OPTIMIZATION AND SCALE-UP PERFORMANCE
OF POLYMER ELECTROLYTE BATTERIES

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ABSTRACT

The rechargeable high energy density polymer electrolyte battery utilizing a lithium anode, polyethylene oxide-salt complex electrolyte and a V_{6}O_{13} composite cathode has been investigated in this laboratory. Cycled tests indicate good adhesion at the anode/electrolyte and electrolyte/cathode interfaces, even after one-hundred deep cycles.

A modified polymer electrolyte with relatively higher room temperature ionic conductivity has also been employed in cells at ambient temperatures. Scaled-up designs are under evaluation.

1. INTRODUCTION.

Fast alkali ion conduction was first observed in polymer materials by Fenton and co-workers in 1973 [1]. Their work demonstrated that polymers such as polyethylene oxide (PEO) complexed with an alkali metal salt exhibited high ionic conductivities at elevated temperatures. The subsequent use of this material as a solid electrolyte in the fabrication of solid state batteries was proposed approximately ten years ago by Armand [2]. Since then intense effort has been made worldwide to produce an all solid state polymeric electrolyte battery.

The discovery of insertion compound in a composite compounds have led to new developments in advanced electrochemical systems for storage and energy conversions. A typical example is a cell utilizing a lithium anode, a polymer electrolyte such as PEO doped with LiCF_{3}SO_{3}, and a V_{6}O_{13} insertion compound in a composite cathode containing carbon and electrolyte phase to enhance electronic and ionic conductivities, respectively.

Since lithium has a low equivalent weight and a high negative electrode potential, high energy density Li-polymer electrolyte batteries are now under study in numerous laboratories. The main attractive features of the polymer electrolyte include, ease of fabrication of the battery components, variable geometry and long
Optimization and Scale-Up Performance of Polymer Electrolyte Batteries

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Abstract:

The rechargeable high energy density polymer electrolyte battery utilizing a lithium anode, polyethylene oxide-salt complex electrolyte and a V6O13 composite cathode has been investigated in this laboratory. Cycled tests indicate good adhesion at the anode/electrolyte and electrolyte/cathode interfaces, even after one-hundred deep cycles.

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shelf life. These ideal properties have led to proposed applications of this system spanning across the whole battery product range from microelectronics to electric vehicles.

The aims of the Anglo-Danish [3] and Canadian-French [4] program have been to develop a solid state secondary battery with the ability to store and deliver energy efficiently and economically. The operating temperature of the cell is 100-140°C and current densities of 0.1 to 1.0 mA cm\(^{-2}\) with PEO-LiCF\(_3\)SO\(_3\) electrolyte are reported to give energy efficiencies of 70-80% and specific powers of 100-300 W dm\(^{-1}\) [4,6].

Cells operating at room temperatures have been fabricated by the Canadian and French group using a modified polyether electrolyte. Current drains of 3-20 \(\mu\)A cm\(^{-2}\) have been demonstrated for MnO\(_2\)-based primary and MoO\(_2\)-based secondary systems [4,7]. The Harwell group also claim to have a polymer electrolyte with sufficient conductivity to be used at room temperature [8]. The cells fabricated with such electrolytes and V\(_6\)O\(_{13}\) cathodes give current outputs of 0.5 mA cm\(^{-2}\).

Reports of scaled-up battery studies have been scarce. However, the construction of "first generation" cells with capacities of 10-30 Ah are under evaluation [4].

The cell studied in this laboratory is based on a lithium anode, a polymer-salt electrolyte (polyethylene oxide complexed with LiCF\(_3\)SO\(_3\)) and a V\(_5\)O\(_{13}\) composite cathode.

2. EXPERIMENTAL

2.1. Materials Fabrication

All manipulation of the cell materials was performed in a < 1% R.H. dry room. The electrolyte was prepared by dissolving known quantities of LiCF\(_3\)SO\(_3\) (3M, pre-dried at 50°C) and PEO (Polysciences, molecular weight 5 x 10\(^6\), pre-dried at 50°C) in acetonitrile (pre-dried using molecular sieves). The weights used were such that the final PEO:Li salt ratio was 8. The solution was allowed to stand in a sealed bottle for 2-5 days to homogenize.

Films of the electrolyte were obtained by a solution casting technique using a doctor blade. They were air-dried for two days followed by careful drying under vacuum over P\(_2\)O\(_5\) for two weeks or more. Films in the 10-20 \(\mu\)m range were obtained.

The cathode process incorporated the materials V\(_5\)O\(_{13}\), Shawinigan Black, PEO, lithium salt and acetonitrile. It was prepared by a complex ball-milling procedure resulting in the final solution being extremely homogeneous. Highly smooth films were cast from the resultant dispersions directly onto aluminum foil current collectors (≈ 17 \(\mu\)m). Film thickness was of the order of 10-30 \(\mu\)m range.
2.2. Cell Design.

Cells were constructed in the dry room; the basic design is shown in Figure 1. Three different sizes of flat, circular cells were tested.

6.4 cm² Cell. Small cells for 100°C operation had geometric surface area of 6.42 cm². The lithium and cathode were separated by concentric cut polypropylene spacers. The electrolyte thickness was 20 μm. The cells were sandwiched between stainless-steel plate current collectors and maintained under constant pressure using a clamping system.

75 cm² Cell. Large cells operating at 100°C were 75 cm² in area. Further scalings were made by connecting the larger area cells in a parallel configuration.

0.8 cm² Cell. Cells operating at room temperature were constructed in the glove-box. The area of the electrolyte was about 0.8 cm², except that in this case the thickness was increased to 50 μm. Polypropylene spacers with a 1 cm diameter void for the electrolyte was used to separate the electrodes. In these cells propylene carbonate (PC) was added to the electrolyte to enhance the ionic conductivity of the electrolyte. The cell was completed by sandwiching the cell between two glass slides and hermetically sealing with epoxy.

2.3 Cell Testing

The cycling of all cells was carried out in the glove-box. The theoretical capacity of the cathode was based on the assumption that Li₄V₆O₁₉ forms at 100% cathode utilization. A constant current discharge and a constant voltage charge through a current limiting resistor were used as the cycling regime.

Post-mortem microscopic examination was carried out on the 6.4 cm² cells discharged at the C/5 rate. The cells were dismantled at room temperature in the dry room and various specimens were carefully peeled from one another to obtain a clean examinable surface. Optical micrographs were obtained using an Olympus SZIII optical microscope equipped with a polaroid camera. A JEOL 840 II scanning electron microscope was used to examine the surfaces at higher magnifications. Low accelerating voltages were used to avoid not only beam damage but also charging the sample. The cathodes were sufficiently electrically conductive to avoid charging. Poor resolution resulted in the case of the electrolyte, either because the accelerating voltage was too low or because of charging. For lithium samples, considerable beam damage occurred. Hence only the cathode was studied in sufficient detail by SEM.
3. RESULTS AND DISCUSSION.

The initial open-circuit voltage (o.c.v.) of the cells without any PC was over 3.5 V at room temperature. However, at 100°C, this value reduced to 2.9-3.1V. Cells containing PC demonstrated o.c.v.'s of around 3.1-3.2V at 20°C.

Figure 2 shows a typical plot of cell voltage versus amount of Li insertion in the cathode for different rates of discharge at 100°C. The cut-off voltage was +1.8V. The curves are characterized by several plateaus and these arise as a result of the change in the oxidation state of the V₆O₁₃ cathode during the lithium insertion. The plateaus are more distinct at the lower rates of discharge. On charge, a loss in capacity is experienced compared to the initial discharge.

Figure 3 shows a plot of cell capacity as a function of cycle number for the 6.4 cm² cells operating at 100°C [9]. The initial capacity was found to be higher at low rates of discharge than at the higher rates. However, greater stabilization in capacity versus cycle number occurred at the higher rate. The cell operating at the C/5 rate was cycled to 100 cycles with greater than 75% of the initial utilization of V₆O₁₃ being maintained at cycle number 100. The other cells were not cycled to the same extent.

Figure 4 shows an optical microscopy cross-section of the electrolyte with lithium and cathode layers on either side. The sample was obtained from the cell cycled at C/5 rate to 100 cycles. The micrograph depicts the Li-electrolyte-cathode layers to be extremely well intact. Although it is not very clear from the micrograph, the interior portion of the electrolyte appeared very crystalline with some amorphous white deposits in sharp contrast to the normal plastic nature of the starting electrolyte. Nonetheless, this layer is highly smooth and uniform at the interfaces of the cathode and anode.

The cathode is also highly uniform at this interface as can be seen from Figure 5. In this micrograph, areas of the crystalline electrolyte are clearly visible. Figure 6 shows an optical micrograph of the electrolyte surface (after 100 cycles) at the cathode/electrolyte interface. The structures appear to be consistent with one another. In all cells examined, the cell materials indicated good adhesion at both the anode/electrolyte and electrolyte/cathode interfaces. Furthermore, the lithium, electrolyte and cathode tended towards a finer grained and smoother structure. In addition, no dendrite was observed on the lithium side.

Figure 7 shows an electron micrograph of the cathode after completing cycle number 1. A micrograph of the cast cathode was not possible because of severe charging arising from the PEO electrolyte. The figure shows the surface to be fairly well intact. The average grain size is about 5 μm. After 35 cycles (Figure 8), the material becomes finer grained with average grain size of <<
2μm. The grains are well-defined and the surface appears quite porous. At cycle number 100, the grains are so small that they could not be resolved clearly. However, results have shown that there is a clear morphological change taking place during cycling [9].

It was found that cells made with thinner cathodes resulted in greater stabilization in capacity with continued cycling. The technique for achieving ultra smooth cathodes, cast as thin films of 15-25 μm, was also established. This ultimately led to the development of thin film cells scaled from 5 mAh to 150 mAh capacity.

Figure 9 depicts the performance of the scaled-up cells. In general, cells discharged at the lower rate give higher capacities than those discharged at higher rates. However, the decline in capacity is much faster at low rates than at the high rate (cf. C/20, C/10, vs C/5). Greater stabilization occurs at the higher rate of discharge. The results are similar to those observed on smaller cells.

Considerable engineering difficulties arose as a result of scaling the cell further. Because of this, several 150 mAh cells were connected in parallel. Using this arrangement, a 750 mAh battery was constructed [9]. The performance was good between C/20 and C/50 discharge rates. However, severe polarizations were encountered at the higher rates of discharge. At C/50 rate over 60% of the theoretical capacity was possible. Even reduced capacities were obtained at C/20 rates. Although the performance of this battery is not comparable to the smaller or larger individual cells, these first results are signs of encouragements.

Figure 10 is a typical plot of capacity versus cycle number for cells operating at room temperature [9]. The data are presented for three PC additions, and the discharge rate was C/50 in all cases. The cell without any PC polarized instantly even with reduced electrolyte thickness (5μm). However, cells containing PC demonstrate good cell performances although there is a steady decline in capacity with cycling.

An initial capacity of 64% is obtained with 10 vol.% PC addition. Only 22 cycles are obtained before the capacity falls below 20% theoretical. With 40 vol.% PC, only 12 cycles are possible before the cell finally shorts.

The optimum result is obtained with 20 vol.% PC. A high initial capacity (86% theoretical) is obtained, but even in this case the decline is inevitable. Up to 26 cycles are obtained before the capacity falls below significant levels.

The addition of small quantities of PC certainly improves the room temperature cell performance. The overall effect is to increase the dielectric property (and hence the ionic conductivity) of the electrolyte. Further studies [9] have shown that discharge
rates greater than $100 \ muAcm^{-2}$ are possible with these systems. This is comparable to cell performance at 100°C with conventional polymer solid electrolytes.

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REFERENCES

Key Words:

polymer, lithium    page 1
cells, ball-milling  page 2
microscopy, cycling  page 3
voltage, propylene carbonate page 4
polarization, rates  page 5
Figure 1. Schematic of the polymer electrolyte cell.

Figure 2. Cell voltage as a function of lithium insertion.
Figure 3. Plot of theoretical capacity vs cycle # for cell at 100 C (Ref. 9).
Figure 9. Performance of large cells at 100 °C (Ref. 9).

Figure 10. Performance of room temperature cells (Ref. 9).
Figure 4. Optical micrograph of the cell cross-section.

Figure 5. Optical micrograph of the cathode at the cathode/electrolyte interface.

Figure 6. Optical micrograph of the electrolyte at the cathode/electrolyte interface.

Figure 7. Electron micrograph of the cathode after discharge # 1.

Figure 8. Electron micrograph of the cathode after discharge # 35.
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