ELECTRICAL PROPERTIES OF A PASSIVE LAYER ON LITHIUM MEASURED IN ABSENCE OF LIQUID ELECTROLYTE

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Abstract: Electrical properties of a passive film formed on lithium in thionyl chloride are measured using impedance spectroscopy. Unlike in all previous investigations published in literature the measuring cells did not include liquid solution. In modelling of the measured impedance spectra the presence of poor electrical contact between the passive film and counter electrode, as well as the passive film porosity, were taken into account. The parameters of electrical transport across the passive film are compared with the corresponding literature data.

Električne lastnosti pasivne plasti na litiju, izmerjene v odsotnosti tekočega elektrolita

Povzetek: Električne lastnosti pasivnega filma, ki se tvori na litiju v prisotnosti tionil klorida, smo merili z impedančno spektroskopijo. Bistvena razlika glede na objavljene meritve v literaturi je, da merjeni sistem ni vseboval tekočega elektrolita. Pri modeliranju izmerjenih impedančnih spektrov smo tudi upoštevali slab električni kontakt med pasivnim filmom in pomožno elektrodo ter poroznost pasivnega filma. Tako dobljene parametre električnega transporta smo primerjali z ustreznimi podatki, objavljenimi v literaturi.

INTRODUCTION

If in contact with terrestrial environment most metallic surfaces are transformed into oxides and/or salts /1/. In cases when the newly formed surface layer prevents the underlying metal from further decay, the system is regarded passivated, the corresponding phenomenon is referred to as passivation and the thin surface layer as a passive layer (or passive film).

The electrical properties of the passive layers formed on lithium in aprotic media have exclusively been studied in systems in which the passive film was in contact with a liquid electrolyte. As lithium passive layers usually include a significant degree of porosity, such measurements only provide information about the combined electrical properties of the liquid electrolyte in layer's pores and those of the solid skeleton of the passive layer (Fig. 1a). As in most cases the pore geometry is not known, nothing can be said about the electrical properties of individual components, especially of the solid part of the passive layer. In this paper we present a technique which allows for direct measurements of the electrical properties of the solid part of the passive film formed on lithium in contact with thionyl chloride (SOCl2). This passive film is polycrystalline LiCl with some inclusions of aluminium and sulphur compounds. The liquid electrolyte is removed from the system and a solid counter electrode is employed instead (Fig. 1b).

The electrical properties of such an all-solid-state system are measured using the impedance spectroscopy and the results are interpreted taking into account both the porosity of the film as well as the poor contact between the passive layer and the solid counter electrode.

EXPERIMENTAL

Electrolyte: A 1.5 M LiAlCl4/SOCl2 electrolyte solution was used. SOCl2 was purified by fractional distillation under an argon atmosphere. AlCl3 (99,99%) was used, as obtained from Aldrich. LiCl (p. a.) from Kemika Zagreb was dried at 175°C under a vacuum for 72h. A 1.5 M solution of LiAlCl4/SOCl2 was prepared in an argon-filled dry box by slowly adding AlCl3 to SOCl2 in order to avoid heating, and then slowly adding LiCl in slight excess.
The water content of the electrolyte as found by IR spectroscopy was less than 10 ppm.

Materials: Thin LiCl films were prepared in two ways:
a) by immersion and spontaneous passivation of metallic lithium in a 1.5 M solution of LiAlCl4/SOCl2. Lithium was stored in the electrolyte for 14 days at 50°C, forming a passive layer of thickness of approx. 80 μm on the surface of the lithium metal. After this treatment the passivated surface was dried for at least two days in Ar atmosphere to remove all liquid electrolyte.

Informacije MIDEM 26(1996)1, str. 21-25

M. Gaberšček, D, Kek, S. Pejovnik: Electrical Properties
of a Passive Layer on Lithium Measured in Absence of Liquid Electrolyte
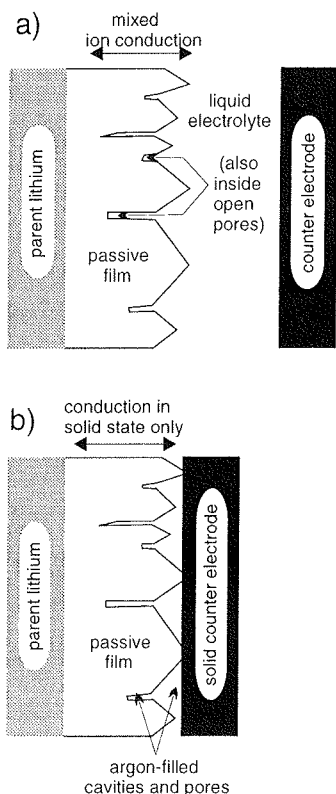

Fig. 1: Cell configurations used to study the electrical properties of passive films on lithium; a) commonly used cells, b) cell configuration used in the present study.

b) by evaporation from a LiCl substrate at a pressure of 10^{-4} mbar at 500°C to 550°C on a polished platinum sheet.

Electrodes: Electronic contacts were made using a conductive carbon cement (CCC) (Neubauer Chemikalien), a conductive silver paint (CSP) (GC Electronic), and a platinum sheet. Ionic contact was made by pressing a sheet of metallic Li against the film surface using a spring contact.

Using the described materials and electrodes the following types of cells were constructed:

a) ionic contacts:

  – Li/passive film LiCl/Li; system A

  – Li/passive film LiCl/Li/Li3N; system B

b) mixed ionic and electronic contacts:

  – Pt/thin film LiCl/Li; system C

  – Li/passive film LiCl/CC; system D

Li3N in system B was prepared by keeping Li/LiCl/Li cells in an argon atmosphere with up to ca 1% of N_2 but with only traces of O_2 and moisture - less than 5 ppm for several days.

Measurements: Impedance measurements were performed using a Solartron 1250 Frequency Response

Analyzer (65000 Hz to 0.01 Hz) combined with a 1286 Electrochemical Interface and a Hewlett-Packard 4284A LCR Meter (1 MHz to 20 Hz). The impedance response was measured at variable DC voltage bias (-2 to +2V).

All measurements and cell preparations were performed in an argon-filled dry box facility.

RESULTS AND DISCUSSION

The shape of impedance response of the Li(parent electrode)/passive film/solid counter electrode system measured in the frequency range from 65000Hz-0.01Hz system may be divided in two cases (Fig.2):

a) if the solid counter electrode is metallic lithium, a slightly depressed arc is observed in the whole frequency range (Fig. 2a),

b) in all other cases a low-frequency tail in addition to the depressed high-frequency arc is observed (Fig. 2b).

Such behaviour may be explained in the following way: the high-frequency arc represents the response due to migration of lithium vacancies in the bulk passive film while the low-frequency tail is due to diffusion of mobile particles (lithium vacancies + the corresponding positively charged carriers) inside the passive film towards the passive film/counter electrode interface. Obviously, if both electrodes consist of metallic lithium the diffusion process is not observed (Fig. 2a). This means that the
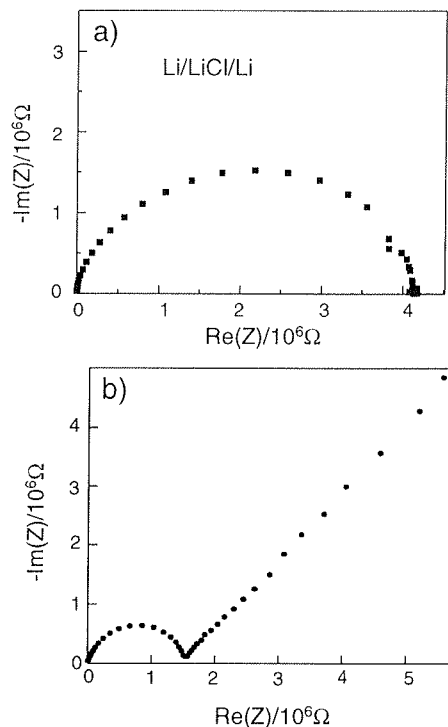

Fig. 2: Typical shape of the impedance response for a) symmetrical Li/passive film/Li cells, b) asymmetrical Li/passive film/solid counter electrode where "solid counter electrode" denotes the following electrodes: platinum, conductive carbon cement, and stainless steel.

impedance of the lithium/passive film interface is very low which prevents the mobile carriers from accumulation at that interface and diffusion is negligible. Conversely, in other systems the measured impedance of the passive film/solid counter electrode interface is high enough to allow for the accumulation of charge carriers and the diffusion process is observed (Fig. 2b).

The fact that the high-frequency arc is depressed (i.e. its centre lies below the real axis) implies that more than just one relaxation process take place within the passive film. Indeed, as shown in Fig. 3, one needs at least 2 RQ terms in order to get a satisfactory fit of a typical measurement. Here R represents the resistance and Q the so-called CPE (constant phase element) defined as

$$ Q = \frac{R^{1-\alpha}}{(j\omega C)^{\alpha}} \qquad (1) $$

where $j = \sqrt{-1}$, ω is the angular frequency of the excitation signal, C is the capacitance and a is a parameter related to distribution of relaxation times. Analysis of many measured impedance responses have shown /2/ that one of the RQ terms probably represents the response of solid skeleton of the passive film while the other is most likely due to a combined effect of i) passive film pores and ii) the poor physical contact at the passive film/solid electrode interface on the impedance re-
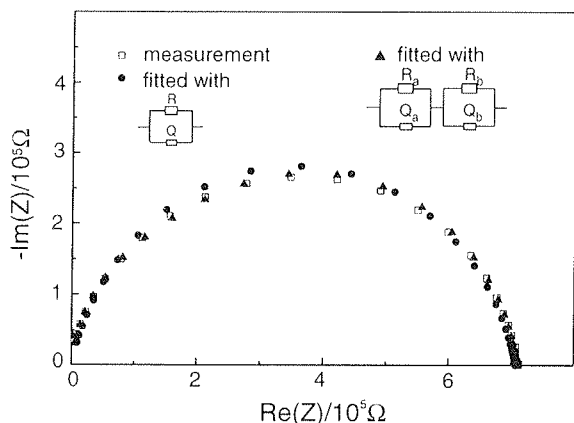

Fig. 3:   Measured impedance spectrum fitted with two different equivalent circuits.

sponse of the system. Building up a simplified model simulating the electrical properties of the system (Fig.4) it was possible to show /2/ that the actual contact area between the passive film and the solid electrode was as low as 2-15% of the geometrical area of the contact. The reason for this is the high surface roughness of the passive film which prevents the solid electrode - unlike in the case of liquid electrolyte systems - from coming into intimate contact with the passive film surface. The second important result of analyses with the model in Fig.4 is the calculated value of average passive film

thickness which lies in the range from 70 to 90 μm. This range agrees well with the values observed using the scanning electron microscopy (20-60 μm) and hence confirms the relevance of the proposed model. Finally, the model gives average values of conductivity of the solid skeleton of the passive film which at 25°C has a value of ca 10^{-9} Scm^{-1}. This is ca 100 times less than the average passive film conductivity found in liquid electrolyte systems /3/. A rough estimation based on the assumption of cylinder-shaped pores, and taking into account that the conductivity of liquid electrolyte is 10^{-2} Scm^{-1}, shows that in average the film porosity is ca 10^{-7} (i.e. the ratio between the cross-section area of pores and the geometrical cross-section area). Expressed in another way this means that if an average cubic single crystal has a base of 10μm, a typical pore diameter would be ca 3.5 nm. Due to difficult handling and chemical reactivity of the systems involving metallic lithium the latter result cannot be verified using, for example, SEM observations.
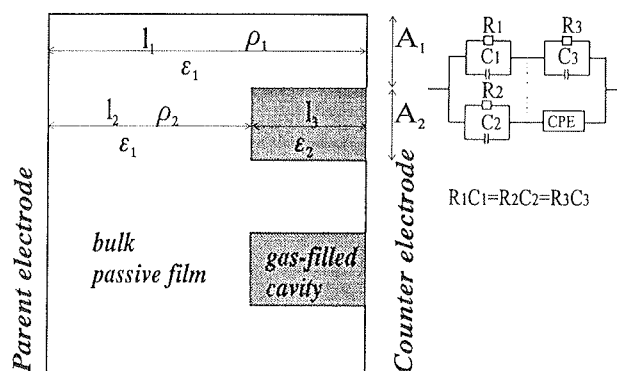

Fig. 4:   Schematics of a model taking into account the poor contact at the passive film/counter electrode interface and/or film porosity.

Impedance response as a function of DC voltage bias:

Measurements of impedance response at variable DC voltage bias (e.g. 0 to ± 2 V) usually serve to distinguish between the contribution of bulk and interfacial response. Typical results are shown in Fig. 5. As expected, the high-frequency arc does not change with bias (Fig. 5 a) while the shape and magnitude of the low-frequency tail show significant dependence on DC voltage bias (Fig.5 b, c). The changes in the low-frequency response are ascribed to deposition (or dissolution) of metallic lithium at the passive film/solid counter electrode interface. For example, if the lithium electrode is biased positively, lithium ions are transferred from this electrode to the counter solid electrode where they are deposited as metallic lithium (Fig. 6 a). Gradually the surface of counter electrode covers completely with metallic lithium which, in terms of the impedance response, means that the low-frequency tail almost disappears (Fig. 5, b - triangles) compare with Fig. 1, curve A). If the deposition of metallic lithium continues, it may

Informacije MIDEM 26(1996)1, str. 21-25

M. Gaberšček, D, Kek, S. Pejovnik: Electrical Properties
of a Passive Layer on Lithium Measured in Absence of Liquid Electrolyte

happen that also the magnitude of high-frequency arc slightly reduces (Fig. 5, c). This result may be explained by taking into account the hypothesis developed for liquid electrolyte systems /3/, viz. that the further deposition of lithium occurs preferentially at grain boundaries which results in the dendritic growth shown in Fig. 6 b. When the dendrites have penetrated deeply enough into the bulk passive film the effective distance between both electrodes is considerably reduced which, in turn, is reflected in the size of the high-frequency arc.

Impedance response as a function of temperature:

Impedance response was measured as function of temperature in the range from 25 to 150°C. Using the model presented in Fig. 4, Arrhenius graph showing temperature dependence of passive film conductivity was constructed (Fig. 7). The activation enthalpy for lithium ion (or vacancy) conductivity was found to be 0.65±0.05 eV. This is 0.24 higher than the value obtained by Haven /4/ for LiCl single crystal in the temperature range 300°C to 450°C. The difference may be due to three reasons:

a) in our case the activation enthalpy has additional term due to extrinsic conductivity;

b) there may be an additional term due to the formation of associates or imperfections /5/;

c) conduction along grain boundaries of LiCl may be activated in a different way as the conduction in LiCl single crystals.
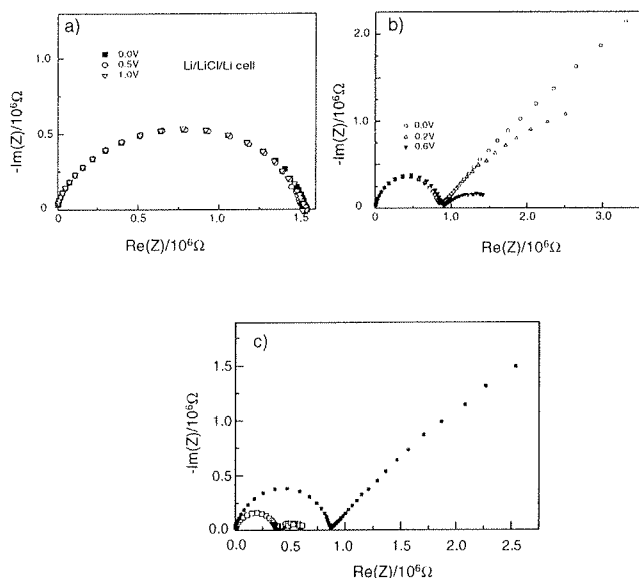

Fig. 5: The influence of dc voltage bias on impedance spectra of the investigated systems:
a) symmetrical cell, b) asymmetrical cells in cases when Li is deposited at the counter electrode as shown in Fig. 6a, c) asymmetrical cells in cases when Li is deposited at the counter electrode as shown in Fig. 6b.
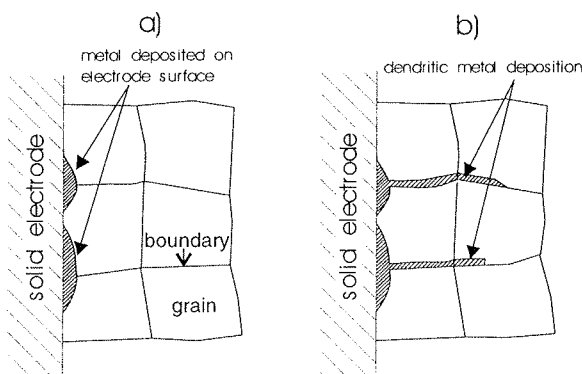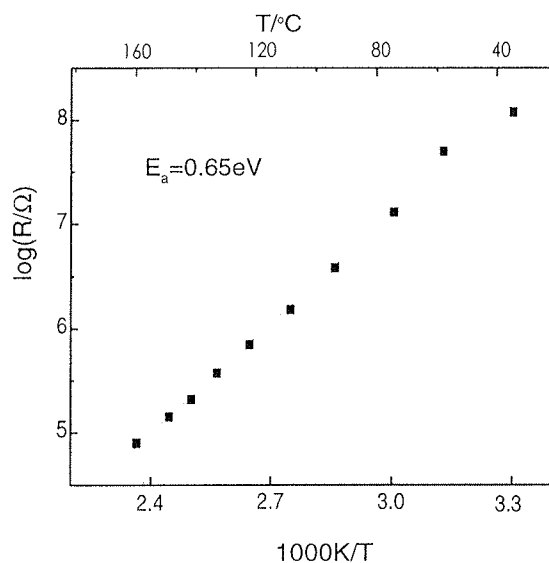

Fig. 7: Arrhenius plot showing temperature dependence of passive film conductivity.

Fig. 6: a) deposition of metallic lithium in the first stage of dc voltage application, b) deposition of Li at after prolonged application of dc voltage.

CONCLUSIONS

The electrical properties of the passive film formed on lithium in thionyl chloride were studied in cells where the liquid electrode was replaced by solid electrodes of different types. Using a simple model describing the electrical properties of the systems under investigation the following results were obtained:

1. The conductivity of the solid part of the passive film was found to be ca 10^{-9} Scm^{-1}, which is ca two orders of magnitude lower than in systems including liquid electrolyte. The ratio between the cross-section area of pores and the solid part of the film was ca 10^{-7}.

M. Gaberšček, D, Kek, S. Pejovnik: Electrical Properties
of a Passive Layer on Lithium Measured in Absence of Liquid Electrolyte

Informacije MIDEM 26(1996)1, str. 21-25

2. If the lithium electrode was biased positively, the deposition of metallic lithium on the counter solid electrode was observed as a pronounced change in the low-frequency part of impedance spectra. Further deposition led to changes in the high-frequency arc as well, which was ascribed to the dendritic growth of metallic lithium into the bulk passive film.

3. The activation enthalpy for lithium ion (or vacancy) conductivity in the temperature range 25 to 150°C was found to be 0.65±0.05 eV.

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