

Two- and three-electrode studies of cycling in experimental polymer electrolyte cells

P. G. Bruce*, F. Krok** and C. A. Vincent

Centre for Electrochemical and Materials Sciences (CEMS), Department of Chemistry, University of St. Andrews, St. Andrews, Fife KY16 9ST, Scotland (UK)

R. Koksang

Innocell, Hestehaven 21D, 5260 Odense S (Denmark)

Abstract

Polymer electrolyte cells have been cycled at different rates and, in some instances, a constant potential has been maintained for an extended period between cycles. These experiments indicate that much of the capacity lost on cycling may be recovered, however, the slow decline in capacity with increasing cycle number appears to be unrecoverable. The latter loss of capacity is probably associated with degradation within the composite cathode. By inserting a third, reference, electrode into the cell the performance of the lithium anode and composite cathode have been measured. These measurements confirm that at low current densities the loss of capacity is associated principally with the cathode.

Introduction

Much effort is being devoted to the development of all-solid-state rechargeable lithium batteries based on polymer electrolytes [1-3]. Such power sources combine high energy density with the advantage of solid-state construction. Test cells, however, suffer a loss of capacity on cycling, and this represents a major obstacle to the further development of polymer batteries. The capacity on cycling cells of the type, Li/polymer electrolyte/ V_6O_{13} , is usually defined as the amount of charge which may be passed while cycling between fixed voltage limits. Therefore, any process within the cell which reduces the cell voltage when on discharge or increases it on charge, compared with the value on open circuit must result in a loss of capacity. Several factors may influence the cell capacity, e.g., the iR drop across the electrolyte, concentration gradients established in the V_6O_{13} electrode or the electrolyte, the finite rate of the electrode reactions [4, 5], loss of contact between the particles of the composite cathode, degradation of the V_6O_{13} particles, etc. Capacity losses due to the iR drop should not vary with the cycle number. Provided the concentration polarizations in the electrode or electrolyte keep pace with the cycling of the cell then they too should not induce a decay in capacity with an increasing number of cycles. On the other hand, an irreversible degradation of the composite cathode due to a loss of particle contact or the formation of phases from which Li cannot be deintercalated could contribute to a permanent loss of capacity on cycling.

*Author to whom correspondence should be addressed.

**Permanent address, Warsaw University of Technology, Poland.

It is observed that the capacity does indeed decrease continuously on cycling. This paper presents results aimed at characterizing the nature of the capacity loss on cycling ambient temperature Li polymer electrolyte cells. Measurements have been carried out using both two- and three-electrode cells, since it is important to establish the relative contribution made by the anode and the cathode to the overall performance of the cell.

Experimental

The cells were prepared in an argon-filled glove box. A thin film of plasticized polymer electrolyte was placed between a Li anode and a composite cathode containing V_6O_{13} , carbon and electrolyte. In the case of the three-electrode cells, a strip of metallic Li was inserted into the electrolyte to act as a reference. After fabrication, the cells were sealed in an evacuated envelope.

Cycling was carried out by connecting the cells to a computer-controlled multi-channel potentiostat based on the Sycopel multistat system. All measurements were carried out at 25 °C.

Two-electrode studies

Cells were cycled between 1.8 and 3.0 V and at charge and discharge rates of $C/8$, $C/50$ and $C/300$. The discharge and charge capacities are expressed as a percentage of the first discharge time of the cell.

Figure 1 shows the variation of both charge and discharge capacity with the number of cycles. The first six cycles were carried out at $C/50$. Of the charge passed on the first discharge only 40% could be recovered on recharging. In subsequent cycles, the charge and discharge capacities were similar. Cycles 7 to 11 were carried out at the higher rate $C/8$ followed by a return to the $C/50$ rate.

On the first high rate cycle, the largest drop in capacity occurred on recharge. This is similar to the behaviour on first cycling the cell. The capacity loss on cycling at the high rate is recovered on returning to the lower $C/50$ rate. To further explore the influence of current density on cycling capacity, two additional experiments were carried out. First the high rate of $C/8$ was imposed from cycle 17 to 21. Again, the loss of capacity was recovered on returning to $C/50$. Second, the cell was cycled at a low rate of $C/300$ (cycle 62); on recharge a value for the cell utilisation of 56% was obtained. It was however noted that when placed on open circuit, after charging to 3.0 V at $C/300$, the cell potential decreased to 2.68 V after 24 h, suggesting that a significant quantity of Li remained in the cathode. Therefore, an attempt was made to fully recharge the cell by maintaining the cell potential at 3.0 V after recharge on cycle 68 until the current fell to 0.5% of its initial value. This took approximately three weeks. However, the capacity on subsequent discharge was only 68% of that obtained on the first discharge of the cell. From these experiments it is apparent that a large proportion of the capacity loss on passing a current through the cell may be recovered, suggesting that it is associated with the iR drop across the electrolyte or concentration polarization in the electrode or electrolyte.

The application of high ($C/8$) or low ($C/300$) rates does not appear to affect the continuous loss of capacity on cycling at $C/50$. On passing from the cycle 2 to cycle 17 the capacity at $C/50$ drops from 40 to 5%; this difference is comparable with the

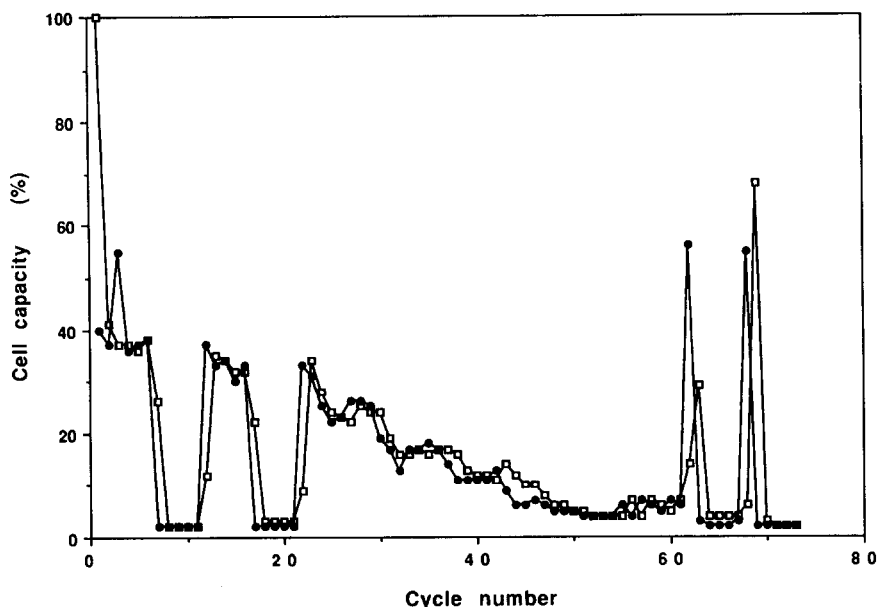


Fig. 1. Variation of (●) the charge and (□) discharge capacities with the number of cycles.

discharge capacity (32%) which cannot be recovered even after the cell is held at 3.0 V for three weeks. These results suggest that the slow decline in capacity with cycle number at $C/50$, after the first cycle, may relate to a permanent and irreversible degradation within the cell.

The degree to which the cell capacity could be recovered was further investigated using a fresh cell. The results are presented in Fig. 2. The cycle rate was $C/50$. Again, on the first cycle the charging capacity is much lower than that on the immediately preceding discharge. After cycle 5 the cell was maintained at 3.0 V until the current decreased to 1% of the charging current. The subsequent discharge capacity was 90% indicating that much of the capacity lost on first recharging the cell may be recovered. However, the recovered capacity is again lost on the following recharge.

Similar behaviour is noted on cycle 11 which was again preceded by maintaining the cell at 3.0 V. It is noteworthy that the charge capacities on cycles 6 and 11 are somewhat lower than on subsequent cycles.

Three-electrode studies

By inserting a third electrode, which acts as a reference, the overpotentials associated with each electrode may be determined and therefore the relative contribution from the anode and cathode to the load voltage may be assessed. The insertion of a reference electrode also permits the potential of the anode or the cathode to be controlled. It therefore becomes possible to cycle the anode or the cathode between fixed voltage limits under a variety of load currents and thus fully characterize the cycleability of each independently of the other.

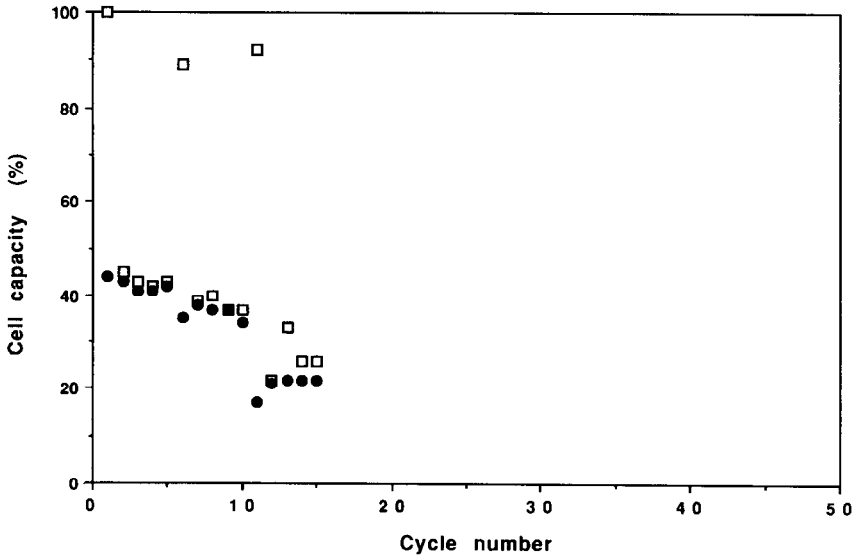


Fig. 2. Variation of (●) the charge and (□) discharge capacities with the number of cycles.

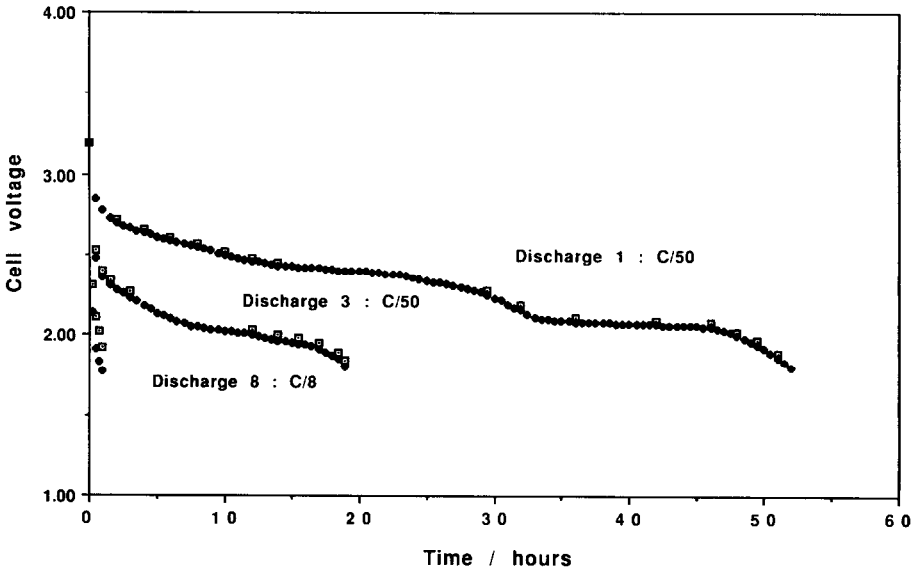


Fig. 3. Variation of electrode potentials with depth-of-discharge: (◆) potential between anode and cathode, and (□) potential between reference and cathode.

The results of three-electrode measurements made during discharge are presented in Fig. 3. On the first discharge at C/50, the difference between the anode-cathode (cell) voltage and the reference-cathode potential does not exceed a few mV. This is also true on the third discharge at the same current density. Therefore the Li anode

contributes little to any reduction in the cell potential and hence capacity during discharge at $C/50$. At higher currents, $C/8$, Li overpotentials of up to 150 mV are however observed indicating that the anode does contribute to a lowering of the cell voltage and capacity on higher rate discharges.

Acknowledgements

PGB and CAV are grateful to the EEC and SERC for financial support, PGB is also indebted to the Royal Society for the award of a Pickering Research Fellowship.

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