

THE Li/LiV₃O₈ POLYMER ELECTROLYTE LITHIUM BATTERY III. INVESTIGATION OF THE ELECTRODE INTERFACES

BRUNO SCROSATI*, ALESSANDRO SELVAGGI, FAUSTO CROCE and
WANG GANG**

Department of Chemistry, University of Rome, 'La Sapienza', Rome (Italy)

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Summary

The characteristics of an Li/LiV₃O₈ polymer electrolyte battery have been examined by charge-discharge cycling tests and by frequency response analysis. The results indicate that cell failures, such as capacity decline upon cycling, are a consequence of geometric inadequacy, probably resulting from electrolyte flow, positive electrode modifications, and lithium dendrite formations.

Improvements in the electrode structure and optimizations in cell design are required to assure high cycling performance of the polymer electrolyte battery.

Introduction

In previous papers [1 - 5] we have shown that LiV₃O₈ vanadium bronze is a very suitable positive electrode material for the development of rechargeable lithium batteries using, as polymer electrolytes, complexes of poly(ethylene oxide), PEO, and lithium salts (*e.g.*, LiClO₄ or LiCF₃SO₃).

In this work we continue the study of these batteries by examining the characteristics and the properties of the electrode interfaces, with the aim of optimizing the electrode structures and of improving cell capacity and cycling behaviour.

Experimental

The PEO-based polymer electrolytes were prepared by casting. The procedures included the dissolution of the two components in purified acetonitrile, the mixing of the solutions, and the slow evaporation of the

* Author to whom correspondence should be addressed.

** On leave from Institute of Physics, Chinese Academy of Sciences, Beijing, China.

solvent onto a Teflon container. The casting and drying procedures were performed in a controlled atmosphere dry-box to avoid moisture contamination. Highly conducting (of the order of 10^{-3} - 10^{-4} S cm^{-1} at 100°C) polymer films (of average thickness 50 - 100 μm) were obtained and stored in the dry-box.

The preparation procedure of the vanadium bronze and its electrochemical properties were described in detail by Pistoia and co-workers [6]. For use as an electrode, LiV_3O_8 was mixed with acetylene black and PEO (weight percent. ratio 40, 20, 40) and the resulting mixture pressed into a single pellet.

Two types of cells were used for the electrochemical tests. A three-electrode cell (described previously [1]) was used for the investigation of the electrode kinetics. This generally used lithium both as the reference and as the counter electrode.

A two-electrode cell of the spring-loaded, button-type was used for the cycling test. This was assembled by contacting a lithium disk (about 1 mm thickness), one or two polymer electrolyte disks (total thickness about 100 μm), the positive electrode pellet (about 1 mm thickness), and a nickel current collector. The surface area of the cell was 0.79 cm^2 .

The cells were assembled in a dry-box and kept at a constant temperature ($\pm 0.5^\circ\text{C}$). The galvanostatic cycling tests used a computer to control the voltage.

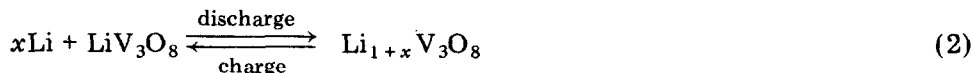
Results and discussion

The cells examined in our laboratory had the typical structure
 $\text{Li}/(\text{PEO})\text{LiX}/\text{LiV}_3\text{O}_8, \text{ ac. black, PEO},$ (1)

where LiX was LiClO_4 or LiCF_3SO_3

Following published recommendations on polymer electrolyte batteries [7, 8], the positive electrode was made by mixing the active material (*i.e.*, the LiV_3O_8 vanadium bronze) with acetylene black (as conductive material) and PEO (as binder material). To obtain homogeneity the components were thoroughly mixed and compressed in a single pellet.

The LiV_3O_8 vanadium bronze is an intercalation electrode and thus the cell reaction may be indicated as:



where the Li insertion may reversibly extend up to an intercalation degree (x) of 3 lithium per mole [3, 6].

Figure 1 illustrates typical charge-discharge cycles of the polymer electrolyte cell at 100°C . The cycles were run with a charge current density, I_c , of 0.1 mA cm^{-2} and a discharge current density, I_d , of 0.2 mA

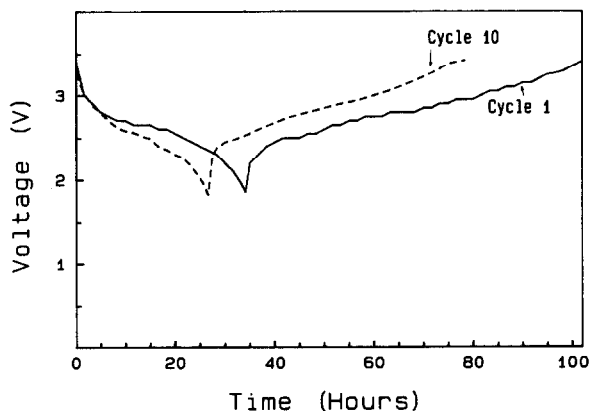


Fig. 1. Typical deep (about 3 Li/mole) charge-discharge cycles of the Li/LiV₃O₈ cell at 100 °C. (PEO)₉LiClO₄ polymer electrolyte. The cycles were run galvanostatically, with a discharge current density (I_d) of 0.2 mA cm⁻² and a charge current density (I_c) of 0.1 mA cm⁻². Upper cut-off 3.5 V, and 2.0 V lower cut-off voltage limits.

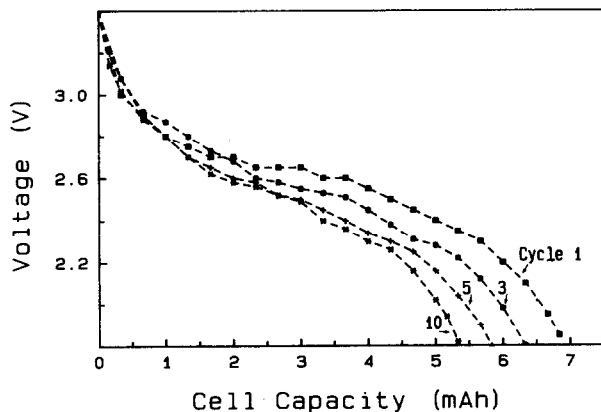


Fig. 2. Consecutive deep discharge cycles of the Li/LiV₃O₈ cell at 100 °C. (PEO)₉LiClO₄ polymer electrolyte. Discharge current density: 0.2 mA cm⁻²; 1.8 V cut-off limit.

cm⁻². Figure 2 shows the first ten consecutive deep ($x \sim 3$) discharge cycles run at the same regime of 0.2 mA cm⁻².

The results confirm the rechargeability of the electrochemical system, but also indicate a capacity decline upon cycling. The latter effect is clearly visible in Fig. 3 which illustrates the long-term discharge behaviour of an Li/LiV₃O₈ cell. From an initial value of 2 mA h (corresponding to an intercalation of approximately 2.2 Li/mole), the cell capacity progressively declines to stabilize at around 0.8 mA h. Such a trend, which has also been observed by other authors in various other systems [9, 10], seems to be a typical feature of polymer electrolyte batteries. In the case examined here it is not connected with an irreversible degradation of the structure of the LiV₃O₈ vanadium bronze, since, as already stressed (3, 6), this cathodic

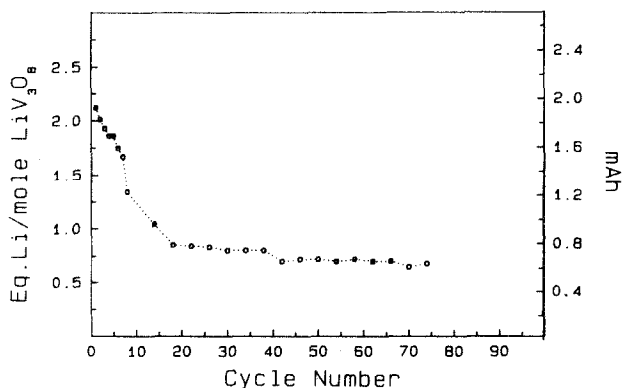


Fig. 3. Long term discharge behaviour of the Li/LiV₃O₈ cell at 120 °C. (PEO)₉LiCF₃SO₃ polymer electrolyte. Discharge current density: 0.5 mA cm⁻².

material can easily accept up to 3 Li⁺/mole without undergoing significant structure alterations. The capacity decline observed in Figs. 2 and 3 must, therefore, be due to macroscopic factors (*i.e.*, lack of contact, increase in resistance, etc.) which ultimately influence the characteristics of the positive electrode interface.

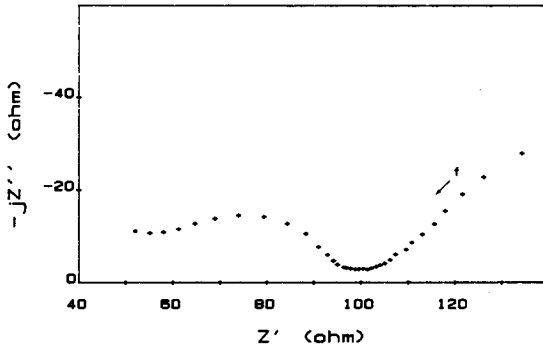
In order to confirm this interpretation and to investigate the nature of the interfacial degradation effects, a detailed a.c. impedance analysis of the Li/LiV₃O₈ cell was carried out under various cell conditions.

Figure 4 compares the impedance diagrams of a freshly made cell (curve (a)), of the same cell after a deep ($x = 2.5$) discharge (curve (b)) and after a complete ($x = 0$) recharge (curve (c)). It can be seen that the impedance diagram reveals three, well defined relaxation effects only after a complete discharge-charge cycle.

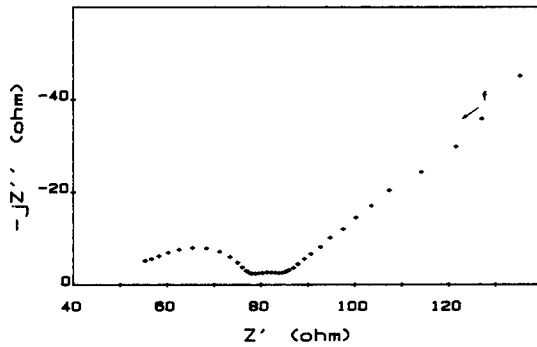
Proceeding in Fig. 4(c) from high to low frequency, the first semicircle may be associated with the Li/electrolyte interface, with a resistance R_a identified by the intercepts to the real axis. The second semicircle, at middle frequency, may be related to the vanadium bronze/electrolyte interface with a resistance R_c , again determined by the intercepts with the real axis. The diagram is completed by a 45° Warburg diffusion line which suggests that the overall kinetics may eventually be controlled by the diffusion of the intercalated lithium in the LiV₃O₈ vanadium bronze.

The fact that the semicircle related to the electrode interfaces becomes defined only after a full discharge-recharge cycle is a preliminary indication of an initially poor electrolyte/electrode adhesion. This may be partly improved by current flow, however, as commonly observed in battery technology, especially for systems operating at high temperature [11].

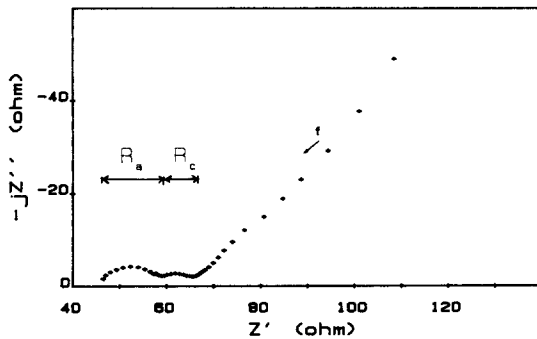
Furthermore, one may see from Fig. 4(c) that the Warburg line does not superimpose on the middle frequency semicircle which, by contrast, almost completely closes on the Z' axis. According to theories on interpretation of a.c. diagrams of intercalation electrodes [12], this indicates that charge transfer polarization prevails over diffusion polarization.



(a)



(b)



(c)

Fig. 4. Complex impedance diagram of a freshly assembled (a), discharged (b), and fully recharged (c) Li/LiV₃O₈ cell at 100 °C. (PEO)₉LiCF₃SO₃ polymer electrolyte.

The very similar impedance diagram (Fig. 4(b)) obtained for almost fully discharged ($x = 2.5$) cells, shows that diffusion limits, even if present, do not consistently influence the electrode kinetics over the entire discharge range. This is not surprising, since fast diffusion of lithium is expected at 100 °C in the intercalation electrode considering that, even at room temper-

ature, high diffusion coefficients (*i.e.*, of the order of 10^{-7} – 10^{-8} $\text{cm}^2 \text{s}^{-1}$) have been found for the intercalated lithium in the LiV_3O_8 vanadium bronze [6].

The decline in capacity illustrated by Figs. 2 and 3, therefore, cannot be totally ascribed to diffusion limits. To clarify the effect, an a.c. impedance analysis of the cell was carried out at progressive cycling stages.

Figure 5 shows the impedance diagram of the cell after the fifth (a) and the fifteenth (b) deep cycle. Comparison with the response of the cell in its initial charged state (see Fig. 4(b)) reveals a consistent expansion of the middle frequency semicircle. This indicates that the interfacial characteristics, after initially improving with current flow, tend to deteriorate progressively. This increase in resistance (R_c) is probably due to a loss of contact between electrode and electrolyte materials. It is reasonable to assume that the physical changes, which accompany the intercalation–deintercalation cycles, may eventually produce electronically isolated masses of active material in the cathodic mixture, as well as continuous changes in the boundary region between the polymer electrolyte disk and the positive electrode pellet.

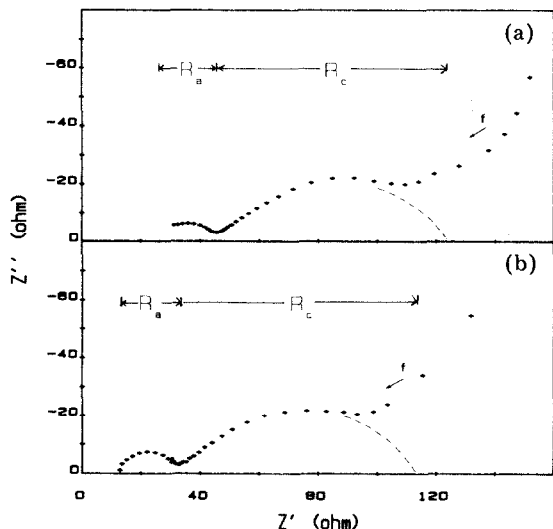


Fig. 5. Complex impedance diagram of an $\text{Li}/\text{LiV}_3\text{O}_8$ cell after the 5th (a), and the 15th (b) cycles at 100°C . $(\text{PEO})_9\text{LiCF}_3\text{SO}_3$ polymer electrolyte.

All the above results tend to indicate that contact failures may represent a serious problem in polymer electrolyte batteries. These failures, however, cannot be exclusively attributed to the positive side of the battery.

In fact, we have often observed that upon prolonged cycling, the voltage of the cell during charge tended to level off or even to decline slightly, as shown in Fig. 6. Since electrolyte decomposition is to be excluded below 3.5 V [3, 13], the voltage profiles of Fig. 6 can be tentatively associated with the growth of lithium microdendrites across the cell.

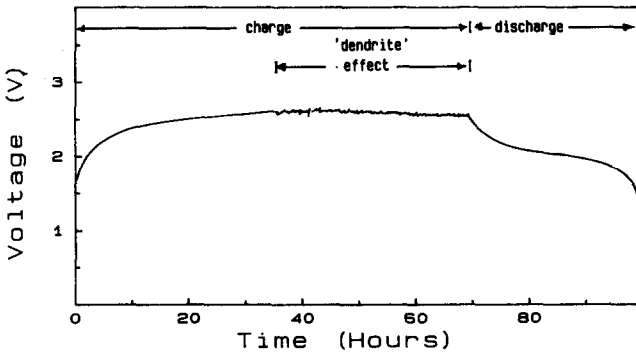


Fig. 6. 'Dendrite effect' in the charge and discharge profiles of the Li/LiV₃O₈ cell during cycling at 100 °C. (PEO)₉LiClO₄ polymer electrolyte.

Under these circumstances, a fraction of the charging current may be 'dissipated' along the dendrite shunts and this may, in turn, produce an 'apparent' loss in capacity in the following discharge.

The formation of lithium microdendrites has also been proposed by Gauthier *et al.* [8]. These authors suggested that the current is sufficient to burn off the dendrites by Joule heating. They also concluded that no permanent cell damage results from occasional dendrites owing to the self-healing properties of the polymer electrolyte. Further investigation, however, is needed to confirm this statement.

Conclusions

From the results described in this work, and from published data, we may conclude that the decline in the capacity of lithium, polymer electrolyte batteries is likely to be a consequence of inadequate cell geometry, probably resulting from electrolyte flow, physical modifications of positive electrode, and lithium dendrite formation. It is possible, however, that the latter effect is not critical in polymer systems, due to the self-healing properties of the electrolyte. Apparently, the modification at the positive interface upon cycling is more serious as it may lead to electronically isolated masses of active material in the cathodic mixture and to losses of contact at the electrolyte/electrode boundary.

Obviously, the positive electrode configuration used in this work, *i.e.*, a mechanical mixture of the three components pressed in a single pellet, cannot ensure a high performance polymer electrolyte battery upon prolonged cycling. Improvements in the cathode structure and optimization in cell design are required, and these are being explored in our laboratories.

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References

- 1 F. Bonino, B. Scrosati, A. Selvaggi, J. Evans and C.A. Vincent, *J. Power Sources*, **18** (1986) 75.
- 2 F. Bonino, B. Scrosati and A. Selvaggi, *Solid State Ionics*, **18 - 19**, (1986) 1050.
- 3 B. Scrosati, *Brit. Polym. J.*, **20** (1988) 219.
- 4 F. Bonino, M. Ottaviani, B. Scrosati and G. Pistoia, *J. Electrochem. Soc.*, **135** (1988) 12.
- 5 F. Bonino, B. Scrosati and A. Selvaggi, *Solid State Ionics*, in press.
- 6 G. Pistoia, S. Panero, M. Tocci, R. V. Moshtev and V. Manev, *Solid State Ionics*, **13** (1984) 311.
- 7 A. Hooper and B.C. Toffield, *J. Power Sources*, **11** (1984) 33.
- 8 M. Gauthier, D. Fauteux, G. Vassort, A. Belanger, M. Duval, P. Ricaux, J. M. Chabagno, D. Mullar, P. Rigaud, M. B. Armand and D. Deroo, *J. Electrochem. Soc.*, **132** (1985) 1333.
- 9 B. B. Owens, M. A. Munshi and P. M. Skarstad, Abst. N. 82 and 83, *Fall Meeting Electrochem. Soc., Honolulu, HI, Oct. 1987*.
- 10 K. West, B. Zachau-Christiansen and T. Jacobson, *J. Power Sources*, **20** (1987) 165.
- 11 C. A. Vincent, F. Bonino, M. Lazzari and B. Scrosati, in C. A. Vincent (ed.), *Modern Batteries*, E. Arnold, London, 1984.
- 12 C. Ho, I. D. Raistrick and R. A. Huggins, *J. Electrochem. Soc.*, **127** (1980) 343.
- 13 B. Scrosati, in C. A. Vincent and J. R. MacCallum (eds.), *Polymer Electrolyte Review I*, Elsevier Applied Science Publishers, Barking, 1987.