

SOME PROBLEMS OF THE CYCLEABILITY OF LITHIUM ELECTRODES

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Summary

Lithium electrode cycleability is influenced by electrochemical and chemical processes occurring during the cathodic deposition and anodic dissolution of lithium. These processes involve the reduction or formation of surface layers, the reduction of the electrolyte, and chemical side reactions.

Dynamic alterations of the protective surface layer properties occur during polarization, and repetitive destruction and formation process takes place. Independently of the electrolyte solution used, during cathodic polarization a sharp decrease in the measured resistance, R , was observed. Distinct differences in the properties of the lithium surface are also obvious during anodic polarization.

Cycling on inert and alloy-forming supports shows remarkable efficiency differences due to the decreased side reactions when using an alloy support.

1. Introduction

Lithium electrode cycleability mainly depends on the nature of the lithium deposition: a dendritic deposition influences its durability. Existing experimental data relating to the cycling behaviour of lithium indicate that improvement in its cycleability in aprotic organic media requires not only chemically and electrochemically stable electrolyte solutions, but also very pure solutions.

Four major approaches to improvement in the cycleability of lithium electrodes are:

- (i) use of additives in the electrolyte;
- (ii) use of lithium alloys;
- (iii) modification of the lithium surface by special layers possessing Li^+ conductivity (solid electrolytes);
- (iv) cycling under mechanical pressure.

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According to Shishikura *et al.* [1] 2-methyltetrahydrofuran (2-MeTHF) seems to have been the only stable solvent used in lithium cycling. In spite of the chemical reactivity of tetrahydrofuran (THF) with lithium it is often mixed with 2-MeTHF. According to our investigations, THF, added to the base solvent in amount 1 - 10 vol.%, is able to modify the passivating surface layer on the lithium electrode.

Lithium is not as stable in propylene carbonate (PC) as it is in 2-MeTHF. However, it is believed by Besenhard *et al.* [2] to be worthy of exploitation if one can succeed in improving the deposition of lithium and retard reduction of the solvent by electrolyte additives.

In this investigation, we have examined the deposition and dissolution of lithium on pure lithium, on an inert substrate (Ni), and on alloying material (Al) in organid aprotic electrolytes.

2. Experimental

PC/LiClO₄ (1 M) and 2-MeTHF/THF(2 vol.)/LiAsF₆ (1 M) were used as electrolyte solutions. These solutions were prepared by dissolving anhydrous LiClO₄ (Merck) and LiAsF₆ (Ventron) in the purified solvents. The latter were carefully dehydrated before use: the PC (Merck) by a twofold vacuum distillation followed by passing through molecular sieves, type 4A; the 2-MeTHF (Merck) and the THF (VEB Laborchemie Apolda) by refluxing over metallic sodium and potassium followed by a vacuum distillation procedure.

Potentiostatic measurements were carried out in glass vessels at room temperature (293 - 295 K) using compact lithium electrodes (0.5 cm²), supported on a nickel collector. The galvanostatic experiments for lithium deposition on Ni and Al were carried out using disc electrodes (0.5 cm dia.), embedded in a poly(ethylene) holder. Some were used as rotating electrodes. In all cases, pure lithium, supported on a nickel collector, served as the counter electrode.

All potentials refer to the Li/Li⁺ couple and have been corrected for the *IR* drop. The resistance, *R*, was estimated by analysing the oscillographic current traces caused by superimposing small amplitude, rectangular potentiostatic pulses of 5 - 10 mV; 250 Hz.

3. Results and discussion

3.1. Lithium deposition and dissolution on compact lithium electrodes under potentiostatic conditions

The current-potential plots were measured under quasi-stationary conditions starting in the cathodic direction (Fig. 1(a)). Due to the thermodynamic instability of metallic lithium in contact with these nonaqueous electrolytes, a potential-dependent surface film is formed possessing

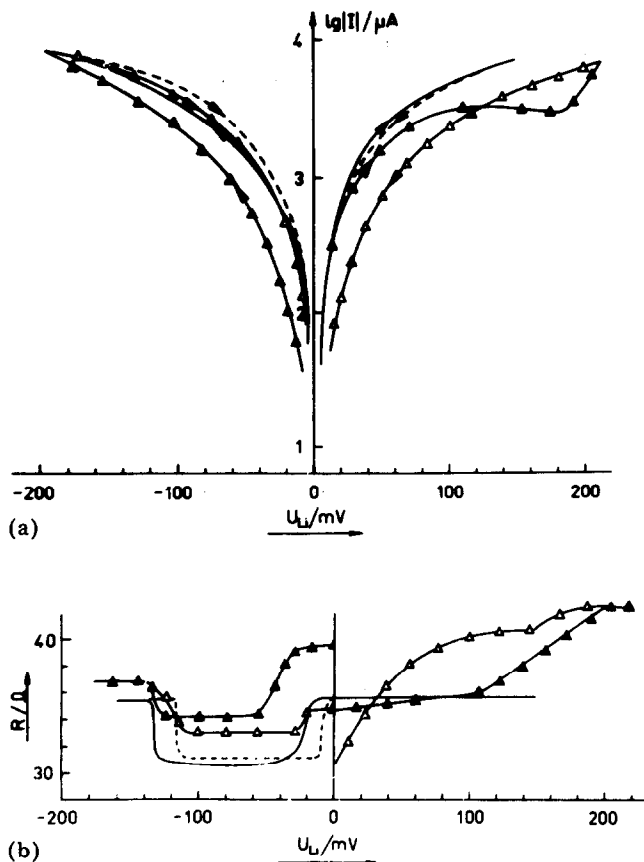


Fig. 1. (a) Polarization plots; and (b) ohmic resistance, R , of lithium deposition and dissolution. ▲, △, (forward, reverse) — PC/1 M LiClO₄; —, — —, (forward, reverse) — 2-MeTHF/THF(2 vol.%) / 1 M LiAsF₆.

protective properties. This is evident from the hysteresis of the forward and reverse curves and from a change in the ohmic resistance measured between the working and the reference electrode (Fig. 1(b)). The measured resistance, R , will change when the current distribution or the resistance R , consisting of at least two components — the electrolyte resistance R_E and a layer resistance R_L representing the conductivity and the thickness of the surface film formed, changes. Assuming the current distribution to be almost constant, and therefore the electrolyte resistance R_E also being constant, we conclude that the protective layer alters its properties dynamically, causing dynamic alteration of the layer resistance R_L .

A significant decrease in the measured resistance occurs in each of the electrolyte systems investigated during cathodic polarization. Under these conditions, the surface film seems to be destroyed or reduced. At high cathodic overvoltages ($|I\eta| > 100$ mV) the resistance increases again, obviously due to an enhanced electrolyte reduction and to the formation of

a new layer. It may be concluded, from the decrease in resistance during the cathodic reverse direction, that the removal of this layer is more or less reversible. The cathodically activated surface represents a better lithium deposition rate, leading to higher cathodic currents during measurements in the reverse direction.

Anodic polarization in the ether electrolyte does not result in any significant change in the layer properties — the resistance is nearly constant, the current-potential plots show no pronounced hysteresis. However, in the PC electrolyte a significant increase is observed in the layer resistance during anodic dissolution. The resistance is almost constant up to 100 mV. From this, it may be assumed that newly deposited lithium in good electronic contact with the base lithium, is dissolved. In the 100 - 200 mV potential region islands of lithium are dissolved which are separated from the base material by a layer of decreasing electronic conductivity. This is evident from the increasing resistance. Only after all the newly deposited lithium ($U > 200$ mV) has dissolved, does the anodic current increase while the resistance remains constant. It could be assumed that the base lithium is involved in the dissolution reaction. In the reverse scan, the dissolution process is retarded due to the remaining layer.

3.2. *Lithium deposition on a foreign substrate under galvanostatic conditions*

It is well known [3] that lithium deposition only occurs on an inert substrate after the formation of a solid electrolyte interface (SEI). This is formed immediately on pure lithium due to the reaction between the metal and the electrolyte components. Therefore, lithium cycling always occurs in the potential range of solvent instability [1]. Cycling outside this instability range should lead to an improvement in cycleability. Substrates possessing lithium alloying properties are known to give a high cycling performance.

To investigate the deposition and dissolution processes in greater detail, lithium was deposited on nickel and aluminum electrodes at varying current densities and then dissolved. Lithium was plated (p) by an amount of charge, Q_p , of 15 mC. After resting for 1 min, the deposited lithium was anodically stripped (s). The required amount of charge for stripping, Q_s , and plating, Q_p , was determined according to Fig. 2. The apparent cycling efficiency was calculated by the fraction, Q_s/Q_p .

3.2.1. *Cycling on nickel*

According to the behaviour of lithium in PC systems [3, 4], the formation of the SEI begins below 1 V *versus* Li/Li⁺. An amount of charge between 5 and 30 mC cm⁻² is required for this process. Only after the formation of this surface layer during cathodic cycling, is lithium deposited at a particular overvoltage. The overvoltage of the pure lithium electrode was measured in the stationary state (Fig. 3).

In our experiments we observed that the formation of the SEI in PC consumed an amount of charge of about 5 - 10 mC cm⁻². In the ether electrolyte, lithium deposition takes place immediately and no SEI forma-

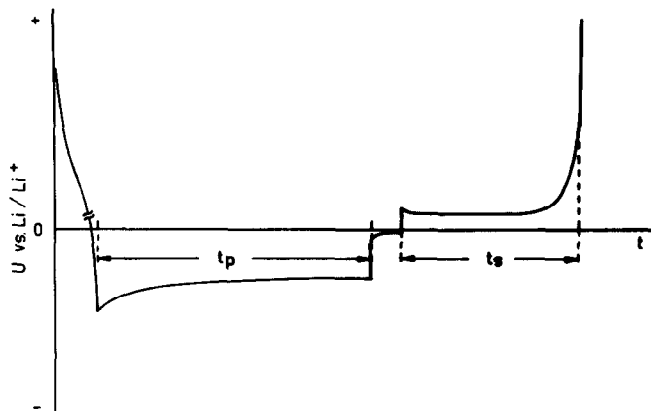


Fig. 2. Potential-time relation during short cycling.

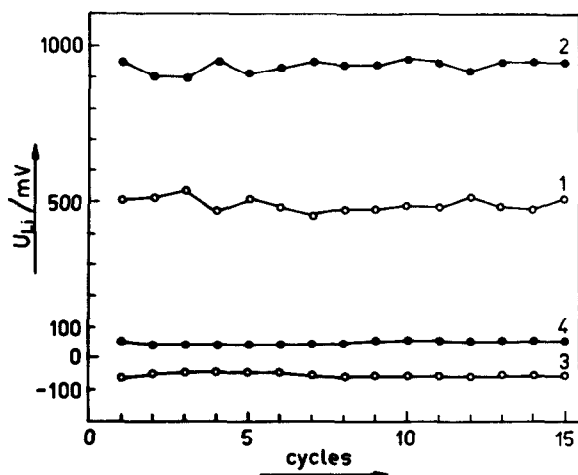


Fig. 3. Potential of lithium deposition and dissolution in dependence on cycle number. Deposition (3) and dissolution (4) on nickel; deposition (1) and dissolution (2) on aluminum.

tion can be detected. This means that the layer formed must be very thin. In the stationary state the overvoltage has almost the same value as that measured in PC. The variation in the plating and stripping current densities up to 1 mA cm^{-2} does not influence cycling efficiency. At current densities above 1 mA cm^{-2} , the efficiency decreases considerably.

With periodic cycling (Fig. 4), the efficiency in PC during the early cycles has a value of about 70% and this decreases later to about 60%. In the ether electrolyte, an efficiency of 85 - 75% was achieved at first but after further cycling the efficiency decreased to approximately 60 - 65%. After the experiments, a visible surface layer was formed in each case. The lack of cycling efficiency is not completely explained by a parasitic

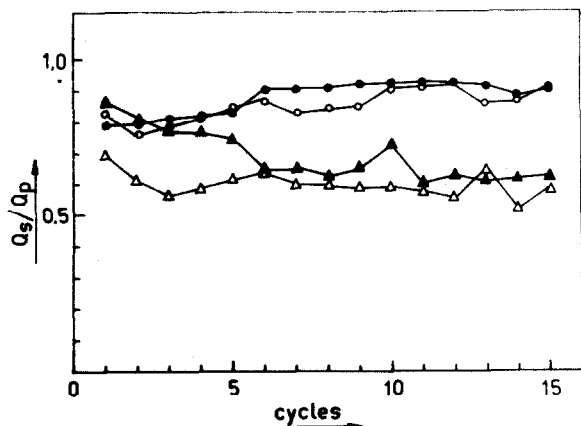


Fig. 4. Cycle efficiency, Q_s/Q_p , in dependence on cycle number in PC/1 M LiClO₄ (○, △); and in 2-MeTHF/THF(2 vol.)/1 M LiAsF₆ (●, ▲). ●, ○, aluminum; ▲, △, nickel.

electrolyte decomposition process; electrochemically insoluble lithium also remains on the surface.

It was shown, using rotating electrodes, that diffusion processes in the solution do not influence the plating and stripping cycles. It was also shown on initial investigation, that with increasing cathodic polarization, the current efficiency of lithium deposition in PC decreases. Under these conditions, PC is mostly reduced to propene and carbonate ions [5] which immediately react with lithium ions, and insoluble lithium carbonate results, producing an additional retarding surface layer. Poorly soluble alkyl carbonates are also formed [6]. In order to achieve a high cycle number, therefore, it is recommended that, in practice, a low cathodic polarization be employed, *i.e.* low current densities ($<0.5 \text{ mA cm}^{-2}$).

3.2.2. Cycling on aluminum

Lithium is deposited in both electrolyte solutions without any unusual SEI formation. The cycling efficiency is distinctly greater than on the inert nickel substrate, and during subsequent cycling it improves to about 90% (Fig. 4). The dissolution of the lithium alloy formed occurs at a high overvoltage (Fig. 3). One may assume that, depending on the more positive potential of the alloying electrode, solvent decomposition is lessened, but a part of the intercalated lithium remains in the alloy and reduces the cycling efficiency. The positive effect of the alloying substrate disappears at higher charge and current densities, when a pure lithium layer is formed on the surface.

In summary, it is necessary to develop an alloying support, which:

- (i) is able to incorporate, reversibly, with sufficient mechanical stability, a large amount of lithium;
- (ii) has a potential at which side reactions with the electrolyte solution are low;

(iii) does not have too great a potential difference compared with lithium.

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