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FILM FORMATION ON LITHIUM IN PROPYLENE CARBONATE SOLUTIONS UNDER OPEN CIRCUIT CONDITIONS

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Conditions

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Lithium is thermodynamically unstable in contact with most non-aqueous battery electrolytes and can be used only because of the formation of protective films on the metal. In a review paper[1] Dey has pointed out the importance of surface layers for battery performance and shown SEM pictures of anode surfaces after reaction under different conditions. In more recent papers by Peled[2,3] the effect of passivating films on electrode kinetic parameters has been shown. It is now generally assumed[2-5] that in most cases the rate determining step (rds) of the dissolution-deposition process of alkali metals in nonaqueous solutions is not electron charge transfer but the migration of cation lattice defects through the surface layer.

Up to now the main effort of investigation of passivity of lithium has dealt with $Li/SOCl_2$ batteries where the "voltage delay" problem is very significant. Studies of the formation of passivating films on Li in PC solutions have been initiated more recently. Their properties have been shown to affect the cycling efficiency of secondary Li electrodes[6,7]. Alloying with an aluminum substrate has been found beneficial[8]. Attempts have been made by Dey[1] to examine the morphology of Li films in PC using

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SEM. His conclusion was that a film of Li_2CO_3 "appears to be extremely thin". The same author, as well as Peled[3], have used the previous data of Scarr[9] dealing with the dual Tafel behavior of Li in PC solutions, in order to support their assumption of the existence of a surface layer and its influence on the electrode kinetics. Scarr has analyzed his experimental results by means of the Butler-Volmer equation.

The aims of the present study are: (1) to investigate the kinetics of film formation on lithium in $PC/LiClO_4$ solutions at ambient temperature under open circuit conditions and to determine some film characteristics such as resistance, conductivity and thickness; (2) to compare film thicknesses, derived from electrochemical capacitance measurements with those calculated from simultaneous ellipsometric measurements.

Experimental

An electrochemical cell was built to make simultaneous electrochemical and ellipsometric measurements in situ. Optically smooth lithium electrodes were prepared and inserted into the cell in inert atmosphere by pressing lithium discs (previously scraped with a blade) on a polycarborate foil in a special jig. The cross-section of a 3.2 mm diam. freshly extruded Li wire, positioned 1 mm from the periphery of the test electrode, served as reference electrode. The electrolyte solution (1 M $LiClO_4$ in PC) was prepared from freshly distilled PC and $LiClO_4$ (Alfa p.a.) previously dried under vacuum (4-5 μm Hg) at 220°C for at least 24 hrs. In order to avoid any possible reaction of PC vapor with

the lithium surface before contact with the liquid, different glove boxes were used for the preparation of electrodes and solutions.

After the ellipsometric measurements on the bare lithium surface were taken, the cell was filled with electrolyte. The delay in electrochemical measurements from the moment of electrode scraping was up to 30-45 minutes; the delay after electrolyte filling was 15-30 seconds. Film formation under open circuit conditions was followed by periodic determinations of electrode capacitance and micropolarization resistance $R_p = (\partial \eta / \partial i)_{\eta=0}$ by means of the galvanostatic pulse polarization technique. The capacitance is estimated from the initial slope of short η-t transients (5-10 μs) (Fig. 1a). The steady-state IR-free overpotential values for the determination of R_p were obtained from oscilloscopic traces with a duration of up to 20 ms. (Fig. 1b). Precautions were taken to avoid damaging the film by applying pulses with the smallest possible electric charge.

Theoretical Considerations

The basic assumption of this study is that lithium in PC is covered by a surface layer. It had been suggested before[3] that this layer is formed instantly by the contact of the metal with the solution. It continues to grow with time. The layer consists of some insoluble products of the reaction of the lithium with propylene carbonate, such as Li_2CO_3, which may form[1] according to the reaction:

$$CH_3-CH-CH_2$$
$$O \quad O$$
$$\backslash \diagup$$
$$C \qquad + 2Li \rightarrow CH_3-CH = CH_2 + Li_2CO_3 \quad .$$
$$\overset{II}{O}$$
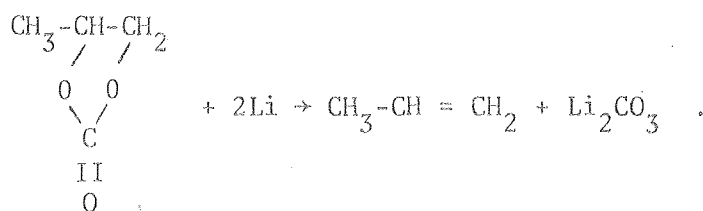
It acts as an Li conducting solid electrolyte[6] with no electronic conductivity and has been called Solid Electrolyte Interphase (SEI)[3]. The capacitance across this film is assumed to be electrically connected in series with that of the electrolytic double layer.

The electrochemical behavior of SEI electrodes will be governed by the properties of the SEI. When the SEI is thick enough the migration of ions through it may be the rate determining step. In this case it is possible to use the basic equation of the classical theory of ionic conduction in solids developed by Frenkel, Varwey, Cabrera and Mott, and Young[10]:

$$i = 4Z \ Fan_+ \nu \ exp \ (-\omega/RT) \ sinh \ (\alpha ZFE/RT), \qquad (1)$$

which at higher electric fields ($E > 2 \times 10^5$ V/cm) can be simplified to:

$$i = i_o \ exp \ (BE) = i_o \ exp \ (B\frac{\eta}{Y}), \qquad (2)$$

where B is the field coefficient, η is the potential difference in the film, E is the electrical field and Y is the film thickness, and a Tafel-like polarization dependence is expected.

From this equation a Tafel slope, b, which increases with the film thickness is obtained:

$$b = 2.3 \ \frac{Y}{B} \quad . \qquad (3)$$

For low field conditions, Eq. (1) reduces to Ohm's law:

$$i = \chi \frac{\eta}{Y} \; ,$$

(4)

where χ is the conductivity of the SEI. The reaction resistance of an electrode is defined as:

$$R_p = (\frac{\eta}{i})_{\eta \to 0}$$

(5)

Thus:

$$R_p = \frac{1}{\chi} \cdot Y$$

(6)

From Eq. (2), for the limiting case, when the field strength tends to be zero:

$$(i)_{E=0} = i_o BE$$

(7)

At low fields, as has been shown, Ohm's law is applicable and hence:

$$\chi = (\partial i / \partial E)_{E=0} = i_o B \; ,$$

(8)

where i_o is the extrapolated zero field ionic current density.

Results and Discussion

The thickness Y of the film formed during the contact of the lithium electrode with the PC-1 M $LiClO_4$ solution has been derived from the capacitance measurements by use of the formula for two capacitors connected in series[3,4],

$$Y = \frac{\sigma \epsilon}{0.113C} - Y' \epsilon / \epsilon' , \; \overset{\circ}{A} \; ,$$

(9)

where $\varepsilon = 4.9$ is dielectric constant of the lithium carbonate film[1], $\varepsilon' = 65$ that of PC, C = the capacitance of the electrode in $\mu F/cm^2$, and σ is the roughness factor, which as a first approximation is asummed to be unity. The thickness Y' of the Helmholz layer in concentrated electrolytes can be approximated by the length of the dipole (c.a. 5 Å for PC); the second right hand term in Eq. (9) can therefore be neglected.

The steady-state iR-free overpotential values were calculated from the transients in the range of current densities between 0.100-20 mA/cm^2 (see Fig. 1b). At higher c.d., i.e. at higher electric fields, $(E > 2.10^5 \ V/cm)$, a Tafel polarization dependence is expected (Eq. 2). Figure 2 presents a series of Tafel plots, obtained by the pulse technique for different film thicknesses. As required for a field-assisted ion current across an insulating film, the Tafel slope, b, increases with film thickness. The extrapolated lines intersect at zero overpotential at the zero field c.d.,

$$i_o = 3 \times 10^{-3} \ A \cdot cm^{-2} \ .$$

The value of the field coefficient B (Eq. 3) may be obtained from the slope of the plot b-Y, presented in Figure 3. This value, $B = 1.24 \times 10^{-6}$ cm/V, is very close to that of typical barrier films[10]. The same value was used to calculate the specific conductivity of the film by the low field approximation Eq. (8):

$$\chi = i_o \cdot B = 3.0110^{-3} \times 1.2410^{-6} = 3.7410^{-9} \ ohm^{-1} \ cm^{-1} \ .$$

For an electric field lower than 2×10^5 V/cm, as has to be expected from Eq. (6), the relationship between the polarization resistance R_p and film thickness is linear. The slope of this relationship yields the specific conductivity χ of the film. However, in our case the plot R_p - Y does not pass through the origin (Fig. 3, curve 2). Figure 4 presents the decrease of the film conductivity χ calculated at c.d. = 0.1 mA/cm^2 with the growth of the film thicness. After a steep decrease up to 60-70 Å thickness, a steady-state value of the conductivity $\chi \approx 3.4 - 3.7 \times 10^{-9}$ ohm^{-1} cm^{-1}, which is very close to that calculated from Eq. (8), was obtained.

The higher conductivity values of thinner films (y < 60 Å) could be attributed to a number of factors among which the most important are: pin-hole porosity, tunnelling effect, the decrease of impurity level and Li$^+$ vacancy concentration with the film growth. The same figure (curve 1) shows film growth with time. The shape of the time dependence of the thickness is not the same as that expected for insulating films growing through ionic transport across the film. Deviations from the parabolic growth law and difficulties of making quantitative analyses from such data also have been found by other authors[1-3].

The experimentally found values of the Tafel slope, b, at different film thicknesses are compared with theoretical values in Fig. 2. As has been seen from Eqs. (1-3), the Tafel slope is equal to:

$$b = \frac{2.3\ RT\ Y}{aZF} \quad . \tag{10}$$

For Z = 1 and a = 3 Å this formula is simplified to:

$$b(mv) = 20 \ Y \ .$$ (11)

A comparison between the experimental and theoretical values of b is given in Table I. If one considers that other combinations of dielectric constant ε and half-jump distance a of the film could be used, the agreement of measured and computed Tafel slopes (for ε = 4.9 and a = 3 Å) is satisfactory.

Ellipsometric Measurements

The ellipsometric measurements of film growth were conducted simultaneously with the electrochemical measurements using a self-compensating automatic ellipsometer. Relative phase Δ and relative amplitude tan ψ were derived from polarizer and analyzer azimuths, respectively. The angle of incidence of the light beam was 75.0°; a mercury lamp was used as light source with a wave length of 5461 Å.

The optical properties of bare lithium have been measured before addition of solution for every experiment. The substrate refractive index proved to be quite reproducible [0.23 ± 0.04 - (2.30 ± 0.03)i].

The thickness of the film was determined by comparing the measurements with calculations based on the experimental substrate refractive index and literature values for refractive indices of different film materials. In Figure 5 the experimental polarizer readings are presented as a function of time. The indicated thicknesses are calculated for a film material with n - 1.5, the refractive index of Li_2CO_3,

using a single-film model. As compared to the film thicknesses obtained from the electrochemical measurements (see Fig. 2) these values are 4 to 5 times higher. A possible reason for this discrepancy is a multiple-layer or inhomogeneous film structure. According to such a model, an inner nonporous insulating region would be accessible by capacitance measurement while the total film, including porous outer regions are observed by ellipsometry.

Conclusion

The experimental results support to the notion that the passivity of Li in PC-LiClO$_4$ solutions at open circuit conditions and ambient temperature can be attributed to the formation of a thin, nonporous, and electronically insulating film (possibly Li$_2$CO$_3$). Differences between the film thickness, calculated by electrochemical and ellipsometric measurements, indicate the presence of a porous, thicker outer region of film material.

Acknowledgement

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TABLE I

Comparison between

Experimental and Theoretical

Tafel Slopes

Y $\overset{\circ}{A}$	b_{exp} mV	$b_{theor.} = 20Y$ mV
25	460	500
37	670	740
65	1150	1300
103	1840	2060
130	2400	2600
138	2650	2760
162	3155	3240

FIGURE CAPTIONS

Figure 1 - Galvanostatic Transients on Li Electrode in 1 M $LiClO_4$ Propylene Carbonate Solution

  (a) Short current pulses for capacitance measurement. Traces for (bottom to top): 0.1, 0.2 and 0.33 mA/cm^{-2}

       Corresponding scales: 2, 5 and 10 mV/div; 2 microseconds/div.

  (b) Long current pulses for overpotential measurement. Traces for (bottom to top): 4, 6, 8, 10, 11.5, 13.3, 15, 16.7, 20 mA/cm^{-2}

       Scales: 0.5 V/div; 1 ms/div.

Figure 2 - Tafel Plots at Constant Film Thickness: 1-25 Å; 2-37 Å; 3-65 Å; 4-103 Å; 5-130 Å; 6-138 Å; 7-162 Å.

Figure 3 - Relationship Between Film Thickness and:

  (1) Tafel slope b

  (2) Polarization resistance R_p

Figure 4 - Time-denpendence of:

  (1) Film conductivity χ

  (2) Film thickness Y

Figure 5 - Change of Polarizer Azimuth Reading with Time for a Lithium Electrode in PC/1 M $LiClO_4$.
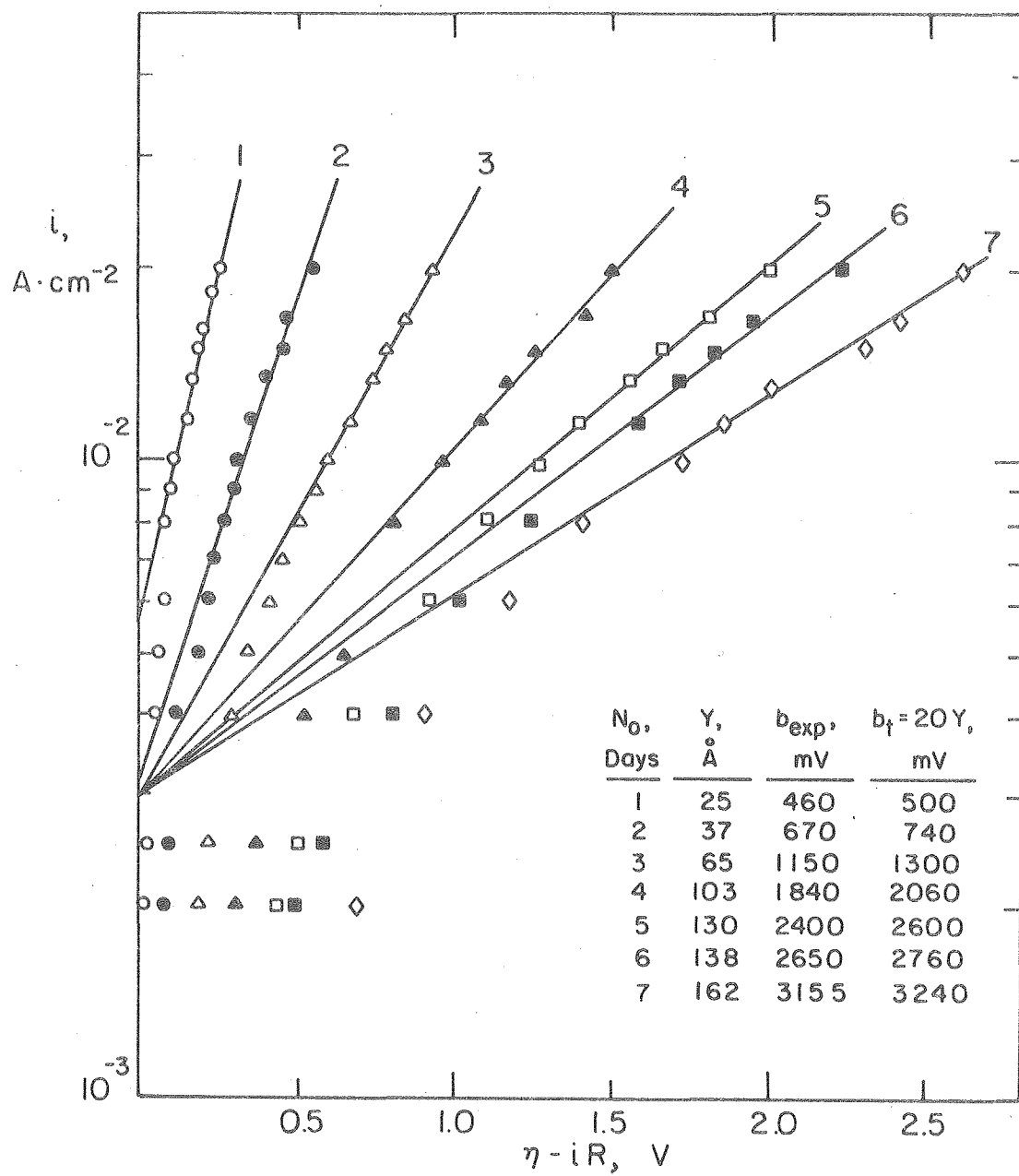   Refractive indices for: Li = 0.2694-2.4776 i; Li_2CO_3 = 1.5; $C_3H_6CO_3$ = 1.429

a)

b)

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Figure 1

N_0, Days	Y, Å	b_{exp}, mV	$b_f = 20Y$, mV
1	25	460	500
2	37	670	740
3	65	1150	1300
4	103	1840	2060
5	130	2400	2600
6	138	2650	2760
7	162	3155	3240

XBL 806-10429

Figure 2

Figure 3

XBL 806-10428

Figure 4

FILM GROWTH ON LITHIUM IN PC/LiClO$_4$-ELECTROLYTE

Figure 5

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