

A STUDY OF THE PROPERTIES OF THE SURFACE LAYERS FORMED ON LITHIUM ELECTRODES IN SULFOLANE-BASED ELECTROLYTES (EXTENDED ABSTRACT)

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Summary

The relevance of the use of lithium in high energy secondary batteries is mainly determined by the properties of the layers which are inevitably formed on the electrode surfaces. The surface layers can be responsible for the limitation of the cycle life of a battery either by giving rise to inhibitory polarization voltages provoked by the passivating properties of the layers, or by excluding some metallic lithium from the cycling processes (insufficiency of protection against corrosion, and/or generation of heterogeneous processes). In this paper we report experimental approaches used to determine the relative importance of these two limiting aspects.

Cycling efficiency measurements (FOM)

As far as the consumption of lithium is concerned, the advantage presented by the use of a lithium anode in a secondary battery rather than in a primary cell is made quite explicit by the use of the so-called Figure of Merit (FOM), defined as the ratio between the total discharge capacity accumulated during cycling until all the lithium initially contained in the electrode has disappeared, and the theoretical capacity Q_1 which would have been delivered if the system had been used as a primary cell:

$$\text{FOM} = \Sigma Q_c / Q_1 \# n Q_c / Q_1$$

(Q_c = quantity of electricity delivered at each cycle by the lithium electrode; n = number of cycles performed.)

To avoid measurements of excessive duration, the Li electrodes must contain small Li masses. In the experiments reported here, the electrodes were lithium-filled ($m = 0.06$ mg) cavities formed by anodic dissolution within tungsten cylinders sealed inside Pyrex tubes. Dissolutions were conducted in order to obtain regular cavities whose surfaces were sufficiently rough to

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ensure good adhesion between the tungsten substrate and the lithium to be pressed on it. Reproducible lithium masses were obtained by pressing Li foils with a dynamometric press inside the cavity, and removing the excess lithium with a blade accurately guided by the plane surface defined by the Pyrex tube. The amount of lithium, Q_i , actually available from this type of electrode, was found to be equal to $Q_i = 30.4 \pm 3 \text{ C cm}^{-2}$.

Relation between the protective and passivating properties of the surface layers

Figure 1 shows the evolution of the charge transfer resistance, R_t , of Li electrodes during storage periods in various sulfolane-based electrolytes. Curves (1), (2), (3) correspond to $\text{LiAsF}_6/\text{sulfolane}$ solutions of various purities. The higher the slope of the curve, the higher the number, n , of cycles achieved with thick lithium electrodes in the same condition ($j = 2 \text{ mA cm}^{-2}$; $Q_c = 10 \text{ C cm}^{-2}$). The fact that the rate of evolution of R_t during storage is linked to the rate of lithium corrosion suggests that the obstacles presented by the surface layer to chemical corrosion and the electrochemical charge-discharge process, increase at the same time. The substitution of LiAsF_6 for LiCF_3SO_3 as the solute (curve (4)) and the use of DME as a cosolvent (1:1) in $\text{LiAsF}_6/\text{sulfolane}$ solutions (curve (5)) confirmed this correlation between the chemical and electrochemical behaviors of the lithium. Scanning electron microscopy (SEM) observations also showed that the thickness of the surface layer formed in the presence of LiCF_3SO_3 reached a stationary value, whereas, under the same conditions, the thickness of the layer formed in presence of LiAsF_6 continued to

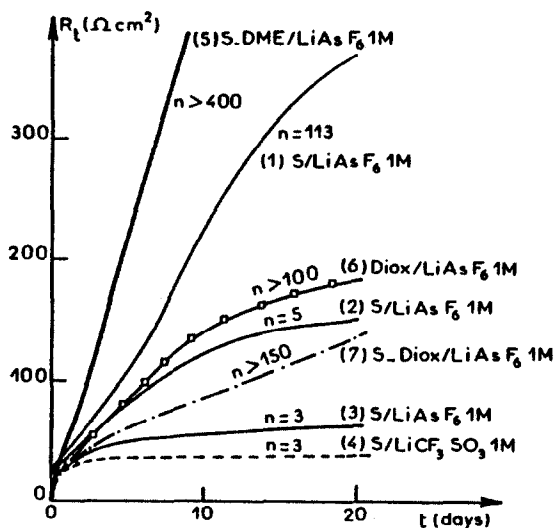


Fig. 1. Evolution of the charge transfer resistance, R_t , during storage tests.

increase regularly. The inability of the Li surface to cycle in presence of LiCF_3SO_3 might then be associated with the mechanism which stops the evolution of surface layers during storage. The use of dioxolane as cosolvent (curve (7)) confirms the absence of blocking for cycling associated with a continuous evolution of R_t during storage periods.

Relation between FOM and cycle-life (n)

The achievement of a large number of cycles, n , is of practical interest only if it is accompanied by high FOM and depth of discharge values. Table 1 gives FOM and n values obtained with a 33% depth of discharge (parts (a, b, d)) using sulfolane-based electrolytes. From Table 1 it appears that the FOM values are determined by the necessary compromise between an excessive and an insufficient chemical and electrochemical protective character which the surface layers must satisfy. Thus, with dioxolane, which is known to be able to lead to high values for n , a relatively important corrosion ($j_1 = 0.19 \text{ mA cm}^{-2}$) can account for the very low value obtained for the FOM. Also, reducing the current and charge densities reduces the development of heterogeneous strippings and platings, and leads to a decrease in j_1 (Table 1 a_1 and c). However, when the duration of the Li/electrolyte contact corresponding to the same charge density (I, a_1) is increased, the reduction of j_1 does not compensate for the increased loss of Li resulting from the chemical attack, and we observe a reduction of the FOM.

TABLE 1

	Electrolytes	j (mA cm^{-2})	Q (C cm^{-2})	n^*	FOM	j_1^{**} (mA cm^{-2})
a_1	S-DME (1:1)	5	10	100	10	0.24
		2	10	>400	7	0.14
a_2	S	2	10	110	9	0.11
a_3	S-D (1:1)	2	10	>150	2	0.75
b	D	2	10	>100	5	0.19
c	S	1	5	>300	13	0.04
d	S-DME (1:1)/separator	2	10	>250	4	0.25

* n : number of cycles achieved with thick Li electrodes (>intentionally interrupted test).

** j_1 : current density equivalent to the mechanisms responsible for the non-electrochemical loss of lithium ($j_1 = j_c$ (due to corrosion) + j_h (due to heterogeneous processes)).
S: sulfolane; D: dioxolane; solute: LiAsF_6 (1 M).

Influence of a separator on the FOM

In order to determine the influence of parameter j_1 on the morphology of the electrode surface, we changed the morphology by modifying the

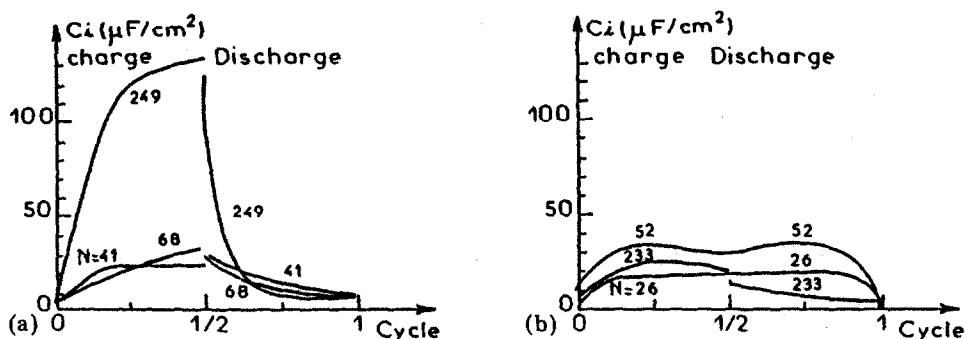


Fig. 2. Variation of the interfacial capacitance, C_i , during the N th cycle ($N = 26, 41, \dots$). (a) Without separator; (b) with separator.

rheology of the cell by pressing a separator against the lithium electrode. A $25 \mu\text{m}$ -thick hydrophilic separator (Celgard 3501) was tested with sulfolane electrolytes. The transfer resistance was found to be multiplied by a factor of about 2000 after 6 days, due to the addition of the separator. The study was continued by adding cosolvents to the sulfolane, with Celgard 2400, in order to wet the separator more suitably. Figure 2 shows the change in the evolution of the interfacial capacity, C_i , during cyclings carried out with, and without, a separator. It appears that the large increase of C_i during the charge observed when $n > 200$ and in the absence of a separator (Fig. 2(a)) must be attributed to a dendritic deposit. Such a dendritic deposit is reduced by the presence of the separator (Fig. 2(b)). SEM observations confirmed this effect on the morphology: the surface layer was found to be thinner, more homogeneous and smoother. However, this apparent improvement did not lead to an increase in the FOM (Table 1). Further investigations are in progress to explain this unexpected result.