

THE A.C. RESPONSE OF LITHIUM, STAINLESS STEEL, AND POROUS CARBON ELECTRODES IN THIONYL CHLORIDE SOLUTIONS

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Summary

Impedance measurements on Li electrodes in SOCl_2 electrolytes indicate that the structure of the passivating surface layer formed in 1.8M LiAlCl_4 differs from that formed in 1.8M AlCl_3 , 1.2M LiCl , 0.6M SO_2 . Also, porous carbon electrodes are found to behave differently in these two electrolytes.

Unpolarised stainless steel electrodes show a 67° constant phase angle impedance over a wide frequency range whereas polarised to 0 mV vs. Li the impedance diagram is very similar to that of Li.

Finally, it is found that passivation may develop differently for Li pressed onto stainless steel from that of Li pressed onto glass.

Introduction

A commercial Li- SOCl_2 battery consists of a Li anode, often swaged against the inner wall of a stainless steel (SS) can, a liquid SOCl_2 cathode made conducting by a Li salt, and a porous carbon cathode on which the reduction of SOCl_2 takes place. The direct contact between the liquid SOCl_2 , Li, and SS is only possible because a passivating solid electrolyte interphase is formed on both metals. The system has been extensively studied and is described in several literature reviews [1 - 4].

This paper provides further information about the a.c. response of Li, SS, and carbon electrodes in SOCl_2 electrolytes. Impedance is a measure of passivation, and examples of measured passivation *versus* time relationships are given.

Experimental

A three-electrode arrangement was used. The reference electrode was lithium in all cases. The details of cell and electrolyte preparation are given elsewhere [5]. Lithium electrode areas were from 21 to 26 cm^2 and SS

electrode areas 33 cm^2 . The electrode area to electrolyte volume ratio was $1.5 \text{ cm}^2/\text{cm}^3$. Carbon electrodes of 1.6 g of Shawinigan acetylene black bonded with PTFE (2.4% PTFE-97.6% carbon) had a geometrical surface area of about 28 cm^2 . Impedance measurements were performed using a Solartron 1250 Impedance Analyzer, and the data were collected automatically by an HP85 computer. At low frequencies the current density amplitude was usually kept below $3 \mu\text{A}/\text{cm}^2$ in order to maintain electrode stability.

Results and discussion

Curve A in Fig. 1 shows the complex plane impedance plot for a Li electrode stored for 6 days in 1.8M LiAlCl_4 at room temperature, and curve B is for Li stored for 13 days at 55°C in 1.8M AlCl_3 , 1.2M LiCl , 0.6M SO_2 . The passivation of Li usually observed in SOCl_2 batteries with LiAlCl_4 salt is alleviated if part of the AlCl_3 is neutralised with SO_2 instead of with LiCl , probably because the passivating LiCl is slowly dissolved, displacing SO_2 from the SO_2AlCl_3 complex [2]. So it is as expected that the impedance (*i.e.*, the degree of passivation) is much less for Li in the SO_2 -containing electrolyte than in the LiAlCl_4 electrolyte, despite the longer storage time at higher temperature in the 0.6M SO_2 electrolyte.

The difference in size is not, however, the only dissimilarity between the curves in Fig. 1. The depression of the semicircles in the frequency range

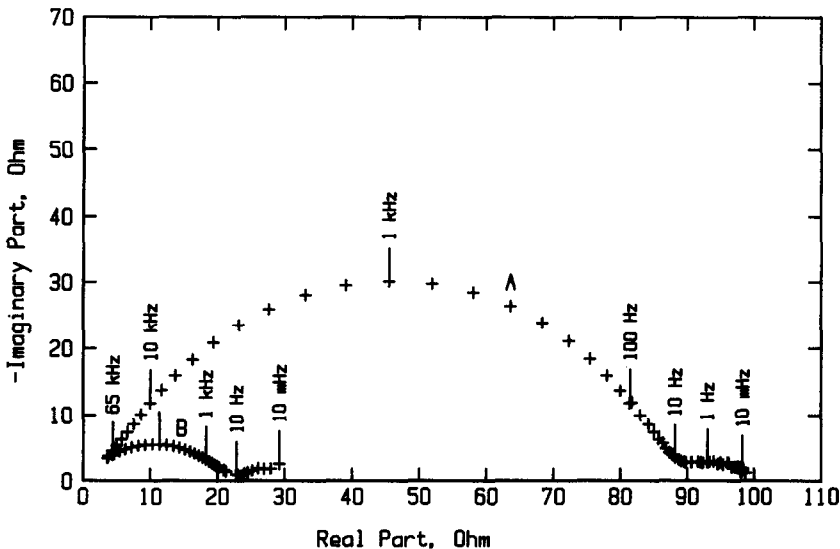


Fig. 1. Complex plane impedance plots for Li after 6 days at room temperature in 1.8M LiAlCl_4 (curve A) and after 13 days at 55°C in 1.8M AlCl_3 , 1.2M LiCl , 0.6M SO_2 (curve B), measured at 55°C in SOCl_2 solutions. Electrode areas: 25 cm^2 .

above 10 Hz is different. If the depression, d , is defined as the "vertical radius" divided by the "horizontal radius" $d = 0.7$ for curve A, and $d = 0.5$ for curve B. These values seem to be characteristic constants of these systems, independent of the size of the interphase impedance and of storage conditions. Another difference is that the "nose" of curve A disappears with increasing impedance (passivation) whereas the beginning of an extremely depressed semicircle on curve B in the frequency range below 10 Hz remains reasonably unchanged by time and temperature. It is thought that these differences in the impedance plot shapes reflect differences in the interphase structure caused by the electrolytes.

Figure 2 shows an impedance plot of a porous carbon electrode in 1.8M LiAlCl₄. The curve is an almost perfect semicircle, $d = 0.9$. Even though the resistance in this electrode is quite low, carbon is passivated in this electrolyte. A current load of 1 mA reduces the electrode resistance from about 9 to 1 ohm within a few seconds. In 1.8M AlCl₃, 1.2M LiCl, 0.6M SO₂ the carbon electrode does not passivate. After three months at room temperature the resistance was 0.3 Ω only.

Figure 3 shows the impedance plot for a SS electrode in 1.8M LiAlCl₄. The impedance shows a constant phase angle of $67 \pm 2^\circ$ in the frequency range 500 Hz - 80 mHz. Below 80 mHz the phase angle falls off and reaches zero at about 8 mHz.

The free potential of SS electrodes in SOCl₂ electrolyte is 3.7 V *vs.* Li. If SS is polarised to 0 mV *vs.* Li an instantaneous current density of 7 mA/cm² is drawn. After 24 h the SS electrode is passivated and the current density is 3 μA/cm². At this point the impedance curve of the electrode has

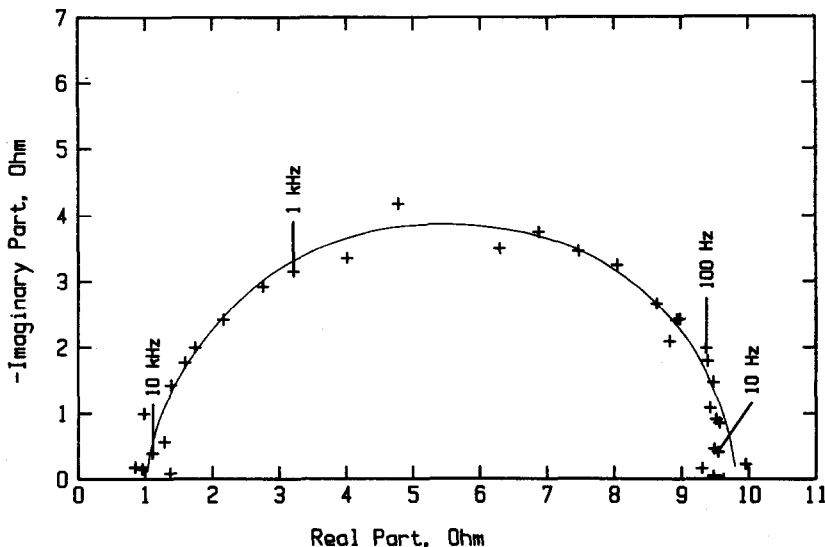


Fig. 2. Complex plane impedance plot for a porous carbon electrode (geometrical surface: 28 cm²) in 1.8M LiAlCl₄ in SOCl₂.

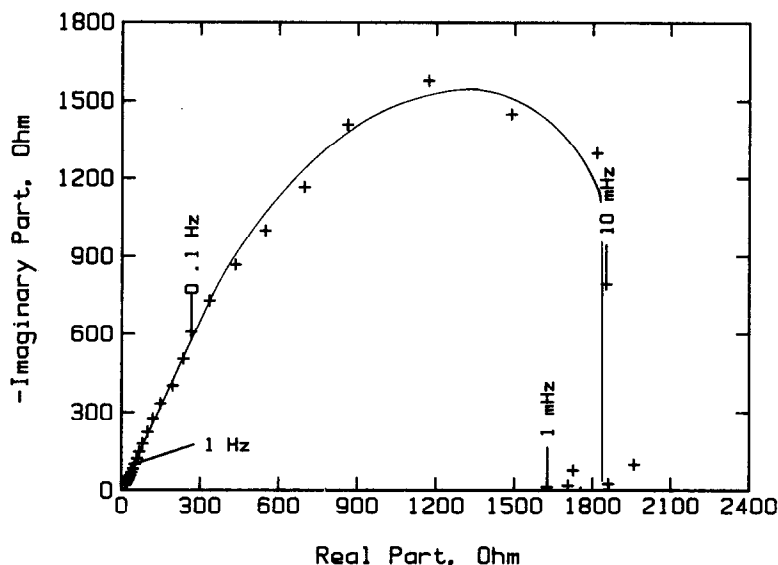


Fig. 3. Complex plane impedance plot for an unpolarised stainless steel electrode (33 cm^2) in 1.8M LiAlCl_4 in SOCl_2 .

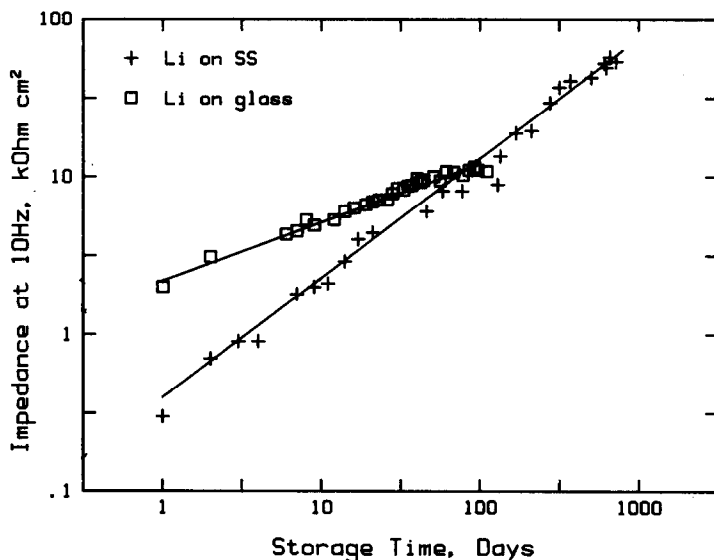


Fig. 4. Log-log plot of impedance at 10 Hz as a function of time for Li on stainless steel and on glass in 1.8M LiAlCl_4 in SOCl_2 at room temperature.

completely changed from that of Fig. 3 to a depressed semicircle with $d = 0.7$, similar to Li in 1.8M LiAlCl_4 .

It has been reported that an anodic current density of $2 \mu\text{A}/\text{cm}^2$ is sufficient to keep the Li electrode free from voltage delay [6]. It was

assumed therefore, that in the case where Li is in contact with SS and both metals are exposed to the electrolyte, the passivation of Li would develop in a different manner from the passivation of Li in contact with inert glass. This was confirmed. Figure 4 shows two log-log plots of impedance at 10 Hz (a measure of the passivation) as a function of time. Over a 2 year period, t was to the power 0.75 for Li on SS and 0.37 for Li on glass in the relationship between impedance Z in $\text{k}\Omega \text{ cm}^2$ and storage time, t , in days. The two examples shown in Fig. 4 were chosen as typical from measurements on more than 10 electrodes of each type.

Acknowledgements

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