

## ELECTRODE KINETICS IN POLY(ETHYLENE OXIDE)-BASED ELECTROLYTES

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### Summary

The behaviour of lithium metal, and of a selected intercalation compound in electrochemical cells with polymeric electrolytes, is discussed on the basis of cyclic voltammetry, polarisation curves, and frequency response analysis. Some preliminary results on a polymeric electrolyte, rechargeable, lithium battery are also presented.

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### Introduction

Following the discovery that combinations of suitable coordinating polymers, such as poly(ethylene oxide) (PEO), and certain metal 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 new types of high energy, rechargeable lithium batteries has been proposed [3, 4].

To date, relatively few studies have been reported on the characteristics of the electrode/polymer electrolyte interface. This is despite the fact that definition of the interfacial processes is most important for the evaluation of the effective cycle life of polymeric electrolyte lithium batteries. Clearly, therefore, it is of interest to conduct studies of the interfacial properties of electrodes in polymeric electrolytes [5, 6]. This work reports the behaviour of the lithium metal electrode and of the  $\text{Li}_{1+x}\text{V}_3\text{O}_8$  intercalation electrode in a  $(\text{PEO})_9\text{LiCF}_3\text{SO}_3$  electrolyte. In addition, some preliminary results related to the combined behaviour of the two electrodes in an  $\text{Li}/\text{Li}_{1+x}\text{V}_3\text{O}_8$  solid-state battery are presented.

### Experimental

The preparation and characterization of the  $(\text{PEO})_9\text{LiCF}_3\text{SO}_3$  electrolyte have already been described [6]. For details of the synthesis of the  $\text{Li}_{1+x}\text{V}_3\text{O}_8$  compound, the reader is referred to ref. 7.

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

## Results and discussion

### *Lithium electrode*

A low-field polarization curve for a lithium electrode in a  $(\text{PEO})_9\text{LiCF}_3\text{SO}_3$  electrolyte at  $110^\circ\text{C}$  is given in Fig. 1 [6]. The absence of hysteresis between the anodic and the cathodic scans demonstrates the inherent reversibility of the electrode. From the slope of the curve, an exchange current density of  $0.45\text{ mA cm}^{-2}$  is obtained, a value in agreement with that reported by other authors [8].

Figure 2 shows a cyclic voltammogram for the lithium deposition and stripping processes on nickel at  $80^\circ\text{C}$  in cells using the above polymeric electrolyte. As expected from the micropolarization results, the cyclability of the electrode is satisfactory. However, the coulombic efficiency depends on the scanning rate: the recovery of lithium decreases from 85% to 30% on decreasing the scanning rate from  $20\text{ mV s}^{-1}$  to  $5\text{ mV s}^{-1}$ .

These results suggest that lithium freshly deposited from the polymer electrolyte may undergo passivation reactions, possibly similar to those found with conventional, liquid electrolyte, lithium cells [9]. Impedance plots obtained for lithium electrodes placed in contact with the  $(\text{PEO})_9\text{LiCF}_3\text{SO}_3$  electrolyte at  $100^\circ\text{C}$ , reveal a progressive expansion of the  $Z''$ - $Z'$  semi-circle with the time of storage (Fig. 3). These results, similar to those recently reported by Fauteux [10], indicate that lithium is passivated by the electrolyte, with the growth of a resistive layer at the interface. Work is in progress in our laboratories to ascertain the mechanism of this passivation reaction and to evaluate its influence on the cyclability of lithium in practical, polymeric electrolyte batteries.

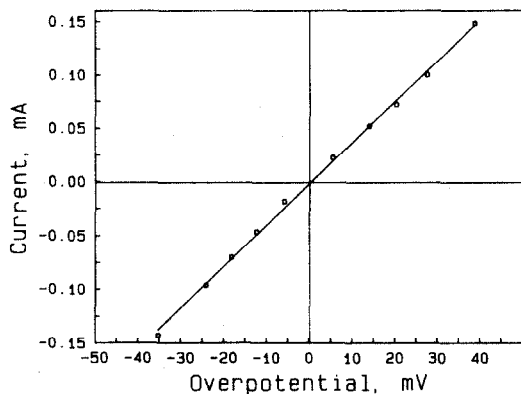


Fig. 1. Micropolarisation curve for lithium electrode in  $(\text{PEO})_9\text{LiCF}_3\text{SO}_3$  electrolyte at  $110^\circ\text{C}$ . Lithium reference electrode. Surface area:  $1.75\text{ cm}^2$ .

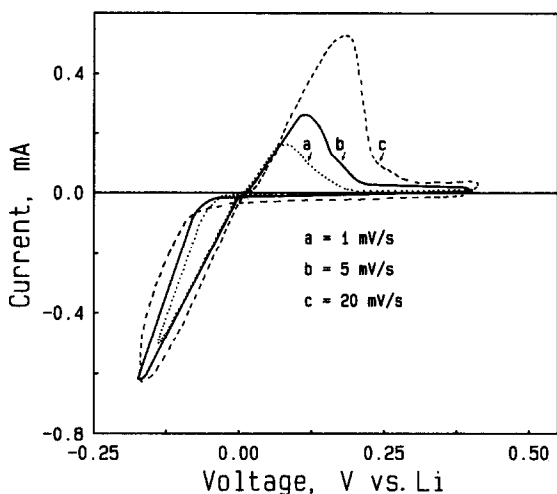


Fig. 2. Voltammograms at various scan rates for lithium plating/stripping process on nickel from  $(\text{PEO})_9\text{LiCF}_3\text{SO}_3$  at  $80^\circ\text{C}$ . Lithium reference electrode. Surface area:  $1.75\text{ cm}^2$ .

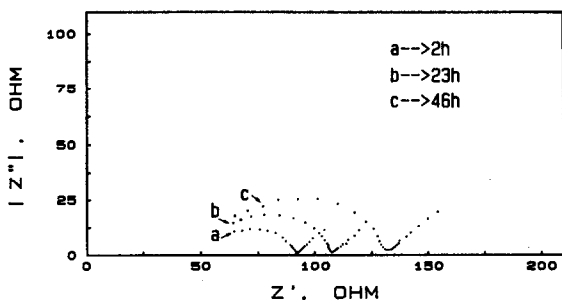


Fig. 3. Complex impedance plot of  $\text{Li}/(\text{PEO})_8\text{LiClO}_4/\text{Li}$  cell at  $100^\circ\text{C}$  as a function of storage time.

### Intercalation electrode

Both  $\text{V}_6\text{O}_{13}$  [3] and  $\text{TiS}_2$  [4] have been proposed as intercalation electrodes for rechargeable, polymeric electrolyte batteries. However, both these compounds may be affected by structural problems during cathodic operation. Consequently, alternative intercalation cathodes are currently being sought.

In previous studies on liquid, organic electrolyte cells [7, 11], it has been shown that a layer-structure compound,  $\text{Li}_{1+x}\text{V}_3\text{O}_8$  exhibits an exceptionally good structure retention, even upon extensive intercalation of  $\text{Li}^+$  ions. Furthermore, the theoretical energy density of the  $\text{Li}/\text{Li}_{1+x}\text{V}_3\text{O}_8$  couple is quite high, *i.e.*, around  $730\text{ W h kg}^{-1}$  for a highly intercalated material [11, 12].

All these favourable aspects have stimulated a programme in our laboratories to test the behaviour of this intercalation compound in poly-

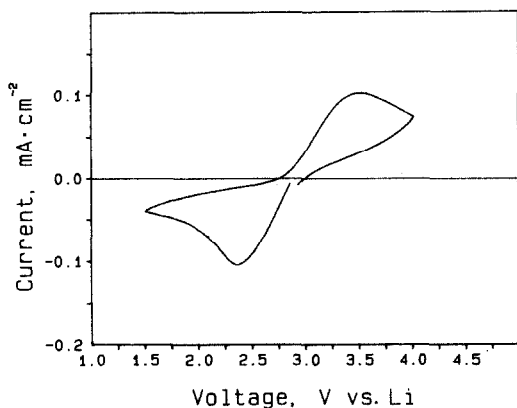


Fig. 4. Voltammogram of  $\text{Li}_{1+x}\text{V}_3\text{O}_8$  electrode in  $(\text{PEO})_9\text{LiCF}_3\text{SO}_3$  electrolyte at  $100^\circ\text{C}$ . Lithium counter electrode. Scan rate:  $1\text{ mV s}^{-1}$ .

meric electrolyte cells. Figure 4 shows the cyclic voltammetry of  $\text{Li}_{1+x}\text{V}_3\text{O}_8$ , obtained at  $100^\circ\text{C}$  in a cell using a  $(\text{PEO})_9\text{LiCF}_3\text{SO}_3$  electrolyte. The data confirm the good cyclability of the material, as expected from the results obtained in liquid electrolyte cells.

#### *Li/Li<sub>1+x</sub>V<sub>3</sub>O<sub>8</sub> battery*

Having confirmed the basic reversibility of the two electrodes, a solid-state battery has been assembled from a strip of lithium metal (anode), a thin layer ( $\sim 50\ \mu\text{m}$  thickness) of  $(\text{PEO})_9\text{LiCF}_3\text{SO}_3$  (electrolyte) and a pellet of a mixture of  $\text{Li}_{1+x}\text{V}_3\text{O}_8$ , PEO, and acetylene black (cathode).

Figure 5 gives a plot of the open-circuit voltage (OCV) of the cell at  $100^\circ\text{C}$  versus the degree of  $\text{Li}^+$  ion intercalation in the vanadium bronze. Values of OCV obtained in discharge (intercalation) and in the following

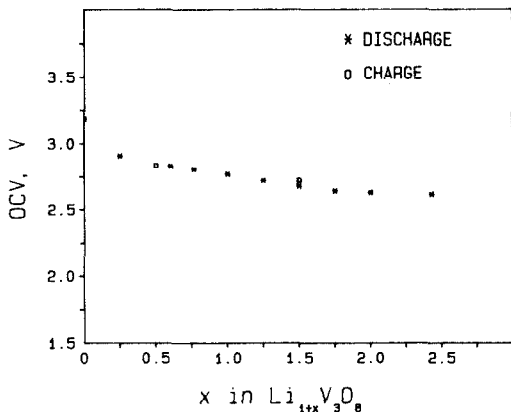


Fig. 5. Open-circuit voltage vs. degree of  $\text{Li}^+$  ion intercalation for  $\text{Li}/\text{Li}_{1+x}\text{V}_3\text{O}_8$  polymeric electrolyte battery at  $100^\circ\text{C}$ .

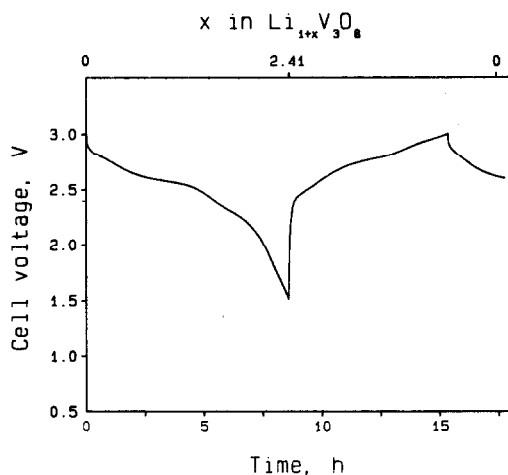


Fig. 6. Charge/discharge cycle for  $\text{Li}/\text{Li}_{1+x}\text{V}_3\text{O}_8$  polymeric electrolyte battery at  $100^\circ\text{C}$ . Discharge current:  $0.1\text{ mA cm}^{-2}$ ; charge current:  $0.1\text{ mA cm}^{-2}$ .

charge (de-intercalation) are reported and clearly demonstrate the favourable characteristics of the cell, both in terms of the degree of intercalation and the cyclability. These results are similar to those of other authors [12] obtained in quasi-thermodynamic conditions.

The good rechargeability of the battery is confirmed by the data given in Fig. 6, which have been collected from a preliminary constant-current cycling test.

These findings suggest that the  $\text{Li}_{1+x}\text{V}_3\text{O}_8$  bronze may find application in polymeric electrolyte, solid-state, lithium batteries:  $\text{Li}^+$  ions can be inserted in considerable amounts and the process is highly reversible.

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