ANODIC DISSOLUTION OF LITHIUM IN
LiClO$_4$-ETHYLENE CARBONATE ELECTROLYTES

L. HEERMAN and J. VAN BAELEN

The anodic dissolution of lithium in LiClO$_4$-ethylene carbonate solutions is complicated by the formation of a film on the electrode effecting a decrease of its activity. This film is not the normal product of the anodisation of lithium metal but is the product of a chemical reaction with the solvent or traces of water in the electrolyte. Anodic dissolution at higher current densities results in a partial breakdown of the film which accounts for an increase of the standard exchange current density from $1,47 \pm 0,25$ mA/cm^2 to $3,28 \pm 0,64$ mA/cm^2 at 40 °C.

The anodic dissolution of lithium in organic electrolytes is of considerable importance for the development of high energy batteries [1, 2].

Most of the investigations previously published were performed with lithium electrodes in LiClO$_4$-propylene carbonate (PC) solutions [3, 4, 5, 6].

In this work some results on the anodic dissolution of lithium in LiClO$_4$-ethylene carbonate (EC) solutions are reported. A study of the kinetics of the solid lithium electrode in these electrolytes has not been published so far though their use in high energy batteries has been described recently [7, 8].

EXPERIMENTAL

EC (UCB) was vacuum distilled at 1-2 mm of mercury and only the middle fraction ($\sim 60\%$) was used for the experiments. The solvent was dried by allowing it to stand for several days over molecular sieves (Merck 5A) which were previously dried at 250 °C for 24 h in vacuum. LiClO$_4$ (Fluka, $\leqslant 0,5\%$ water) was dried at 200 °C for 24 h in vacuum, molten under an argon atmosphere at 280 °C and a stream of dry chlorine gas was passed through it, until the melt became completely clear. After solidification the salt was promptly transferred to a dry box where all subsequent operations were carried out. Solutions stored in the presence of lithium metal contained < 40 ppm water as determined by Karl Fischer titration in an apparatus exposed to the air.

Electrodes were prepared by pressing lithium metal (Merck, 1% Na) in cylindrical teflon holders and chipping off to expose fresh surfaces prior to each measurement. Three such electrodes served as test, reference and counter electrodes. Bias potentials between different electrodes were very low, generally not exceeding a few tenths of a millivolt.

Graphite electrodes of spectroscopic purity (National Carbon Company) were used to study the electrochemical decomposition of the solvent.

All measurements were performed galvanostatically. Overvoltages were corrected for the ohmic potential drop between the test and reference electrodes using $\eta = \eta$ (obs)-iR.

The iR loss was determined from pulse measurements where the largest current used was always greater than the maximum current used during a micropolarisation run. Double layer capacities C_{dl} were evaluated from the initial slope of the oscilloscopic trace of a single current pulse (with the oscilloscope operating at 20 µs/cm) using $C_{dl} = i/(\partial\eta/\partial t)_{t\to 0}$.

RESULTS AND DISCUSSION

All experiments reported here were performed with electrodes exposed for at least one hour to the electrolyte before the commencement of the measurements.

The micropolarisation behaviour of lithium electrodes in 1.0 M LiClO$_4$–EC electrolyte at 40 °C is shown in figure 1. Curve a (fig. 1) was recorded without any further pretreatment of the electrodes. Each point of curve b (fig. 1) however was recorded after steady state anodic polarisation at 10 mA/cm^2 just preceeding to the measurement. A rapid decrease of overvoltage within the first minutes of closing the circuit was observed at this higher current density. When the potential remained constant the current density was changed abruptly to the indicated value in the micropolarisation region and the corresponding overvoltage value was noted.
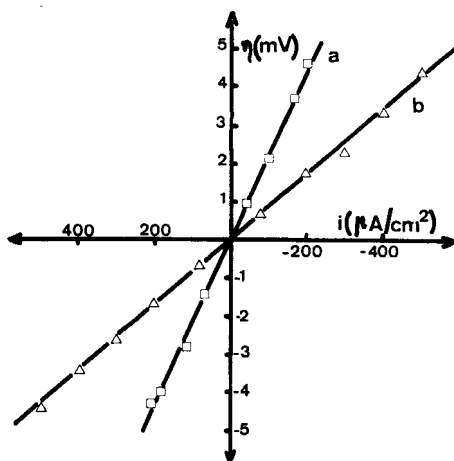

Fig. 1 — Micropolarisation behaviour of lithium electrodes in 1.0 M LiClO$_4$–EC electrolytes at 40 °C (a) without pretreatment of the electrode (b) after anodic dissolution at 10 mA/cm^2.

From these measurements it is clear that anodic dissolution at higher current densities results in an activation of the electrode. This effect cannot be explained by surface roughening since the electrode subsequently returned slowly back to the original level of lower activity.

Exchange current densities calculated from the micropolarisation curves using the well known expression for the charge transfer resistance $R_t = -(\partial\eta/\partial i)_{i\to 0} = (RT/F)/i_0$ together with the double layer capacities (determined at $2\ \text{mA/cm}^2$) for the results of figure 1 are given in table 1. Thus the exchange current density increases roughly in proportion to the increase of the real surface available for the transfer reaction.

TABLE I

Charge transfer resitance, exchange current density and double layer capacity for lithium electrodes in 1.0 M LiClO$_4$–EC *electrolyte at* 40 °C *(results of fig.* 1)

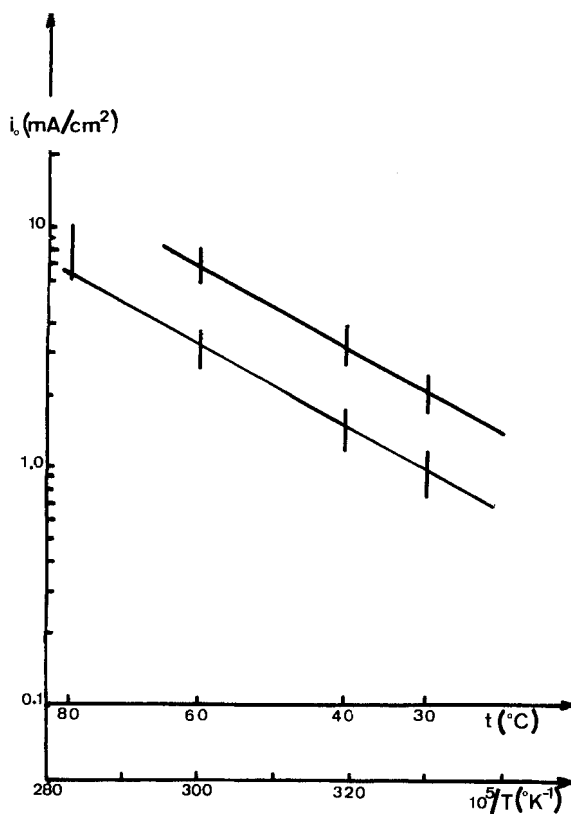|	R_t (ohm cm^2)	i_0 (mA/cm^2)	C_{dl} (μF/cm^2)
Level of lower activity	21.4	1.26	1.9
Level of higher activity	8.7	3.11	4.9

Fig. 2 — Determination of the activation energy for lithium electrodes in 1.0 M LiClO$_4$–EC electrolytes. Lower curve: without pretreatment of the electrodes; upper curve: after anodic dissolution at 10 mA/cm^2.

A similar behaviour was observed for solutions of different concentrations and at different temperatures. Exchange current densities for 1.0 M $LiClO_4$–EC electrolytes as a function of temperature are plotted in figure 2 where the upper curve gives the results obtained after anodic pretreatment at 10 mA/cm^2. Increase of the current density during anodic activation above this value did not result in a further increase of the exchange current density for the experimental conditions reported in this work. The heat of activation calculated from the results in figure 2 using $\partial \log i_0 / \partial (1/T) =$
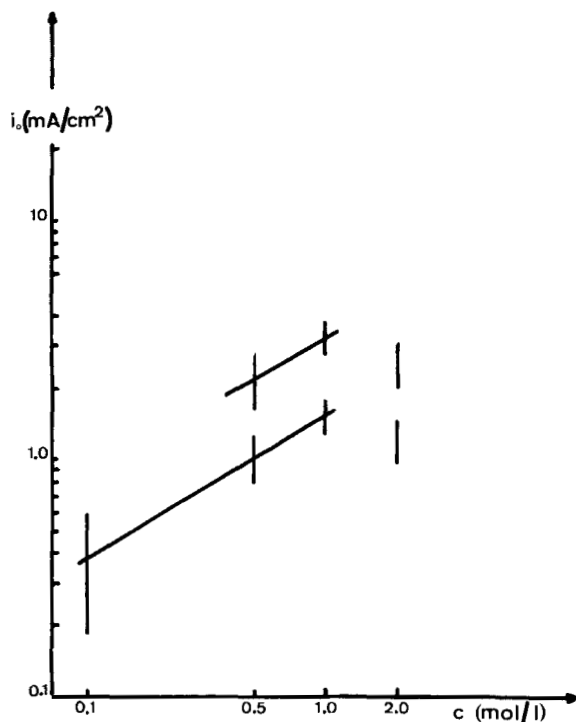

Fig. 3 — Exchange current density-concentration plot for lithium electrodes in $LiClO_4$–EC electrolytes at 40 °C. Lower curve: without pretreatment of the electrodes; upper curve: after anodic dissolution at 10 mA/cm^2.

$-\Delta H_0^{\neq}/2{,}303\ R$ was found to be 7,90 kcal/mole. Exchange current densities as a tion of concentration at 40 °C are given in figure 3. From the variation of the exchange current density with the concentration in the range 0.1-1.0 M, using the expression $\partial \log i_0 / \partial \log c_{LiClO_4} = 1 - \alpha$, the value of the charge transfer coefficient was estimated to be about 0,60.

　　　Exchange current densities for solutions > 1.0 M are lower than expected from the results for the less concentrated solutions. This effect can be attributed to the formation of ion pairs and the incomplete dissociation of the electrolyte resulting in an apparent reaction order less than unity with respect to the concentration of $LiClO_4$.
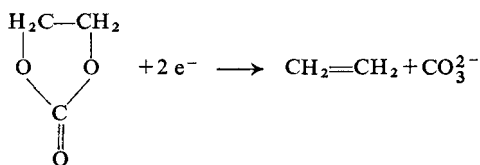
Some experiments have also been performed on the influence of water in the electrolyte. Addition of 400 ppm water causes the exchange current density to drop to a value as low as 0,03 mA/cm² and the double layer capacity to $\sim 0,5$ μF/cm². It was however found that lithium electrodes in the presence of such small quantities of water can be activated to almost the same extent as found for an anhydrous electrolyte but the electrode returns rapidly back to the level of lower activity after interruption of the current.

The results reported here are consistent with the idea of film formation on the electrodes as was advocated previously for lithium in $LiClO_4$–PC solutions [3, 4, 5].

The formation of this film takes place within the first minutes after exposing a fresh lithium surface to the electrolyte as was shown by Butler *et al.*, [3] for lithium electrodes in $LiClO_4$–PC solutions.

Anodic dissolution at higher current densities results however in a partial breakdown of the film which accounts for the observed increase of the exchange current density corroborated by an increase of the double layer capacity. A similar effect was noted by Scarr [4] for lithium electrodes in $LiClO_4$–PC solutions.

The film may be formed by a chemical reaction between lithium metal and the solvent. Dey [5] established that the chemical reaction between lithium and PC is thermodynamically favorable. Dey and Sullivan [6] found that the electrochemical decomposition of PC on graphite electrodes in $LiClO_4$–PC solutions occurs at potentials $+ 0,6$ V vs. Li/Li^+ (1.0 M). It was confirmed that the electrochemical decomposition of EC on graphite electrodes occurs in the same potential region. Analysis of the reaction products after constant current electrolysis showed that the reaction can be written as

$$\underset{\substack{\text{O} \qquad \text{O} \\ \diagdown \text{C} \diagup \\ \parallel \\ \text{O}}}{\text{H}_2\text{C}\text{---}\text{CH}_2} \quad + 2\,e^- \quad \longrightarrow \quad CH_2{=}CH_2 + CO_3^{2-}$$

in complete agreement with the previous work of Dey and Sullivan [6]. Since Li_2CO_3 is virtually insoluble in the electrolyte a carbonate layer can be formed on the surface of a lithium electrode after exposure of a fresh surface to the electrolytes considered here.

It is however clear that the almost inevitable presence of small quantities of water in the electrolyte can lead also to the formation of a hydroxide film on lithium surface, since the reduction of water in these electrolytes occurs at potentials $+ 1,4$ V vs. Li/Li^+ (1.0 M) in $LiClO_4$–PC or $LiClO_4$–EC electrolytes. It is therefore impossible to give a more detailed description of the film formation process on basis of present results.

In conclusion it can be stated that the solid lithium electrode in $LiClO_4$–EC electrolytes, despite the formation of a film on the surface, behaves as a relatively active and almost reversible electrode though a direct comparison with alkali metal electrodes in other media, e.g. amalgam electrodes in aqueous solutions, is difficult.

ACKNOWLEDGEMENT

UNIVERSITEIT TE LEUVEN
Laboratorium voor Anorganische Chemie
(Dir.: prof. R. Breckpot)
Leuven

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