A.C. IMPEDANCE STUDIES ON THE LITHIUM PASSIVATING LAYER OF AN Li–SOCl$_2$ CELL (EXTENDED ABSTRACT)

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The lithium electrode becomes passivated by a thin layer of insoluble LiCl upon contact with LiAlCl$_4$–SOCl$_2$ electrolyte. This passivating layer retards the chemical interaction between lithium and SOCl$_2$, which prolongs the shelf life of the cell. It also causes the so-called "voltage delay" problem. Considerable efforts have been made to determine the morphology and kinetic properties of the passivating layer. Significant results have been obtained in recent years by means of a.c. impedance analyses [1 - 3]. In this study, the a.c. impedance method was also used to investigate the effects of anodic pulses and cyanoacrylate coatings on lithium electrodes.

The electrochemical cell consisted of three Li metal (Foote) electrodes held in position by PTFE spacers. The free surface area of the working electrode was well defined by plugging Li into a 2.4 mm glass tube, and then cutting with a knife to acquire a fresh surface. A nickel wire inside the glass tube was attached to the lithium so that a mixed potential problem was avoided. The reference electrode, manufactured in the same way, was spaced about 5 mm from the working electrode and was arranged in such a way as not to shield the latter. The counter electrode was also at a distance of 5 mm from the working electrode. The electrolyte was 1.5 M LiAlCl$_4$ in SOCl$_2$ throughout the experiment. An EG&G M378 electrochemical impedance system (Princeton Applied Research Co.) interfaced with an IBM XT computer was used to carry out the experiments. Test frequencies were set from 10^{-1} to 10^5 Hz with an amplitude of 10 mV. One experiment took about 8 min to complete.

Figure 1 illustrates the Nyquist plots for a non-coated Li electrode. Curve a represents the case when the Li electrode had been stored in electrolyte for 1 day at room temperature. Curves b - f represent the cases when an anodic pulse of 1.5 V s^{-1} was applied and a.c. impedances were measured at times 0, 9.5, 18.5, 27.5 and 36 min, respectively, after the anodic pulse. An equivalent circuit of parallel resistor–capacitor combination is proposed for the semi-circular Nyquist plot. The solution resistance was negligible, as shown on the high frequency part at the left-hand side of the plots. The low
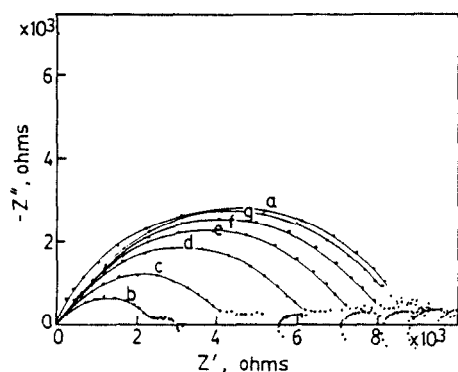
Fig. 1. Impedance loci for Li electrode after (a) one-day electrode/electrolyte contact at room temperature and then, at (b) 0 min, (c) 9.5 min, (d) 18.5 min, (e) 27.5 min, (f) 36 min, and (g) 46 min after the anodic pulse (1.5 V vs. Li-ref. s^{-1}).
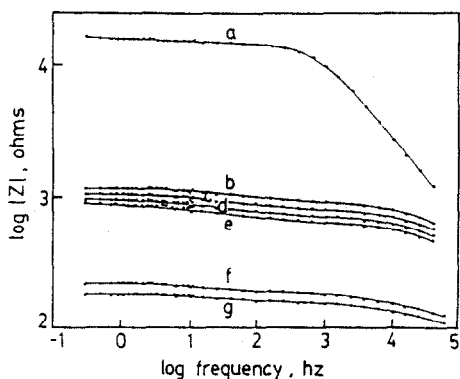
Fig. 2. Bode plots for Li electrode after (a) one-day electrode/electrolyte contact at room temperature and then consecutive anodic pulses of (b) 1.5 V s^{-1}, (c) 1.5 V s^{-1}, (d) 2.0 V s^{-1}, (e) 2.0 V s^{-1}, and that immersed in acid electrolyte for (f) 32 min, (g) 5.5 h.

frequency part at the right-hand side of the plots represents the resistance of the passivating layer, which was broken by an anodic pulse (curve b). However, this passivating layer recovered in less than one hour. An extrapolation of the polarization resistances will show that the solid electrolyte interphase (SEI) of the passivating layer cannot be removed completely. This is further evidenced by repeated anodic pulses, as shown in the Bode plots of Fig. 2. The SEI existed even in the acid electrolyte (1.5 M $LiAlCl_4$ + 0.3 M $AlCl_3$ in $SOCl_2$) where $AlCl_3$ reacted with the LiCl film. The result is in agreement with Meitav and Peled's [4] measurements of SEI thickness.

The voltage delay problem caused by the passivating layer can be overcome by cyanoacrylate (CA) coatings on fresh-cut lithium, as demonstrated by Fleischer et $al.$ [5]. The CA-coated Li electrode has a much lower polarization resistance than the non-coated electrode, as shown in Fig. 3. Fleischer and Ekern [6] attributed the polarization reduction to the CA coatings because of the change in morphology and the growth kinetics of the LiCl film. Higher temperature storage at 50 °C accelerated the formation of the passivating layer. The a.c. impedance measurements at −10 °C (Fig. 4) showed a second semi-circle for the non-coated Li electrode which could be attributed to the increase in viscosity and the decrease in conductivity of the electrolyte inside the second porous layer. The linear Warburg curve cannot be seen clearly because of the effect of a combination of migration and diffusion. No second semi-circle was found for the CA coated electrode, which could be attributed to the lack of a secondary porous layer.

In conclusion:

(i) An anodic pulse breaks the passivating layer on the Li electrode, but the SEI cannot be removed completely.

(ii) The CA coated Li electrode substantially reduces the polarization resistance and the voltage delay time.
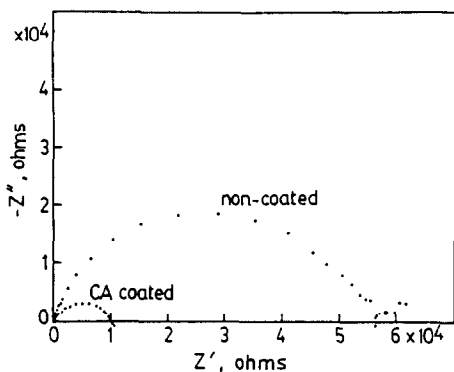
Fig. 3. Impedance loci for Li electrode after 16 h immersion in electrolyte at 50 °C and test at room temperature.
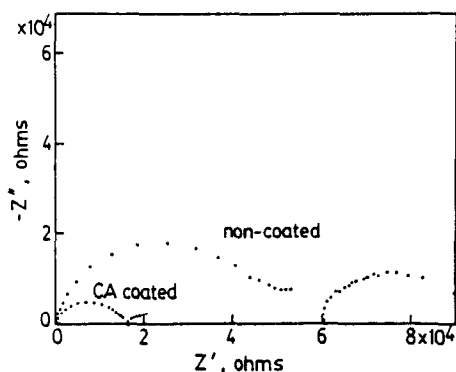
Fig. 4. Impedance loci for Li electrode after 16 h immersion in electrolyte at 50 °C and test at −10 °C.

(iii) A second parallel resistance–capacitor combination appears at −10 °C caused by the electrolyte inside the second porous layer.

References

1 M. Hughes, S. A. G. R. Karunathilaka and N. A. Hampson, *J. Appl. Electrochem.*, *13* (1983) 669.
2 J. Thevenin, *J. Power Sources*, *14* (1985) 45.
3 A. J. Hills, N. A. Hampson and M. Hayes, *J. Electroanal. Chem.*, *209* (1986) 351.
4 A. Meitav and E. Peled, *J. Electrochem. Soc.*, *128* (1981) 825.
5 N. A. Fleischer, J. R. Thomas and R. J. Ekern, *Proc. 30th Power Sources Symp.*, *1982*, p. 172.
6 N. A. Fleischer and R. J. Ekern, *J. Power Sources*, *10* (1983) 179.