

PERFORMANCE OF MAGNESIUM POLYTHIOPHENE PERCHLORATE CELL

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The characteristics of electrochemically synthesised polythiophene perchlorate electrodes have been examined in the application of assembling a primary cell in conjunction with magnesium perchlorate solutions. The cell so assembled is found to behave satisfactorily and discharge characteristics are found to be influenced by the different doping levels in the polymer. This indicates the possibility of assembling a cell with different doped levels of conducting polythiophene, each giving a different open circuit voltage and capacity and energy density. The cell voltage is found to be appreciably stable and on prolonged storage, it is affected by self discharge characteristics.

Key words: Primary magnesium polythiophene cell, discharge studies

INTRODUCTION

Conducting polymers are an interesting class of synthetic metals which find application in a variety of technological avenues. Of all the avenues of applications, the use of these polymers as electroactive materials in batteries is quite attractive, as they possess reversibility in doping and undoping process accompanied by wide conductivity changes which in turn can be successfully monitored through their method of synthesis. Among the various polymers that are available now, polyacetylene is a well studied example in this direction delivering good characteristics [1-4], but suffers from scarce stability [4]. On the other hand, polymers based on heterocyclic monomers such as thiophene or pyrrole possess better stability and can be electrosynthesised in a cleaner and stable form [5-6]. Studies on these polymers relating to the application in battery systems are emerging [7-9] and polythiophene is a better and attractive candidate. The possibility of using polythiophene both as anode and cathode or as cathode in conjunction with metals like Li has been recently reported leading to a secondary cell. However, there is no report on the use of this polymer in a primary cell application and this paper deals with the possibility of assembling such a cell.

EXPERIMENTAL

Materials

Thiophene (Aldrich), acetonitrile (GR E Merck), NaClO_4 (Riedel) were used after purification through standard procedures. Stainless steel (SS) mesh was used as current collector and acrylic container was used to pack the cell.

Preparation of polythiophene electrode

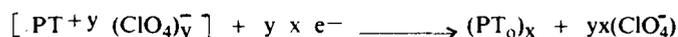
Polythiophene was grown on a SS mesh by electro-oxidation from the monomer in a degased acetonitrile containing NaClO_4 as electrolyte. The electrochemical synthesis was carried out as reported earlier [10]. Doping and redoping were also carried out as described previously [11]. Doping level for $y = 0.10$ to $y = 0.28$ was imparted by careful electrosynthesis.

Cell assembling and evaluation

Polythiophene grown on SS mesh (10 cm^2) which serves as current collector was employed as cathode active material and a magnesium plate (10 cm^2) was used as anode. The electrolyte employed was 1M aqueous magnesium perchlorate solution. The electrodes were sandwiched on both sides with a cellophane paper which served as the separator and packed in an acrylic container. The discharge characteristics were studied at different current densities for different doping levels.

RESULTS AND DISCUSSION

Polythiophene doped with perchlorate, $\text{PT}(\text{ClO}_4)_y$ can act as electroactive material because of its metallic behaviour. Besides, doping process can be reversed and reintroduced and such phenomenon can be equated to charging-discharging reaction of a battery system. In this present case, $\text{PT}(\text{ClO}_4)_y$ can be used as cathode active material, as a result of dedoping and redoping process with ClO_4^- ion. The release of ClO_4^- ion during dedoping can be considered as a discharge reaction of a given cathode which can be represented as follows:



where

y represents the dopant level of the polymer
 x represents the number of repeat units in the polymer
 PT_0 represents neutral polythiophene possessing no counter ions, assuming a complete discharge.

Polythiophene perchlorate electrode [$\text{PT}(\text{ClO}_4)_y$] of varying dopant level (y) when coupled with magnesium anode gives rise to different open circuit voltages (OCVs). Fig. 1 shows the different OCVs obtained with respect to varying dopant levels of conducting polythiophene. It can be seen that from $y = 0.1$ to $y = 0.22$, there is a sharp increase in OCV and after a level at $y = 0.25$, the increasing trend is rather slow. It indicates that electrochemical potential of $\text{PT}(\text{ClO}_4)_y$ cathode can be varied over a relatively large range depending on the degree of oxidation (y).

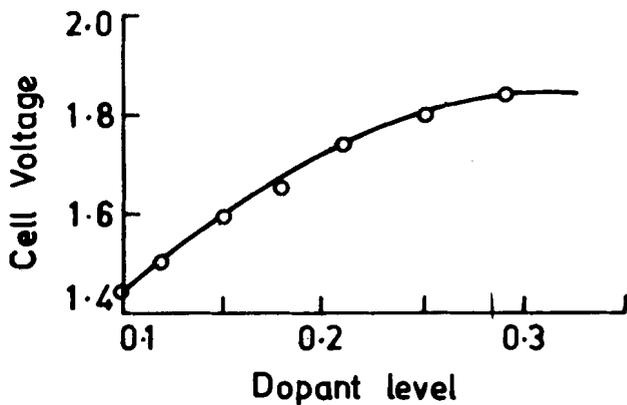


Fig.1: Open circuit voltage as a function of dopant level

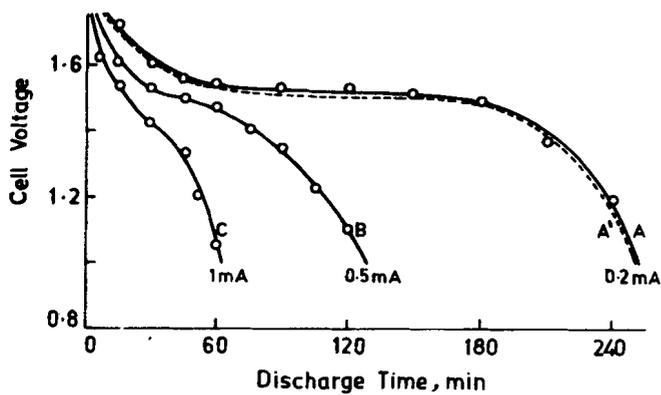


Fig.2: Discharge of Mg/PT(ClO₄)_{0.25} cell

Fig.2 represents the discharge characteristics of the cell Mg/aq. Mg(ClO₄)₂/PT(ClO₄)_{0.25} at different currents. It can be seen that an operating voltage of 1.5V is obtained at different discharge rates studied. The curve depicted by curve A (0.2 mA) delivers a capacity of 16.2 Ah/kg of cathode material. Curves B and C show the discharge behaviour, when the cell is discharged at higher current densities, namely 0.5mA and 1mA respectively. At such high discharge rates, the discharge time corresponds to 2 hr and 1 hr respectively with the decrease in flat voltage plateau.

Fig.3 shows the discharge characteristics of Mg [aq.Mg(ClO₄)₂] PT(ClO₄)_{0.18} at different current densities. An operating voltage of 1.3V is obtained at this doping level. $y = 0.18$ is 8.8 Ah/kg of cathode material. The discharge behaviour shows similar trend at higher current densities.

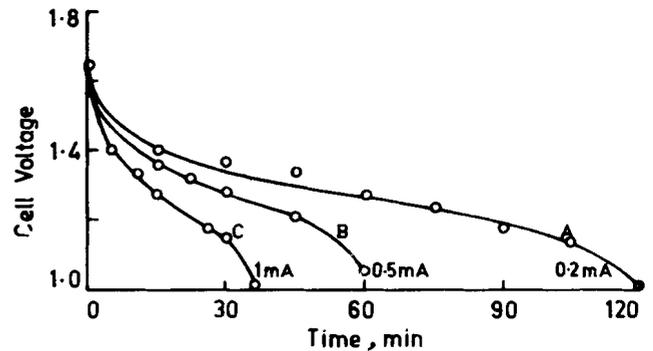


Fig.3: Discharge of Mg/[PT(ClO₄)_{1.8}] cell

Fig.4 presents the discharge characteristics for Mg/aq. Mg(ClO₄)₂ PT(ClO₄)_{0.12}. All the curves show that the discharge duration is comparatively shorter than in the previous cells. In this case, the maximum discharge time obtained is 1 hr which confirms that lowering of doping levels of the cathode under study lowers the performance.

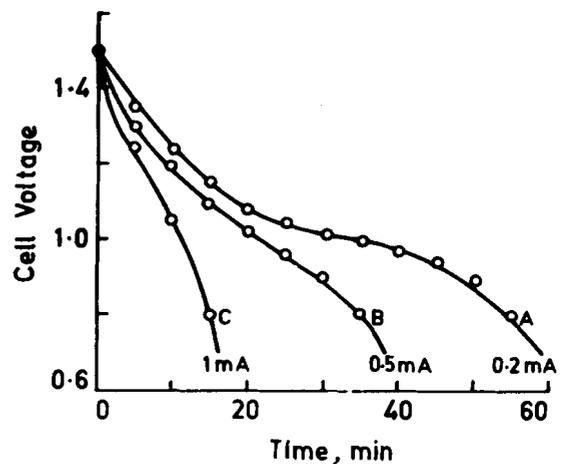


Fig.4: Discharge of Mg/PT(ClO₄)_{0.12} cell

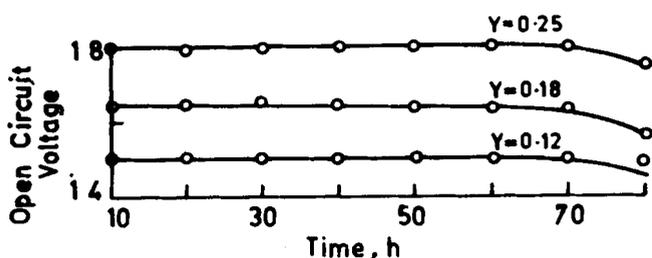
All these discharge curves for the cells under different chemical configurations indicate that an appreciable working voltage is obtained only at higher dopant levels. Table I shows the increase in trend of capacities of the cells with respect to dopant levels in polythiophene. This indicates the possibility of assembling cells of varying capacity by altering the dopant levels in the conducting polythiophene, a salient feature in cells based on conducting polymers.

TABLE-I: Characteristics of Mg [aq.Mg(ClO₄)₂] PT(ClO₄)_y cells

Sl.No.	Dopant level y	Capacity A.hr/kg	Energy density Whr/kg
1	0.25	16.2	24.3
2	0.18	8.8	11.55
3	0.12	4.0	4.4

Another important observation made in this investigation is the reusability of discharged polythiophene electrode. After discharge, the polythiophene electrode can be redoped externally to the same dopant level [11] and recharged. Curve "A" in Fig.2 shows one such discharge characteristic of redoped polythiophene. It can be seen that a similar discharge trend is followed as in curve "A". It should also be noted that such redoping and recharging is possible for number of times which is due to the reversibility of doped and undoped state in polythiophene.

The stability of the cell is another important factor to assess the stability of polymer electrode. The stability of electrode here under study has been examined by following time dependence of the OCVs of a charged Mg [aq.Mg(ClO₄)₂] PT(ClO₄)_y cell. Fig.5 illustrates the results obtained for dopant levels studies. It can be seen that OCV remains constant for 72 hours and falls slowly. The fall of OCV after 10 days has indeed been sharp which can be accounted for slow self discharge characteristics of PT(ClO₄)_y electrode

Fig.5: Stability of Mg/[PT(ClO₄)_y]_x cell

Such an observation is consistent with the self discharge characteristics of PT(ClO₄)_y even in nonaqueous media [9]. This is also similar to even polyacetylene perchlorate electrode in lithium cells too.

As seen from the above characteristics of polythiophene perchlorate it can be summarised that coupling of conducting PT(ClO₄)_y electrode with magnesium anode forms a primary cell giving rise to a maximum working voltage of 1.5V. Besides, the polymer electrode can be used in secondary cells, as a result of repeatability in doping-undoping cycles.

CONCLUSION

Cells of different chemical configurations Mg [aq.Mg(ClO₄)₂] PT(ClO₄)_y have been assembled with varying dopant levels (y) of conducting polythiophene giving rise to OCV in the range of 1.5 - 1.8V. The maximum capacity obtained is 16.2 Ah/kg.

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