

## ELECTRODE PROCESSES AT THE LITHIUM-POLYMER ELECTROLYTE INTERFACE

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### Summary

The electrochemical deposition and stripping of lithium have been examined using three-electrode cells with a polyethylene oxide-lithium trifluoromethanesulphonate polymer electrolyte. The results show that the process is reversible, but that the kinetics are influenced by the nature of the electrode substrate and the formation of passivating films.

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### Introduction

Following the discovery that combinations of suitable coordinating polymers such as polyethylene oxide (PEO) and certain salts have a relatively high ionic conductivity [1], many studies on the bulk properties of such 'polymer electrolytes' have been reported [2]. Since these electrolytes can be fabricated in the form of thin films, the possibility of developing a new type of high energy, rechargeable lithium battery has been proposed [3, 4]. There have, however, been relatively few reports so far [5 - 8] on the characteristics of electrodes involving such phases.

It therefore seemed of interest to undertake some systematic studies of the interfacial properties of such systems [9]. Here we report preliminary results of experiments on lithium deposition and stripping carried out on a number of electrode materials.

### Experimental

Polyethylene oxide (average molecular weight 4 000 000) from B.D.H. Ltd., and lithium trifluoromethanesulphonate, reagent grade from 3M Ltd., were used after drying, but without further purification. (PEO)<sub>9</sub>LiCF<sub>3</sub>SO<sub>3</sub>

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electrolyte was prepared by solvent-casting from acetonitrile as described by Weston and Steele [10]. The conductivity of this material was  $1.6 \times 10^{-7} \text{ S cm}^{-1}$  at  $25^\circ\text{C}$  and  $7.9 \times 10^{-5} \text{ S cm}^{-1}$  at  $80^\circ\text{C}$ , the temperature of the majority of the measurements. The electrochemical stability range of this electrolyte at  $80^\circ\text{C}$ , Fig. 1, is approximately 4.5 V with respect to lithium, confirming the earlier results of Armand and co-workers [6].

The majority of the electrochemical measurements were performed in a new design of three electrode cell, illustrated schematically in Fig. 2. The cell was constructed of Macor (9658), Corning Inc., a machinable glass ceramic, and was provided with stainless steel electrode contacts. The working electrode had a nominal area of  $0.125 \text{ cm}^2$  and was in the form of an easily replaceable disc. The lithium reference electrode consisted of a miniature stainless steel syringe whose threaded tip enabled it to be attached to the base of the cell. The lithium contact was formed by extruding lithium from the syringe tip and cutting a fresh surface. The counter electrode was, generally, a disc of diameter 1.3 cm cut from lithium ribbon. For some experiments, a symmetric, two-electrode glass cell with nominal electrode surfaces of  $1.7 \text{ cm}^2$  was used. The temperature of the cells was maintained using a thermostatically controlled oil bath.

Polarisation and cyclic voltammetry curves were obtained using standard potentiostatic equipment. Complex impedance studies were carried out with a frequency response analyser.

## Results and discussion

Lithium electrode kinetics were studied on four substrates: lithium metal itself, nickel, stainless steel, and vitreous carbon.

### (i) Lithium

A typical example of a low-field polarisation experiment for a lithium electrode in  $(\text{PEO})_9 \text{LiCF}_3\text{SO}_3$  electrolyte at  $112^\circ\text{C}$  is shown in Fig. 3. From the slope of this curve, an exchange current density of  $0.45 \text{ mA cm}^{-2}$  was

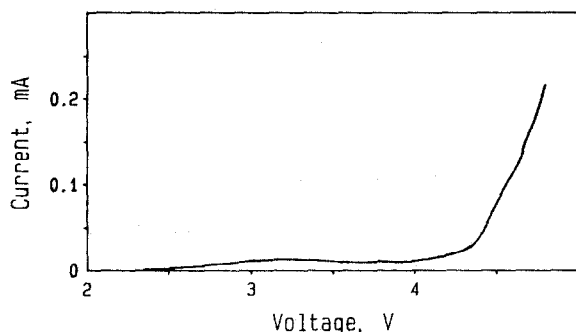


Fig. 1. Polarisation curve for a  $\text{Li(s)}|(\text{PEO})_9 \text{LiCF}_3\text{SO}_3(\text{s})|\text{Pt(s)}$  cell at  $80^\circ\text{C}$ .

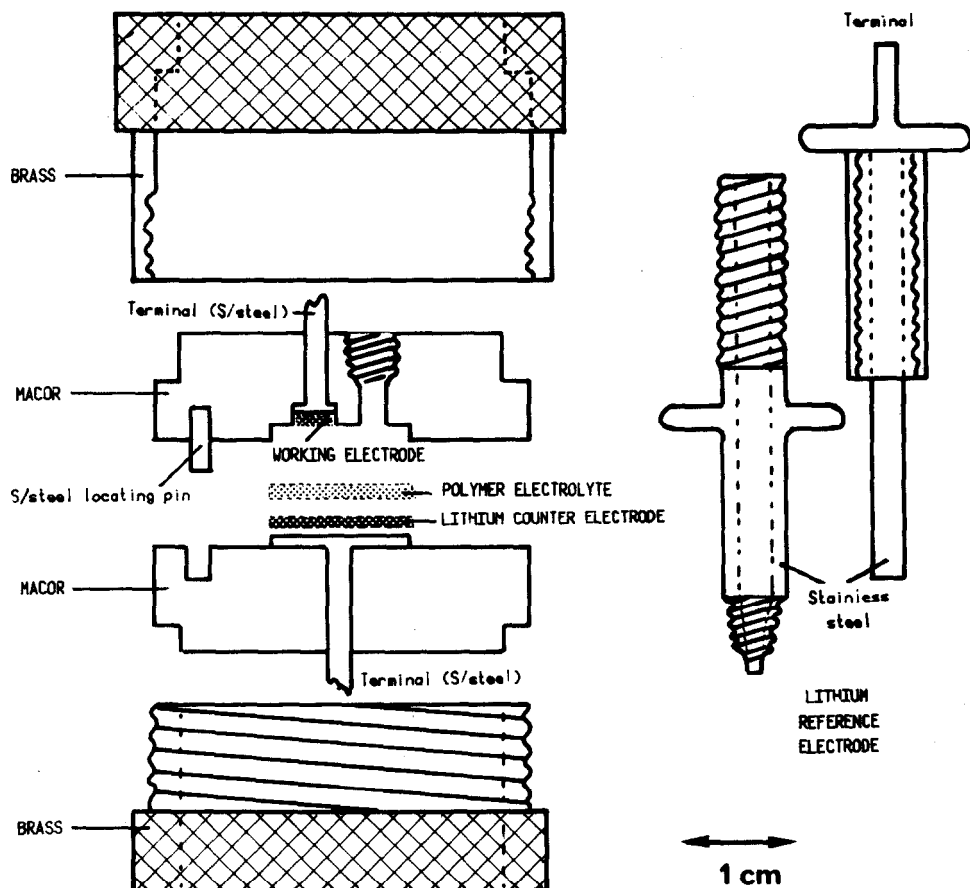


Fig. 2. Three electrode cell.

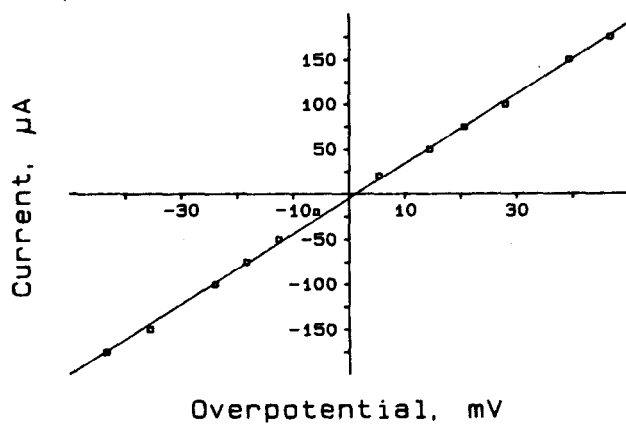


Fig. 3. Micropolarisation curve for a lithium electrode in  $(\text{PEO})_9 \text{LiCF}_3\text{SO}_3$  electrolyte at  $112^\circ\text{C}$ . Lithium reference electrode. Surface area:  $1.75 \text{ cm}^2$ .

obtained, a value which compares well with that reported by Sequeira and Hooper [11]. As pointed out by these authors, difficulties may be experienced in obtaining a consistent contact between the electrode and the polymer film: irreproducible behaviour was observed when insufficient pressure was applied to this interface. Further evidence of contact problems was noted in experiments in which a lithium electrode underwent a series of 0.7 C charge/discharge cycles using constant current steps of  $200 \mu\text{A}$ . After a number of cycles the a.c. impedance of the electrode was measured, which enabled the double layer capacitance to be evaluated. A steady fall in capacitance with increasing cycle number was noted (Fig. 4), indicating continuous geometric changes at the interface, most probably brought about by irregular lithium deposition. Further experiments are now being undertaken to study this effect in more detail.

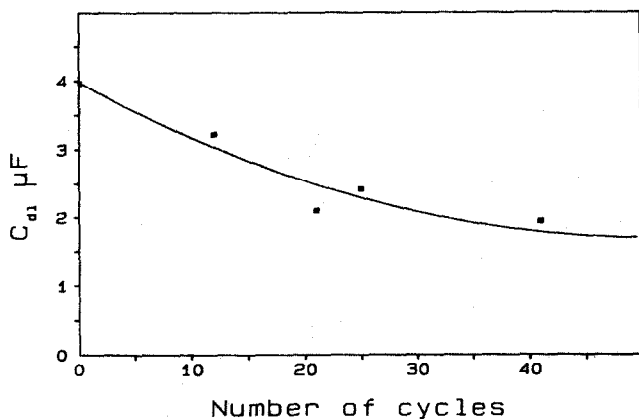


Fig. 4. Double layer capacitance at the  $\text{Li(s)}|(\text{PEO})_9 \text{LiCF}_3\text{SO}_3(\text{s})$  interface as a function of cycle number.

#### (ii) Nickel

Figure 5 shows a cyclic voltammogram for lithium plating and stripping on nickel at  $80^\circ\text{C}$ . The form of this trace is very similar to that observed in cells with conventional organic solvent-based electrolytes [12]. On the cathodic scan, the voltage required to deposit lithium metal on the nickel surface is some 250 mV more negative than on lithium itself. Once a monolayer has been formed, however, further plating can occur at any potential below zero volts, so that a "reverse peak" is formed on commencing the anodic scan. At positive potentials lithium is reoxidised. At high rates the cyclability is good, but at lower rates (Fig. 6), recovery of lithium decreases from 85% at  $20 \text{ mV s}^{-1}$  to 30% at  $5 \text{ mV s}^{-1}$ . These results suggest that lithium, freshly deposited from the polymer electrolyte, undergoes some passivation reaction, again similar to that found with conventional lithium cells [13]. Fauteux [14] has also proposed the formation of passivating films in similar systems on the basis of a.c. analysis. It is not clear, however, whether the observed passivation is a consequence of reaction with the poly-

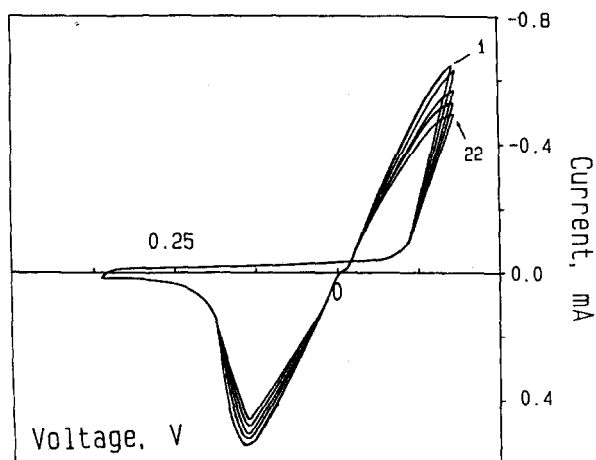


Fig. 5. Cyclic voltammograms of the lithium plating/stripping process on nickel from  $(\text{PEO})_9\text{LiCF}_3\text{SO}_3$  at  $80^\circ\text{C}$ . Surface area:  $1.75\text{ cm}^2$ .

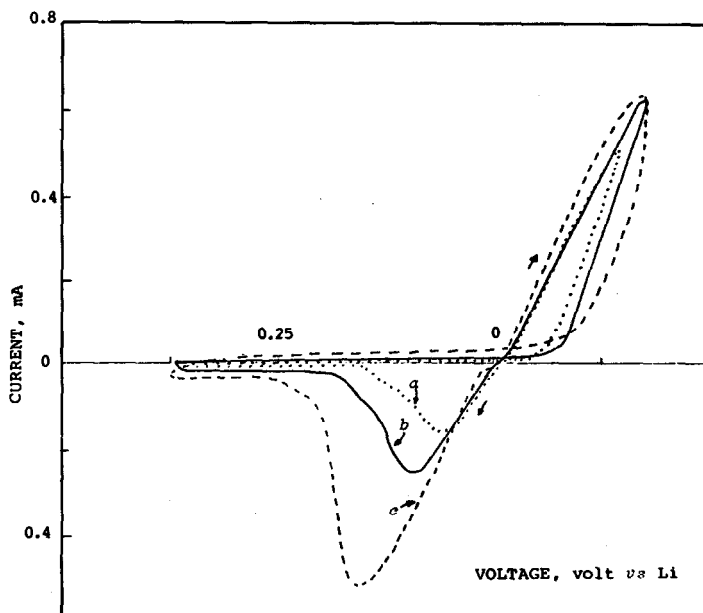


Fig. 6. Cyclic voltammograms of the lithium plating/stripping process on nickel from  $(\text{PEO})_9\text{LiCF}_3\text{SO}_3$  at  $80^\circ\text{C}$  as a function of scan rate. a:  $1\text{ mV s}^{-1}$ ; b:  $5\text{ mV s}^{-1}$ ; c:  $20\text{ mV s}^{-1}$ .

mer, or the salt as suggested by this author or, as seems possible, reaction with impurities such as water, catalyst residues, residual solvent from the casting procedure, etc. Indeed, the presence of impurities in the electrolyte used in the present work was revealed on scanning the potential to  $+2.0\text{ V}$ ,

when small, quasi-reversible, parasitic peaks were noted at +0.5 V and +1.3 V. Peaks at the latter voltage have been observed previously [8, 15] and attributed to water.

*(iii) Stainless steel*

Results are shown in Fig. 7 for similar experiments using stainless steel electrodes — another substrate of practical interest. The overvoltage for the formation of the initial monolayer is lower than in the case of nickel. While the cyclability is fair, the anodic wave is seen to consist of a double peak, the origin of which is the subject of further study.

*(iv) Vitreous carbon*

Figure 8 shows the lithium deposition/stripping process on vitreous carbon. Reduction of lithium ions commences at approximately one volt

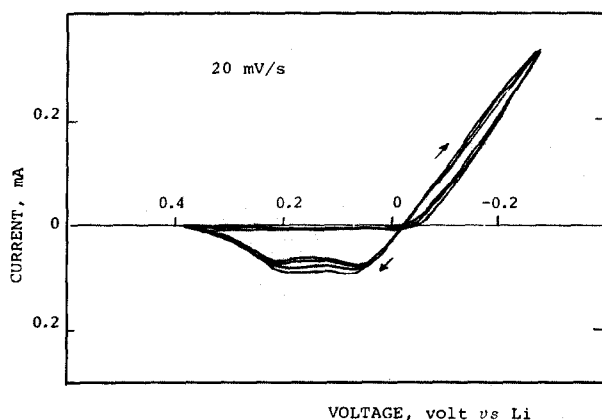


Fig. 7. Cyclic voltammograms of the lithium plating/stripping process on stainless steel from  $(\text{PEO})_9 \text{LiCF}_3\text{SO}_3$  at 80 °C. Surface area:  $0.125 \text{ cm}^2$ . Li reference.

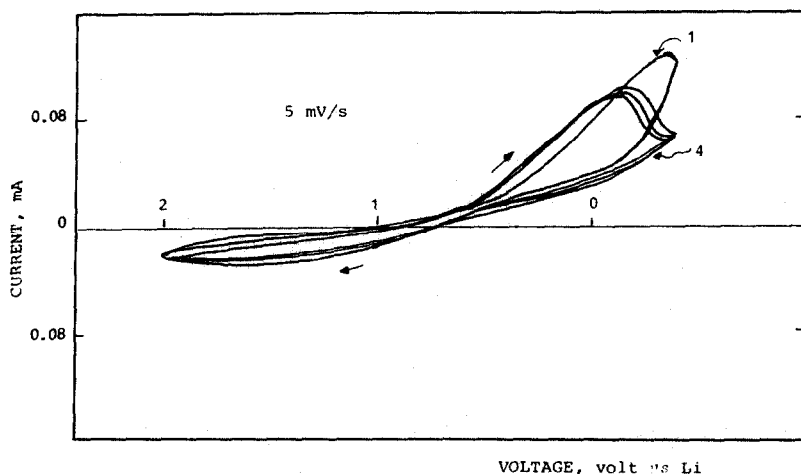


Fig. 8. Cyclic voltammogram of the lithium plating/stripping process on vitreous carbon from  $(\text{PEO})_9 \text{LiCF}_3\text{SO}_3$  at 80 °C. Surface area:  $0.125 \text{ cm}^2$ . Li reference.

anodic of the reversible lithium potential, suggesting the formation of some lithium carbide phase. The reversibility of this process is seen to be very poor: this may be due to a slow diffusion of lithium into the bulk of the carbon, as in an intercalation reaction.

## Conclusions

The cyclability of lithium deposited from a solvent-cast polymer electrolyte, (PEO)<sub>n</sub>LiCF<sub>3</sub>SO<sub>3</sub>, shows similarities to the behaviour observed in conventional non-aqueous cells. As might be expected, the nature of the substrate has a significant effect on the electrochemical characteristics. Two further subtle variables have been identified, however, which require strict control, namely, the efficacy of the physical contact between the electrode and the polymer film and the impurity content of the electrolyte.

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