CAPSULES
notes and applications from Bioanalytical Systems, Inc.
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Electrochemical Impedance Spectroscopy #6
Characterization of Lithium Anodes for Secondary Batteries

Purpose

Although there are many potential advantages to using lithium anodes in secondary (rechargeable) batteries, due to its high energy density and negative redox potential, development of such batteries has been limited. Dendritic deposition of lithium metal during the charging step reduces cycle life and produces a highly reactive system. In addition, the dendrites can break away from the anode, which leads to loss of active material. The dendrites can also short-circuit the battery.

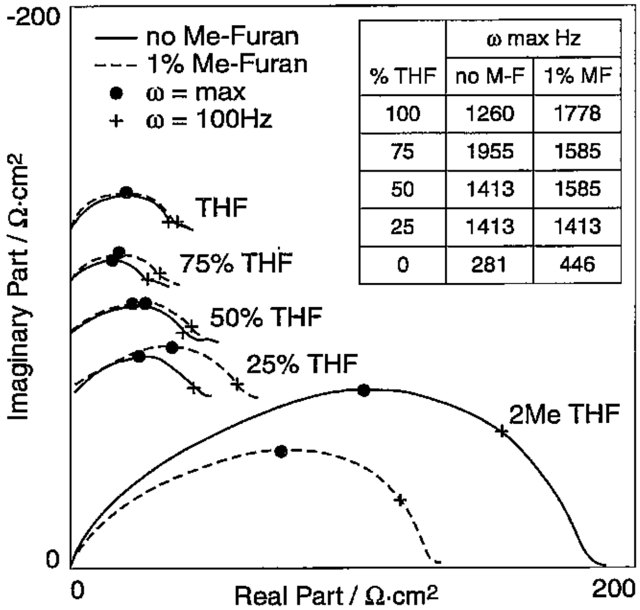
Therefore, there has been much interest in choosing an electrolyte system that can lead to smooth and uniform lithium deposition. It is known that the deposition is affected by the films that form on the surface of lithium electrodes, caused by the high reactivity of lithium. The composition of this film is determined by the nature of the electrolyte (the solvent or polymer and the salt), and any contaminants (e.g., water) or additives (e.g., carbon dioxide) that may be present. This study is one of a number of papers in which the authors attempted to correlate the morphology and composition of the surface film (as determined using surface-sensitive Fourier transform infrared (FTIR) spectroscopy, energy dispersive X-ray analysis (EDAX), and scanning electron microscopy (SEM)) with the interfacial properties of the lithium electrode (as determined by Electrochemical Impedance Spectroscopy (EIS)) and its cycling efficiency.

Reference

Studies of Li anodes in the Electrolyte System 2Me-THF/THF/Me-Furan/$LiAsF_6$, D. Aurbach, A. Zaban, Y. Gofer, O. Abramson and M. Ben-Zion, J. Electrochem. Soc. 142 (1995) 687-696.

Method

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.



% THF	ω max Hz no M-F	ω max Hz 1% MF
100	1260	1778
75	1955	1585
50	1413	1585
25	1413	1413
0	281	446

Figure 1. Nyquist plots obtained from lithium electrodes stored for 4 days in 1 M $LiAsF_6$ solutions. Solid lines, no additives; dashed lines, 1% Me-Furan. Figure adapted from reference.

Results

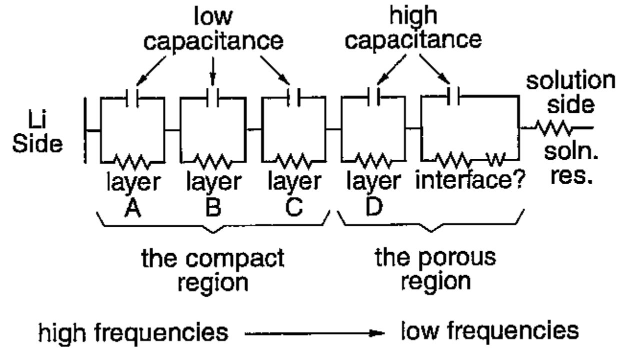
Exposure of a fresh, highly reactive, lithium surface to an electrolyte leads to the instantaneous formation of a film composed of insoluble lithium salts. The composition of this film depends upon the nature of the electrolyte, and varies with time. Since any lithium dissolution or deposition must occur through this film, the film has a significant effect on the discharging and charging behavior of secondary lithium anode batteries.

In this study, the effects of various ethereal solvents (THF, 2Me-THF, and 2Me-Furan (MF)), different concentrations of the $LiAsF_6$ salt and different water concentrations were examined. The impedance spectra of various solvent combinations are shown in F1 (it should be noted that MF was used as an additive for some of these measurements; spectra measured in the presence of 1% MF are shown as dashed lines). It can be seen that the major feature of all these spectra is a semi-circle; however, the radius of the semi-circle varies considerably with solvent composition.

An equivalent circuit consisting of 5 parallel RC circuits in series (F2) was used for these systems, reflecting the multi-layer structure of the surface films (it was found that 4 parallel RC circuits did not produce an adequate fit between the experimental and the simulated data, and that there was no noticeable improvement when 6 RC circuits were used). The values of the individual R and C components were calculated, and these values were used to estimate the total film resistance and the total film thickness (the thickness of the individual layers was calculated from the individual capacitances, the electrode surface area, and the average dielectric constant of the surface species (estimated at 5)). These values were plotted as a function of time for the various experimental conditions used. The plot of resistance *vs.* time for different solvent mixtures are shown in F3. It can be seen that the addition of THF to 2Me-THF decreases the resistance and stabilizes the interface (as shown by the time independence of the resistance for THF-containing mixtures); the addition of 1% MF has little effect if THF is also present, but it again stabilizes the interface for the 100% 2Me-THF system.

More information can be gained about the nature of the film by using analytical techniques such as surface-sensitive FTIR and EDAX. It was shown by FTIR that the major surface species for all solvents used in this study were lithium alkoxide species, produced by reduction of the ether solvents. Inorganic and organic lithium carbonates are also present, due to the reaction of the lithium alkoxide species with carbon dioxide. Lithium oxides and hydroxides were produced by reaction with trace water. EDAX detected the presence of arsenic and fluoride containing compounds in the surface films, which is consistent with the reduction of the $LiAsF_6$ salt used in these studies. The addition of MF to both THF and 2Me-THF caused a decrease in the film concentrations of species derived from the reduction of THF, 2Me-THF, and the $LiAsF_6$ salt; this was attributed to the preferential reduction of MF and the deposition of MF reduction products on the electrode surface.

The difference in the impedance spectra for 100% 2Me-THF and the other solvent mixtures was attributed to the lower reactivity of 2Me-THF. This leads to a greater contribution to the film of the reduction products of the salt and of trace water. The presence of increased concentrations of lithium hydroxide and lithium oxide in the film allows diffusion of water through the film; that is, there is no passivation for water. The increasing resistance of the film when using 100% 2Me-THF was therefore attributed to a continuing reaction with water. The addition of the more reactive THF and/or MF prevented this process.



Scheme 2

Figure 2. Equivalent circuit used for modeling film on lithium anode. Figure adapted from reference.

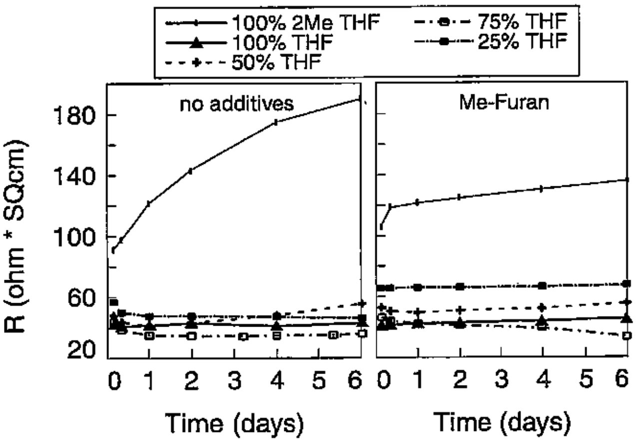


Figure 3. Interfacial resistance of lithium electrodes stored in 1 M $LiAsF_6$ solutions of THF, 2Me-THF and THF/2Me-THF mixtures with a) no additives and b) 1% Me-Furan. Figure adapted from reference.

The nature of the surface film was also studied using SEM. The morphology was found to be essentially smooth for all solvent combinations; although, the morphology of films grown in 2Me-THF solvent was sensitive to the presence of contaminants (this was attributed to the relatively low reactivity of this solvent). The cycling efficiency was also slightly decreased for solvents with a high 2Me-THF components, but this could again be reversed by the addition of the more reactive MF.

Although the composition of the surface film (and hence its effect on the performance of the lithium anode) can be affected by many factors, the use of EIS in conjunction with surface-analysis techniques can lead to a better understanding of the lithium-electrolyte interface.