

## CORROSION PROTECTION OF SECONDARY LITHIUM ELECTRODES IN ORGANIC ELECTROLYTES

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### Summary

Hydrocarbons show considerable surface activity in organic electrolytes; they, at least partially, displace the polar organic solvent molecules from any solid/electrolyte interface. Saturated hydrocarbons are chemically stable even *versus* lithium or lithium-rich alloys, and thus they are able to delay the irreversible reduction of organic electrolytes by these highly active negatives, *i.e.*, they delay corrosion and surface filming of the negatives.

As surface filming of lithium strongly controls the growth of lithium dendrites during electroplating, a delay in the filming process significantly decreases dendrite growth. Prevention of dendrite growth, however, requires speedy protection of freshly created "dynamic" surfaces and, hence, a high concentration (and solubility) of the hydrocarbon surfactant. On the other hand, for the protection of "static" electrodes under open cell conditions, even relatively insoluble surfactants may suffice.

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### Introduction

Metallic lithium is chemically unstable in organic electrolytes; it is covered with at least a monolayer of reaction products. The same holds for lithium alloys with high lithium activity, such as  $\beta$ -LiAl or lithium-rich alloys of B, Si, Sn, etc.

Suitable electrolytes for lithium batteries all form thin surface layers that are permeable to  $\text{Li}^+$  ions. The layers are reasonably "electrolyte-tight" and so protect the metal from further attack. This protection mechanism is sufficient for primary batteries. In secondary systems there is a permanent renewal of the surface layers during cycling. Therefore, the considerable irreversible consumption of lithium and electrolyte, as well as the accumulation of electronically insulating film material, cause severe problems.

For the above reasons, attempts have been made to slow down the reaction between the lithium (or highly active lithium alloys) and the electrolyte solution. One method is to use surface-active electrolyte additives which are at least "quasi-inert" with respect to lithium, *i.e.*, the additives react at a much lower rate than the electrolyte solution itself.

## Results and discussion

### *Choice of surfactant*

For solubility reasons, conventional surfactant molecules carry a strongly polar, or even an ionic, group. These surfactants cannot provide the required inertness with respect to lithium. On the other hand, non-polar surfactants, such as *saturated* hydrocarbons, are practically inert at room temperature and thereby limit the access of electrolyte components to the electrolyte surface. Considerable corrosion inhibition of lithium-alloy negatives by adsorbed long-chain hydrocarbons has been demonstrated, *e.g.*, for  $\text{Li}_x\text{In}$  electrodes ( $x \approx 1$ ) in  $\text{LiClO}_4$ /propylene carbonate (PC) electrolytes [1].

A problem with non-polar surfactants is that the solubility and the surface activity are conflicting properties. As a rule, low molecular weight hydrocarbons are more soluble in organic electrolytes but are less surface active than high molecular weight compounds. Furthermore, in most cases, the solubility of hydrocarbons increases and, hence, surface activity decreases, with decrease in the dielectric constant of the organic solvent.

Surfactants, which are only *reversibly* adsorbed on the electrode surface, cannot permanently avoid the *irreversible* reaction with the electrolyte solution. Nevertheless, even a very preliminary protection may be extremely useful when "dynamic" surfaces are to be protected. Electroplating lithium at  $1 \text{ mA cm}^{-2}$  represents a deposition of 5 monolayers of the metal per second.

Since a quick protection of freshly created electrode surfaces requires a reasonable concentration of surfactant in the bulk electrolyte, highly-surface-active but scarcely soluble surfactants cannot be used for this purpose. For long-lasting "static" protection (*e.g.*, under open-circuit conditions) large surfactant molecules with a high surface activity will be more effective, although because of diffusion limitations, the low solubility may cause delay times of the order of minutes until an equilibrium coverage of the electrode is achieved [2].

### *Tensammetric studies*

A convenient measure of surface activity is by the depression of the double-layer capacity of a mercury electrode in the presence of a surfactant. Such "tensammetric" studies allow concentration-independent determinations of the surface coverage to be made. Tensammetry with lithium electrodes in  $\text{Li}^+$  electrolytes is not possible, but because the chemical interactions

between saturated hydrocarbons and either mercury or lithium are weak, so the type of metal should not play an important role.

Surfactants cover the electrode surface only within a limited range of potential. When the potential is distant from zero charge, the surfactant molecules are "pushed away" by the ions from the electrolyte solution which are attracted by the oppositely-charged electrode. Unfortunately, no data exist for the potential of zero charge of lithium or lithium alloys in organic electrolytes. The reversible potentials of metallic electrodes ( $M/M^{n+}$ ), however, are generally close to the corresponding zero-charge potentials.

The technique of tensammetry has been used [1, 3] to study various saturated hydrocarbons in different electrolytes. As a rule, the attainment of a favourable combination of surface activity plus reasonable solubility (of the order of 1%) was found to be more difficult with chain-type hydrocarbons than with polycyclic types. In  $\text{LiClO}_4$ /propylene carbonate (PC) electrolytes, *cis*- and *trans*-decalin (decahydronaphthalene), tricyclo(5.2.1.0<sup>2,6</sup>) decane and perhydrofluorene proved to be both sufficiently soluble and highly surface active. The degree of broadness of the potential range of adsorption,  $\Delta E$ , (*i.e.*, the separation between the tensammetric desorption peaks) and the depression of the double-layer capacity,  $\Delta C$ , at the potential of zero charge are both useful parameters for characterizing the strength of adsorption. Adsorption energies, etc., can be calculated [2, 4] from the concentration dependence of these two parameters. In Table 1,  $\Delta E$  and  $\Delta C$  are listed for saturated solutions of various surfactants in organic electrolytes.

TABLE 1

Potential range of adsorption,  $\Delta E$ , and depression of double-layer capacity at zero charge,  $\Delta C$ , determined by tensammetry ( $f = 60$  Hz, phase angle =  $90^\circ$ ) with a dropping Hg electrode

Surfactant	Electrolyte	$E$ (mV)	$C$ ( $\mu\text{F cm}^{-2}$ )
$\alpha$ -Cholestane	PC/LiClO <sub>4</sub> 0.5 M	1000	6.9
Hexadecane	PC/LiClO <sub>4</sub> 0.5 M	565	7.1
<i>cis</i> -Decalin	PC/LiClO <sub>4</sub> 0.5 M	740	7.7
<i>trans</i> -Decalin	PC/LiClO <sub>4</sub> 0.5 M	695	7.9
1,2-Dicyclohexylethane	PC/LiClO <sub>4</sub> 0.5 M	775	8.0
Longicyclen*	PC/LiClO <sub>4</sub> 0.5 M	620	8.2
Perhydrofluorene	PC/LiClO <sub>4</sub> 0.5 M	930	9.8
<i>trans</i> -Decalin	PC/DME 90/10 LiClO <sub>4</sub> 0.5 M	700	7.6
<i>cis</i> -Decalin	PC/DME 90/10 LiClO <sub>4</sub> 0.5 M	725	7.9
<i>cis</i> -Decalin	$\gamma$ -Butyrolactone LiBF <sub>4</sub> 1 M	530	6.3

\*C<sub>15</sub>H<sub>24</sub>.

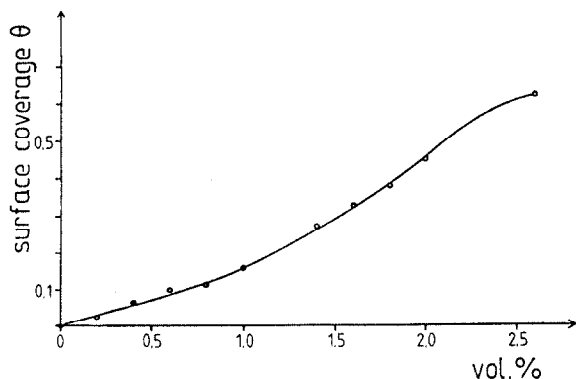


Fig. 1. Adsorption isotherm (room temperature) of *cis*-decalin on mercury, electrolyte: 1 M LiClO<sub>4</sub>/γ-BL.

To date, studies of the concentration dependence of the adsorption of saturated hydrocarbons from organic electrolytes have revealed a Frumkin-type (S-shaped) adsorption isotherm (Fig. 1). This suggests that small amounts of surfactant are not very effective, because there is a strong interaction between the adsorbed surfactant molecules which causes a more than linear increase in surface concentration with bulk concentration of the surfactant.

#### Surfactants on "static" Li<sub>x</sub>In surfaces

The corrosion protection of Li<sub>x</sub>In electrodes (under open-circuit conditions) in PC electrolytes by adsorbed *n*-paraffins has been reported previously [1]. Comparable results are also obtained with various polycyclic hydrocarbons. It would appear that the choice of surfactant is not critical. However, significant differences can occur, *e.g.*, *cis*-decalin in LiClO<sub>4</sub>/PC is more effective in protecting Li<sub>x</sub>In than *trans*-decalin. In addition, corrosion protection does not specifically depend on PC as the solvent; markedly decreased corrosion of Li<sub>x</sub>In due to adsorbed, saturated hydrocarbons is also observed in other solvents, *e.g.*, in γ-butyrolactone or in PC + 1,2-dimethoxyethane mixtures. Li<sub>x</sub>In electrodes exhibit only a small additional polarization in surfactant-containing electrolytes. In saturated solutions of *cis*-decalin, *trans*-decalin, and perhydrofluorene in 0.5 M LiClO<sub>4</sub>/PC, the polarization is about 20 mV in the current density range ±1 to ±5 mA cm<sup>-2</sup>. The extra polarisation does not increase linearly with current density; it is rather a "polarisation offset".

No undesired interferences of hydrocarbon surfactants were observed during long-term cycling of Li<sub>x</sub>In. An unsupported hanging In rod was cycled for more than 1000 times ( $i_c = i_a = 1 \text{ mA cm}^{-2}$ ,  $Q = 3600 \text{ mA s cm}^{-2}$ ) in 1 M LiClO<sub>4</sub>/PC-DME (1:1) + 3% *cis*-decalin, corresponding to an efficiency of 98.5%. The efficiency in the absence of *cis*-decalin was ~97.5%.

### Surfactants on "dynamic" lithium surfaces

Surfactants strongly affect the morphology of electroplated metals in so far as they reduce the formation of dendrites. This phenomenon is associated with a promotion of nucleation and an hindrance of crystal growth. In the case of lithium electrodes, there appears to be a second mechanism that retards dendrite formation. The production of lithium dendrites is commonly due to the fact that most of the lithium electrode is blocked, and the remaining active surface area has to accommodate a very high current density. Adsorbed, chemically inert surfactants obviously provide the lithium surface with a more uniform activity and, hence, cause more uniform and smoother metal deposits that are more stable towards corrosive processes.

The addition of *cis*- or *trans*-decalin or of tricyclo(5,2,1,0<sup>2,6</sup>) decane to LiClO<sub>4</sub>/PC electrolyte has a marked beneficial effect on the morphology of electroplated lithium (Fig. 2(a), (b)). Similar effects have been observed with other surfactants, such as quinoneimine dyes [5]. Because of the signifi-

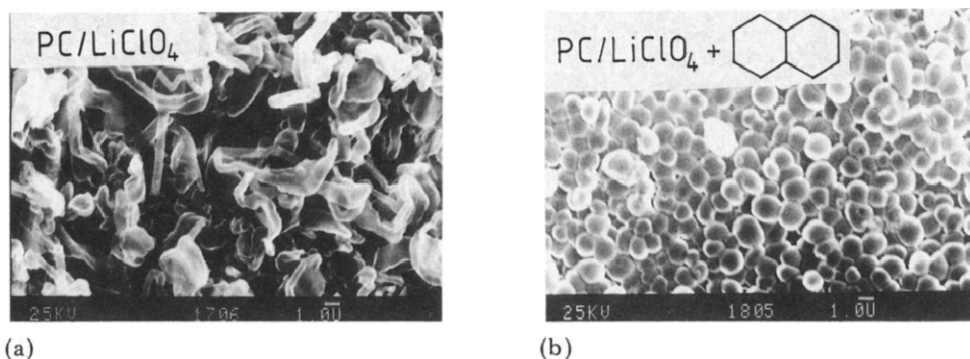


Fig. 2. Electron micrographs of Li electroplated at  $1 \text{ mA cm}^{-2}$  from (a)  $0.5 \text{ M LiClO}_4/\text{PC}$  and (b)  $0.5 \text{ M LiClO}_4/\text{PC} + \text{ca.}1\% \text{ decalin}$ .

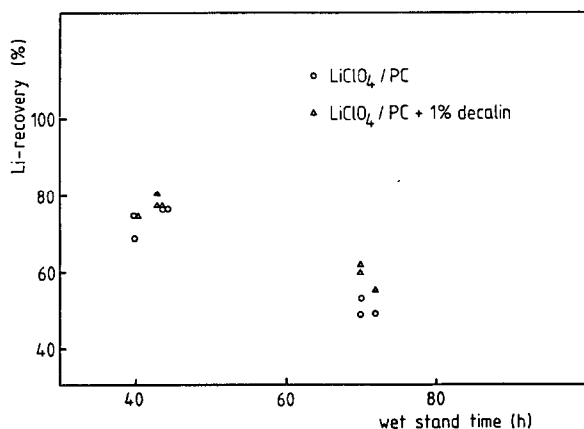


Fig. 3. Li-recovery after plating (on stainless steel) and storage in  $0.5 \text{ M LiClO}_4/\text{PC}$  and  $0.5 \text{ M LiClO}_4/\text{PC} + 1\% \text{ decalin}$ ,  $i_c = i_a = 1 \text{ mA cm}^{-2}$ ,  $Q = 2700 \text{ mA s}$ .

cantly reduced dendritic morphology of lithium electroplated in presence of decalin, improved cycling and corrosion behaviour is to be expected. However, preliminary experiments have been to some extent disappointing. Whereas there was no change in the cycling behaviour, the long-term storage characteristics were found to have improved (Fig. 3).

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### References

- 1 J. O. Besenhard, P. Komenda, A. Paxinos, E. Wudy and M. Josowicz, *Solid State Ionics*, 18 & 19 (1986) 823.
- 2 H. Jehring, *Elektrosorptionsanalyse mit der Wechselstrompolarographie*, Akademie Verlag, Berlin, 1974.
- 3 J. O. Besenhard, H. P. Fritz, E. Wudy, K. Dietz and H. Meyer, *J. Power Sources*, 14 (1985) 193.
- 4 J. O. Besenhard, J. Gürtler, P. Komenda, A. Paxinos and Zhu Shutao, to be published.
- 5 Shin-Ichi Tobishima and Takeshi Okada, *J. Appl. Electrochem.*, 15 (1985) 901.