JOURNAL OF APPLIED ELECTROCHEMISTRY **26** (1996) 689–692

Electrochemical characterization of polymer precoated lithium electrodes

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Received 23 September 1994; revised 2 February 1996

The electrochemical behaviour of lithium electrodes in contact with solutions of propylene carbonate is investigated as a function of different polymer precoating materials (poly-(2-vinylpyridine) and poly-(ethylene oxide)). Impedance and polarization measurements show that the electrochemical behaviour of the surface is influenced markedly by precoating due to a modification of the passivating layer. Such information is important for lithium electrodes in batteries with organic electrolytes.

1. Introduction

The electrochemical behaviour of lithium electrodes is strongly influenced by the thin passivating layer built up by reduction products of the organic electrolyte [1–5]. In the last decade much effort has been devoted to improving the cycling efficiency of lithium electrodes for application in rechargeable batteries containing electrolytes by modifying either the electrolyte or the electrode surface. It has been shown that addition of small amounts of hydrocarbons influences the morphology of lithium deposited from solution [6] and, thereby, the electrochemical behaviour of the electrode [7]. Beneficial effects on the cycling behaviour of lithium electrodes were also observed using inorganic additives such as CO_2, N_2O and CO. These additives promote the formation of thin inorganic films on the lithium surface [8].

In this paper the influence of precoating the lithium electrode with two kinds of polymers is described. The first polymer is poly-2-vinylpyridine (P2VP) having successfully been applied in lithium iodine pacemaker batteries [9], and the second is poly-(ethylene oxide) (PEO) which shows sufficiently high ionic conductivity in combination with lithium salts [10]. Moreover, P2VP reacts with metallic lithium itself, an effect which is accelerated in the presence of anthracene (atc), forming lithium addition compounds as intermediates [11].

2. Experimental details

A 0.5 molar solution of $LiClO_4$ in propylene carbonate (PC) was used as electrolyte. The solvent was distilled under vacuum, dried over molecular sieves, and finally redistilled. $LiClO_4$ was stored over P_2O_5 and dried in high vacuum at 140 °C for 6 h. The polymers were carefully dried over P_2O_5 in vacuum at 80 °C.

For the precoating process the lithium electrodes were cleaned by abrading the surface layer, then immediately dipped into a solution of 1 g P2VP ($M = 50\,000$) in 10 cm^3 benzene or of 1 g PEO ($M = 100\,000$) in 10 cm^3 acetonitrile (ACN). After evaporating the solvent, the electrodes had a coating of polymer of thickness 50–100 μm. In some cases lithium electrodes were precoated with a solution of 1 g P2VP solved in 10 cm^3 tetrahydrofuran (THF) which had previously been saturated with anthracene (0.34 g in 10 cm^3 THF). For the electrochemical measurements a four-electrode cell was used, the working electrode (surface area 1 cm^2) being place between two counterelectrodes (lithium, surface area 4 cm^2). A lithium reference electrode was used. All potentials refer to the Li/Li^+ (0.5 M)-couple. The polarization experiments were carried out with a slow voltage sweep of 1 $mV\,s^{-1}$, starting at 0 V, in the cathodic direction up to −250 mV, then returning to 0 V and going on to +250 mV, finally returning to 0 V (potentiostat PS 5 Sensortechnik Meinsberg). The curves were recorded 10 min after immersion of the electrodes in the electrolyte. For the impedance measurements a Solartron 1250 FRA coupled with an 1286 ECI was used. The frequency range was 65 kHz to 0.01 Hz. All operations were carried out in an argon atmosphere in a glove box.

3. Results and discussion

Current-potential curves were recorded in the case of uncoated and pre-coated lithium electrodes (Fig. 1). The current densities of P2VP and PEO-precoated electrodes are only slightly smaller than those of uncoated electrodes and are therefore omitted in Fig. 1. As the upper range of the curve (a) forms a nearly straight line, the data were fitted to a Tafel-like equation (Equation 1) developed by Peled for describing the passivating layer on lithium electrodes in nonaqueous solvents [2, 3, 12]. Assuming that the passivating layer is not dissolved due to anodic polarization, the migration of the lithium ions through it should be the rate-determining step and i_0 is defined as an ionic exchange current density. The slope $1/b$

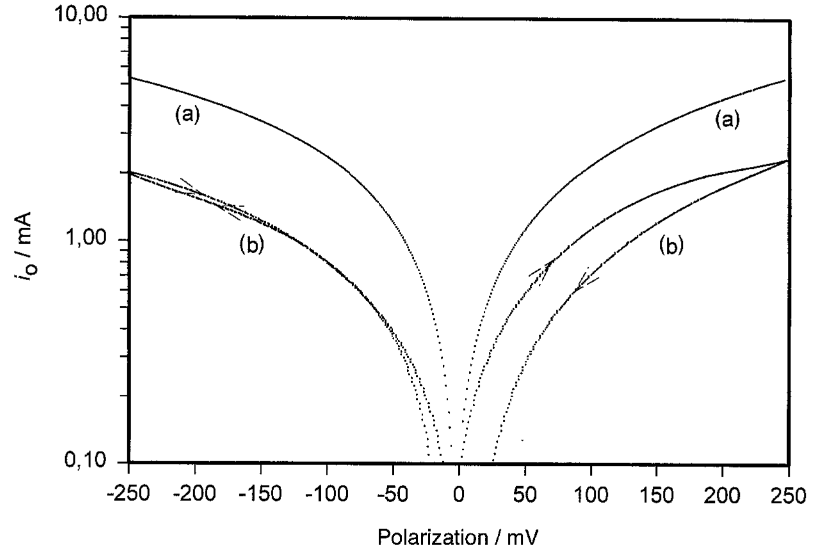

Fig. 1. Polarization plot (a) uncoated lithium electrode and (b) P2VP (atc)-coated lithium electrode ($d_{\mathrm{P2VP}} \sim 100\,\mu\mathrm{m}$) after 10 min immersion in the electrolyte at 20 °C.

of the line is mainly determined by the thickness of the passivating layer.

$$\log i = \log i_o + \frac{1}{b}\eta \qquad (1)$$

where η is the overpotential.

As the electrode surface may change during the cathodic deposition or anodic dissolution of lithium in a different way the cathodic and the anodic branches of the Tafel-plot were separately evaluated. The results are summarized in Table 1. The cathodic i_o-values show only a slight difference to the anodic value for the same electrode. This means that the passivating layer is not dissolved due to anodic dissolution of the lithium electrode. It can be seen that i_o is influenced by the kind of precoating layer. The b-values are similar to those estimated by Peled [2] and seem not to be influenced by the precoating layer, at least for the anodic branch. This means that the thickness of the effective passivating layer build up on the lithium surface has not been changed due to polymer precoating

The P2VP/atc-coated electrode shows different behaviour. The current densities are much lower (Fig. 1, curve (b)). Furthermore, a marked difference in the current values at equal overpotentials, while going forward and backward, respectively, is a characteristic feature of this electrode. The electrode surface changes during the polarization experiment due to cathodic deposition and anodic dissolution of lithium. No linear segment was observed in the Tafel-plot of the P2VP/atc-coated electrode, so the foregoing interpretation was not used in this case.

Table 1. Ionic exchange current densities i_o and Tafel slopes b for uncoated and precoated lithium electrodes in 0.5 M $LiClO_4/PC$ at 20 °C

Coating	Cathodic		Anodic	
	i_o/mA cm^{-2}	b/mV	i_o/mA cm^{-2}	b/mV
Uncoated	1.5	447	1.4	410
P2VP precoated	0.9	390	1.0	400
PEO precoated	0.6	440	0.7	405

To study the formation and alteration of the effective surface layer in greater detail, impedance spectroscopy measurements were performed for different immersion times. For the interpretation of the impedance plots an equivalent circuit (Fig. 2(a)) according to the PEI model proposed by Thevenin [13] was applied. This model describes the impedance behaviour of an electrode covered by a polymer membrane swollen by the electrolyte. The corresponding impedance spectrum consists of three semicircles which may be assigned to three separate electrode processes, the first being related to the bulk resistance $R_b (f \geqslant 1\,\mathrm{kHz})$, which means migration of ions through the membrane, the second to the charge transfer resistance R_{ct} $(1000\,\mathrm{Hz} \geqslant f \geqslant 1\,\mathrm{Hz})$, and the third to the resistance $R_d (f \geqslant 0.1\,\mathrm{Hz})$ related to the

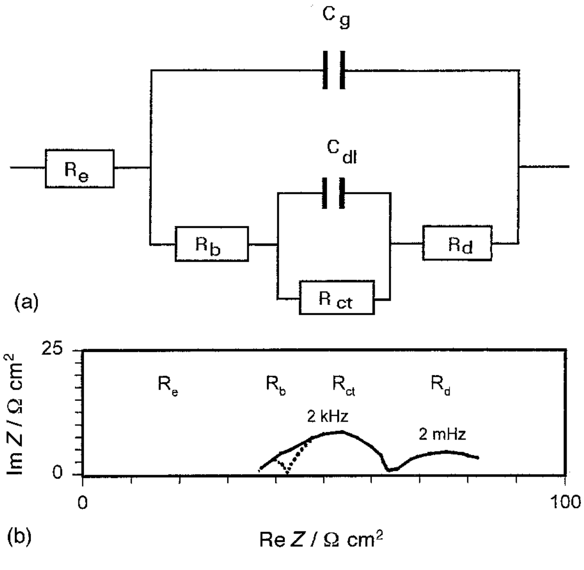

Fig. 2. (a) Equivalent circuit and (b) ideal impedance plot (dotted line) real impedance plot of an uncoated lithium electrode (continuous line).

diffusion of ions in the pores of the polymer film (Fig. 2(b)).

The actual impedance plot of uncoated, as well as precoated lithium electrodes shows asymmetrical semicircles which are broadened in the higher frequency region ($f \geqslant 1$ Hz), suggesting the existence of at least two processes [13]. In Figs 3, 4 and 5 the separate resistances for uncoated and precoated electrodes

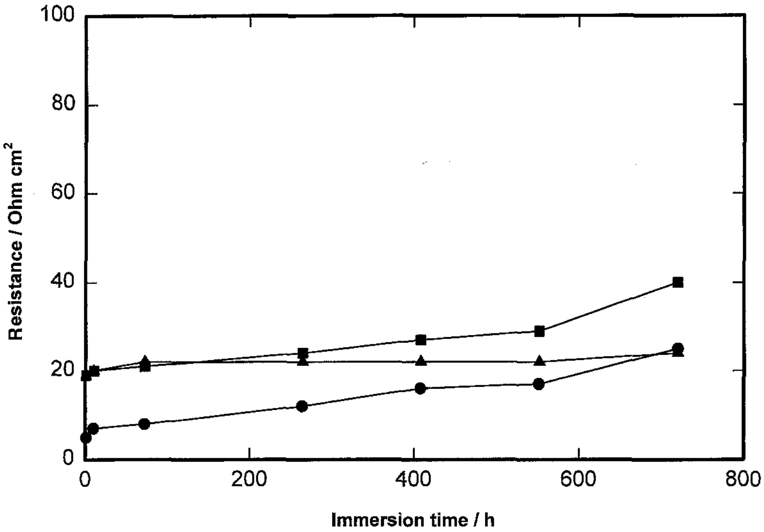

Fig. 3. Resistances R_b (●), R_{ct} (■) and R_d (▲) of an uncoated lithium electrode with immersion time.

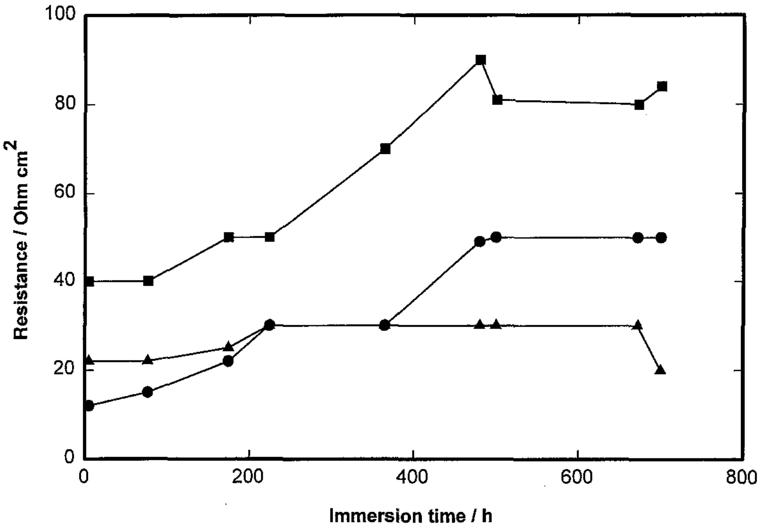

Fig. 4. Resistances R_b (●), R_{ct} (■) and R_d (▲) of an P2VP-precoated lithium electrode with immersion time.

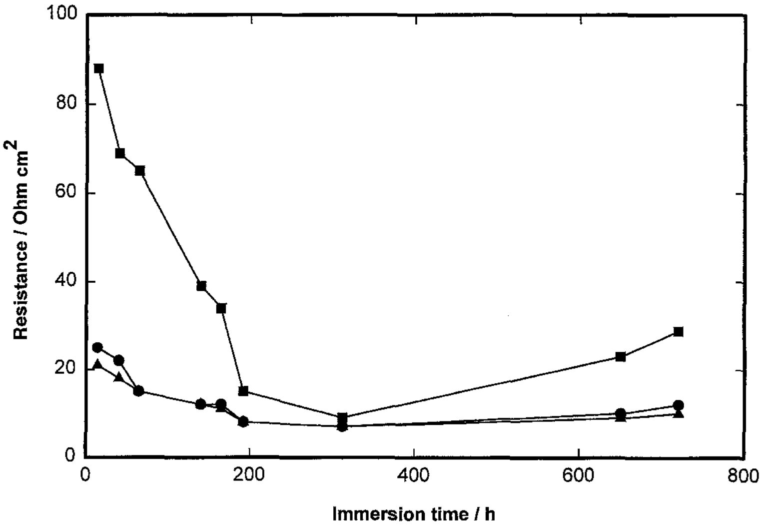

Fig. 5. Resistances R_b (●), R_{ct} (■) and R_d (▲) of an PEO-precoated lithium electrode with immersion time.

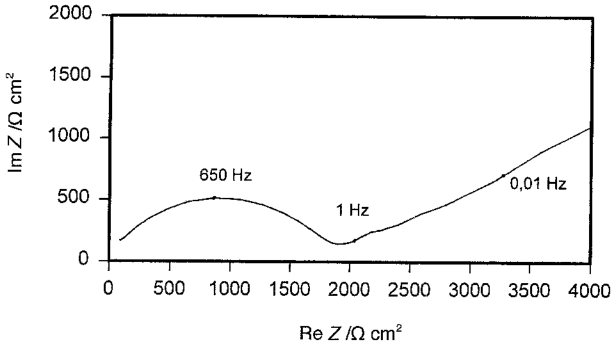

Fig. 6. Impedance plot of a P2VP/atc precoated lithium electrode after 10 min immersion in the electrolyte.

are plotted as a function of immersion time. As in the case of the uncoated electrode (Fig. 3), R_b and R_{ct} increase slightly, while R_d remains nearly constant. Similar behaviour can be observed for the P2VP-precoated electrode (Fig. 4), but the values are higher and show a stronger increase during immersion. The PEO-precoated electrode (Fig. 5) shows a different behaviour. The bulk resistance, as well as R_{ct} and R_d, fall from an initial high value to a relatively low one, this being somewhat lower than that for the uncoated electrode. As PEO is easily soluble in PC ($\geqslant 1\,\mathrm{mol\,dm^{-3}}$); this effect can not be caused by gradual dissolution of the PEO-layer. The passivating layer on the lithium is modified by incorporation of reduction products of the coating material.

The P2VP/atc-precoated electrode (Fig. 6) is marked by a much higher overall resistance than all the other electrodes. In addition, the shape of the impedance plot is different from the others, consisting of a broadened semicircle and a straight line in the low frequency region (Fig. 6). This means that the impedance behaviour is caused by the coating layer itself, not by the electrode/electrolyte interface. The overall resistance decreases during storage time.

A distinction must be made between the precoated layer and the intrinsic effective layer which is formed after some time on the lithium surface. The initial PEO and P2VP layers do not remain on the surface, but are dissolved after a short time, as can be seen from alterations of the electrode impedance during the first minutes of electrode immersion in the electrolyte. The polymer materials seem to modify the passivating layer and do not work as a layer themselves. This modification can be explained by the reaction of lithium with both the solvent and precoating material simultaneously.

Apart from this effect all the layers do not have constant electrochemical qualities, but undergo further change with time.

In contrast to PEO and P2VP, precoating with a mixture of P2VP and anthracene leads to a gel-like layer, insoluble in PC because of its network structure [11]. After an experiment this layer could be removed from the electrode surface as a thin skin. The increased R_b and R_{ct} values in the case of pure P2VP (Fig. 4) also suggest that a reaction with lithium takes place, forming a higher polymer.

4. Conclusions

The passivating layer formed on lithium in contact with organic electrolytes can be modified by precoating the electrode with polymer materials to alter the electrochemical behaviour. Further aspects which are important for applying lithium electrodes in batteries are the cycling behaviour combined with impedance measurements at different potentials and the morphology of lithium deposited during cathodic reduction. These points will be considered in a following paper.

Acknowledgement

We wish to thank Prof. J. O. Besenhard and Dr M. Hess for helpful assistance. This work was supported by 'Deutsche Forschungsgemeinschaft'.

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