

BEHAVIOUR OF THE LITHIUM ELECTRODE DURING CYCLING IN NONAQUEOUS SOLUTIONS

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Summary

The behaviour, in different electrolytes, of Li during cycling in anode limited close packed cells has been studied.

The highest efficiency (\bar{E}) at a current density of 4 mA cm^{-2} and a charge density of 2 mA h cm^{-2} is obtained in LiAsF_6 containing a mixture of THF/2-MeTHF with 2 vol.% 2-MeF.

The effect on E of current density and depth of discharge in ether solutions has also been examined.

The change of polarization resistance, ohmic drop in the solution and geometric capacitance with cycling, has been investigated by the galvanostatic pulse method.

An assumption for the Li passivation observed during cycling in ether electrolytes is discussed.

Introduction

Most of the many papers dedicated to the study of the Li secondary electrode in various electrolytes related to work carried out at the EIC laboratories [1, 2]. Recently, Yamaki [3] and Matsuda *et al.* [4] have also shown the possibility of cycling Li in different solvent mixtures. The feasibility of secondary Li cells was, however, exhibited for the first time by the MoliceL, where a solution of LiAsF_6 in PC or PC/EC mixture is used [5, 6].

Many recently published investigations were performed with cathode limited cells by following the shape of the discharge curves and not the potential of the Li anode. This makes an assessment of the actual behaviour of the anode during cycling difficult.

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This study was aimed at the elucidation of the processes occurring during Li cycling in different electrolytes under conditions closely relating to those prevailing in real cells.

Experimental

Anode limited close-packed cells were employed. Two types of cell models were used:

(i) rectangular glass cells with a Li electrode closely packed against 2 cathodes with the aid of a Teflon spacer. The electrolyte volume was approx. 1.2 ml cm^{-2} of Li.

(ii) metal cells of stainless steel. The Li electrode was pressed against the cathode by a coil spring at 2 kg cm^{-2} . The electrolyte volume was approx. 0.2 ml cm^{-2} of Li.

Each cell type was provided with a Li reference at a distance of about 1 mm from the Li electrode.

The results presented in this study were mainly obtained using cell type (i).

The cathode capacity was at least 4 times greater than that of the plated/stripped Li. The cycling process was followed by the potential-time curves of the anode and the cathode with respect to the Li reference. In most cases the cycle life ended as a result of the high polarization of Li (0.5 V). The cathode potential during the cycling period was in the range of 2.2 - 2.8 V.

The solvents were purified according to procedures broadly described in the literature [1 - 5]. LiAsF_6 (USS Agri-Chemicals) was used as received. The moisture content of the solutions was below 100 ppm. The cathode material was either LiV_3O_8 or $\text{LiCr}_{0.9}\text{V}_{0.1}\text{S}_2$ both developed in our laboratories [7, 8]. The cathodes were prepared by pressing a mixture of the active material with 20 - 30 vol.% Teflonized acetylene black on a Ni screen. The separators were either glass mat or Cellgard 2400.

Results and discussion

Table 1 presents the average cycling efficiency, \bar{E} , obtained in this study of Li in electrolytes recommended for Li secondary cells [1 - 5]. The efficiency, \bar{E} , is calculated according to the formula given by Koch [1]:

$$\bar{E} = 1 - \frac{Q_{\text{ex}}}{n Q_{\text{d}}} = 1 - \frac{1}{n \text{DOD}} \quad (1)$$

were Q_{ex} is the amount of excess Li; n the number of "100%" cycles; Q_{d} , the charge of Li stripped; DOD, the depth of discharge equal to $Q_{\text{d}}/Q_{\text{ex}}$.

All tests were carried out at 4 mA cm^{-2} , $Q_{\text{c}} = Q_{\text{d}} = 2 \text{ mA h cm}^{-2}$. Cycling was stopped when the Li overpotential exceeded 500 mV, with the

TABLE 1
Cell type (i)

Solutions	Li (mg)	DOD (%)	Cycles	\bar{E} (%)	FOM
1.5 M LiAsF ₆ -THF/2-MeTHF (1:1)	18.1	4.9	71.0	72.0	3.5
1.0 M LiAsF ₆ -EC/2-MeTHF (1:1)	18.2	4.9	21.0	3.8	1.0
1.0 M LiClO ₄ -PC/2-MeTHF (1:1)	12.4	7.2	10.0	—	0.7
1.0 M LiClO ₄ -PC/DME (1:1)	12.5	7.1	21.0	33.0	1.5
1.0 M LiAsF ₆ -PC/DME (1:1)	18.7	4.8	22.0	6.0	1.0

exception of EC-containing solutions where the overpotential of Li was 600 mV from the beginning. The results in Table 1 reveal that the highest efficiency is obtained in the ether solvent mixture, the so-called "EIC electrolyte" with 0.2 vol.% 2-MeF, and that under the present conditions the efficiency values are lower than those reported earlier [1, 2]. A possible reason for this discrepancy is the use of higher c.d. in this study. As seen from the results in Fig. 1, the increase of c.d. brings about a decrease in \bar{E} . It was established, however, that the change of DOD in the range from 4 to 30% at a constant c.d. does not affect the \bar{E} value substantially. For example, at 2 mA cm⁻² this value remains close to 80% (Fig. 2).

It was noted that neither the cell type (glass or metal) nor the kind of cathode material (LiV₃O₈ or LiCr_{0.9}V_{0.1}S₂) had any substantial effect on the efficiency data.

A potential maximum (point 1 in Fig. 3(a)) was observed at the start of the cathodic cycle in the EIC solution. This maximum can be related either to the deposition of Li on a partially passivated substrate or to the crystallization overpotential (new phase formation) [9]. It is assumed here

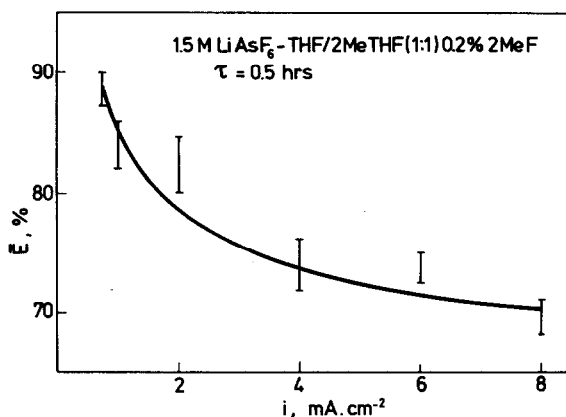


Fig. 1. Effect of current density (c.d.) on lithium cycling efficiency (\bar{E}). $\tau_d = \tau_c = 0.5$ h; cell type ((i) and (ii)).

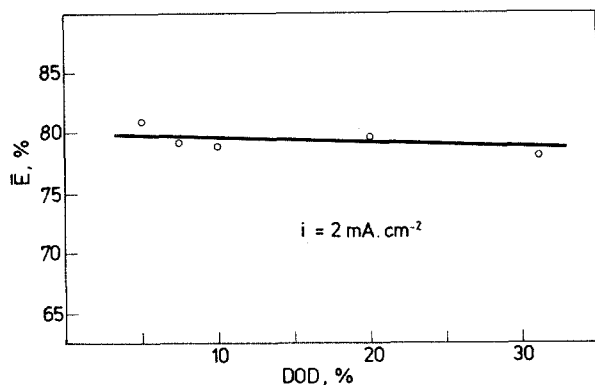


Fig. 2. Effect of depth of discharge (DOD) on lithium cycling efficiency at a constant current density: $i = 2 \text{ mA cm}^{-2}$; electrolyte, 1.5 M $\text{LiAsF}_6\text{-THF}/2\text{-MeTHF}$ (1:1) 0.2% 2-MeF; cell type ((i) and (ii)).

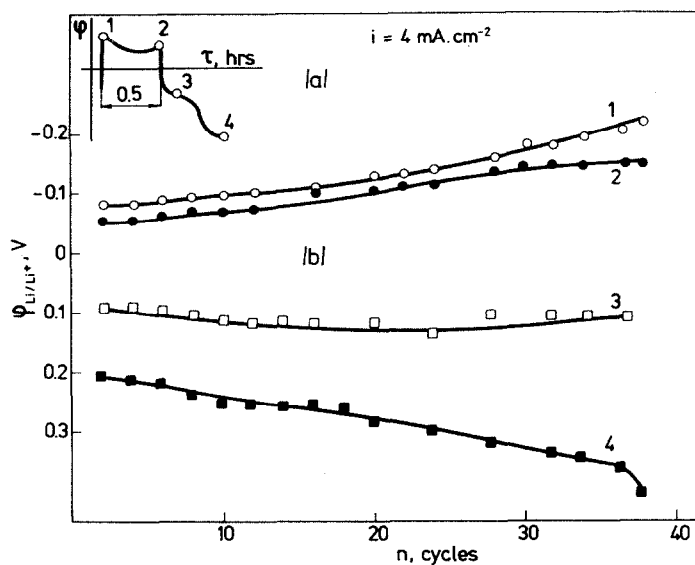


Fig. 3. (a) Typical Li cathodic-anodic polarization curve; $i = 4 \text{ mA cm}^{-2}$, $\tau_c = \tau_d = 0.5 \text{ h}$; cell type (i). (b) Change of cathodic (1, 2) and anodic (3, 4) overpotentials of Li in EIC electrolyte.

that the maximum is related to the partial passivation of the Li substrate during discharge. This assumption is supported by the experimentally observed correlation (Fig. 3(b)) between the increase in the anodic dissolution overpotential at the end of the discharge (curve 4) and the height of the maximum at the beginning of the charge curve (curve i).

It is likely that during cycling the Li substrate is gradually blocked by passivation products which increase the polarization. In some cases this

could bring about an earlier failure of the Li electrode than that expected by eqn. (1).

It was found in the case of EIC electrolytes that when cycling is interrupted after charging, the storage at open circuit results in a deterioration of the Li anode efficiency in subsequent cycling. Figure 4 illustrates the effect of storage time on the single cycle efficiency, E_c , which in this case is estimated from the Q_a/Q_c ratio for the respective cycle. Here Q_a is the charge measured from the beginning of the potential-time discharge curves to the point of the sharp increase in the Li anodic polarization (see Fig. 3(a)). Thus after 24 h of storage in a charged state the E_c of Li in the next cycle is only 50% of its previous value. This efficiency decay is accompanied by an increase in Li polarization from 200 to 300 mV during discharge at 2 mA cm⁻².

These results indicate that the study of Li passivation during cycling is of definite interest. As shown in our previous investigation [10] the galvanostatic pulse method (GPM) can be used successfully to elucidate the kinetics and mechanism of Li passivation. The method is applied here in an attempt to study Li passivation during cycling in EIC electrolytes. The cell was cycled at 1 mA cm⁻² for 1 h and the pulses were applied at different time intervals during cycling. As can be seen from Fig. 5 the polarization resistance R_p (resp. the overpotential at 1 mA cm⁻²) measured by GPM at the end of the discharge remains constant as the number of cycles increases. After 80 cycles a considerable increase in the reciprocal capacitance, C^{-1} , is also observed. This is accompanied by a simultaneous increase in the steady overpotential, φ_s , measured at the end of discharge. It was found that the steady state overpotential φ_s during discharge is higher than the sum of the ohmic, $\eta_{s01} = iR_{s01}$, and polarization, $\eta_p = iR_p$ overpotentials measured by the GPM. The difference, $\varphi_d = \varphi_s - (iR_p + iR_{s01})$ is plotted in Fig. 6 as a function of the square root of time of discharge. The linearity of these relationships suggests that some diffusion limitations are operative. The slope of the $\varphi_s - \tau^{1/2}$ plots increases with the number of cycles (see Fig. 6(b)).

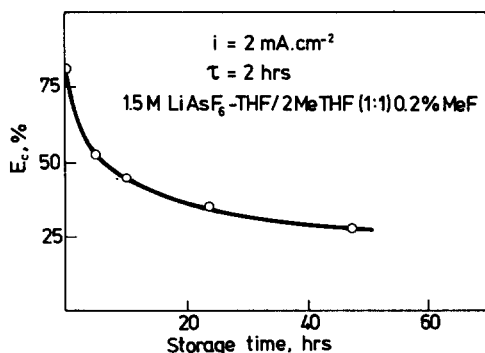


Fig. 4. Effect on the efficiency, E_c , in the next cycle of storage of charged Li electrode at open circuit. $i = 2 \text{ mA cm}^{-2}$, $\tau = 2 \text{ h}$; cell type (i).

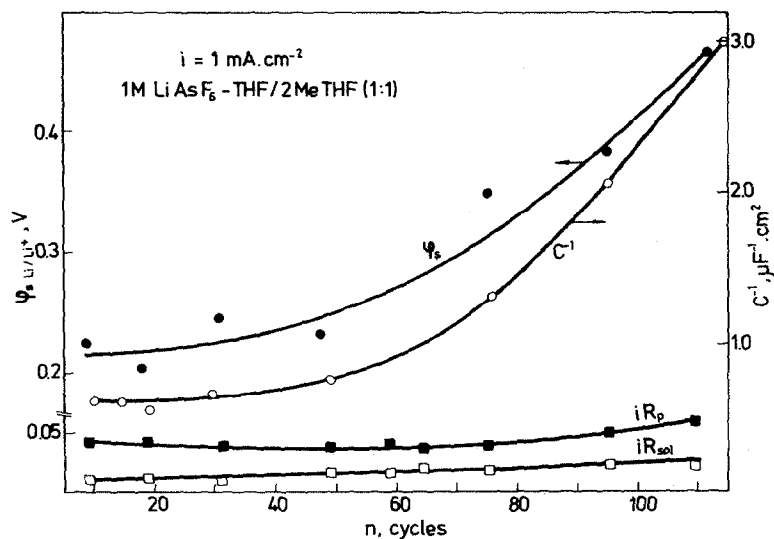


Fig. 5. Change of polarization resistance R_p , ohmic drop iR_{sol} , reciprocal capacitance C^{-1} and overall steady state overpotential φ_s at the end of discharge of Li during cycling at 1 mA cm^{-2} ; cell type (i).

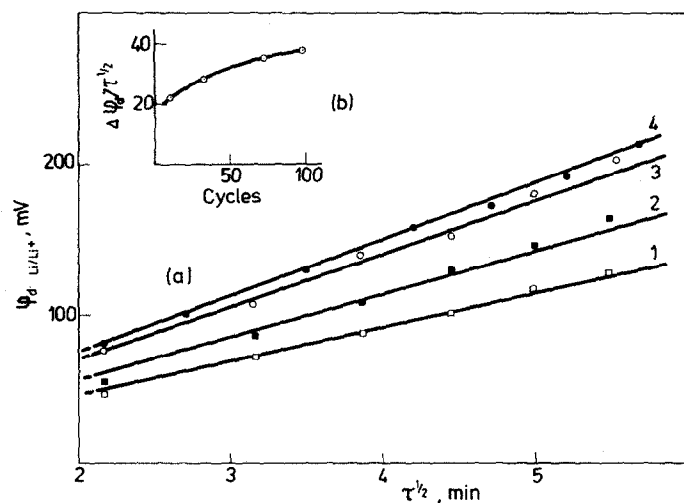


Fig. 6. (a) Dependence of the overpotential, $\varphi_d = \varphi_s - (iR_p + iR_{sol})$, of Li on the square root of time discharge: 1, 9th; 2, 32nd; 3, 73rd; 4, 98th cycle. (b) Change of the slope $d\varphi_d/d\tau^{1/2}$ with the number of cycles.

A similar dependence was observed by Volkov and Povarov [11] during cycling of free Li electrodes in an excess of aprotic solutions.

The experimental data accumulated so far do not allow us to arrive at definite conclusions on the nature of this diffusion process. However, the

degradation of ether electrolytes containing LiAsF_6 [12] could be one of the reasons for the blocking of the Li electrode surface as cycling proceeds.

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