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F. Schwager and R.H. Muller

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IMPEDEANCE AND ELLIPSOMETER MEASUREMENTS
OF LITHIUM ELECTRODES IN PROPYLENE
CARBONATE SOLUTIONS
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Berkeley, CA 94720

ABSTRACT

Complex electrode impedance has been measured for lithium after exposure to nitrogen, propylene carbonate and LiC₆O₄ solutions in propylene carbonate. Results for zero-field exchange current density and polarization resistance are in agreement with earlier current pulse measurements. Ellipsometer measurements show a different electrode behavior for anodic and cathodic reactions in perchlorate solution.
INTRODUCTION

Film formation on lithium in propylene carbonate solutions has been studied by electrochemical pulse techniques and ellipsometry. There was some indication that the constant current pulses used for micropolarization measurements might have affected the surface film. Also, a discrepancy had been found between ellipsometrically and electrochemically determined film thicknesses. By using an ac-impedance technique, damage to the film is minimized and the frequency dependence of the impedance contains more information about the electrode processes than dc-measurements. The disadvantage of ac-impedance measurements is the rather complicated analysis of the experimental results. Young\(^1\) presents ac-measurements on different valve metals in the form of plots of the dielectric loss function without giving a physical interpretation. More detailed theoretical treatment of ac-behavior are given by Sluyters-Rehbach,\(^2\) Bard and Faulkner,\(^3\) deLevie\(^4\) (for porous electrodes) and McDonald and McKubre\(^5\) (for theory and application).

A. Transport Properties of Film Materials

Different lithium electrodes have been investigated in propylene-carbonate solutions by the ac-impedance method. One set of experiments concerned the behavior of lithium electrodes with a nitride film.

One of the basic assumptions for the interpretation of data of films on lithium is that Li\(^+\) is the mobile ion.\(^6\) Relaxation time measurements by NMR on lithium-aluminates and LiOH\(^7\) justify this assumption. Values of diffusion coefficients in LiOH can be found in the literature.\(^7-9\)
Kujnets and Yakimenko\(^8\) give a value of \(7.3 \times 10^{-11} \text{ cm}^2/\text{s}\) at 25°C. The electric conductivity obtained by Johnson, et al.\(^9\) has been extrapolated to 25°C and shows a value of \(7 \times 10^{-13} (\Omega\text{-cm})^{-1}\).

In contrast, diffusion coefficients of \(\text{Li}^+\) and electric conductivities in \(\text{Li}_3\text{N}\) are so high that this material has been proposed as a solid electrolyte.\(^11\)–\(^13\) Huggins, et al. give a room temperature value of \(3.7 \times 10^{-8} (\Omega\text{-cm})^{-1}\) for the ionic conductivity in polycrystalline \(\text{Li}_3\text{N}\). For sintered \(\text{Li}_3\text{N}\) pellets, conductivities of \(4 \times 10^{-4} (\Omega\text{-cm})^{-1}\) have been obtained.\(^14\) An electronic conductivity is also indicated by the optical properties of \(\text{Li}_3\text{N}\) which is black. A study of light absorption was done by H. Brendecke and W. Bludan.\(^15\) Not much has been published on the diffusion and conductivity of \(\text{Li}_2\text{O}\). Most data are available for mixtures of \(\text{Li}_2\text{O}\) with other compounds at high temperature. A relation for the diffusion coefficient between 500 and 1000°C is given by Oishi, et al., from which one extrapolates a value of \(D = 2.65 \times 10^{-20} \text{ cm}^2/\text{s}\) at room temperature. The conductivity of \(\text{Li}_2\text{O}\) is expected to be much lower than that of \(\text{LiOH}\) and \(\text{Li}_3\text{N}\).

### B. ac-Experiments

#### I. Experimental Technique

Tracing of Lissajous figures was the technique used because all the instrumentation was available in our laboratory. These include an oscil­lator (0.1Hz-1MHz), Hewlett-Packard Model 3311A, which drives a Potentiostat Princeton Applied Research Mod. 371 with a rise time of 2\(\mu\)s. The oscillating potential (usually 4mV amplitude) was applied between reference and working electrode (Fig. 1), and the current was measured over a resistor in series with the electrochemical cell. Current vs. potential were displayed on a Tektronix Mod. 511 oscilloscope.
The resulting elliptical traces (Lissajous figures) were photographed (Fig. 2a) and analyzed by the method indicated below which is straightforward but quite cumbersome and time consuming. The accuracy by measuring the photographs is also limited. The rise time of the potentiostat (2\(\mu\)s) restricts the use of high frequencies.

The geometric parameters of the ellipse (Fig. 2b) are related by simple equations to the complex impedance.\(^5\)

\[
\begin{align*}
\hat{Z} &= Z_{\text{Re}} - j Z_{\text{Im}} \\
|\hat{Z}| &= \Delta E/\Delta I \\
\frac{\Delta I'}{\Delta I} &= \sin \phi \\
Z_{\text{Re}} &= |\hat{Z}| \cos \phi \\
Z_{\text{Im}} &= |\hat{Z}| \sin \phi
\end{align*}
\]

where \(|\hat{Z}|\) is the magnitude (modulus) of the complex impedance \(\equiv (Z_{\text{Re}}^2 + Z_{\text{Im}}^2)^{1/2}\), \(\Delta E\) is twice the amplitude of the voltage between reference and working electrode, \(\Delta I\) is twice the current amplitude measured over the resistor and \(\phi\) the phase lag of the current behind the voltage.

II. Electrode and Cell Preparation

The cell consisted of two compartments made of polypropylene. The electrode compartment had two opposing holes for the electrode holders, two windows for the light beam (incident angle 75°) and an extrusion compartment for the lithium reference electrode. A reservoir containing the solution before the beginning of the measurements was located on top of the electrode compartment. This separation of electrodes and solution enabled optical and electrochemical measurements to be made shortly after solution contact of the electrodes. The electrodes were lithium discs of
19 mm diameter which were scraped and pressed into a holder. For the preparation of the Li₃N- films, the freshly pressed electrodes were scraped again and put under varying pressures of N₂ for different periods of time in the antechamber of the glove box. Although the delay between scraping and the first contact with nitrogen was only on the order of 5 sec, it was difficult to form nitride films. The nitride formed patch-wise round islands (see also (17,18)). Lithium nitride is very brittle and it has been found to flake off very easily from the supporting lithium substrate. In one case, a film of approximately 0.2 mm thickness fell off when dry and exploded in the glove box atmosphere on hitting a stainless steel surface.

III. Results

Figure 3 shows impedance plots for a lithium electrode immersed in a 1M LiC₂O₄/PC solution after different periods of time. The impedance in the medium and lower frequency range is obviously dependent on the time of immersion whereas the extrapolated curve at high frequencies intercepts the real axis always at the same point. The assumption that the lower point of intersection with the real axis represents the solution resistance $R_Ω$, between reference and working electrode, is supported by a comparison with the values obtained by micropolarization (Table I).

The intersection of the curve with the real axis at low frequencies represents the resistance of the film and thus is related to the film thickness. For low field strengths (as is the case with a 4mV- amplitude ac-polarization) a linear relation between current density $i$ and applied potential $\eta$ holds

$$ \left( \frac{\eta}{i} \right)_{\eta \to 0} = R_p = Z_{Re} (\nu \to 0) - R_Ω $$

(5)
The low-field film resistances $R_p$ thus derived are the same as those obtained by galvanostatic pulse polarizations (Table II). By applying the terminology used by Geronov\textsuperscript{6} of treating the activated diffusion process in the film like a charge controlled reaction using Tafel plots and exchange current densities $i_0$, we obtain for zero field

$$R_p = \frac{RT}{nF i_0}$$

(6)

Exchange current densities obtained by the two techniques are comparable (Table III). Figure 4 shows impedance plots for different lithium electrodes after approximately the same immersion times. For convenience the solution resistances have been subtracted in all of these plots. Curves I and II are obtained on films grown in 1M LiC\textsubscript{6}O\textsubscript{4}- solution and in PC without salt,\textsuperscript{1} respectively. Curves III-V are obtained for Li\textsubscript{3}N-films in 1M LiC\textsubscript{6}O\textsubscript{4}- solution. The salt has obviously a large influence on the film formation (Curves I and II). The Li\textsubscript{3}N film either increases the film conductivity by a factor of about two or slows down the film formation rate.

The low-field film resistance $R_p$ for the different electrodes is presented in Fig. 5 as a function of time. The nitride films (III, IV, V) are found to be more conducting than the films grown in 1M LiC\textsubscript{6}O\textsubscript{4} alone. Curve II is obtained for a 0.5M LiC\textsubscript{6}O\textsubscript{4} solution. It seems that in one case (Curve IV) the resistance reaches a maximum. This can be explained by diffusion of solution through micropores in the Li\textsubscript{3}N.

IV. Mathematical Models

In a first approximation an insulating surface layer can be considered as a capacitor of capacitance $C_f$. This model is used for the capacitance
measurements with short current pulses. A small leakage current through this capacitor can be represented by a parallel resistor of resistance $R_{fr}$. Experimental impedance plots are similar to those expected for such a circuit, but the theoretical plot is an exact semi-circle\(^2,3\)

\[
\left(\frac{Z_{\text{Re}} - \frac{R_{fr}}{2}}{Z_{\text{Im}}}\right)^2 + \frac{Z_{\text{Im}}^2}{\left(\frac{R_{fr}}{2}\right)^2} = 1
\]

For the present experimental plots the left side of Eq. 7 is always smaller than the right. Note that the film resistance $R_{fr}$ is equal to $R_p$ for low polarizations.

Figure 6 shows the deviation from the semi-circle (represented by a value of 1.0) as a function of time for the different electrodes. After short immersion times the semi-circle is approximated much better. The ratios of $2\times Z_{\text{Im}}(\text{max})/Z_{\text{Re}}(\nu \rightarrow \infty)$ reach a constant value after an initial drop. In the electrical circuit this can only be accounted for by a frequency dependent resistance, capacitance or both. In analogy to solutions we introduce the Warburg impedance\(^2,3\) which describes the lag of the current behind the voltage due to diffusion.

The simplest circuit, taking into account the film and the solution, is shown in Fig. 7. It consists basically of two RC-circuits in series. $R_{\Omega}$ is the solution resistance, $Z_s$ the Warburg impedance of the solution, $C_d$ the double layer capacitance, $C_f$ the film capacitance, $Z_f$ the Warburg impedance of the film, and $R_{fr}$ the film resistance. Because of the much higher diffusion coefficient in solution, $Z_s$ is negligible and also as $C_d$ is much larger than $C_f$, we can concentrate our discussion on the circuit representing the film. An alternate circuit which has been derived for transport in membranes\(^2,3\) is discussed in Appendix II.
a) **High Frequency Limit Approximation**

In the first case, we look only at the parallel capacitance due to the film \( C_f = \varepsilon_0 \varepsilon_f / d_f \), and due to diffusion in the film \( C_w = \sigma \omega^{-1/2} \). We thus obtain \(^2\)

\[
C_{\text{tot}} = \frac{\varepsilon_0 \varepsilon_f}{d_f} + \sigma \omega^{-1/2} = \frac{1}{\omega Z_{\text{Im}}}
\]  

(8)

where the kinetic parameter \( \sigma \) is a function of the temperature \( T \), the diffusion coefficients of the oxidized \( (D_0) \) and reduced \( (D_R) \) species and the concentration of this species.

Plots of \( 1/\omega Z_{\text{Im}} \) vs. \( \omega^{-1/2} \) are presented for two different electrodes in Figs. 8 and 9 for very high frequencies. In this range, the curves are linear (following Eq. 8), and the parameter \( \sigma \) is obtained as the slope (Table IV). The intercept with the y-axis is not accurate enough to give information about the film capacitance \( C_f \).

b) **Low Frequency Limit Approximation**

In the second case we look only at the real parts of the impedance which are due to the ohmic resistance in the film \( R_{fr} \) and the real part \( R_w \) of the Warburg impedance \( Z_f \) which are in series

\[
R_{\text{tot}} = \left( \frac{1}{R_{fr}} + \frac{1}{R_w} \right)^{-1}
\]  

(9)

with

\[
R_{fr} = \frac{d_2}{\varepsilon_0 B} = \frac{d_2}{\kappa}
\]  

(10)

\[
R_w = \sigma \omega^{-1/2}
\]  

(11)
\( i_0 \) is the exchange current density, \( d_2 \) the film thickness, \( B \) the field coefficient and \( \kappa \) the film conductivity. With 9, 10 and 11 we obtain the following equation for \( \omega \cdot \sigma \):

\[
\frac{1}{A \cdot Z_{Re}} = \frac{1}{R_{tot}} = \frac{i_0}{b} + \frac{1}{\sigma} \omega^{1/2}
\]  

(12)

In Figs. 10 and 11, experimental values of \( 1/(Z_{Re} - R_{\infty}) \) are plotted vs. \( \omega^{1/2} \) for two different experiments. From the linear range we obtain \( 1/\sigma \) which is compared in Table IV with the values from Figs. 8 and 9. For a redox-couple the following relation holds:

\[
\sigma = \frac{RT}{n^2 F^2 A \sqrt{2}} \left\{ \frac{1}{D_0^{1/2} C_0^*} + \frac{1}{D_R^{1/2} C_R^*} \right\}
\]  

(13)

In the film the bulk concentration \( C_R^* \) of the reduced species \( Li^0 \), is much lower than that of the oxidized species \( C_0^* \). Equation 13 is thus simplified to:

\[
\sigma = \frac{RT}{n^2 F^2 A \sqrt{2}} \frac{1}{D_R^{1/2} C_R^*}
\]  

(13')

or

\[
\frac{1}{\sigma} = 1.5 \cdot 10^7 \cdot D_R^{1/2} C_R^*
\]  

(13'')

The \( 1/\sigma \)- values obtained from Figs. 8 and 9 according to Eqs. 8 and 12 differ by a factor 2 to 3 but show the same trends with increasing film thickness. It is difficult to see why, with increasing film thickness according to Eqn. 13, the term \( D_R^{1/2} C_R^* \) should become smaller. For a constant \( C_R^* \) the diffusion coefficient should become smaller.
In Table V the y-axis intercepts in Figs. 10 and 11 are presented. The film thickness in Eqn. 10 can be expressed by the Tafel slope \( b \) (from polarization curves) and by the field coefficient \( B \),

\[
B = 2.3 \cdot \frac{d_2^2}{B} .
\]  

(14)

With Eqns. 14 and 10 we can eliminate \( d_2 \) and obtain:

\[
\frac{1}{R_{fr}} = \frac{a}{\lambda} = 2.3 \cdot \frac{i_0}{b}
\]  

(15)

In Table V, exchange current densities calculated with Eqn. 15 are presented for 2 experiments. They are of the same order as those presented in Table III.

c) Whole frequencies range

A mathematical treatment of the film part of the circuit in Fig. 7 over the whole frequency range follows. The circuit consists of 3 parallel elements with the complex impedances:

\[
\hat{Z}_{C_f} = -j \cdot \frac{1}{\omega C_f}
\]  

(16)

\[
\hat{Z}_{R_{fr}} = R_{fr}
\]  

(17)

\[
\hat{Z}_f = \sigma \cdot \omega^{-1/2} - j \cdot \sigma \cdot \omega^{-1/2}
\]  

(18)

\[
1/\hat{Z}_{tot} = 1/\hat{Z}_{C_f} + 1/\hat{Z}_{R_{fr}} + 1/\hat{Z}_f
\]  

(19)

or

\[
\hat{Z}_{tot} = Z_{Re} - j \cdot Z_{Im}
\]  

(20)
with
\[
Z_{\text{Re}} = \frac{R_{fr}\sigma\omega^{-1/2}}{G} \left[ 2\sigma\omega^{-1/2} + R_{fr} \right]
\]
and
\[
Z_{\text{Im}} = \frac{R_{fr}^2\sigma\omega^{-1/2}}{G} \left[ 2\sigma\omega^{1/2} + 1 \right]
\]

and
\[
G = R_{fr}^2 + 2\sigma\omega^{-1/2} \left( R_{fr} + \sigma\omega^{-1/2} \right) + 2 R_{fr}^2\omega^{1/2}C \left( C_{\omega}^{1/2} + 1 \right)
\]

It can be shown that these equations fulfill the conditions

with \( \omega \to 0 \) and \( \omega \to \infty \):

\[
\omega = 0: \quad Z_{\text{Re}} = R_{fr} \quad \omega \to \infty: \quad Z_{\text{Re}} = 0
\]
\[
Z_{\text{Im}} = 0 \quad Z_{\text{Im}} = 0
\]

A computer program which calculates the impedance as a function of frequency with \( \sigma, C_f \) and \( R_{fr} \) as parameters has been used.

V. Discussion

ac-measurements confirmed the results obtained by current pulse techniques for zero-field exchange current densities \( i_0 \) and polarization resistances \( R_p \).

The conductivities of the films formed on lithium in perchlorate solutions are of the order of \( 10^{-9} \text{ ohm}^{-1} \text{ cm}^{-1} \). This value is at least four orders of magnitude higher than that for LiOH.\(^10\) Micropores or a large amount of defects could account for this high value but the optical properties indicate that the electronic conductivity in the films may not be negligible.
Cabrera and Mott\textsuperscript{19} present a model for the growth of thin oxide films on metal which is in good agreement with our experimental results. The thickness of their films is on the order of 100 Å and less (which is about the magnitude of the films obtained by capacitance measurements). The reason for this limit lies in the transport mechanism through the film which implies the motion of an Li\textsuperscript{+} ion as well as the transfer of an electron from the metal/film to the film/solution interface where it reduces a species such as an adsorbed solvent molecule. The electron transport may be due to thermionic emission or tunneling.

The film growth deduced from the capacitance measurements is parabolic:

\[
\frac{dx}{dt} = A \frac{x}{x} \tag{24}
\]

The experimental value of A is obtained from a plot of film thickness vs. time (Fig. 12). The value for A in this case is $2.3 \times 10^{-18}$ cm\textsuperscript{2}/s.

a) Film growth by Li\textsuperscript{0} diffusion only

In this model we assume that metallic lithium is diffusing through the film and reacts at the film/solution interface with e.g. H\textsubscript{2}O: the growth can be expressed as:

\[
\frac{dx}{dt} = \frac{n^*}{\rho} \cdot MG \tag{25}
\]

with $n^*$ the flux density of Li\textsuperscript{0}, $\rho$ the density and MG the molecular mass of LiOH. The quantity A (Eq. 24) may be written as:\textsuperscript{19}

\[
A = D \frac{MG}{\rho} \Delta C(\text{Li}^0) \tag{26}
\]

For LiOH as film material and assuming the same diffusion coefficient for Li\textsuperscript{0} as for Li\textsuperscript{+} in LiOH, $D = 7.3 \times 10^{-11}$ cm\textsuperscript{2}/s, we obtain a Li\textsuperscript{0} concentration...
difference of $1.9 \cdot 10^{-9}$ mol/cm$^3$ in the film.

b) **Field assisted film growth**

Knowing $A$ from capacitance measurements and the conductivity $\kappa$ from ac-measurements (Table II), we can calculate the potential difference $V$ across the film:

$$V = \frac{Z^2 F^2 \cdot \delta}{MG} \cdot \frac{A}{\kappa}$$

With $\kappa = 3.5 \cdot 10^{-9}$ ohm$^{-1}$ cm$^{-1}$ we obtain:

- $V = 0.40$ V for LiOH
- $V = 0.90$ V for Li$_2$O

The same potential difference is likely to occur across the film of the Li- reference electrode and is therefore not measurable.

C) **Ellipsometry and Cyclic Voltammetry**

I. **Experiment**

A lithium electrode was investigated after 5 days immersion in 1 M LiC$\text{ClO}_4$/PC- solution by ellipsometry and cyclic voltammetry. Figures 13 and 14 show the change in the ellipsometer parameters $\Delta$ and $\psi$ during an anodic and a cathodic sweep. The current is proportional to the sweep-potential. At +2V it had a value of 15 mA/cm$^2$ on an electrode immersed for 250 h in a 1 M LiC$\text{ClO}_4$/PC- solution, corresponding to a resistance of 134 $\Omega$cm$^2$ which is also obtained by ac- measurements on the same electrode. The charge transferred during one sweep corresponds to the thickness of a metallic Li- layer of 5000 Å. During the anodic sweep changes were $1.5^\circ$ in $\Delta$ and $0.5^\circ$ in $\psi$. The direction of the sweep is also reflected in $\Delta$ and $\psi$. The changes in the ellipsometer parameters lag slightly behind the potential changes, thus indicating a diffusion process.
The cathodic sweep shows completely different features. Except for the first cycle, the changes are much larger, $20^\circ$ in the $\Delta$- and $5^\circ$ in the $\psi$- value. $\Delta$ increases in the direction of the value of metallic lithium.

II. Discussion

If Li$^+$ was the only charge transferring species we should expect the same optical response during anodic and cathodic polarization. The discrepancy may be explained by the electronic conductivity of the film. During dissolution, the Li$^+$-ions formed at the metal/film-interface diffuse through the film, during deposition diffusing Li$^+$-ions are reduced at the film/solution-interface or in the film. It is not clear why the deposition seems to take place to a greater extent during the decreasing phase of the cathodic sweep. The anodic behavior is consistent with a simultaneous roughening of the substrate and film growth. The cathodic behavior agrees qualitatively with a gradual accumulation of metal deposits in the surface layer and its penetration by metal filaments, followed by the formation of metallic islands on top of the film. This mechanism agrees with the formation of insulated lithium deposits, proposed by Rauh and Brummer$^{24}$ to account for the grey surface appearance and the isolation and encapsulation processes proposed by Koch and Brummer$^{25}$ to account for capacity loss.

D. Precipitation on Inert Electrodes in LiC$_2$O$_4$/PC Solutions

In B. V. and C. II we have proposed a mechanism for the formation of the electrochemically detectable film. Ellipsometry, SEM and depth profiling by Auger spectroscopy, however, indicate the presence of a much thicker, porous film. Geronov, et al.$^6$ proposed that this film is a secondary film resulting from a corrosion of the primary compact film. Another possibility has been tested on inert electrodes. The film could
be formed by a precipitation of insoluble products of a reaction between electrolyte salt and propylene carbonate.

I. Experiments

A stainless steel electrode and independently a silver electrode were immersed in a 1 M LiClO₄/PC solution for several days. ac-impedance measurements on the stainless steel electrode (Fig. 15) indicate a shift of the low frequency range of the real part of the impedance with time similar to that in Figs. 3 and 4. This change could be attributed to growth of a film.

Ellipsometric measurements on a silver electrode immersed in 1 M LiClO₄/PC were carried out at a wavelength of 5145 Å. No reliable data on film growth was obtained because the system was very unstable. The light influenced the optical properties of the surface. The formation of a film, however, is visible and has been investigated by Auger and SIMS.

For the Auger and SIMS investigation, the silver electrode was, after 100 h immersion in 1 M LiClO₄/PC, washed in pure PC and dried in vacuum at room temperature. After transferring the sample into the SAM a background analysis showed outgassing of water (Fig. 16), indicating that the film material is hygroscopic.

a) Auger

The Auger-peaks were shifted due to charging of the surface. Very short sputtering and flooding of the surface with electrons improved the spectra.

Figure 17 shows a spectrum with a beam size of 1μm. The main components of the film are chlorine, carbon and oxygen in the atomic ratio 5.6:71:28.4 at a spot where the film was thick. Figure 18 shows a
spectrum taken at a thin part of the film. Li, Cl, C, O and the substrate Ag can be distinguished. The spectrum taken on a crystal of ~4μm diameter by pulse counting with a beam of 6nA and 3000 A diameter showed chlorine, carbon and oxygen in the atomic ratios 15:67:19.

The Auger-spectra show a large amount of carbon in the film, even after sputtering.

b) SIMS

Positive ion SIMS (Fig. 19) shows the presence of a large amount of lithium (M 6, 7) in the film. The peaks at mass 13, 14, 15 can be attributed to CH+, CH₂⁺, CH₃⁺. Peaks at high positive masses (M 51, 63, 73, 81) may support the presence of polymeric material (Fig. 20).

The negative ion SIMS (Fig. 21) was not very sensitive and only the peaks of O⁻(16), OH⁻(17) and Cl⁻(35 can be found.

II. Discussion

The experimental observations indicate that propylene carbonate is unstable to lithium- salts and that degradation products could form less soluble lithium- salts like Li₂CO₃²⁰,²¹ and even polymers. The degradation of PC would, of course, also influence the formation of the primary film by supplying film material more readily than a reaction between a tunnelling electron and a solvent molecule. The formation of a precipitate film is also supported by the dependence of film growth on the water content, the importance of the anion of the electrolyte salt, and by the linear growth law of the film determined by ellipsometry.

Conclusions

ac-impedance measurements allow an easy determination of film resistances on lithium. The experimental results are in good agreement
with values obtained by micro-polarization.

A complete analysis of the experimental impedance plots has not yet been carried out and the kinetic parameter $1/\sigma$ has been obtained only for the limits where $\omega \to \infty$ and $\omega \to 0$, respectively. Qualitatively it has been found that the complex impedance plot deviates from a semicircle increasingly with immersion time of the electrode. This could be explained by conductivity.

Lithium nitride films have a lower resistance than films formed by immersion in solution only. It is, however, difficult to form homogeneous $\text{Li}_3\text{N}$-films, the reactivity of $\text{N}_2$ is much lower than that of $\text{O}_2$ and $\text{H}_2\text{O}$ so that a native oxide film formed during electrode cleaning prevents the reaction with $\text{N}_2$. $\text{Li}_3\text{N}$ usually forms in islands which easily separate from the metal.

The high film conductivity as well as results from cyclic voltammetry indicate that the film is $\text{Li}^+$ and $\text{e}^-$ conductive. Cabrera and Mott\textsuperscript{19} describe a mechanism of thin film formation which is based on this assumption and describes the observed growth rate and final thickness of the film.

The film observed by ellipsometry and SEM seems to be a precipitate of insoluble products formed by a reaction of the propylene carbonate with the electrolyte salt.
ACKNOWLEDGMENTS

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This paper was presented at the Detroit, Michigan meeting of the Electrochemical Society, October 17-21, 1982, extended abstract No. 295.
References

Table I. IR-drop in PC, 1 M LiC\textsubscript{4}O\textsubscript{4} solution obtained by micropolarization and ac-measurements: Variations due to different location of reference electrode.

<table>
<thead>
<tr>
<th>Immersion Time (h)</th>
<th>$R_\Omega$ dc</th>
<th>$R_\Omega$ ac</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>70 ± 3</td>
<td>66 ± 4</td>
</tr>
<tr>
<td>115</td>
<td>70 ± 3</td>
<td>66 ± 4</td>
</tr>
<tr>
<td>211</td>
<td>139 ± 7</td>
<td>121 ± 10</td>
</tr>
</tbody>
</table>
Table II. Comparison of film reaction resistances obtained by ac-impedance measurements and by micropolarization (galvanostatic pulse) measurements in PC, 1 M LiClO₄.

<table>
<thead>
<tr>
<th>N₂-Exposure (torr-min)</th>
<th>Immersion Time (hours)</th>
<th>( R_p ) ac-impedance (ohm-cm²)</th>
<th>( R_p ) Galvanostatic pulse (ohm-cm²)</th>
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Table III. Comparison of exchange current density $i_0$ on lithium obtained by extrapolation of Tafel-plot (galvanostatic pulse) and ac-impedance measurement in PC, 1 M LiClO$_4$.

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<th>N$_2$-exposure (torr-min)</th>
<th>$i_0$ (mA/cm$^2$) ac-impedance</th>
<th>$i_0$ (mA/cm$^2$) galvanostatic pulse</th>
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Table IV. Kinetic parameters $1/\sigma$ from Figures 8, 9, 10 and 11.

$1/\sigma = \tan \alpha$

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<th>Figure 11</th>
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Table V. Exchange current densities for Li in 1 M LiClO₄ calculated from y-axis intercepts (Figs. 10 and 11), electrode area 2.85 cm².

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<th>Immersion time, h</th>
<th>y-axis intercept, a</th>
<th>Tafel slope b of polarization curve</th>
<th>Exchange current density iₒ (mA/cm²)</th>
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<td>4.5x10⁻³</td>
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<td>650</td>
<td>4.5x10⁻³</td>
<td>1.3</td>
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</table>
Figure Captions

Fig. 1. Electrical circuit used to measure Lissajous-figures.

Fig. 2a. Lissajous-figure on oscilloscope.

Fig. 2b. Parameters of Lissajous-figure used for impedance calculation.

Fig. 3. Change of impedance $Z$ during growth of film in 1 M LiC$_4$/PC solution, electrode area 2.85 cm$^2$.

Fig. 4. Impedance plots for different lithium electrodes in 1 M LiC$_4$/PC solutions after 250 h immersion time: I-1 M LiC$_4$; II-PC only; III-thick Li$_3$N film (3800 torr-min., completely black); IV-medium Li$_3$N-film (2000 torr-min., black islands visible); V-thin Li$_3$N-film (1050 torr-min., not visible); electrode area 2.85 cm$^2$.

Fig. 5. Time dependence of the electrode resistance $R_p$ of differently prepared lithium electrodes: I-1 M LiC$_4$; II-0.5 M LiC$_4$; III-thick nitride layer; IV-thin nitride layer; V-medium nitride layer.

Fig. 6. Deviation of experimental complex impedance plots from semi-circle (value 1): I-0.5 M LiC$_4$; II-no salt; III-thick nitride layer; IV-thin nitride layer.

Fig. 7. Simple model of film on lithium in electrolyte solution with its electrical equivalent circuit.

Fig. 8. Evaluation of the kinetic parameter $1/\sigma = \tan \alpha$ for high frequency limits for different immersion times. (PC, 1 M LiC$_4$).

Fig. 9. Evaluation of the kinetic parameter $1/\sigma = \tan \alpha$ for high frequency limits for different immersion times.
Fig. 10. Evaluation of the kinetic parameter $1/\sigma$ at the low frequencies for different immersion times in PC, 1 M LiC$_2$O$_4$ (times as in Fig. 9).

Fig. 11. Evaluation of the kinetic parameter $1/\sigma$ at low frequencies for different immersion times, 2000 torr-min N$_2$ (times as in Fig. 9).

Fig. 12. Film growth obtained with dielectric constant 4.8 from short current pulse capacitance measurements. Solution: 1 M LiC$_2$O$_4$/PC.

Fig. 13. Relative phase $\Delta$ and amplitude $\psi$ during anodic polarization of film grown in PC, 1 M LiC$_2$O$_4$, 10 days, open circuit. Thickness of capacitance measurements = 90 A.

Fig. 14. Relative phase $\Delta$ and amplitude $\psi$ during cathodic polarization of film grown in PC, 1 M LiC$_2$O$_4$, 10 days, open circuit. Thickness from capacitance measurements = 90 A.

Fig. 15. Impedance plots of stainless steel electrode in 1 M LiC$_2$O$_4$/PC solution.

Fig. 16. Mass spectrum of background from outgassing of precipitate film on silver.

Fig. 17. Auger spectrum of precipitate film formed on silver in 1 M LiC$_2$O$_4$, 8 days, open circuit.

Fig. 18. Auger spectrum of thin part of film used in Fig. 17, showing silver substrate.

Fig. 19. Positive ion SIMS spectrum of precipitate film on silver, low-mass range.

Fig. 20. Positive ion SIMS spectrum of precipitate film on silver, high-mass range.
Fig. 21. Negative ion SIMS spectrum of precipitate film on silver.
Fig. 1
Fig. 2a
Fig. 2b
CHANGE OF Li-ELECTRODE IMPEDANCE WITH DIFFERENT TIME OF IMMERSION IN PC/IM LiClO₄-SOLUTION (OPEN CIRCUIT)

Fig. 3

- a. after 1 h
- b. " 45 h
- c. " 250 h
- d. " 650 h
IMPEDEANCE PLANE PLOTS FOR DIFFERENT LITHIUM ELECTRODES IN PC-SOLUTIONS UNDER OPEN CIRCUIT CONDITIONS AFTER 250hr. IMMERSION TIME

Fig. 4
Fig. 5

Resistance $R_p$ (ohm.cm$^2$) vs Time (hrs)

- Line I
- Line II
- Line III
- Line IV
- Line V

XBL 8012-13352 A
Film Model With Equivalent Circuit

Reference electrode

Solution

Double layer

Film

Metal

\[ R_{\Omega} \]

\[ C_d \]

\[ Z_s \]

\[ C_f \]

\[ R_{fr} \]

\[ Z_f \]
Fig. 8

\[ \frac{1}{|Z_{lm}|} \times 10^6 \Omega^{-1} \]

- Axis labels:
  - \( y \)-axis: \( \frac{1}{|Z_{lm}|} \times 10^6 \Omega^{-1} \)
  - \( x \)-axis: \( \omega^{-1/2} \) (rad\(^{-1/2}\))

- Graph lines:
  - Line I: 1h after immersion, \( \tan \alpha(\Omega \cdot \text{rad}^{-1/2}) = 6.7 \times 10^{-4} \)
  - Line II: 45h, \( \tan \alpha(\Omega \cdot \text{rad}^{-1/2}) = 4.7 \times 10^{-4} \)
  - Line III: 275h, \( \tan \alpha(\Omega \cdot \text{rad}^{-1/2}) = 2.4 \times 10^{-4} \)
  - Line IV: 650h, \( \tan \alpha(\Omega \cdot \text{rad}^{-1/2}) = 2.4 \times 10^{-4} \)
Fig. 9

\[
\frac{1}{|Z_{im}|} \times 10^6 \Omega^{-1}
\]

\[
\tan \alpha (\Omega \cdot \text{rad}^{-1/2})
\]

- I: 1 h after immersion \(1.1 \times 10^{-3}\)
- II: 50h \(7.5 \times 10^{-4}\)
- III: 115h \(6.7 \times 10^{-4}\)
- IV: 210h \(5.4 \times 10^{-4}\)
Fig. 12

Slope = $2.1 \times 10^{-9}$ cm·s$^{0.5}$
Fig. 13
Fig. 14
Stainless steel electrode in Im LiClO$_4$/PC

I 0h after immersion
II 70h after immersion
III 100h after immersion

Fig. 15
Outgassing of precipitate film on Ag

Fig. 16
Auger spectrum on Ag-electrode immersed for 8 day in PC/1M LiClO$_4$
Fig. 18

Auger spectrum precipitate film on Ag thin part
Fig. 19

Positive-ion SIMS precipitate film on Ag

Counts

Mass/charge

Fig. 19
Positive SIMS on film grown on Ag in PC/1M LiClO$_4$

Fig. 20
Negative-ion SIMS of precipitate film on Ag

Fig. 21
Appendix

After conclusion of this work, an alternate equivalent circuit, shown in Fig. A-1, was found to provide a better interpretation of the experimental results. This circuit had originally been proposed for use with biological membranes. The three branches of the circuit represent migration through the film, capacitance across and adsorption on it.

A listing of the program, written for an LSI 11-23 minicomputer (Table A-I), together with a sample of tabulated (Table A-II) and graphic (Fig. A-2) output are shown.

Figure Captions

Fig. A-1. Alternative equivalent circuit.

Fig. A-2. Sample of graphic output of computer program.
Film Model With Equivalent Circuit

Fig. A-1
Table A-1. LSI-11 Program for circuit shown in Fig. A-1.

```plaintext
PROGRAM ACHEOD
OPEN(UNIT=1, NAME='DY1:PLTDAI.DAT', TYPE='UNKNOWN')
DUMMY=0.
WRITE(1,98)DUMMY
WRITE(1,98)DUMMY
98 FORMAT(F10.0)
   REAL CH,CD,CM,RF,CF,FR,RE,ZIM,RA,CA
   COMPLEX YM,YD,YLI,YRE,YTJOT,ZLI,ZTOT,ZF,YF,ZHI,YH:
1   FORMAT(F12.9)
   TYPE 10
   10 FORMAT(*CA='-')
       ACCEPT 1,CH
       TYPE 11
   11 FORMAT(*CD='-')
       ACCEPT 1,CD
       TYPE 12
   12 FORMAT(*RM='-')
       ACCEPT 1,RM
       TYPE 13
   13 FORMAT(*RF='-')
       ACCEPT 1,RF
       TYPE 14
   14 FORMAT(*CF='-')
       ACCEPT 1,CF
       TYPE 15
   15 FORMAT(*FR='-')
       ACCEPT 1,FR
       TYPE 5
   5 FORMAT(*RA='-')
       ACCEPT 1,RA
       TYPE 6
   6 FORMAT(*CA='-')
       ACCEPT 1,CA
PRINT 20
20 FORMAT(' FREQUENZ',8X,'REAL TEIL',6X,' IMAG.TEIL')
GOTO 2000
1001 FR=10.
   GOTO 2000
1002 FR=50.
   GOTO 2000
1003 FR=100.
   GOTO 2000
1004 FR=300.
   GOTO 2000
1005 FR=600.
   GOTO 2000
1006 FR=1000.
   GOTO 2000
1007 FR=3000.
   GOTO 2000
1008 FR=5000.
   GOTO 2000
1009 FR=7000.
   GOTO 2000
1010 FR=10000.
   GOTO 2000
```

1011 FR=20000.
    GOTO 2000
1012 FR=50000.
    GOTO 2000
2000 DM=6.28*FR
     S1=1./RM
     S2=DM*CM
     S3=DM*CD*CF/(CD+CF)
     ZMI=CMPLX(RA,1./(DM*CA))
     YMI=1./ZMI
     YM=CMPLX(S1,S2)
     YD=CMPLX(0.,S3)
     YF=CMPLX(1./RF,0.)
     ZM=1./YM
     ZD=1./YD
     ZF=1./YF
     ZLI=ZM+ZF
     YLI=1./ZLI
     YRE=YD
     YTDT=YLI+YRE+YMI
     ZTOT=1./YTDT
     ZRE=REAL(ZTOT)
     ZIM=AIMAG(ZTOT)
     PRINT 16,FR,ZRE,ZIM
     BB=0.
     WRITE(1,99)FR,ZRE,ZIM,BB,BB,BB,BB,BB
99 FORMAT(1X,F9.0,711X,F9.3))
   IF(FR.LT.10.)GOTO 1001
   IF(FR.LT.50.)GOTO 1002
   IF(FR.LT.100.)GOTO 1003
   IF(FR.LT.300.)GOTO 1004
   IF(FR.LT.600.)GOTO 1005
   IF(FR.LT.1000.)GOTO 1006
   IF(FR.LT.3000.)GOTO 1007
   IF(FR.LT.5000.)GOTO 1008
   IF(FR.LT.7000.)GOTO 1009
   IF(FR.LT.9999.)GOTO 1010
   IF(FR.LT.19999.)GOTO 1011
   IF(FR.LT.49999.)GOTO 1012
16 FORMAT(3F12.2)
   PRINT 17,CM,CD
   PRINT 18,RM,RF
   PRINT 19,CF
   PRINT 21,CA,RA
21 FORMAT(' AD.CAPAC CA=','F12.4/' ABS.RES RA=','F12.4)
18 FORMAT(' MIGR.RESISTANCE RM=','/ FILM RESISTANCE RF=','CF12.4)
19 FORMAT(' FILM CAPACITANCE CF=','F12.9)
17 FORMAT(' DIFF.CAPAC. CM=','F12.9/ DOUBLE LAYER CAPAC. LD=','CF12.9)
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