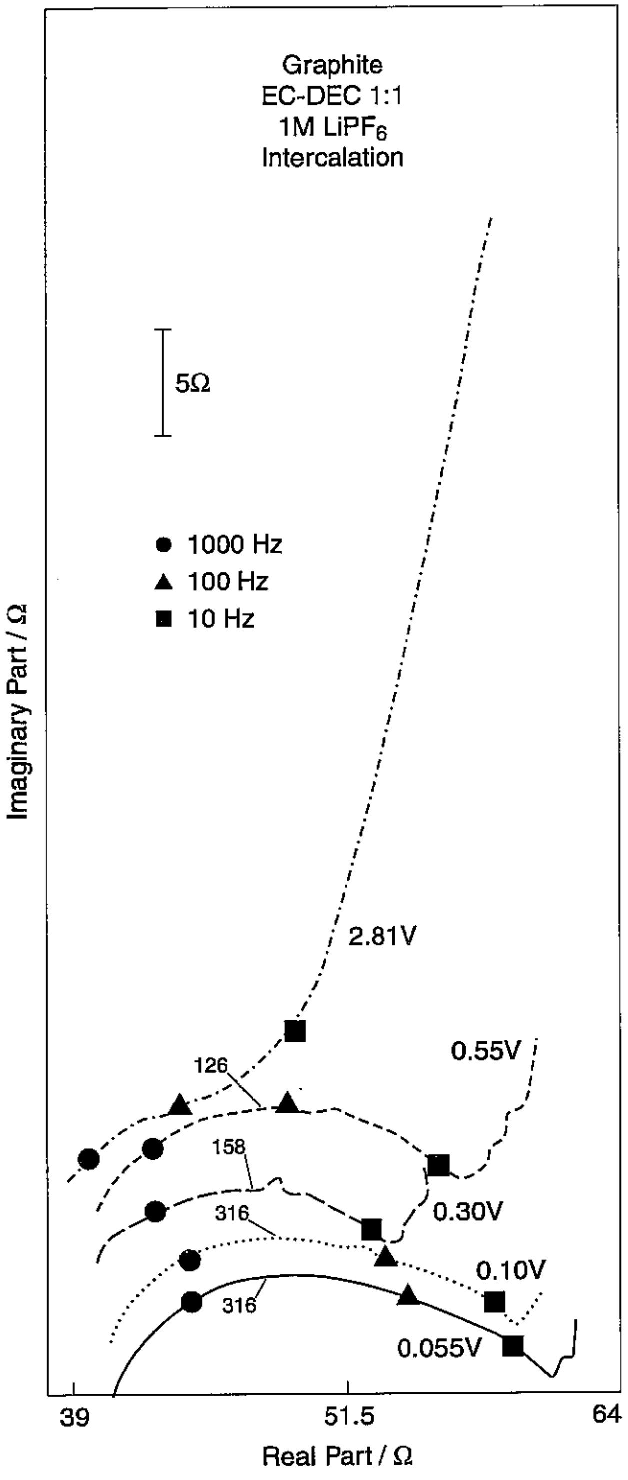

Figure 4. Nyquist plots for a graphite electrode during intercalation in 1M $LiPF_6$/EC-DEC (1:1 mixture). All potentials measured with reference to Li/Li^+. The spectra are vertically offset. Figure adapted from reference.

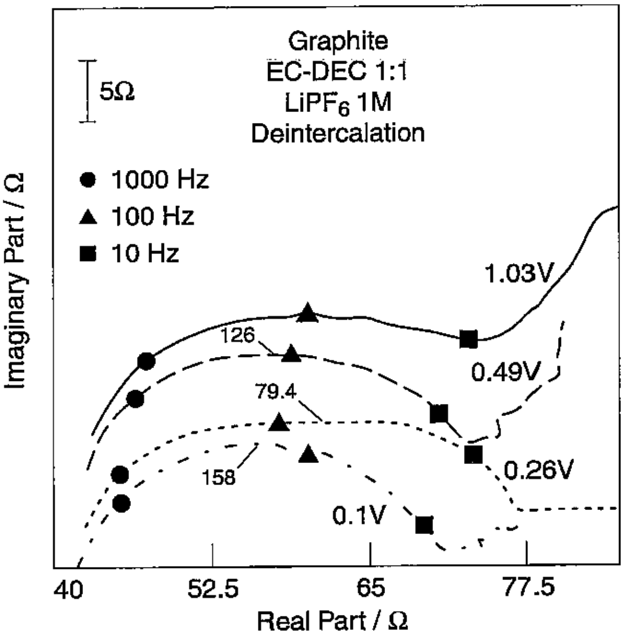

Figure 5. Nyquist plots for a graphite electrode during deintercalation in 1M $LiPF_6$/EC-DEC (1:1 mixture). All potentials measured with reference to Li/Li^+. The spectra are vertically offset. Figure adapted from reference.