

ELECTROCHEMICAL STUDIES OF P3-MT ELECTRODES IN $\text{LiAlCl}_4\text{-SO}_2$ ELECTROLYTE (EXTENDED ABSTRACT)

DONALD FOSTER*, BENJAMIN BAHARY, SOL GILMAN and MICHAEL BINDER

Power Sources Division, U.S. Army Electronics Technology and Devices Laboratory (LABCOM), Fort Monmouth, NJ 07703-5000 (U.S.A.)

Introduction

Requirements are emerging both within the Armed Forces and elsewhere for batteries with greatly expanded capabilities that can deliver unprecedented high power levels during relatively short time periods. Power Sources Division has therefore undertaken a bold technology initiative in developing novel, high energy density/power battery systems. A recent advance in electrolyte development is based on $\text{LiAlCl}_4\text{-SO}_2$ electrolyte complexes, first reported in a 1980 doctoral dissertation by Koslowski [1]. This electrolyte has ambient temperature specific conductivity of $0.13 \text{ ohm}^{-1} \text{ cm}^{-1}$ which is the highest known conductivity of any nonaqueous electrolyte.

Special attributes of conducting polymers such as high porosity, flexibility, electroactivity, and electronic and ionic conductivity offer considerable attractions for positive electrodes. After screening various conducting polymers for use as a cathode, we chose to investigate poly(3-methylthiophene) films. In order to study the possibility of using P3-MT as a cathode substrate for high pulse power applications in this electrolyte, we applied cyclic voltammetry, chronoamperometry, and a.c. impedance to study electrochemical performance of platinum rods coated with thin films of P3-MT in $\text{LiAlCl}_4\text{-SO}_2$ electrolyte. This particular combination of polymer cathode, $\text{LiAlCl}_4\text{-3SO}_2$ electrolyte, and lithium anode has not been studied previously.

Experimental

Experimental arrangements and methods of polymer preparation have been described previously [2]. Poly(3-methylthiophene) was prepared in 0.1 M solutions of tetrabutylammonium tetrafluoroborate in acetonitrile also containing 0.1 M 3-methylthiophene. The charge required to electropolymerize one micron of polymer was taken to be $0.33 \text{ coulombs cm}^{-2}$ [3].

* Author to whom correspondence should be addressed.

Electrochemical polymerizations were carried out at 1 mA cm^{-2} current at room temperature.

Results and discussion

Figure 1 shows a 100 mV s^{-1} cyclic voltammogram of a $0.4 \text{ }\mu\text{m}$ P3-MT film polymerized on a 0.07 cm^2 smooth platinum rod and also a scan of a bare, smooth 0.07 cm^2 carbon rod in $\text{LiAlCl}_4\text{-SO}_2$ electrolyte. Both voltammograms show a large reduction peak at 2.9 V . This reduction peak in the case of carbon has been shown to be due to SO_2 reduction [4]. We assume that in the case of the polymer also, the 2.9 V reduction peak is due to SO_2 reduction in/on the polymer. Reduction currents due to polymer anion undoping appearing at approximately 3.5 V [2] are negligible when compared with the 2.9 V peak reduction current intensity. For a bare carbon rod, as expected for diffusion controlled processes, a plot of peak reduction current plotted against the square root of scan rate was linear. However, for the polymer coated platinum rod, a plot of peak reduction current at 2.9 V was linear with the scan rate.

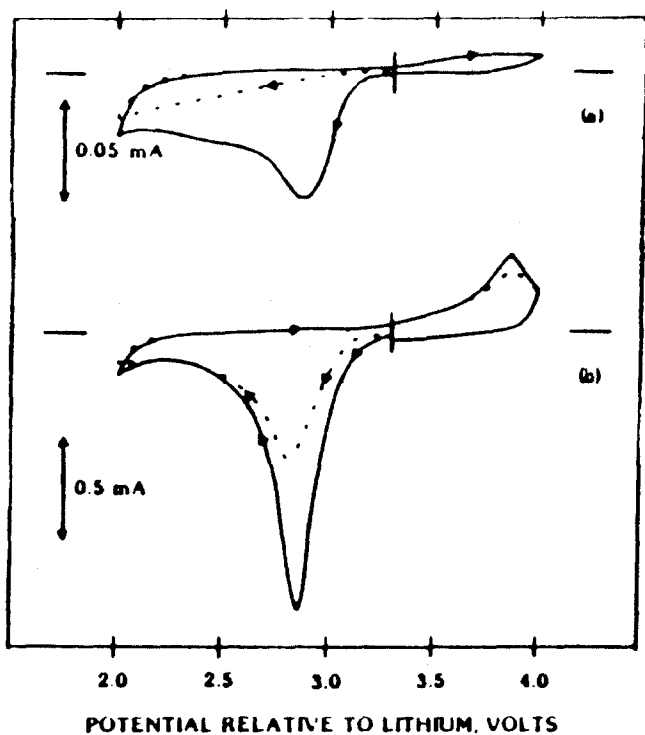


Fig. 1. Cyclic voltammogram of (a) bare carbon and (b) $0.4 \text{ }\mu\text{m}$ poly(3-methylthiophene) coated carbon rod.

Results of chronoamperometric experiments, where the potential was stepped from 3.7 V to 2.0 V on polymer-coated platinum rods, are shown in Fig. 2. It is of interest that currents as high as 1 A cm^{-2} can be achieved for the polymer electrode. This translates into a power density of 2 W cm^{-2} of apparent electrode surface. Stepping the current from 3.7 V to 3.1 V in 0.1 V increments has shown that there is a linear relationship between charge delivered in the first 5 ms and the magnitude of the potential step. This relationship is expected for a capacitance due to polymer undoping and double layer effects.

a.c. Impedance measurements were made on $2 \mu\text{m}$ P3-MT films held at 3.7 V vs. lithium reference in this electrolyte. The capacitance was 0.0059 F cm^{-2} . This value is typical of results found for polymer films in organic electrolytes [5 - 8].

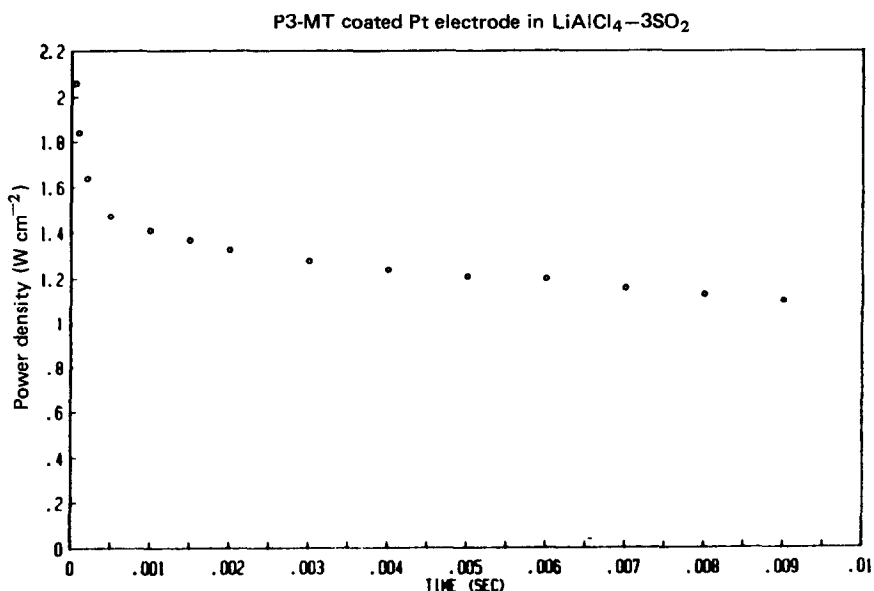


Fig. 2. Power vs. time for $1 \mu\text{m}$ poly(3-methylthiophene) coated Pt. The pulse step was from 3.7 to 2.0 V.

Conclusions

High current densities of 1 A cm^{-2} can be attained on thin poly(3-methylthiophene) electrodes in $\text{LiAlCl}_4\text{-3SO}_2$ electrolyte. Cyclic voltammetric studies have shown that SO_2 reduction is primarily responsible for the reduction current at low scan rates. Chronoamperometric and a.c. impedance studies show that for very short time scales, polymer undoping and double layer capacitance contribute to the total current.

Acknowledgements

This research was sponsored, in part, by SDIO/IST and managed by ONR under the auspices of Dr James J. Auburn of Bell Laboratories. We thank Dr Robert Mammone for his expert help and advice in initial experiments.

References

- 1 B. Koslowski, *Dissertation*, The University of Hanover, F.R.G., 1979.
- 2 R. J. Waltman, A. F. Diaz and J. Bargon, *J. Electrochem. Soc.*, **131** (1987) 1452.
- 3 D. Peramunage and M. Tomkiewicz, *J. Electrochem. Soc.*, **134** (1987) 1384.
- 4 R. Mammone and M. Binder, *J. Electrochem. Soc.*, **133** (1987) 1312.
- 5 B. J. Feldman, P. Burgmayer and R. W. Murray, *J. Am. Chem. Soc.*, **107** (1985) 872.
- 6 R. A. Bull, F. F. Fan and A. J. Bard, *J. Electrochem. Soc.*, **129** (1982) 1009.
- 7 S. W. Feldberg, *J. Am. Chem. Soc.*, **106** (1984) 4671.
- 8 A. F. Diaz, J. Isd. Castillo, J. A. Logan and W. Y. Lee, *J. Electroanal. Chem.*, **129** (1981) 115.