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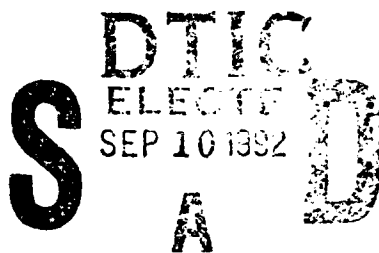


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SLCET-TR-91-31

Lithium Rechargeable Cell with a Poly 3-Methylthiophene Cathode

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Electronics Technology and Devices Laboratory

August 1992



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13. ABSTRACT (Maximum 200 words) A poly 3-methylthiophene (PMT) cathode showed excellent coulombic efficiency during cycling in a lithium rechargeable cell. An electrolyte containing dimethyl carbonate was used since it is stable at the high anodic potentials reached during cell charging. The polymer cathode tolerated modest overcharge and was able to continue cycling after a severe short-circuit with minimal loss of capacity.				
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PMT 1.4 microns thick

INTRODUCTION

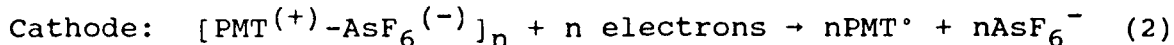
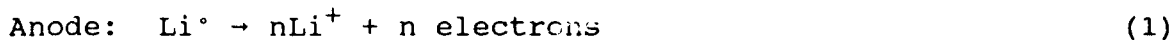
Presently there is considerable attention being given to electrically conductive polymers as cathode materials for rechargeable batteries. They can be reversibly doped (oxidized, conductive state) and dedoped (reduced, insulating state), exhibiting good stability over many cycles. Microns-thick polymer films hold promise for the development of thin, light-weight rechargeable batteries and for use in bipolar stacks to provide high power.

One material which is stable at the high anodic potentials encountered with lithium rechargeable cells is poly 3-methylthiophene (PMT). Recently, thin films of PMT were successfully cycled in rechargeable lithium/sulfur dioxide cells [1]. PMT is insoluble in strong acids, bases, and common organic solvents [2], and films are able to be polymerized electrochemically. Depending on the method of polymerization, solvent, anion dopant and extent of doping, conductivities between 10-2000 have been measured [3-6]. The nature of the dopant anion also influences PMT redox potentials [7].

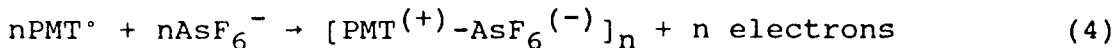
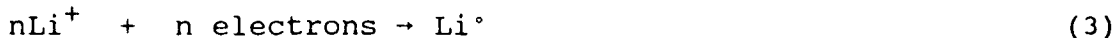
Rechargeable lithium batteries containing organic liquid based electrolytes have generally suffered from diminishing cell capacity with increased cycling. This is often traceable to poor lithium cycling efficiencies and/or solvent oxidation on charge. Significant improvement in these two areas has been made with the use of solvent mixtures. Lithium cycling studies with LiAsF_6 electrolyte containing methyl formate (MF), dimethyl carbonate (DMC), diethyl carbonate (DEC), and mixtures of MF with DMC or DEC have determined the order of stability (resistance to oxidation) to be: $\text{MF} \ll \text{DMC} < \text{MF/DMC} < \text{MF/DEC} < \text{DEC}$ [8]. Although DEC was the most stable, lithium cycling efficiency and electrolyte conductivity were very poor. The highest lithium cycling efficiencies (about 85%) and conductivities were with the binary mixtures. However, it was found that cells containing these solvent mixtures were not stable at open circuit (potentials approaching 4.0 V) during storage. Pure DMC has an 80% lithium cycling efficiency and is less conductive [8], but cells are more stable during storage in this solvent. For these reasons we chose to study the PMT cathode in DMC-based electrolyte.

In this study we constructed a rechargeable lithium cell using a 1.4 micron thick PMT cathode in 1.46 M LiAsF_6 -DMC electrolyte. Knowing that this electrolyte is stable at potentials above 4.2 V [8], we cycled the cell between 3.8 and 2.7 V. In this way we were confident that the electrolyte was stable at normal cell operating potentials as well as to what was later determined to be mild overcharge (a 4.0 V cutoff). The cell reactions involve the shuttle of AsF_6^- anions at the PMT cathode and the cycling of lithium at the anode. On discharge,

Li^+ and AsF_6^- are released into the electrolyte:



On charge, Li^+ is reduced, and plates onto the lithium electrode as AsF_6^- migrates into the matrix of the oxidized PMT, re/establishing electrical neutrality:



EXPERIMENTAL

PMT was electrochemically polymerized in a 125 ml European flask (Ace Glass) using a 1 cm² platinum flag counter electrode, a saturated sodium calomel reference electrode, and a platinum rod working electrode. The platinum rod was polished to a mirror finish with 0.1 micron alumina/water paste and sheathed in heat shrinkable Teflon so as to expose only the 0.071 cm² cross-sectional area at the polished end of the rod. The cell was flooded with 30 ml of electrolyte containing 0.1 M 3-methylthiophene monomer (Sigma Chemical) and 0.1 M lithium hexafluoroarsenate in redistilled acetonitrile. The LiAsF_6 provides the counter anion (AsF_6^-) to electrically neutralize the polymer which is formed in the oxidized state (positive charge). The salt also enhances electrolyte conductivity. The successful use of this salt in the preparation of PMT was significant in that the dopant anion is the same as that which occurs in the electrolyte used in the cell. If polymerization were with another anion of a size different than AsF_6^- , there would be the possibility of a competition between ions during cycling, as well as the possibility of additional mechanical stresses to the polymer matrix. Ultra high purity dry argon was bubbled through the electrolyte to remove oxygen. An adherent film 1.4 microns thick (measured by SEM) was produced by pulse deposition. This was carried out at a constant current of 10 mA cm⁻² by passing 0.25 coulombs per cm² on five successive cycles with five minute rest periods (at open circuit) between cycles. If the rest periods were omitted, films of poor quality resulted. The PMT-coated platinum surface was then rinsed in acetonitrile and dried under vacuum at 50°C. Based on film thickness and cross-sectional area, the volume of the PMT was 9.95×10^{-6} . Assuming the ideal case (100% efficiency) for polymerization, a maximum of 4.52×10^{-5} g of 3-methylthiophene was deposited on the substrate; the true mass of PMT was not determined but was certainly less. The experimental cell was constructed with a lithium metal anode, a 1.4 micron thick PMT cathode doped with AsF_6^- , and a lithium reference electrode. The cell was flooded

with 10 ml of 1.46 M LiAsF_6 -DMC (approximately 0.01 S cm^{-1}), prepared with dry, high purity salt in redistilled solvent. A PAR Model 273 Potentiostat/Galvanostat controlled by a Hewlett Packard Model 85 computer was used to perform polymerizations and cycling experiments, all at ambient temperature.

RESULTS AND DISCUSSION

Initially, cells were discharged at 0.1 mA cm^{-2} to 2.0 V (versus a lithium reference) and showed two reduction plateaus, the second plateau beginning at about 2.3 V. To avoid this second, unidentified reduction, cells were subsequently discharged only to a 2.7 V cutoff. After a one minute rest period at open circuit, cells were charged at 0.05 mA cm^{-2} constant current until cell potential reached 3.8 V, allowing a one minute rest period prior to the next discharge. Under these conditions, cell discharge and recharge of PMT was reproducible over many cycles, exchanging nearly the same number of coulombs during each half cycle. The performance of one cell will be discussed, although other cells performed similarly.

Figure 1 shows cell potential vs time at a discharge rate of 0.1 mA cm^{-2} for cycles 1-3, 5 and 20. The first few discharges were atypical, especially the first discharge which was particularly poor. This is explained by the fact that the polymer was not sufficiently doped, especially on the first cycle. After polymerizing PMT, some of the anions were probably leached out of the polymer matrix during the rinsing process. Even so, load potential was greater than 3 V. Charging PMT to 3.8 V after the first discharge replaced anions removed during discharge as well as making up for the "missing" anions. The slight increase over the next few cycles resulted from swelling of the polymer as it was more thoroughly wetted with electrolyte. This would further open the polymer structure and create more surface area, allowing an additional increase in the level of polymer doping. After the initial "conditioning" of the PMT electrode, discharge capacity was very reproducible.

Three consecutive charge and discharge cycles of PMT are shown (charge cycle number 19 through discharge cycle number 22) in Figure 2. Cell capacity and load voltage were extremely reproducible. The operating potential exceeded 3 V during most of the discharge, then dropped precipitously once cell potential reached 2.8 V. Each recharge cycle (to a 3.8 V cutoff) replaced 100% of the charge previously removed.

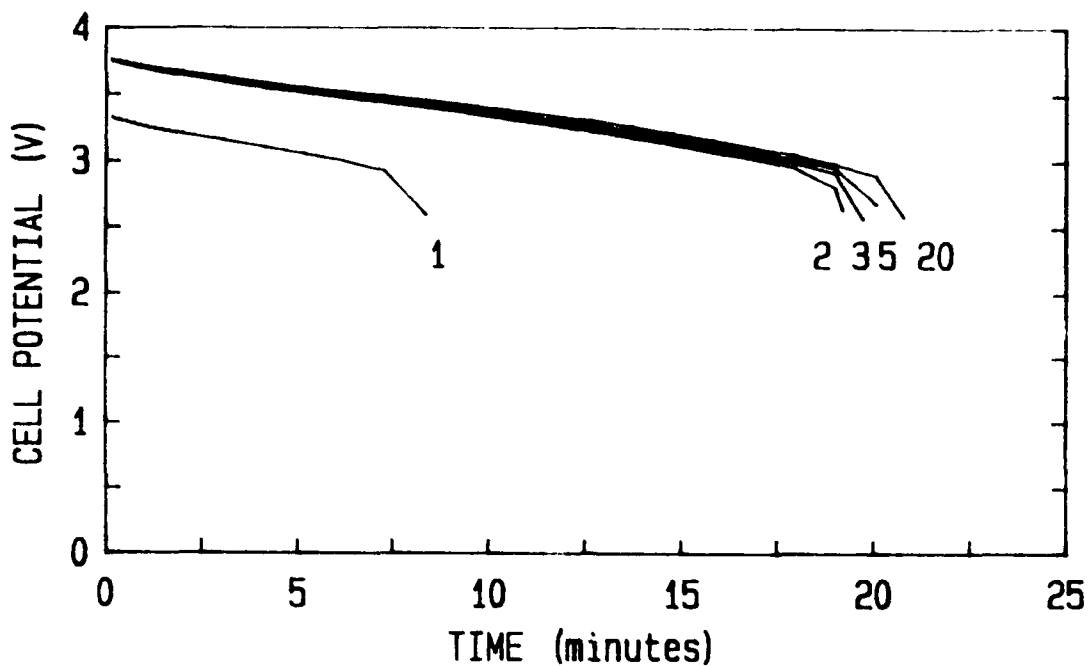


Figure 1. Cell potential vs discharge time for cycles 1-3, 5, and 20 for a Li/1.46 M LiAsF₆-DMC/PMT cell. Discharge rate 0.1 mA cm⁻², charge rate 0.05 mA cm⁻² to a 3.8 V cutoff. PMT 1.4 microns thick.

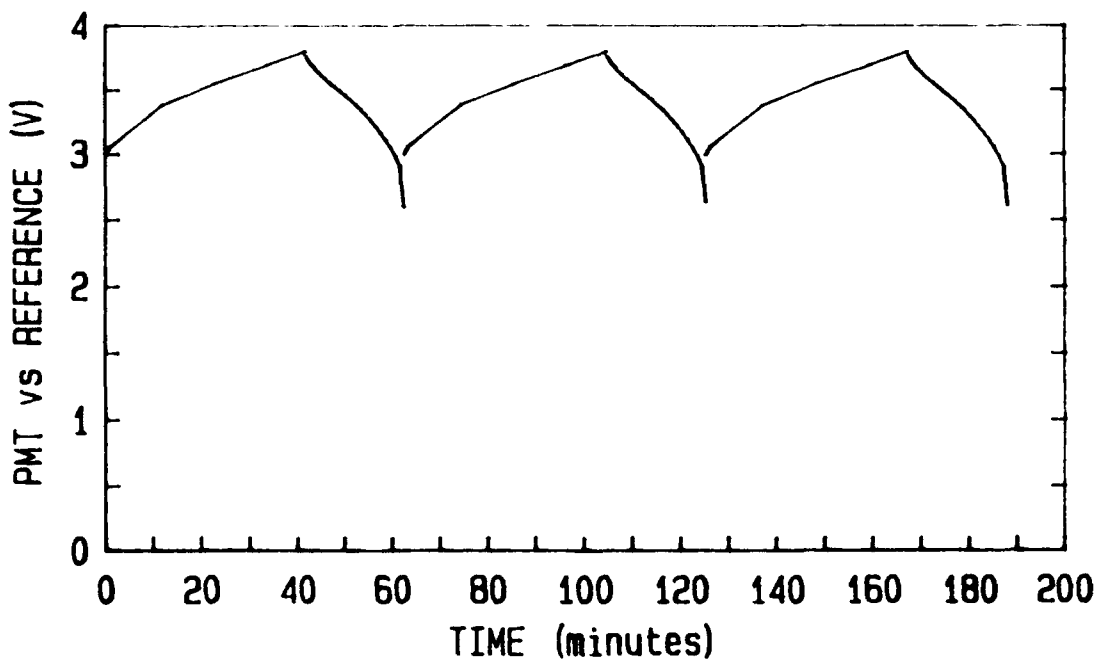


Figure 2. Cell potential vs time from charge cycle 19 through discharge cycle 22. Charging rate 0.05 mA cm⁻² to a 3.8 V cutoff, discharge rate 0.1 mA cm⁻².

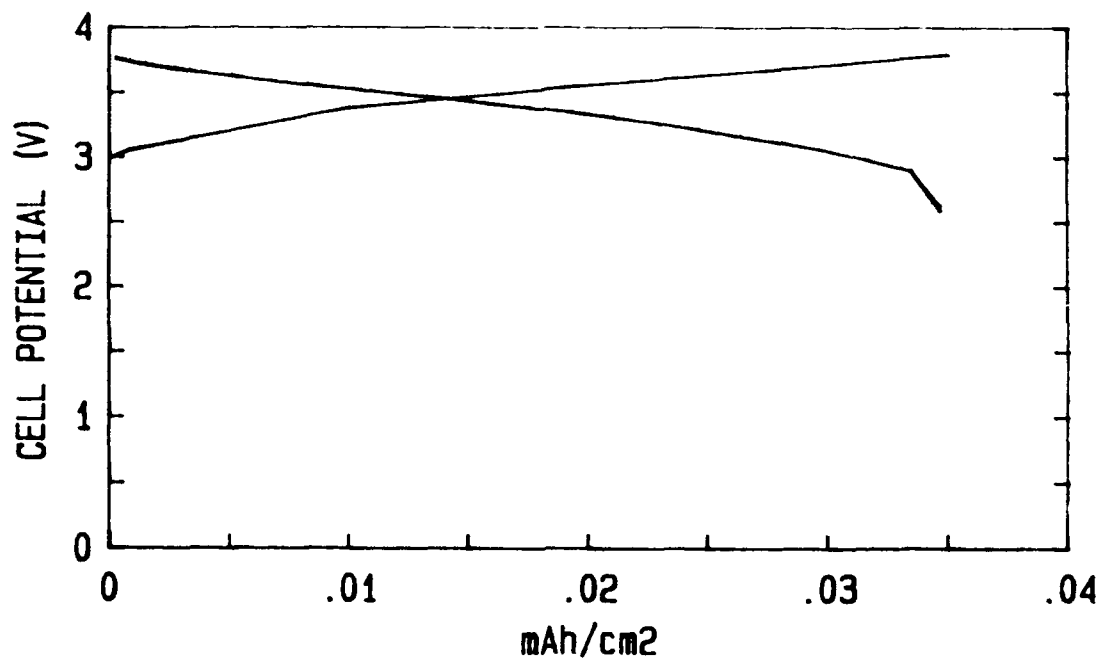


Figure 3. Cell potential and capacity for cycles 20 through 22. Charging (ascending line) was at 0.05 mA cm^{-2} to a 3.8 V cutoff and discharge (descending line) at 0.1 mA cm^{-2} .

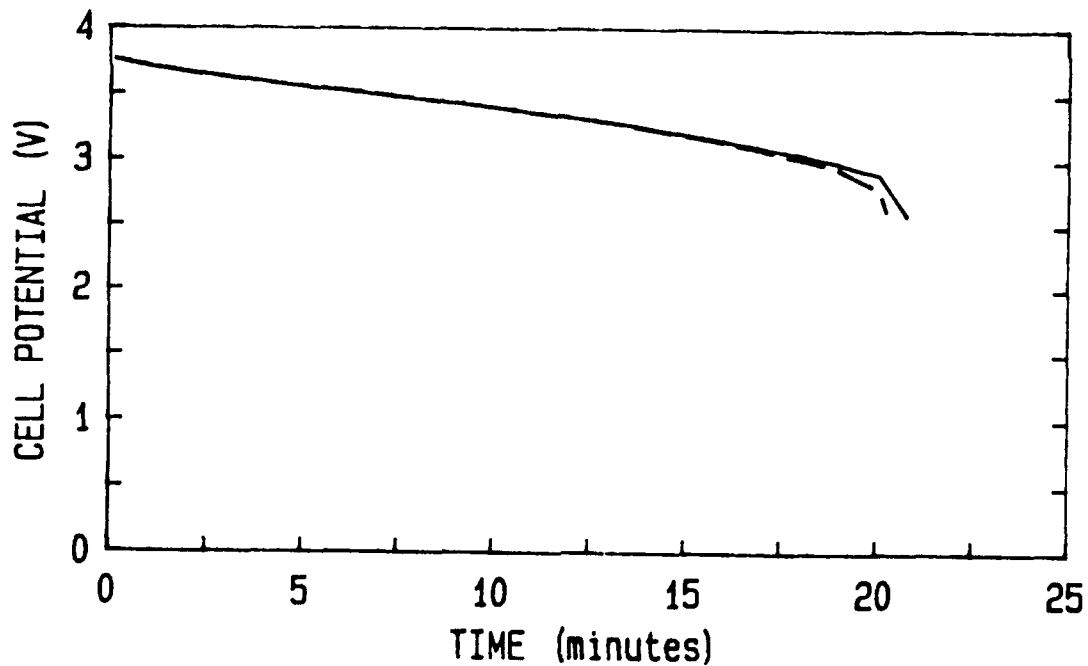


Figure 4. Voltage vs time for a 0.1 mA cm^{-2} discharge for cycles 20 (solid line) and 63 (dashed line). Recharge at 0.05 mA cm^{-2} to a 3.8 V cutoff.

The excellent coulombic efficiency is best illustrated in Figure 3, which shows potential and amp-hour capacity for consecutive cycles. Three charge cycles (numbers 20-22) at 0.05 mA cm^{-2} are plotted over top of each other, and appear as a single ascending line. Likewise, the three corresponding discharges also appear as a single descending trace when plotted over each other.

Cell voltages during discharge cycles 20 and 63 are shown in Figure 4. PMT discharge capacity loss between the 20th to the 63rd cycle was only 2.5%.

After cycle 63, the cell was intentionally short-circuited for eight hours and allowed to stand for two days. The cell was recharged (to 3.8 V) and cycling continued. Approximately 12% of the cell discharge capacity (compared to cycle 63) was irreversibly lost (Figure 5, curves A and B). Only a small, permanent loss in cell operating potential occurred, which increased from 10 to 50 mV over the course of a discharge. No further losses in capacity or operating potential were observed over the next 53 cycles to cycle 116 (curve C).

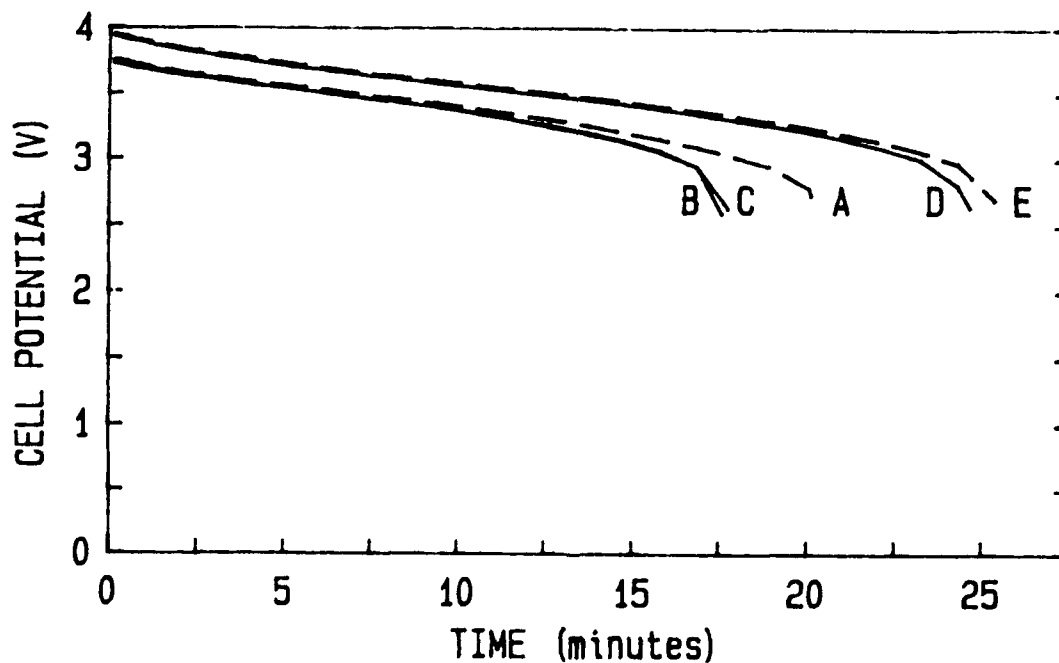


Figure 5. Cell discharge at 0.1 mA cm^{-2} for cycle 63 (A), following severe short-circuit and recharge to 3.8 V, cycle 65 (B), and cycle 116 (C). Cell discharge following recharge to a 4.0 V cutoff is shown for the first (D, cycle 117) and fourteenth (E, cycle 130) cycles.

The next 14 cycles (cycles 117 through 130) were performed with a recharge voltage cutoff of 4.0 V. Capacity increased over the first couple of cycles and then stabilized for the remaining cycles (Figure 5, curves D and E), with a net increase in capacity of 25% compared to the first 63 cycles. The increase in discharge capacity is presumed the result of more completely doping the polymer with AsF_6^- anions. Operating potential was also increased by about 170 mV. Recharging to 4.0 V created an overcharge condition, replacing approximately 108% of the coulombs removed on discharge. After the initial increase in discharge capacity, overcharge remained at 8%, and discharge capacity remained constant. This implied that the PMT cathode was stable to an overcharge potential of 4.0 V (as is the electrolyte), and was capable of continuing to provide a reproducible discharge. There is some charging voltage cutoff between 3.8 V and 4.0 V which would optimize cell cycling; precluding cell overcharging while allowing maximum discharge capacity and operating potential.

We increased the discharge rate to 0.5 mA cm^{-2} with recharge to 4.0 V for eight cycles, and obtained reproducible discharge and charge cycles. Figure 6 compares capacity (mAh cm^{-2}) of PMT discharged at 0.1 mA cm^{-2} (solid line) and 0.5 mA cm^{-2} (dashed line). Although the rate was increased fivefold, the cell was able to deliver nearly the same capacity as was obtained at the lower rate.

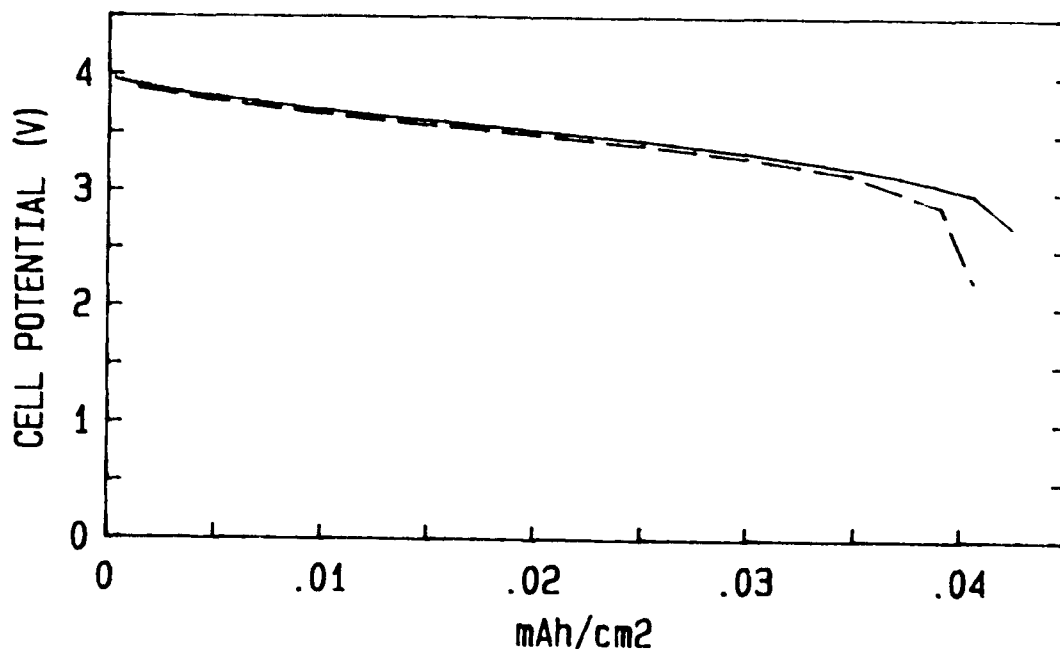


Figure 6. Discharge capacity of PMT at two discharge rates, 0.1 mA cm^{-2} (solid line) and 0.5 mA cm^{-2} (dashed line.)

A safety advantage of this cell lies in the polymer itself, since it becomes electrically more insulating during undoping (discharge). During short-circuit or overdischarge, cell resistance would increase, and the polymer might act as an internal fuse to terminate cell operation. Our experiments have shown (Figure 5) that the cell could then recover from a severe short-circuit and continue to cycle with minimal loss in performance.

To augment cell safety by minimizing the quantity of lithium in a cell, one could also use an anode consisting of a lithium intercalating compound, such as graphite or one of the metal oxide compounds. This could reduce hazards associated with metallic lithium, such as cell shorting as a result of dendrite formation.

CONCLUSIONS

Thin (1.4 micron) PMT films exhibited excellent cycling efficiency in Li/LiAsF₆-DMC/PMT cells, operating well within the limits of electrolyte stability. A capacity loss of less than 3% occurred after 63 cycles in lab cells. Perhaps cycling efficiency would be even better in a hermetically sealed cell, protected from the introduction of contaminants such as water or oxygen. It is expected that hundreds of cycles are possible with little loss in capacity of the PMT cathode. The limiting factor for cycle life is the cycling efficiency of the lithium. Lithium cycling efficiencies may be improved by the discovery of new solvent mixtures which will also allow good cell stability on storage.

Maximum capacity is achieved by constant current charging to a potential cutoff between 3.8 V (undercharged) and 4.0 V (overcharged). The Ah capacity of PMT was insensitive to a fivefold increase in discharge rate, from 0.1 to 0.5 mA cm⁻². Further, PMT was stable during several overcharge cycles without degradation of discharge capacity.

Other attractive features are the ability to recover most of the cell capacity after severe cell shorting, and the ability to continue cycling without further loss in capacity. This high voltage rechargeable cell could be useful as a rechargeable battery, and may be suitable for pulse power applications in a bipolar construction composed of many thin cells.

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