

## PROPERTIES OF A PASSIVATING FILM ON THE SURFACE OF LITHIUM ELECTRODES

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### Summary

The properties of the primary passivation film formed on a lithium electrode in a solution of  $\text{LiAlCl}_4$  in thionyl chloride are described. The thickness of the film grows rapidly to 1 - 1.5 nm during the first few hours after contact of the lithium with the electrolyte, and then becomes  $\sim 5$  nm after a certain period of time. The film has a continuous, not obviously crystalline, structure, and its conductivity for lithium ions has a semiconductor nature that is determined by the presence of defects in the crystal. The film exhibits a p-type electronic conductivity that is caused by electron holes as the minority current carriers, and its presence leads to the further growth of a continuous film. The decrease in the concentration of the minority carriers in the bulk of the film during exposure of the electrode to the solution can be associated with slow structure-ordering processes. The formation of a thick, crystalline secondary film after long electrode exposure hinders mass transfer in the solution layers adjacent to the electrode and preserves the primary film.

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### Introduction

During the past decade, numerous studies have been made of the passivating film formed on a lithium surface in contact with aprotic electrolyte solutions using either comparatively inert organic solvents (*e.g.*, propylene carbonate) or oxidative solvents (*e.g.*, thionyl chloride). Nevertheless, many aspects of the structure and the operating mechanism of such films have not been fully elucidated, and they are still widely debated.

### Experimental and results

The data available at present indicate that the formation of the surface layer passes through a succession of consecutive steps and that the thickness

is not uniform. After a sufficiently long contact of the lithium with the electrolyte solution, a rather thick film is formed with a clearly defined crystalline structure. The presence of a crystalline film at the interface between lithium and thionyl chloride was first demonstrated in 1976 by Dey [1] using scanning electron microscopy. The quantitative relationships in the growth of such a film were examined in the authors' laboratories by means of the isotope method. As an illustration, Fig. 1 shows a curve of the amount of chloride ion increase in the surface layer of lithium with time, measured for a solution of  $\text{LiAlCl}_4$  in thionyl chloride containing the isotope  $^{36}\text{Cl}$ . It can be seen that the rate of accumulation of chloride ions in the film gradually slows down, but even after 2200 h this process is still in progress. If the film in this solution is considered to consist entirely of  $\text{LiCl}$ , the density of which is known, then it is possible to estimate the thickness of the film. According to this estimation, the thickness reaches 3 - 4  $\mu\text{m}$  in the time of the experiment. This value is the lowest possible, since the film is porous, has a loose structure, and may include components without chloride ions.

As early as 1977, Moshtev and coworkers [2, 3] pointed out that in addition to a comparatively thick crystalline film, a thin, continuous film (a so-called "primary passivating film") is formed on the lithium surface. The properties of this latter film were investigated by Povarov *et al.* [4] employing various experimental procedures. Electron-microscopic studies revealed that in the presence of thionyl chloride the formation of the first crystals on a lithium surface only begins several hours after contact with the solution. A continuous crystalline layer is only produced after the passage of hundreds of hours. However, sharp changes in the electrochemical parameters of the lithium occur much earlier. During the first 5 - 10 h, the polarization resistance of the electrode increases from 1 - 2  $\text{ohm cm}^2$  to about 30 - 50  $\text{ohm cm}^2$ .

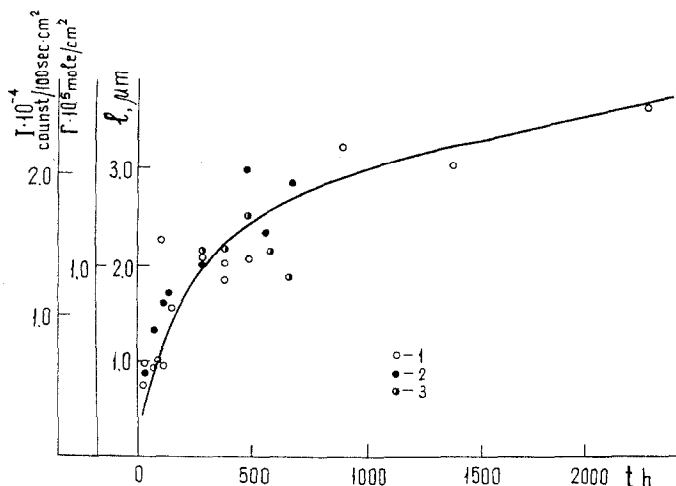


Fig. 1. Dependence of sample radioactivity, amount of chlorine ion, and film thickness on the exposure time in the electrolyte. Temperature: (1) 20, (2) 50 and (3) 70 °C.

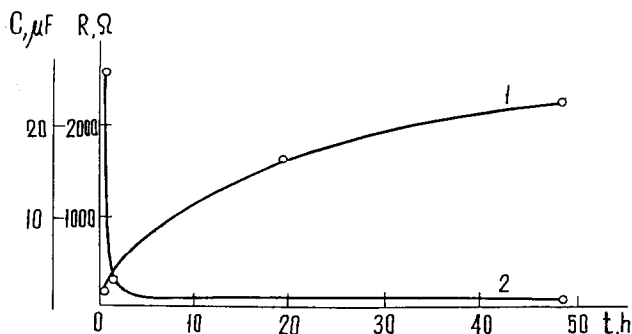


Fig. 2. Time dependence of the resistance (1) and capacitance (2) of the lithium electrode in 1 M  $\text{LiAlCl}_4$  in thionyl chloride at a frequency of 1 kHz.

$\text{cm}^2$ . As demonstrated by the data in Fig. 2, during this period the measured values of the impedance components (*i.e.*, resistance  $R$  and capacity  $C$ ) also undergo major changes. These observations suggest that the change in the state of the lithium surface commences immediately following its contact with the solution, *i.e.*, long before a visible crystalline layer is formed. These changes are due to the appearance of a thin, not obviously crystalline, passivating film.

An electrode covered with a primary passivating film exhibits certain characteristic features. The first of these is a pronounced photosensitivity. By illumination of the electrode with visible light, the current in the anodic polarization region decreases markedly, especially in the first few hours of electrode contact with the solution. With a more prolonged electrode exposure, the effect decreases in intensity but still persists.

The second feature is the anomalous effect of temperature on the polarization resistance of the electrode: the resistance decreases with decrease in temperature from 30 to  $-10^\circ\text{C}$ , but then increases as the temperature is taken to lower values.

The main specific feature of the primary passivating film is that the electrode impedance curve in the medium and high frequency range is a semi-circle whose centre always lies below the abscissa (Fig. 3). This feature is confirmed by the results obtained by many other authors. The impedance

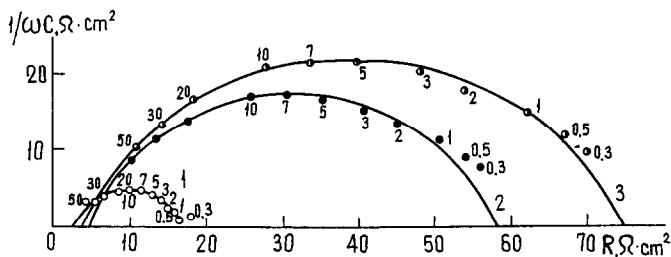


Fig. 3. Impedance curves for a lithium electrode, obtained in 1 M  $\text{LiAlCl}_4$  in thionyl chloride, after (1) 3, (2) 100 and (3) 240 h contact between electrode and electrolyte. Numbers on the curves represent frequencies in kHz.

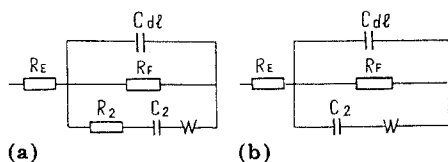


Fig. 4. Equivalent circuits for (a) the electrode/solid electrolyte boundary and (b) the lithium-LiAlCl<sub>4</sub> boundary in thionyl chloride.

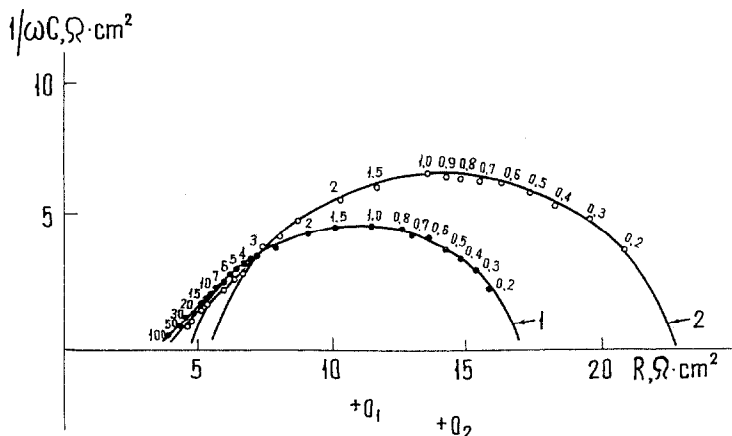


Fig. 5. Impedance curves for a lithium electrode in 1 M LiClO<sub>4</sub> in propylene carbonate after (1) 6 and (2) 28 h contact between the electrode and the electrolyte. Numbers on the curves represent frequencies in kHz.

behaviour can be interpreted by means of the equivalent circuit given in Fig. 4. In this circuit,  $R_E$  is the electrolyte resistance,  $R_F$  is the polarization resistance of the faradaic process of transfer of lithium ions across the film/electrolyte interface, and  $C_{d1}$  is the double-layer capacity at this interface. The string  $R_2-C_2-W$  represents the presence in the film of both lithium ions and of other current carriers whose concentrations are small. Recalculation of the experimental data using this circuit shows the resistance  $R_2$  to be close to zero. By determining the values of Warburg impedance components,  $W$ , it is possible to estimate the concentration of the minority current carriers. At a particular relationship between the element parameters of the above circuit, the electrode behaviour is absolutely determined by the Warburg impedance, and in the high-frequency region, the impedance diagram shows linear sections specific to this case (Fig. 5).

Similar results are also obtained in solutions in the presence of other oxidants (e.g., SO<sub>2</sub>, CH<sub>3</sub>NO<sub>3</sub>) as well as in solutions with organic solvents in the absence of specially added oxidants. In the latter case, the capacity  $C_{d1}$  is close to zero, while in oxidant solutions it is small but still different from zero.

## Conclusion

On the basis of the above results and other experimental data, it is possible to draw the following conclusions about the properties of the primary passivating film:

(i) The primary film is formed directly upon contact of lithium with the electrolyte and grows quickly during the first few hours; its thickness at the initial stage is 1 - 1.5 nm and after a certain period of time it is about 5 nm.

(ii) The primary film has a continuous, not obviously crystalline, structure; it exhibits self-healing properties when its continuity is impaired.

(iii) The main conductivity of the film for lithium ions is of a semiconductor nature and arises from the presence of defects in the crystal lattice; roughly it is equal to  $10^{-7} - 10^{-6} \text{ ohm}^{-1} \text{ cm}^{-1}$ .

(iv) The film has a certain p-type electronic conductivity; the concentration of the minority current carriers (*i.e.*, electron holes) upon contact in solutions using organic solvents is about  $10^{15} \text{ cm}^{-3}$  and in solutions containing oxidants is about  $10^{14} \text{ cm}^{-3}$ . The presence of electronic conductivity leads to further growth of the continuous primary film and to subsequent formation of a crystalline secondary film.

(v) The properties of the primary film change to a certain extent during exposure of the electrode to the solution. In particular, there is a certain decrease in the concentration of the minority carriers in the bulk of the film and also a decrease in the value of  $C_2$ . These changes can be associated with slow structure-ordering processes in the primary film.

(vi) After prolonged exposure of the electrode to the solution and the formation of a thick, crystalline (secondary) film, the primary film is preserved and, as before, exerts a decisive influence on the electrochemical behaviour of the electrode. The effect of the secondary film is to cause partial screening of the surface and to hinder mass transfer in the solution layers adjacent to the electrode.

## References

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