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High-rate discharge of poly 3-methylthiophene cathodes in inorganic electrolytes

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Lithium cells with thin film electrodes of poly 3-methylthiophene were discharged at high current densities in electrolytes containing either sulphur dioxide, thionyl chloride, or sulphuryl chloride. Highest capactiy was obtained with thionyl chloride electrolyte for current densities as high as $30\,\mathrm{mA\,cm^{-2}}$ (up to $600\,\mathrm{W\,cm^{-3}}$). Cells containing sulphur dioxide electrolyte were rechargeable, but constant current discharge performance was less than in either thionyl chloride or sulphuryl chloride. However, pulse discharge in sulphur dioxide permitted comparable power densities to be achieved, and reproducible results were obtained over many cycles.

1. Introduction

The study of electrically conductive polymers as electrodes in electrochemical cells is popular because extremely thin films are easy to prepare, holding promise for the development of ultra-thin batteries. If used in conjunction with an ionically conducting polymer electrolyte, it should be possible to construct a relatively small bipolar cell able to deliver high power pulses. Early studies of conductive polymers began with polyacetylene, but many polymers have been explored since, especially those with structures containing aromatic rings, such as the polythiophenes. The present interest is with poly 3-methylthiophene, in which conductivities as high as $2000\,\mathrm{S\,cm^{-2}}$ have been reported [1]. In the oxidized (conductive) state, the positively charged polymer is doped with anions to electrically neutralize the charge. On cell discharge, the polymer cathode becomes reduced to a neutral state (electrically insulating), and anions diffuse out of the polymer matrix into the electrolyte.

Polymer electrodes can be cycled (charged and discharged) many times with excellent efficiency. Nagatomo and Omoto cycled a lithium cell containing a poly 3-methylthiophene cathode for 1200 cycles with 97% coulombic efficiency [2]. Kawai *et al.* [3] report similar coulombic efficiencies for poly 3-alkythiophenes containing various alkyl groups. Generally, studies have involved electrolytes containing organic solvents. Little work has been done with inorganic electrolytes such as sulphur dioxide (SO_2), thionyl chloride ($SOCl_2$) and sulphuryl chloride (SO_2Cl_2), which themselves become reduced. These solvents have been extensively studied in lithium cells, most commonly with porous carbon cathodes.

In earlier work, we electrochemically prepared $1.4\,\mu\mathrm{m}$ thick films of poly 3-methylthiophene (PMT) and successfully cycled lab cells containing a lithium anode and $Li(SO_2)_3AlCl_4$ electrolyte [4]. Operating potentials above 3.0 V were observed for discharge current densities of $1\,\mathrm{mA\,cm^{-2}}$, and cells were charged without exceeding 3.9 V to minimize formation of chlorine and the accompanying corrosive effects. The purpose of this study was to explore high current density discharge of PMT in the SO_2-based electrolyte as well as in $SOCl_2$ and SO_2Cl_2-based electrolytes.

2. Experimental details

Electrochemical polymerization of PMT was performed in a 125 ml European flask using a $1\,\mathrm{cm^2}$ platinum flag counter electrode, a SSCE reference electrode, and a platinum or glassy carbon rod working electrode. The working electrode was polished to a mirror finish with $0.1\,\mu\mathrm{m}$ alumina/water paste and sheathed in heat shrinkable Teflon, exposing a $0.071\,\mathrm{cm^2}$ surface area. The cell was flooded with electrolyte containing 0.1 M 3-methylthiophene monomer (Sigma Chemical) and 0.1 M tetrabutylammonium tetrafluoroborate, dissolved in redistilled acetonitrile. Ultra high purity argon was bubbled through the electrolyte to remove any oxygen. PMT films, $1.4\,\mu\mathrm{m}$ thick (measured by SEM), were polymerized at $10\,\mathrm{mA\,cm^{-2}}$ by passing $0.25\,\mathrm{C\,cm^{-2}}$ five times ($1.25\,\mathrm{C\,cm^{-2}}$ total), with five minute periods at open circuit between depositions. The PMT-coated electrode was then rinsed in acetonitrile and dried under vacuum at 50° C. Based on the cross-sectional area and thickness, the volume of the film was $9.95 \times 10^{-6}\,\mathrm{cm^3}$, containing a maximum of $4.52 \times 10^{-5}\,\mathrm{g}$ of material assuming 100% efficiency of polymerization. The polymer was in its conductive state at this point, containing BF_4^- dopant anions. Since the electrolytes were to contain $AlCl_4^-$, we also tried to prepare PMT with a $AlCl_4^-$ counter-ion. Although we were able to form PMT with two different tetrachloroaluminate-containing salts, coverage and adherence to the substrate were poor. Therefore, we were confined to using the BF_4^--doped PMT.

Electrolytes containing $SOCl_2$ and SO_2Cl_2 were prepared after redistilling each solvent over lithium ribbon while bubbling dry argon, then dissolving anhydrous $LiAlCl_4$ (Anderson Physics) to form a

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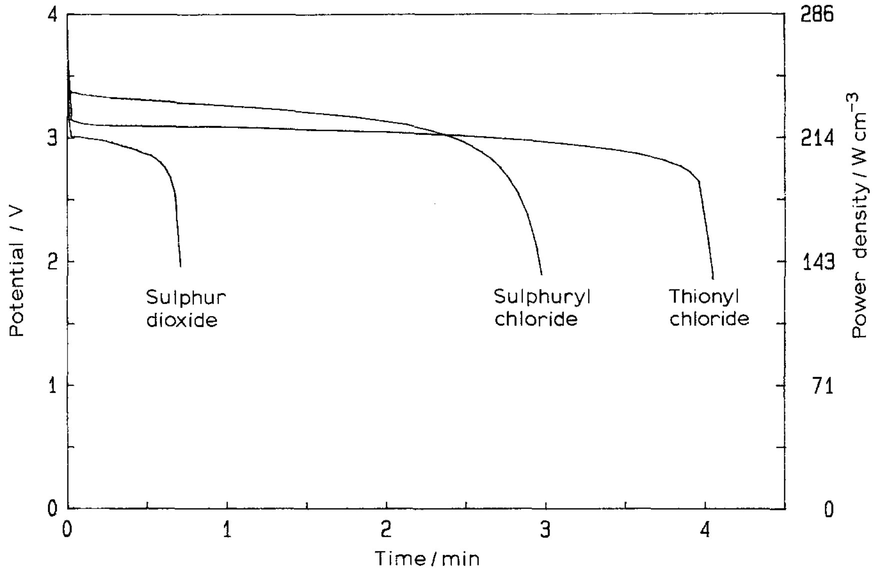

Fig. 1. Potential and power density of 1.4 μm PMT as a function of discharge time at 10 mA cm^{-2} constant current in various electrolytes.

1.0 M solution. A small amount of excess anhydrous LiCl was then added to ensure solution neutrality. $Li(SO_2)_3AlCl_4$ electrolyte was prepared with $LiAlCl_4$ and excess anhydrous liquid SO_2 by combining them in an evacuated Teflon vessel that was able to withstand pressure. After dissolution of the salt, excess SO_2 was slowly bled off through a bubbler containing halocarbon oil. The resultant electrolyte was between 3 and 3.5 SO_2 molecules per $LiAlCl_4$ molecule as measured by weight.

Electropolymerization, galvanostatic discharge/charge, and data collection were under the control of a Hewlett Packard HP 86 computer connected to a PAR model 173 potentiostat/galvanostat with a model 276 plug-in interface, and a Fluke 8842A digital multimeter. The experimental cell was a 125 ml European flask flooded with 20 ml of the electrolyte of interest, a large lithium counter electrode and a lithium reference electrode.

A $Li|Li(SO_2)_3AlCl_4|PMT$ cell is a rechargeable system, performing better when BF_4^- is replaced with $AlCl_4^-$ as the dopant anion [4]. It has been suggested that improved coulombic efficiency of poly alkylthiophenes over the first few cycles is also due to structural changes in the polymer matrix, resulting from swelling of the polymer with electrolyte and the accumulation of retained dopant ions [3]. For these reasons, in the experiments with SO_2 electrolyte, BF_4^- was first undoped from the PMT by holding the cell potential at 3.0 V. The cell was then held at 3.8 V to dope the PMT with $AlCl_4^-$ from the electrolyte. After running a discharge, recharge of the PMT electrode was done at 0.1 mA cm^{-2} constant current to a 3.8 V cut-off. Soon after charging, cell potential in $Li(SO_2)_3AlCl_4$ electrolyte was about 3.6 V. After equilibration overnight, open circuit cell potential stabilized at 3.4 V. Cells with the $SOCl_2$ (3.55 o.c.v.) and SO_2Cl_2 (3.83 o.c.v.) electrolytes were used as non-rechargeable cells, so a fresh BF_4^--doped PMT electrode was required for each run. We tried to increase the dopant level by

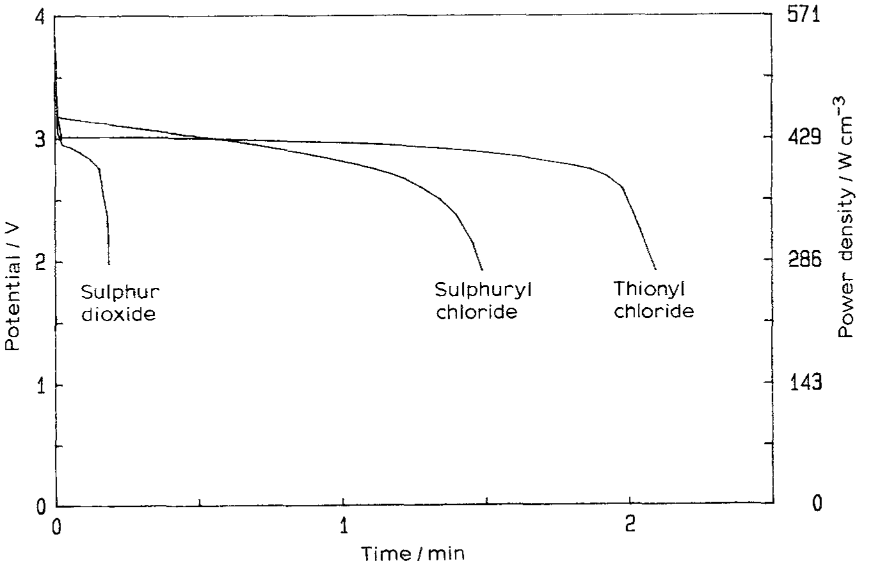

Fig. 2. Potential and power density of 1.4 μm PMT as a function of discharge time at 20 mA cm^{-2} constant current in various electrolytes.

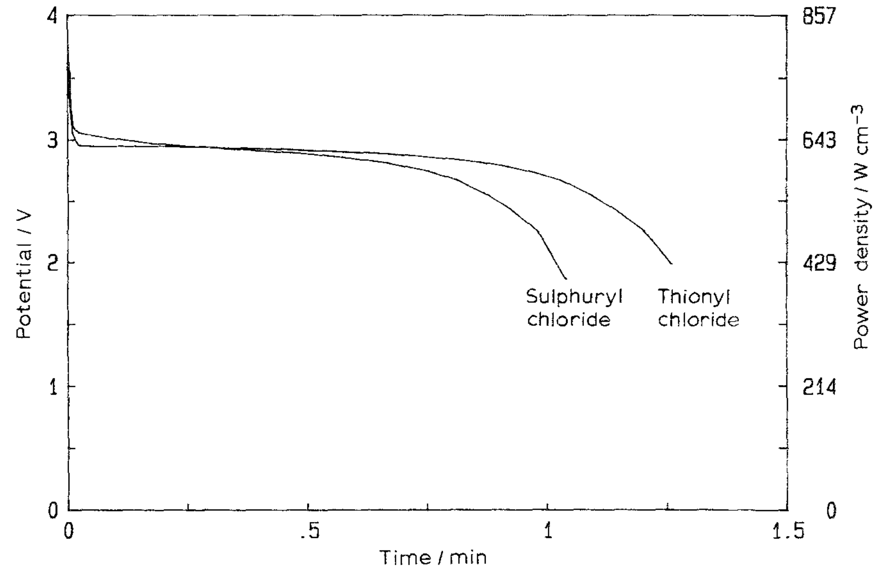

Fig. 3. Potential and power density of 1.4 μm PMT as a function of discharge time at 30 mA cm^{-2} constant current in $SOCl_2$ and SO_2Cl_2 electrolytes.

holding cell potential at 3.8 V for 30 min in the thionyl chloride-based electrolyte, presumably further doping the PMT with $AlCl_4^-$. Charge delivered from polymer undoping is insignificant compared to that derived from electrolyte reduction, but we surmized that this doping process might favourably alter structural and performance characteristics (as is observed in SO_2 electrolyte). However, no change in performance was observed, indicating that at high rates of discharge, the dopant anion and level of doping had little effect on discharge capacity in $SOCl_2$ electrolyte.

3. Results and discussion

Operating potential and volumetric power density are shown for constant current discharge of PMT at 10, 20 and 30 mA cm^{-2} in Figs 1–3, and energy densities are given in Table 1. The values represent the average of several discharges. Bare platinum and bare glassy carbon electrodes were used as controls. When discharged at 10 mA cm^{-2}, they gave no capacity in $SOCl_2$, and even at a lower current density of 1.0 mA cm^{-2}, only 0.8 min of discharge was obtained to a 2.0 V cut-off. Thus, none of the capacity observed for the PMT electrodes can be attributed to electrolyte penetration through the film with subsequent reduction at the substrate on which the film was polymerized.

Table 1. Capacity of 1.4 μm thick PMT at various discharge rates in SO_2, $SOCl_2$, and SO_2Cl_2 electrolytes

Solvent	*Rate/ mA cm^{-2}*	*Discharge time/min*	*/Ah g^{-1}**	*/mAh cm^{-2}*	*/Ah cm^{-3}*
SO_2	10	0.72	0.189	0.120	0.857
	20	0.20	0.105	0.067	0.476
$SOCl_2$	10	4.10	1.075	0.683	4.883
	20	2.10	1.101	0.700	5.002
	30	1.25	0.983	0.625	4.466
SO_2Cl_2	10	3.04	0.797	0.507	3.621
	20	1.54	0.807	0.513	3.668
	30	1.03	0.810	0.515	3.680

* Based on theoretical maximum deposited.

Although the sulphuryl chloride electrolyte provided the highest operating potential during the initial part of a discharge, the thionyl chloride-based electrolyte delivered the highest cell capacity at all current densities. Also, operating potential was most constant in the $SOCl_2$ electrolyte. Lowest operating potential and shortest discharge times were observed in the SO_2-based electrolyte (Figs 1 and 2). At the 20 mA cm^{-2} rate (Fig. 2), PMT in $SOCl_2$ was discharged for nearly 2 min at an operating potential of 3.0 V and 429 W cm^{-3} power density. At 30 mA cm^{-2} (Fig. 3), PMT delivered about 600 W cm^{-3} at a potential of 3.0 V in both $SOCl_2$ and SO_2Cl_2 for at least 0.5 min. At the 10 and 20 mA cm^{-2} discharge rates, PMT in $SOCl_2$ had a capacity of about 1.1 Ah g^{-1} (Table 1). This is comparable to the results reported by Calvert *et al.* [5] for 50 to 330 μm thick films of poly(acetylene) in $SOCl_2$. In flooded cells, at discharge rates of 12.5 and 25 mA cm^{-2}, they observed capacities of 1.37 and 1.06 Ah g^{-1}, respectively. A BET surface area of 4.13 m^2 g^{-1} has been measured for PMT [4], which is low compared to surface areas of 60 to 1500 m^2 g^{-1} which is typical for porous carbon electrodes. Thus, the high energy density of PMT cannot be explained as electrolyte reduction on a high surface area material. One possibility is that PMT presents a highly catalytic surface which facilitates charge transfer during reduction of electrolyte.

By comparison, constant current discharge in SO_2 electrolyte is poor at high current densities. However, PMT performs well at high current for short pulses, and is able to be recharged for many cycles in this electrolyte. This would be the preferred system if only short pulses were required, and a period for recharge were allowable. Figure 4 demonstrates this application for pulses of four second duration at 25 mA cm^{-2} with one second periods at open circuit between pulses. Cell potential at the end of each pulse is shown, each

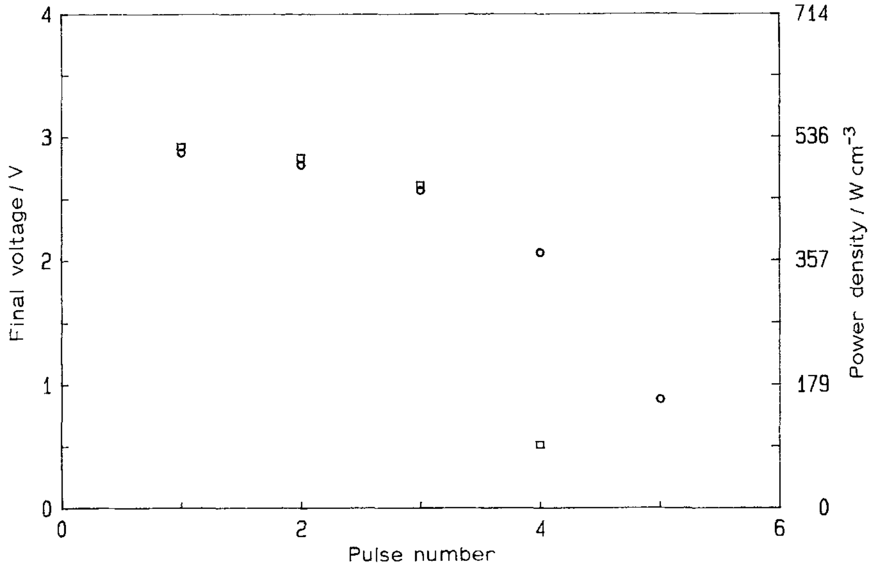

Fig. 4. Final potential of PMT with multiple 4 s, 25 mA cm^{-2}, pulses with one second rest periods in Li(SO$_2$)$_3$AlCl$_4$ electrolyte. Second (square) and 35th (circle) pulse sets, with recharge to a 3.8 V cut-off at 0.2 mA cm^{-2}.

cycle (set of pulses) ending when cell potential fell below 2.0 V. Cell recharge was at 0.2 mA cm^{-2} to a 3.8 V cut-off. The cell was cycled 35 times, each cycle delivering four or five 25 mA cm^{-2} pulses. The first three pulses of each set were very reproducible, with a final potential of between 2.9 and 2.6 V, corresponding to power densities of 518 to 464 W cm^{-3} of PMT, respectively. At a lower rate of 15 mA cm^{-2}, eight pulses were possible to the 2.0 V cut-off, the first seven being reproducible from cycle to cycle. Final potential of the first six pulses ranged from 3.0 to 2.7 V (321–289 W cm^{-3}, respectively). Although shorter in duration, these pulses provided power densities comparable to those obtained at constant current in SOCl$_2$ and SO$_2$Cl$_2$ electrolytes, yet were reproducibly repeated over many cycles.

4. Conclusion

Very thin films of PMT were able to be discharged at high current densities in SO$_2$, SOCl$_2$ and SO$_2$Cl$_2$ electrolytes. Power densities of 600 W cm^{-3} for 0.5 min and 429 W cm^{-3} for nearly 2 min were obtained for 1.4 μm thick PMT electrodes in SOCl$_2$. In SO$_2$-based electrolyte, PMT is rechargeable, and multiple 4-second pulses at about 500 W cm^{-3} were delivered for many cycles.

Thionyl chloride-based electrolyte would be a preferred choice for a single, high capacity cell discharge. The sulphur dioxide-based electrolyte would be useful as a rechargeable system, but discharge capacity is lower than in either SOCl$_2$ or SO$_2$Cl$_2$. The stability of PMT in the oxyhalide electrolytes was not studied, but we have observed it to be stable in the SOCl$_2$ electrolyte over a period of five days. Long term stability of PMT in these electrolytes is questionable, but this and other polymers could be attractive if used for bipolar reserve cell applications. If used in conjunction with ionically conducting polymer electrolytes, a high power solid state cell is possible.

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