

Lithium rechargeability on different substrates

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Abstract

The rechargeability of lithium and its alloys is considered by applying new parameters of cycleability. Such parameters are the corrosion current during cycling (j_c), shedding degree of the anode ($0 \leq \gamma \leq 1$) and the maximal cycling efficiency (E^{\max}). The corrosion current is a measure of the protective properties of the film formed on the anode; E^{\max} and γ are related to the deposit morphology. A number of similarities has been revealed during lithium cycling in 15 electrolytes at an inert electrode substrate. The morphology of the lithium deposit is determined by the most reactive component of the solution, with respect to lithium. This component can be a solvent, solute or impurity (additive). The corrosion current is influenced by the solvent or some impurities (additives). When cycling lithium at alloying substrates the cycleability parameters also depend upon the kind of alloy. The new parameters give a simple possibility of choosing the most suitable electrolyte solution and selecting the lithium alloy with the least shedding degree during cycling and with the best capacity retention.

Introduction

Recently some attempts to connect the cycling efficiency of lithium on an inert substrate with the electric properties of aprotic polar media (conductivity, viscosity, solvation parameters) have been undertaken [1, 2]. It becomes clear, however, that the main factor controlling the electrochemical behaviour of lithium electrodes is the nature of their surface films [3]. Lithium cycleability depends on the solution properties solely via the film properties.

To investigate how the components of the electrolyte solution and the type of substrate influence film formation and, therefore, lithium cycleability, it is expedient to select good criteria, characterizing this process. The most common criteria are cycling efficiency, determined by various methods [4-6] and FOM of lithium [7]. The known criteria are not universal. In some cases they depend essentially on current density [8]. Consequently, difficulties arise in comparing the degrees of lithium cycleability in different media. We use, here, new criteria of rechargeability which are independent of current density. They allow the anode film properties and the deposit morphology to be characterized more accurately.

Approach

The dependence of the capacity loss rate during cycling upon the cycling current is the basis for the new criteria to be defined. The capacity loss rate is calculated

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from the formula:

$$j_i = \frac{Q_p - Q_s}{t_p + t_s} = \frac{100 - E}{100 + E} j \quad (1)$$

where Q_p , t_p are the capacity ($C \text{ cm}^{-2}$) and time (s) of charge, Q_s , t_s the capacity and time of discharge and $E = Q_s/Q_p$ is the coulombic efficiency (%). The dependence $j_i = j_i(j)$ is linear as a rule (as an example see Fig. 1). $j_i = j_c + j_{\text{cap}} = j_c + \gamma j$, $\gamma = \tan \alpha$.

The capacity loss rate contains two terms. The first one j_c , does not depend on current and may be considered as a corrosion current for freshly deposited lithium. The corrosion current characterizes the passivating properties of the film (the presence of defects, solubility, electron conductivity) in total. The second term, $j_{\text{cap}} = \gamma j$ is the shedding rate of the anode. In the case of lithium electrodeposition on an inert substrate the shedding rate of the anode may be considered as an encapsulation current.

The linearity of the plot of encapsulation current density versus cycling current is due to the fact that a constant part of deposited lithium is isolated in each discharge semicycle at different current densities. Thus, the slope γ of the $j_i = j_i(j)$ dependence reflects the deposit morphology in a certain solution and may be called the degree of anode shedding (or encapsulation degree). It ranges from 0 to 1.

The E , j_c and γ parameters are related to each other by the following expression:

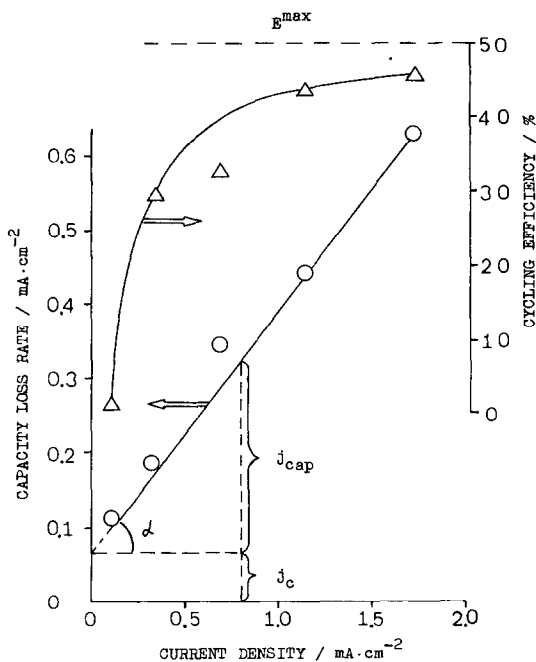


Fig. 1. Dependence of cycling efficiency (Δ) and capacity loss rate (\circ) of electrodeposited lithium on cycling current density in 1 M LiAsF₆/PC-DME (60:40) containing trace water. Charging capacity = 0.2 C cm⁻².

$$E = \frac{1 - \frac{j_c}{j} - \gamma}{1 + \frac{j_c}{j} + \gamma} 100\% \quad (2)$$

At $j_c=0$ or $j \gg j_c$ this function reaches a maximum value:

$$E^{\max} = \frac{1 - \gamma}{1 + \gamma} 100\% \quad (3)$$

E^{\max} is representative of both the anode morphology and the degree of its cycleability in the given solution. The utmost compact and adherent deposit corresponds to $\gamma=0$ and $E^{\max}=100\%$. On the contrary, the values $\gamma=1$ and $E^{\max}=0\%$ correspond to a badly adherent deposit which has completely lost electrical contact with the bulk substrate.

It can be assumed that in the case of lithium deposited on an inert substrate the higher the Li^+ conductivity of the film the smoother the morphology.

Experimental

Lithium was cycled on different substrates in hermetic cells under galvanostatic conditions at $j=j_p=j_s$. The counter and reference electrodes were lithium. The cells were assembled in air dried over P_2O_5 . In the discharge process lithium was dissolved up to a cutoff potential of 1 V versus Li/Li^+ in most cases. The electrolyte solutions, based on propylene carbonate (PC), dimethoxyethane (DME), γ -butyrolactone (BL), dimethyl sulfoxide (DMSO) and ethylene carbonate (EC) were thoroughly dehydrated using a lithium-aluminium alloy.

The capacity loss current density j_l was determined in terms of eqn. (1) as an average value from the 2nd to the 6th cycle. The dependences $j_l=j_l(j)$ were determined using the lowest experimental points. Such dependences correspond to the highest cycling efficiency for each current.

Discussion

We have carried out cycling of lithium in 15 thoroughly dehydrated solutions of electrolytes on a stainless-steel substrate. The cycling parameters are summarized in Table 1, for corrosion currents greater than $5 \mu\text{A cm}^{-2}$. Two groups of solution can be identified. LiClO_4 and LiCF_3SO_3 solutions make up the first group in which the parameters γ and E^{\max} do not change much between one solvent and another. LiAsF_6 and LiBF_4 solutions make up the second group, where the above parameters depend on the solvent to a greater extent; DME exerts the strongest negative influence. These observations can be interpreted as follows. The morphology of the lithium deposit depends on the film properties which are determined by the reduction products of the most Li-reactive component of the solution. Since LiBF_4 and LiAsF_6 are not such strong oxidizers as the solvents, lithium reacts preferentially with the solvent. Since the reduction products of various solvents are different, the film properties differ from

TABLE 1

Parameters of lithium cycling on a stainless-steel substrate in 1 M solutions of electrolytes (0.2 C cm⁻² charge, 50 °C)

Salt	Solvent	Parameter		
		γ	E^{\max} (%)	j_c ($\mu\text{A cm}^{-2}$)
LiClO ₄	PC	0.310	52.7	
	BL	0.450	37.9	20
	PC-DME (60:40)	0.345	48.7	
	DMSO	0.345	48.7	40
LiBF ₄	PC	0.180	69.5	
	BL	0.265	58.0	5
	PC-DME	0.600	25.0	
	DME	0.600	25.0	
LiAsF ₆	PC	0.270–0.330	57.5	
	BL	0.370	46.0	15
	PC-DME	0.830	9.3	
	PC-EC	0.455	37.5	
LiCF ₃ SO ₃	PC	0.225	63.3	
	BL	0.245	60.6	40
	PC-DME	0.285	55.6	

each other markedly. On the other hand, LiClO₄ and LiCF₃SO₃ are stronger oxidizers than the solvents and lithium reacts preferentially with the salts, forming a primary inorganic solid film which inhibits further reduction of the solvent. Since in this case the same films are formed in different solvents, the interface properties are not strongly different from each other.

The corrosion current is influenced by the nature of the solvent and impurities facilitating the dissolution of surface films, e.g. water. It follows from Table 1 that BL and DMSO form films which do not prevent lithium corrosion.

In the case of lithium cycling on Li-inserting substrates, the parameters of cycling are also dependent on the nature of the substrate, as shown in Table 2, for corrosion currents greater than 2.5 $\mu\text{A cm}^{-2}$. The shedding degree on lithium cycling on the inserting substrate at 0.2 C cm⁻² is from 5 to 35 times smaller than that obtained upon cycling on the stainless-steel substrate. This is due to the lack of dendrite formation and more reliable contact between the particles of alloy than between those of lithium. In this case the anode shedding is caused by the alloy dispersion which is much less than the encapsulation of the lithium dendrites.

In addition, the following peculiarities are observed. Upon lithium cycling to a depth of 0.2 C cm⁻² on Sn and Pb substrates, corrosion currents are observed but at 2 C cm⁻² they disappear. This can be accounted for by the influence of surface oxide layers on the metal substrates. Due to their considerable electron conductivity the oxide layers cause corrosion of the alloy. With increasing depth of charge these layers break down, and their influence on the process reduces. The shedding degree of Li_xAl and Li_xZn alloys increases with current density due to volumetric changes in

TABLE 2

Parameters of lithium cycling on various substrates in 1 M LiClO₄/PC-DME (50 °C)

Substrate	Charge (C cm ⁻²)	Parameter		
		$\gamma \times 10^2$	E^{\max} (%)	j_c ($\mu\text{A cm}^{-2}$)
S.s.	0.2	34.5	48.7	
Ga (20 °C)	0.2	2.54	95.0	
Al	0.2	2.50–3.17	95.1	
	2.0	0.5	99.0	
Cd	0.2	2.08	95.9	
	2.0	1.00	98.0	
Zn	0.2	2.08–3.83	95.9	
	2.0	2.08–3.83	95.9	
Sn	0.2	1.00	98.0	17.0
	2.0	0.5	99.0	
In	0.2	7.5	86.0	
	2.0	3.3	93.6	
Pb	0.2	6.63	87.6	27.5
	2.0	4.50	91.4	

the alloy on cycling. For most of the alloys an increase in charge depth by an order of magnitude decreases shedding, whereas for Li_xZn it remains constant. This suggests that for the Zn substrate the oxide layers do not influence the process.

Cycling studies of coin cells (20 mm diameter, 1.6 mm thickness) with various anodes for a discharge depth of 10 mAh have also been carried out. Vanadium and niobium oxides have been used as cathode active materials and 1 M LiClO₄/PC-DME as electrolyte solution. The cells with a lithium anode gave 20 cycles, those with an Li_xPb anode 140–150 cycles and those with an Li_xIn anode 230–240 cycles. Unlike the cells with lithium anodes, those with alloys provide good capacity retention.

Conclusions

The application of new cycleability parameters to the study of lithium rechargeability has allowed us to improve our understanding of the process at the electrolyte/lithium-containing anode interface.

Careful selection of all the solution components is required for the optimal electrolyte to be defined. The reduction products of the most Li-reactive component of the solution must form a non-porous elastic film. The Li⁺ conductivity of the film must also be as high as possible.

It appears undesirable to use BL or DMSO in rechargeable batteries. The films formed in these media on cathodically deposited lithium do not protect it from further corrosion, and thus the internal resistance of the battery increases during wet-stand storage and the necessary cycle life is not obtained.

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