

## Short Communication

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### Lithium rechargeable cell with a poly 3-methylthiophene cathode and $\text{LiAsF}_6$ -dimethyl carbonate electrolyte

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#### Abstract

A poly 3-methylthiophene cathode showed excellent coulombic efficiency during cycling in a lithium rechargeable cell. A dimethyl carbonate electrolyte 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 in capacity.

#### 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. Micron-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). PMT is insoluble in strong acids, bases, and common organic solvents [1], and films are able to be polymerized electrochemically. Depending on the method of polymerization, solvent, anion dopant and extent of doping, conductivities between  $10\text{--}2000\text{ S cm}^{-1}$  [2-5] have been measured. The nature of the dopant anion also influences PMT redox potentials [6].

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  $\text{LiAsF}_6$  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 [7].

MF  $\ll$  DMC < MF/DMC < MF/DEC < DEC

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 [7], 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  $\mu\text{m}$  thick PMT cathode in 1.46 M  $\text{LiAsF}_6$ -DMC electrolyte. Knowing that this electrolyte is stable at potentials above 4.2 V [7], we cycled the cell between 3.8–2.7 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  $\text{AsF}_6^-$  anions at the PMT cathode and the cycling of lithium at the anode. On discharge,  $\text{Li}^+$  and  $\text{AsF}_6^-$  are released into the electrolyte.

Anode  $\text{Li}^0 \longrightarrow n\text{Li}^+ + n \text{ electrons}$

Cathode  $[\text{PMT}^{(+)}-\text{AsF}_6^{(-)}]_n + n \text{ electrons} \longrightarrow n\text{PMT}^0 + n\text{AsF}_6^-$

On charge,  $\text{Li}^+$  is reduced, and plates onto the lithium electrode as  $\text{AsF}_6^-$  migrates into the matrix of the oxidized PMT, re-establishing electrical neutrality.

$n\text{Li}^+ + n \text{ electrons} \longrightarrow \text{Li}^0$

$n\text{PMT}^0 + n\text{AsF}_6^- \longrightarrow [\text{PMT}^{(+)}-\text{AsF}_6^{(-)}]_n + n \text{ electrons}$

## Experimental

PMT was electrochemically polymerized in a 125 ml European flask (Ace Glass) using a 1  $\text{cm}^2$  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  $\mu\text{m}$  alumina/water paste and sheathed in heat shrinkable Teflon so as to expose only the 0.071  $\text{cm}^2$  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. Ultra high purity dry argon was bubbled through the electrolyte to remove oxygen. An adherent film 1.4  $\mu\text{m}$  thick (measured by SEM) was produced by pulse deposition. This was carried out at a constant current of 10  $\text{mA cm}^{-2}$  by passing 0.25 coulombs per  $\text{cm}^2$  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  $9.95 \times 10^{-6} \text{ cm}^3$ . Assuming the ideal case (100% efficiency) for polymerization, a maximum of  $4.52 \times 10^{-5} \text{ g}$  of 3-methylthiophene was deposited on the substrate, the true mass of PMT was not determined but was certainly less. The experimental cell was assembled in a glove box filled with dry argon, and contained a lithium metal anode, 1.4  $\mu\text{m}$  thick PMT cathode doped with  $\text{AsF}_6^-$ , and a lithium reference electrode. It was flooded with 10 ml of 1.46 M  $\text{LiAsF}_6$ -DMC (approximately 0.01  $\text{S cm}^{-1}$ ), prepared with dry, high purity salt in redistilled solvent. To prevent the introduction of moisture during cycling, experiments were performed within the glove box, and all cell ports were closed via ground glass joints or threaded fittings with gaskets. 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  $\text{mA cm}^{-2}$  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  $\text{mA cm}^{-2}$  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.

Cell voltages during discharge cycles 20 and 63 are shown in Fig. 1. Cell capacity and load voltage were extremely reproducible. Cell operating potential exceeded 3 V during most of the discharge, then dropped precipitously once cell potential reached 2.8 V. PMT discharge capacity loss between the 20th to the 63rd cycle was only 2.5%. Each recharge cycle (to a 3.8 V cutoff) replaced 100% of the charge previously removed (see Fig. 3, curves A and A').

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 (Fig. 2, curves A and B). The reason for this loss was not investigated, but is most likely a consequence of reduction processes occurring at or below the plateau observed at 2.3 V. 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).

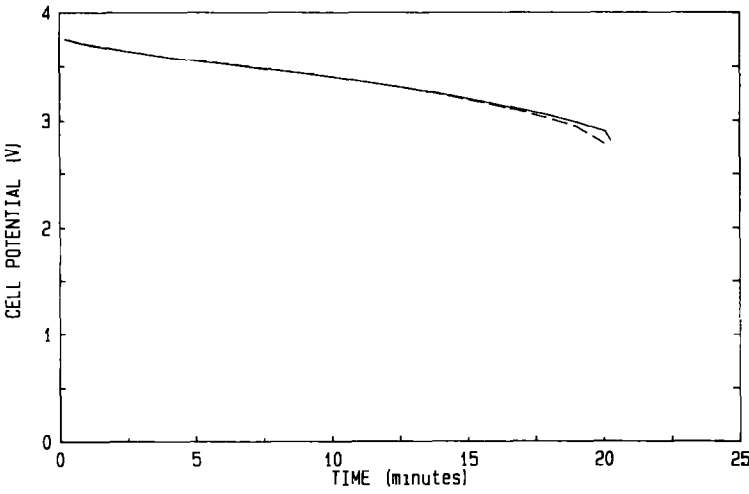


Fig 1 Voltage as a function of discharge time for a Li/1.46 M LiAsF<sub>6</sub>-DMC/1.4 μm thick PMT cell discharged at 0.1 mA cm<sup>-2</sup> constant current to a 2.7 V cutoff. Discharge curves are shown for cycles 20 (solid line) and 63 (dashed line). Recharge was to a 3.8 V cutoff at 0.05 mA cm<sup>-2</sup> constant current.

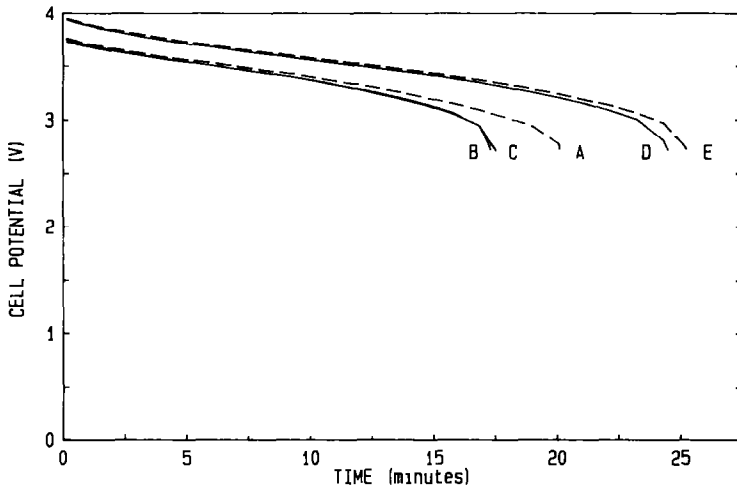


Fig 2 Li/1.46 M LiAsF<sub>6</sub>-DMC/1.4 μm thick PMT cell discharge curves during cycle 63 (A), following severe short-circuit and recharge, cycle 65 (B), and cycle 116 (C). Discharge was at 0.1 mA cm<sup>-2</sup> and recharge at 0.05 mA cm<sup>-2</sup> to 3.8 V. Cell discharge following recharge to 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 (Fig 2, 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 to be the result of more

completely doping the polymer with  $\text{AsF}_6^-$  anions. Operating potential was also increased by about 170 mV. Recharging to 4.0 V resulted in 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 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  $0.5 \text{ mA cm}^{-2}$  with recharge to 4.0 V for eight cycles, and obtained reproducible discharge and charge cycles. Figure 3 compares capacity ( $\text{mA h cm}^{-2}$ ) of PMT discharged at  $0.1 \text{ mA cm}^{-2}$  (curve B) and  $0.5 \text{ mA cm}^{-2}$  (curve C). Although the rate was increased five-fold, the cell was able to deliver nearly the same capacity as was obtained at the lower rate. Also compared are the capacity removed during discharge at  $0.1 \text{ mA cm}^{-2}$  (curve A) and replaced on the subsequent recharge to a 3.8 V cutoff (A') to demonstrate the excellent coulombic efficiency of PMT.

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 (Fig. 2) that the cell could then recover from 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,

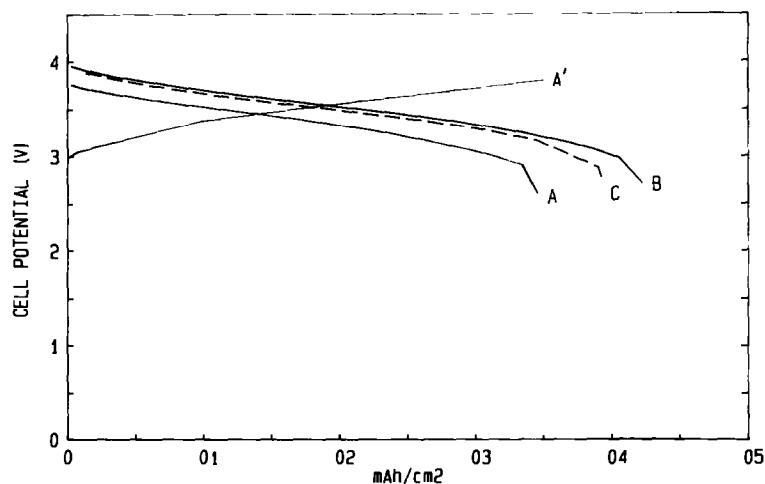


Fig. 3 Capacity removed during discharge (A) at  $0.1 \text{ mA cm}^{-2}$  and replaced upon recharge (A') at  $0.05 \text{ mA cm}^{-2}$  to a 3.8 V cutoff for a Li/1.46 M  $\text{LiAsF}_6$ -DMC/1.4  $\mu\text{m}$  thick PMT cell. Discharge capacity is also compared for two rates,  $0.1 \text{ mA cm}^{-2}$  (B) and  $0.5 \text{ mA cm}^{-2}$  (C) with a 4.0 V charging cutoff.

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  $\mu\text{m}$ ) PMT films exhibited excellent cycling efficiency in  $\text{Li}/\text{LiAsF}_6\text{-DMC/PMT}$  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.

Maximum capacity is achieved by constant current charging to a potential cutoff between 3.8 V (undercharged) and 4.0 V (overcharged). The A h capacity of PMT was insensitive to a five-fold increase in discharge rate, from 0.1 to 0.5  $\text{mA cm}^{-2}$ . 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 stable, high voltage rechargeable cell should be able to provide hundreds of cycles, limited only by the lithium cycling efficiency. Lithium cycling efficiencies may be improved by the discovery of new solvent mixtures which will also allow good cell stability on storage.

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