

POLARIZATION OF THE LITHIUM ELECTRODE IN SULFURYL CHLORIDE SOLUTIONS

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Summary

The growth of the passivating film on a lithium electrode in contact with sulfonyl chloride solutions has been examined by micropolarization and complex impedance measurements. The results tend to confirm the hypothesis of a two-layer film, where probably the first layer is thin and compact and the second layer is porous and defective.

Introduction

The behaviour and performance of lithium-sulfonyl chloride batteries are largely influenced by the anodic passivation phenomena which result in the formation of a poorly conductive film on the surface of the lithium electrode. The understanding of the nature and of the morphology of this passivating film and the control of its growth are of primary importance in the general development of lithium-inorganic electrolyte batteries.

To achieve this understanding, we have undertaken an electrochemical study of the polarization of the lithium electrode in sulfonyl chloride solutions, and the results obtained by micropolarization and complex impedance measurements are summarized in this work.

Experimental

Lithium chloride (LiCl, Merck, reagent grade) was dried under vacuum at 150 °C for 48 h. Aluminum trichloride (AlCl₃, Fluka, reagent grade) was further purified by sublimation in the presence of excess of Al metal.

The purification of sulfonyl chloride, as well as the preparation of the electrolyte solutions, were described in an earlier paper [1]. The conductiv-

ity of the solutions was controlled by a conventional glass cell having two platinum electrodes.

For the micropolarization studies, a three-electrode cell (entirely assembled in a dry-box containing less than 2 ppm of water) was used. The structure of this cell has been described in detail elsewhere [1]. Basically, the lithium working, the lithium reference, and the lithium counter electrodes, respectively, were pressed into a suitable Teflon holder and contacted by nickel terminals. The Teflon holder was then housed in a glass container and sealed with Teflon gaskets. Known amounts of electrolyte were then syringed into the cell. A similar configuration, with only two facing lithium electrodes, was adopted for the cell used for the impedance measurements.

The micropolarization sweeps were obtained with a galvanostat driven by a fast function generator. The a.c. impedance measurements were controlled and run by a Solartron apparatus: 10 mV r.m.s. sine waves (frequency range from 1 Hz to 1 MHz) were imposed on the cell and the response was analyzed by an Apple Computer.

Results and discussion

As is typical of lithium-inorganic electrolyte systems, the lithium electrode is readily passivated in sulfuryl chloride solutions, with the formation of a non-conductive film which grows on its surface continuously and causes severe voltage delay effects upon discharge [2, 3].

We have studied the growth rate of this film by fast micropolarization sweeps (0 - 10 μA amplitude and 10 $\mu\text{A s}^{-1}$ rate) progressively carried out on a lithium electrode kept in contact with a LiAlCl_4 , SO_2Cl_2 solution. Since, under this condition, the electrode polarization is mainly ohmic, it is possible to obtain the resistance of the electrode from the slope of the related current-voltage curve, following its increase with the time of contact with the electrolyte, and thus evaluate the rate of growth of the passivating film. This is shown in Fig. 1, where a typical micropolarisation sweep is also inserted. The growth of the film appears to be parabolic, with a very fast rate at the initial period of contact with the electrolyte solution.

We have postulated in previous papers [2, 3] that, as proposed in the case of thionyl chloride systems [4 - 6], and in sulfuryl chloride solutions also, the lithium passivating film has a two-layer configuration. The inner layer is probably thin and compact and it is formed immediately upon contact with the electrolyte. This layer protects the electrode from corrosion by the solvent. The second layer, which grows continuously on the first one, is porous and defective and is probably responsible for the voltage delay effects experienced in stored $\text{Li}/\text{SO}_2\text{Cl}_2$ cells [1].

Upon discharge, lithium migrates through the first layer (probably *via* an ionic transport, since the film is basically formed by LiCl which is an Li^+ ionic conductor) and then through channels in the porous outer layer, the latter being progressively eliminated by thermal and gravitational stresses.

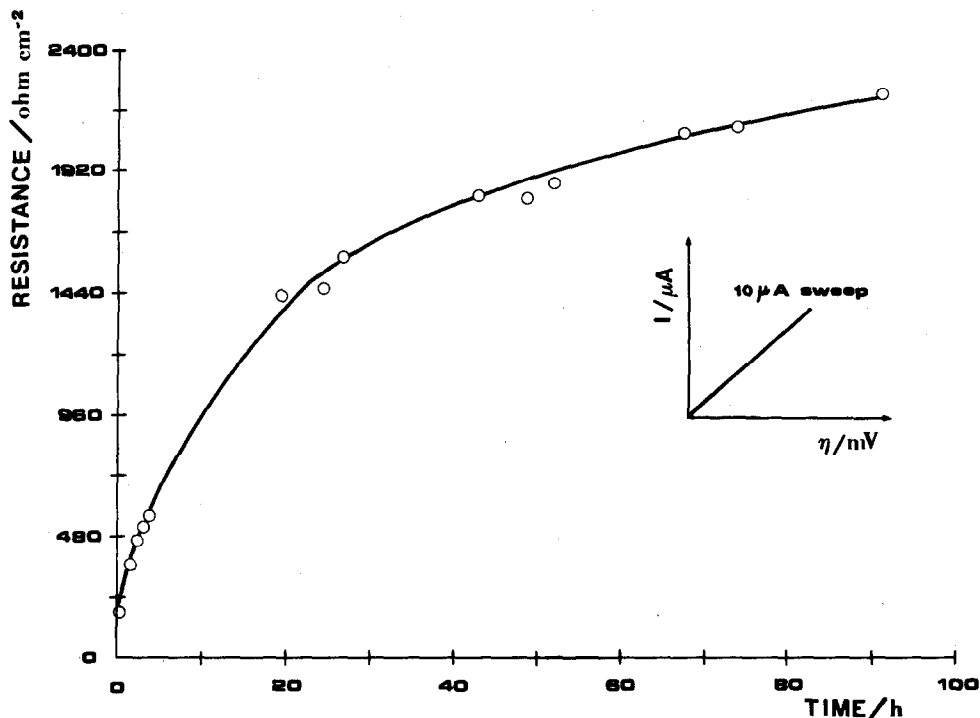


Fig. 1. Resistance growth of the lithium electrode in an LiAlCl_4 solution, determined by fast micropolarization sweeps ($10 \mu\text{A/s}$). Electrode surface: 1.2 cm^2 .

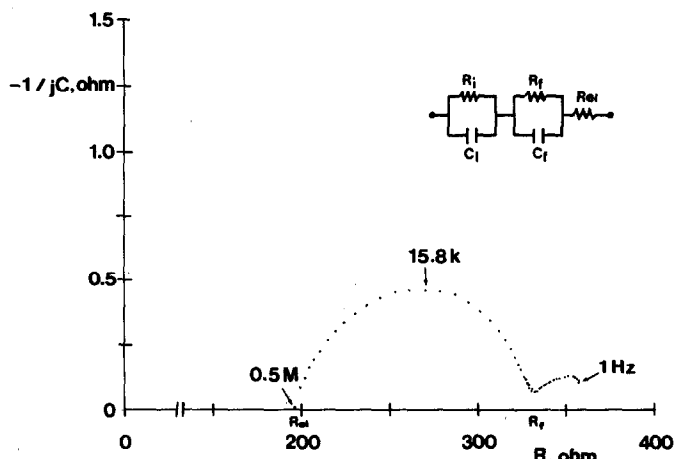


Fig. 2. Complex impedance plot for an Li/LiAlCl_4 , $\text{SO}_2\text{Cl}_2/\text{Li}$ cell after 1.5 h of storage. Electrode surface: 0.12 cm^2 .

To support this model further, we have carried out an a.c. impedance study of cells having two facing lithium electrodes in SO_2Cl_2 solutions. Figure 2 shows a complex plane impedance Nyquist plot of a cell using a 0.83M

LiAlCl_4 solution in SO_2Cl_2 . The measurements were taken after 1.5 h storage. The plot clearly shows the presence of two semicircles. The low-frequency semicircle probably represents the process of lithium dissolution and thus is associated with the electrode-electrolyte interface. Indeed, the capacitance (C_i) derived from this low-frequency semicircle is of the order of several microfarads.

The second semicircle represents the impedance of the passivating film on the lithium electrode. Here, in fact, the electrode capacitance (C_f), being of the order of $0.15 \mu\text{F}/\text{cm}^2$, is much smaller than that normally associated with double-layer capacitance and thus must be related to the geometric capacitance of the lithium passivating film. It should be pointed out that a two-semicircle complex impedance plot has also been noted in the case of lithium-thionyl chloride cells [7].

Using the equation of a parallel plate capacitor as discussed by Peled [5], the minimum thickness of the film is here calculated to be of the order of 10^{-5} cm and this value again agrees well with those reported as typical for passivating films in other lithium-inorganic electrolyte systems [5, 7].

The simplest equivalent circuit which may describe the lithium electrode in contact with an LiAlCl_4 , SO_2Cl_2 solution is that shown in the inset of Fig. 2, consisting of a series combination of resistance and capacitance. In this circuit, R_{e1} represents the resistance of the LiAlCl_4 , SO_2Cl_2 electrolyte solution interposed between the two lithium electrodes, R_f and C_f , the

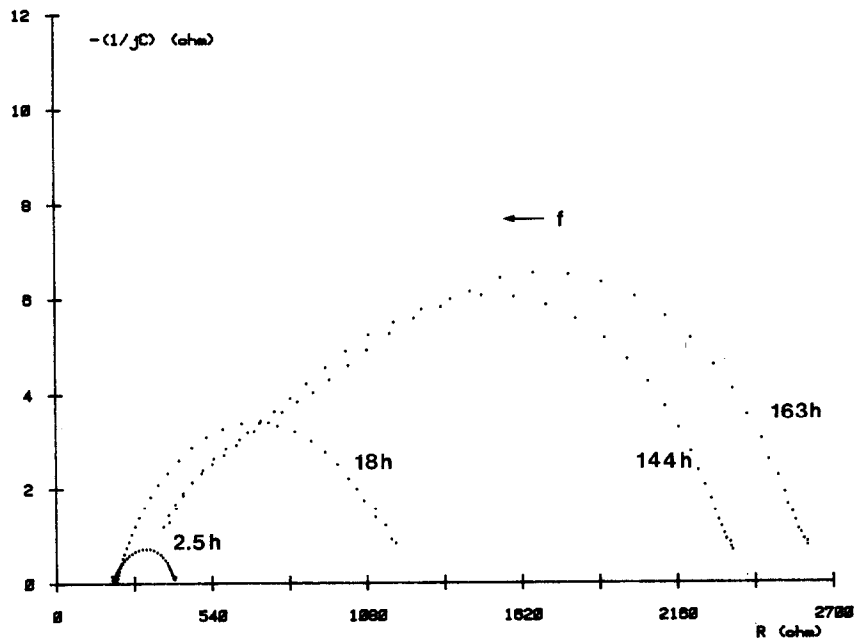


Fig. 3. Complex impedance plot for an $\text{Li}/\text{LiAlCl}_4$, $\text{SO}_2\text{Cl}_2/\text{Li}$ cell after various times of storage. Electrode surface: 0.12 cm^2 .

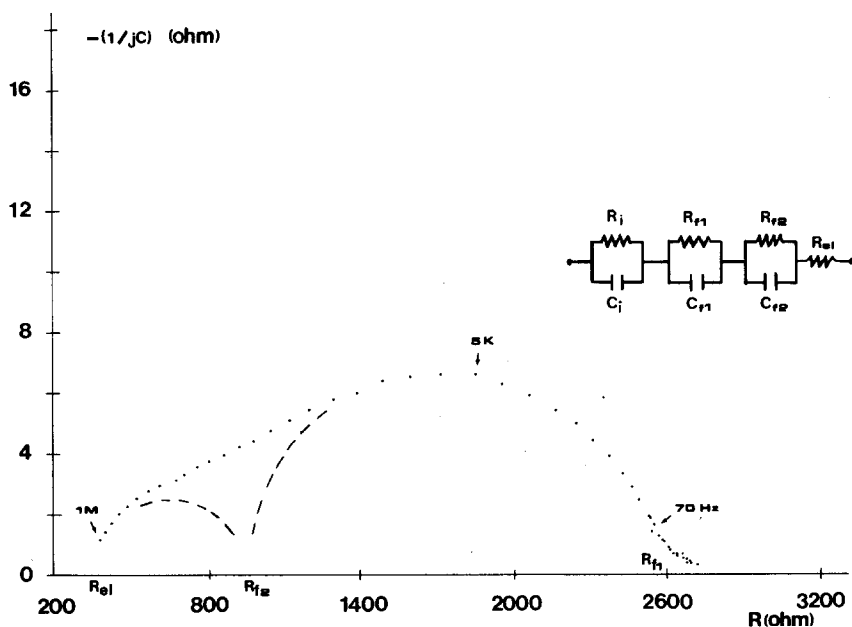


Fig. 4. Complex impedance plot for an Li/LiAlCl₄, SO₂Cl₂/Li cell after 163 h of storage. Electrode surface: 0.12 cm².

resistance and the capacitance respectively of the passivating film, and C_i the capacitance of the interface.

Figure 3 shows complex impedance plane plots for the same cells, obtained after progressively increasing times of storage. It may be noticed that the prolonged contact with the electrolyte results in a progressive increase in the film resistance R_f (as expected on the basis of the already discussed growth of the film) while the resistance of the electrolyte, R_{e1} , changes very little (as also expected, since the passivation of the electrodes should not greatly influence the measure of the electrolyte resistance at high frequencies). This behaviour supports the equivalent circuit of Fig. 2.

However, another important feature is deducible from Fig. 3: the semi-circle representing the impedance of the lithium passivating film is progressively splitting into two semicircles. This reveals two polarization events whose time constants become increasingly different. Such an effect might, indeed, indicate that the growing film has a different morphology from that formed immediately upon contact with the electrolyte.

On the above assumptions, the equivalent circuit may be considered as being formed by the sequence of series combinations of resistance and capacitance indicated in Fig. 4, where the complex impedance plane for a cell stored for 163 h is illustrated. Here R_{f1} and C_{f1} represent the resistance and the capacitance respectively of the first inner layer, and R_{f2} and C_{f2} the resistance and capacitance respectively of the growing film.

Acknowledgements

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