

A.C. IMPEDANCE STUDIES OF THE LITHIUM/POLYMER ELECTROLYTE INTERFACE IN SOLID-STATE LITHIUM CELLS

C. C. HUNTER*, D. C. SINCLAIR and A. R. WEST

University of Aberdeen, Department of Chemistry, Meston Walk, Aberdeen AB9 2UE (U.K.)

A. HOOPER**

Applied Electrochemistry Centre, The Harwell Laboratory, Oxon. OX11 0RA (U.K.)

(Received April 20, 1987; in revised form January 20, 1988)

Summary

Cells containing either $\text{LiClO}_4/\text{poly}(\text{ethylene oxide})$ or $\text{LiCF}_3\text{SO}_3/\text{poly}(\text{ethylene oxide})$ complexes as the electrolyte with lithium metal and/or V_6O_{13} -based composite electrodes have been assembled and their a.c. impedance measured at temperatures in the range of room temperature to 120°C .

Two resistances are identified from the equivalent circuit analysis. One is attributed to the polymer and shows a characteristic, non linear, Arrhenius plot with a change in slope at about 70°C . The other is attributed to the lithium/polymer interface and gives an essentially linear Arrhenius plot. The magnitude of this second resistance in $\text{Li}/\text{V}_6\text{O}_{13}$ cells decreases during an initial period of open circuit voltage stabilisation from about 3.5 to 3.2 V. Possible origins of this second resistance are discussed.

Introduction

Lithium/solid-solution cathode rechargeable cells containing polymeric electrolytes based on poly(ethylene oxide), PEO, are currently under development for ambient and high temperature battery applications [1 - 3]. A.c. impedance techniques provide one possible means of monitoring cell performance and for yielding information on the chemical reactions and interfacial effects that occur during cell assembly and operation. Various a.c. impedance studies of such cells have been reported [4 - 6] including

*Now at Robert Gordons Institute of Technology, Department of Chemistry, Aberdeen, U.K.

**Author to whom correspondence should be addressed.

measurement of the polymer conductivity [7] and the formation of a passivation layer at the Li/polymer interface [6].

An effect in these cells that has not been explained satisfactorily concerns their initial open circuit voltage behaviour. Immediately after assembly and heating to their normal operating temperature, cells with standard poly(ethylene oxide) electrolytes have reproducibly high open circuit voltages (OCV); for example, 3.65 V at 120 °C for cells containing V_6O_{13} -based cathodes. However, on standing, the OCV quickly falls before levelling out to a steady value (*e.g.*, 3.2 V for V_6O_{13}). One purpose of the present study was to use a.c. impedance techniques to shed light on this OCV stabilisation period.

Experimental

Cells were assembled using lithium metal foil electrodes (150 μm), polymer electrolyte (50 μm) of composition $(\text{PEO})_9\text{LiCF}_3\text{SO}_3$ or $(\text{PEO})_9\text{LiClO}_4$ and V_6O_{13} /polymer electrolyte/acetylene black composite cathodes (75 μm) on nickel current collectors. The cells, of approximate area 1 cm^2 , were assembled in an atmosphere of dried argon, placed between nickel foil electrodes in a spring-loaded conductivity jig, and the jig placed inside a vertical tube furnace whose temperature was controlled and measured to ± 2 °C. An atmosphere of flowing dry argon was used throughout the measurement cycle.

Experiments were carried out on four types of cell:

Li/ $(\text{PEO})_9\text{LiCF}_3\text{SO}_3$ /Li

Li/ $(\text{PEO})_9\text{LiCF}_3\text{SO}_3$ /cathode

cathode/ $(\text{PEO})_9\text{LiCF}_3\text{SO}_3$ /cathode

Li/ $(\text{PEO})_9\text{LiClO}_4$ /cathode

A.c. impedance measurements were made with a Solartron 1250 Frequency Response Analyser linked to a 1286 Electrochemical Interface and controlled by a BBC microcomputer. For the cells that were not symmetric and generated an OCV, an equal and opposite potential was applied to the cell by the 1250 FRA for the duration of the a.c. measurements. Applied a.c. voltages were 100 mV and the frequency range was 30 mHz to 65 kHz.

Results

A Li/ $(\text{PEO})_9\text{LiCF}_3\text{SO}_3$ /cathode cell was placed in the furnace at 120 °C and rapidly developed an OCV of ~ 3.60 V. The temperature was then reduced to 103 ± 2 °C and the cell left standing on open circuit over a period of 44 h. Periodically, a.c. impedance measurements were made and

the cell OCV recorded. The OCV decreased from 3.51 to 3.47 V over the first 5 h period, to 3.20 V after 20 h and to 3.15 V after 44 h.

The a.c. impedance spectra had a similar form throughout the equilibration period to that obtained initially (Fig. 1(a)). This comprised a single arc or 'semicircle' with a low angle spike at lower frequencies. The high frequency end of the arc clearly did not pass through the origin and gave a non-zero intercept, $R(1)$. From the low frequency intercept of the arc on the real, Z' axis, a second resistance, $R(2)$, could also be obtained, as shown. The value of the parallel capacitance, $C(2)$, associated with the arc was estimated using the relation:

$$2\pi f(\max)R(2)C(2) = 1$$

which holds at the frequency, $f(\max)$, of the highest point of the arc. No detailed analysis of the parameters responsible for the low frequency spike was made.

During the period of OCV stabilisation, the resistance $R(2)$ decreased markedly, by between 1 and 2 orders of magnitude, as shown in Fig. 2, but $R(1)$ showed little, if any, variation. The capacitance $C(2)$ was also essentially unchanged throughout, with a value of 310 ± 80 nF.

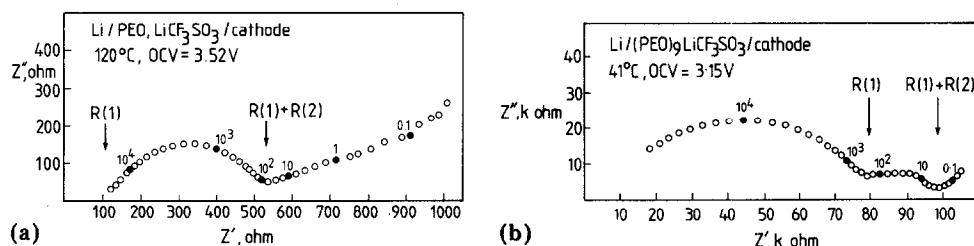


Fig. 1. Complex impedance plane plots for a freshly prepared cell. Selected frequencies, in Hz are marked.

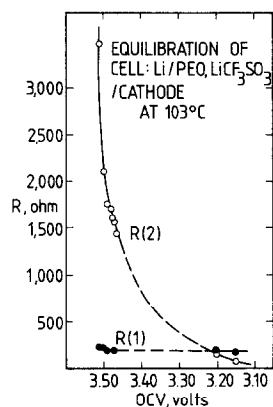


Fig. 2. Resistances $R(1)$ and $R(2)$ against OCV during the OCV stabilisation period.

A similar study was made of a cell that contained $(\text{PEO})_9\text{LiClO}_4$ as the electrolyte, although, in this case, the cell was placed in the furnace at 120°C and left at that temperature. The complex impedance plane plots were similar to that shown in Fig. 1, with an arc and a low frequency spike from which $R(1)$ and $R(2)$ were extracted, as above. The results are shown in Fig. 3. The OCV decreased from 3.43 to 3.15 V over a period of 3.5 h, as shown in the top part of the Figure. During this time $R(1)$ was essentially unchanged, although its initial value appears to be somewhat higher, probably because the cell had not equilibrated at the temperature of the furnace. By contrast, $R(2)$ showed a dramatic decrease with decreasing OCV, similar to that obtained with the LiCF_3SO_3 -containing cell (Fig. 2). The capacitance $C(2)$ showed some scatter and was in the range 30 - 100 nF.

Shown in Table 1 are the results obtained from a symmetrical $\text{Li}/(\text{PEO})_9\text{LiCF}_3\text{SO}_3/\text{Li}$ cell, both after a few minutes and also after a 24 h stand at 103°C . Again, two resistive components, $R(1)$ and $R(2)$, are identified but, in contrast to the earlier results, $R(2)$ showed no significant change with time. Its value corresponds more closely to the lower, 'equilibrated', values shown in Figs. 2 and 3, rather than to the initially high values.

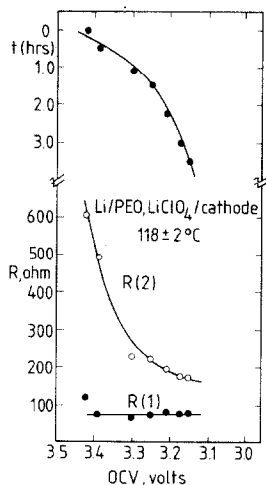


Fig. 3. Resistances $R(1)$ and $R(2)$ against OCV, and OCV against time, during the OCV stabilisation period.

TABLE 1

Cell: $\text{Li}/(\text{PEO})_9\text{LiCF}_3\text{SO}_3/\text{Li}$; equilibration at 103°C

	$R(1)$ (Ω)	$R(2)$ (Ω)	$C(2)$ (nF)
Initial values	327	147	66
After 24 h	324	142	69

In order to gain further insight into the origins of the two resistances $R(1)$ and $R(2)$, a.c. impedance measurements were made for two cells over the temperature range ambient to 120 °C. A Li/(PEO)₉LiCF₃SO₃/cathode cell was left at 103 °C for two days and then cooled slowly to room temperature over a period of 24 h. The a.c. measurements were then made on the reheating cycle. A Li/(PEO)₉LiCF₃SO₃/Li cell was assembled, held at 120 °C for a few hours, cooled slowly to room temperature over 24 h, and the impedance measurements again made during reheating.

Results are given in Fig. 4 in the form of log conductance *versus* reciprocal absolute temperature (no corrections were made for the cell constants). The resistances $R(1)$ show markedly non-linear behaviour, with a change in slope at about 70 °C, characteristic of poly (ethylene oxide) electrolytes [7]. The low temperature $R(1)$ values are similar in the two cells, but differ by a factor of 3 - 4 above 70 °C. The reasons for this difference are not presently understood. The $R(2)$ plots, by contrast, show essentially linear temperature dependence with no discontinuity at ~70 °C. The $R(2)$ values for the two cells over the whole temperature range differ by about one order of magnitude and are larger for the symmetric lithium cell.

The impedance data obtained below ~50 °C confirmed that $R(1)$ was the bulk resistance of the electrolyte. An additional high frequency arc was also seen between the origin and the intercept $R(1)$ in the impedance plots (Fig. 1(b)). This had an associated capacitance value, $C(1)$, of ~200 pF. This is consistent with the bulk capacitance of thin layer cells.

A symmetric cell, cathode/(PEO)₉LiCF₃SO₃/cathode, was also prepared and its a.c. impedance recorded at different temperatures over the range room temperature - 120 °C. At temperatures above 70 °C, the only feature present in the complex impedance plane was a spike inclined at 30 - 40° to the horizontal. At lower temperatures, part of a high frequency arc was

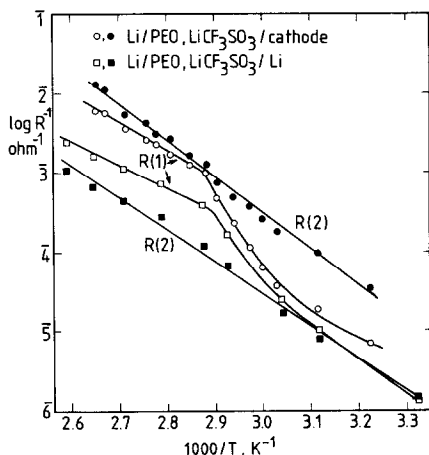


Fig. 4. Temperature dependence of resistances $R(1)$ and $R(2)$ for two cells.

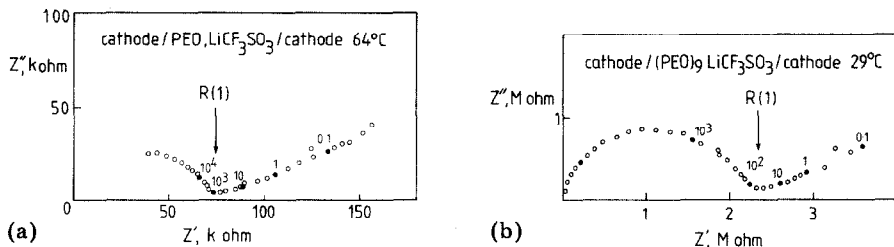


Fig. 5. Complex impedance plane plots for a symmetric cathode cell. Selected frequencies, in Hz, are marked.

also observed, as shown in Fig. 5(a), for 64 °C. At still lower temperatures (Fig. 5(b)), the complete high frequency arc was seen and clearly extrapolated to the origin of the plot. The high frequency arc, with an associated capacitance of ~ 40 pF, was attributed to the bulk response of the electrolyte. Its low frequency intercept, $R(1)$, had a similar temperature dependence to that of the other $R(1)$ values such as those shown in Fig. 4.

In this symmetric cathode cell, therefore, the impedance data show a high frequency arc, representing the bulk response of the electrolyte, and a low frequency electrode response. There was no evidence for the arc at intermediate frequencies, characterised by the element $R(2)C(2)$, that was observed in cells containing a lithium metal electrode(s).

Discussion

The a.c. impedance results on cells with different electrode-electrolyte combinations enable us to identify certain features of the equivalent electrical circuit of the cells. From the limited range of temperature and frequency-dependent data that have been obtained in this work, the impedance data may be analysed in terms of the ideal equivalent circuit shown in Fig. 6. The resistance $R(1)$ represents the electrolyte resistance and is shunted by the cell geometric capacitance, $C(1)$. Given the geometry of our cells, a value of $C(1)$ in the range 30 - 300 pF is reasonable. Arrhenius plots of the $[R(1)]^{-1}$ values were of a similar form (Fig. 4) and, by comparison with literature reports, $R(1)$ is consistent with the resistance of the polymeric electrolyte.

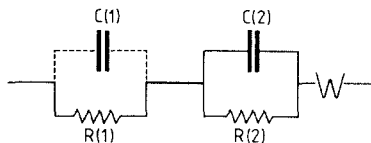


Fig. 6. Equivalent electrical circuit used to model the impedance data.

The parallel $R(2) C(2)$ element of Fig. 6 was evident only in the impedance data for cells containing at least one lithium electrode. One obvious interpretation of this element is therefore in terms of the lithium/electrolyte interface. If so, then the magnitude of the capacitance $C(2)$, in the range 30 - 400 nF, suggests a thin layer effect extending over the range 100 - 1000 Å. Although there was considerable scatter between the values of $R(2)$ and $C(2)$ for different cells, possibly associated with differences in interfacial contact arising from their fabrication, the value of $C(2)$ for any given cell was relatively independent of both temperature and time. This would indicate, for such a model, that the layer thickness remains essentially constant. Although this precludes its interpretation in terms of a growing passivation layer, as observed by other workers [6], we do not believe that this necessarily rules out its association with the lithium/electrolyte interface. We note that none of the resistance terms observed in this work shows the increasing values with time associated with such layer growth, and therefore conclude that the behaviour of our system is somehow different. This may relate possibly to differences in the nature of the lithium surfaces prior to cell assembly or to assembly procedures.

The lack of any time dependence for the $R(2)$ component in a symmetric lithium-lithium cell (Table 1) suggests that the observed variations of this term in the lithium/ V_6O_{13} cells are associated directly with the presence of a high initial open circuit voltage and its subsequent decline. Since it is known that $(\text{PEO})_9\text{LiCF}_3\text{SO}_3$ electrolytes will decompose at voltages greater than 3.4 - 3.5 V versus lithium at 120 °C [8], it is possible that the initial open circuit voltage decay is associated with a local decomposition of the electrolyte. In this case the $R(2)$ and $C(2)$ terms would then be related to some aspect of this phenomenon. However, further studies are required to establish a definite interpretation of these components.

The Warburg resistance, Fig. 6, is evidenced in complex impedance plots by a spike, inclined ideally at 45°, and the low frequency behaviour of Fig. 1 may thus be attributed to a Warburg. A similar response was observed in all cells containing a V_6O_{13} electrode. It is likely, therefore, that the origin of the Warburg lies in the cathode material or at the electrolyte/cathode interface.

Acknowledgements

The authors gratefully acknowledge the financial support of the industrial members of the Harwell-based, Solid State Battery Working Party and The Department of Trade and Industry. J.T.S. Irvine is thanked for advice on impedance measurements.

References

- 1 M. Gauthier, A. Belanger, D. Fauteux, M. Duval, B. Kapfer, M. Robitaille, R. Bellemare, Y. Giguere, G. Vassort, P. Ricoux, P. E. Harvey and F. Brochu, *Proc. 3rd Int. Meet. on Lithium Batteries, Kyoto, Japan, May 1986*, Abstract nos. ST11 and ST12.
- 2 A. Hooper, in C. A. C. Sequeira and A. Hooper (eds.), *Solid State Batteries*, NATO ASI Series, Martinus Nijhoff, 's-Gravenhage, The Netherlands, 1985, p. 399.
- 3 A. Hooper and J. Jensen (eds.), *Advanced Battery Development*, Anglo-Danish Project: Final Summary Report, Odense University Press, 1984.
- 4 N. C. Chaklanabish and H. S. Maiti, *J. Power Sources*, 16 (1985) 97.
- 5 J. Thevenin, *J. Power Sources*, 14 (1985) 45.
- 6 D. Fauteux, *Solid State Ionics*, 17 (1985) 133.
- 7 J. E. Weston and B. C. H. Steele, *Solid State Ionics*, 2 (1981) 347.
- 8 C. A. C. Sequeira, J. M. North and A. Hooper, *Solid State Ionics*, 13 (1984) 175.