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EFFECT OF POLYMERIZATION CURRENT DENSITY ON THE PERFORMANCE OF ZN AND CONDUCTING POLYMER BASED RECHARGEABLE CELLS

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ABSTRACT

Recent years, polypyrrole (PPy) has identified as a extensively studied conducting polymer (CP). Although there are several early studies on PPy based rechargeable cells, Lithium (Li) based polymer rechargeable cells have been dominated for a long time. Non-ecofriendliness, disposal problems, cost are the major drawbacks of Li based rechargeable cells. Hence Zn has been reported as a worthy consideration to replace Li. Zn has been identified as a material with ecofriendliness and excellent electrical conductivity. In this study, preliminary work of the effect of polymerization current density on the performance of Zn based rechargeable cells is reported. The cells were fabricated in the array of Zn as anode / PVdF:PC:EC:ZnTF gel polymer electrolyte / PPy cathode doped with a surfactant anion. Cells were tested for their cycling ability by using cyclic voltammetry, continuous charge-discharge tests and electrochemical impedance spectroscopy test. In these cells, maximum open circuit voltage of 1.0 V was obtained for 2.0 mA cm^{-2} current density. Also current density 2.0 mA cm^{-2} has highest capacity value of 0.03288 F. Better discharging characteristic also obtained for the same current density. Form the results obtained it is evident that PPy prepared with high current density are more suitable as a cathode materials in rechargeable cells.

Keywords: Polypyrrole, Cyclic Voltammetry, Rechargeable cells, Surfactant, Electrochemical Impedance Spectroscopy

1.0 INTRODUCTION

Most widely studied CPs are Polyacetylene (PA), Polypyrrole (PPy), Polythiophene (PT) and Polyaniline (PANI). These polymers have several advantages including stability, easy preparation, high conductivity, flexibility, high optical response and non-toxicity[1]. CPs have

been identified as promising candidates for cathode materials in rechargeable cells since they can be easily synthesized by using chemical or electrochemical method. In the past few years, many different types of CPs such as PA, PPy, PT have been widely studied as cathode material for Li rechargeable cells[2]. Among those PPy has received more attention due to its superior electro activity, good electrical conductivity and chemical stability[3]. Lithium based cells have some safety issues, including highly reactivity environment hazards in disposing[4]. Li can be replaced with metals like Zn, Cu and Mg. Out of them Zn is an excellent material for battery application due to its low toxicity, low cost, high availability, high stability[5]. In this study, effect of polymerization current density on the performance of Zn and PPy based rechargeable cells is reported.

2.0 EXPERIMENTAL

2.1 Preparation of cathode

PPy films were prepared using 0.1 M Pyrrole (ALDRICH) monomer and 0.05 M Sodium Dedecylbenzenesulfonate (SDBS, ALDRICH). PPy:DBS films were electrochemically polymerized on to a stainless steel(SS) electrode galvanostatically using a three electrode set up. An Ag/AgCl and Pt wire were used as reference and counter electrodes respectively and the SS electrode was used as the working electrode. The polymerization electrolyte was an aqueous solution of PPy and SDBS. Three different films were prepared at current densities 1.00, 1.50, 2.00 mA cm^{-2}. PPy film thickness was calculated with the assumption of charge density of 240 mC cm^{-2} provides a 1 μm thick film.

2.2 Preparation of the gel polymer electrolyte

Polyvinylidenefluoride (PVdF, ALDRICH), Ethylene Carbonate (EC, ALDRICH), Propylene Carbonate (PC, ALDRICH) and Zinc Trifluoromethanesulfonate (ZnTF, ALDRICH) were used as the starting materials for preparing gel polymer electrolyte. Equal weights of PC and EC were measured and were thoroughly mixed. Then PVdF was added to the mixture and stirred for 30 minutes. Then required amount of ZnTF was added to the mixture and the new mixture was stirred another 30 minutes. After that solution was heated at 130 °C for 15 minutes. The hot, viscous mixture was taken in between two well cleaned glass plates and pressed one glass plate by another to form a thin electrolyte layer.

2.3 Fabrication of the cells

The PPy: DBS film deposited on the SS electrode was used as the cathode of the cell. A circular shape membrane was cut to the size of the SS cathode from the electrolyte was added on to the PPy: DBS film and the same size Zn disk was used as the anode. Cells were fabricated in the configuration of Zn / PVdF:PC:EC:ZnTF / PPy:DBS.

2.4 Characterization of the cells:

First, the open circuit voltages (OCVs) of the cells were measured. Cyclic voltammetry tests were performed within the potential window 1.0 V to 0.01 V using a computer controlled Potentiostat / galvanostat (Metrohm-AUTOLAB) at the scan rate of 0.5 mV s^{-1}. This procedure was repeated for all current densities. Thereafter these cells were tested for their ability to withstand for continuous charge and discharge cycles. In this test charging cutoff voltage was held at 2.0 V and discharging cutoff voltage was held at 0 V. First, cells were galvanostatically discharged to 0.5 V, immediately subjected to a galvanostatic charge up to 2.0 V and maintained at that potential until the desired current was reached and then discharged using a computer controlled charge-discharge setup. Charging-discharging current was kept at 0.075 mA. Electrochemical impedance spectroscopy(EIS) measurements were performed using frequencies ranging from 400 kHz to 10 mHz using Metrohm Frequency Response Analyzer (M101). Measurements were taken at time intervals of 15 minutes. These tests were repeated for all cells fabricated with different PPy current densities.

3.0 RESULTS AND DISCUSSION

Table 1: OCVs of the cells with respect to current density used

Current Density (mA cm^{-2})	Open Circuit Voltages (mV)
1.0	890
1.5	940
2.0	1008

The observed OCVs of the cells with respect to varying current densities are shown in table 1. It can be clearly noticed that with the increase in current density, open circuit voltage has been increased. This result proposes to choose higher current densities for CP cathode to obtain higher voltage output from the cells. When the oxidation and reduction processes of the conducting polymer electrode are being carried out, electrochemical reactions will take

place on the CP electrode due to ion movements. Electrochemical reactions on the cathode and anode can be formulated as follows,

At the cathode: $2PPy^{-}DBS^{+} + Zn^{2+} + 2e \Leftrightarrow 2PPy^{0}Zn(DBS)_2$ [1]

At the anode: $Zn \Leftrightarrow Zn^{2+} + 2e^{-}$ [2]

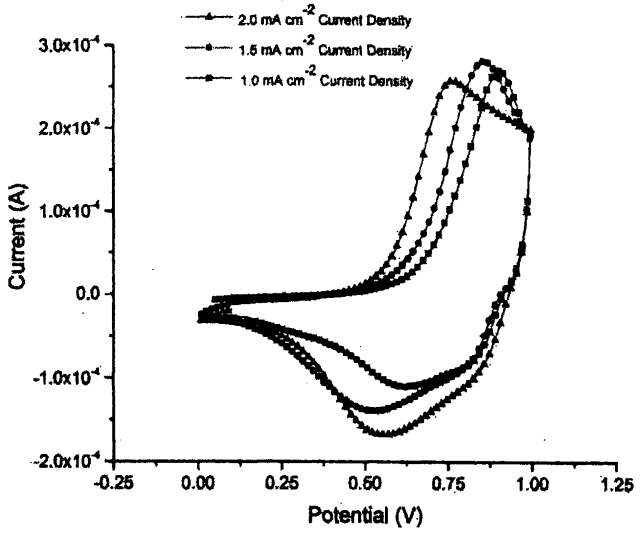

Figure 1: Cyclic voltammograms (CV) obtained for Zn/GPE/PPy: DBS cells having PPy cathode of 1μm thickness with respect to polymerization current densities scan rate 5 mVs^{-1}

The cathodic peak of the CV is assigned to the reduction and the anodic peak is assigned to the oxidation at which redox reactions of the cells corresponds to discharging and charging. If the reactions are fully reversible, the ion insertion and desertion to the cathode during charging and discharging should occur at identical potentials at each cycle. Hence, the corresponding peaks should appear at the same potential values resulting zero peak separation. Here the cathodic peaks and anodic peaks appeared well but peak separation of cells are very smaller. It is seen that the current density also affecting the peak separation. When current density increased, peak positions shift to the lower potentials in both peaks. But the corresponding capacity of the cells increased. The amount of charge available during the cell reactions were calculated from the area of the CVs. They are given in the Table 2.

Table 2: Differential capacity variation with current density

Current Densities (mA cm^{-2})	Differential capacity (F)
1.00	0.02236
1.50	0.02844
2.00	0.03288

During charging-discharging cells were tested for their ability to withstand in continuous charge discharge cycling. Figure 2 shows discharging capacity variation with the cycle number for the cells having cathodes of different current densities.

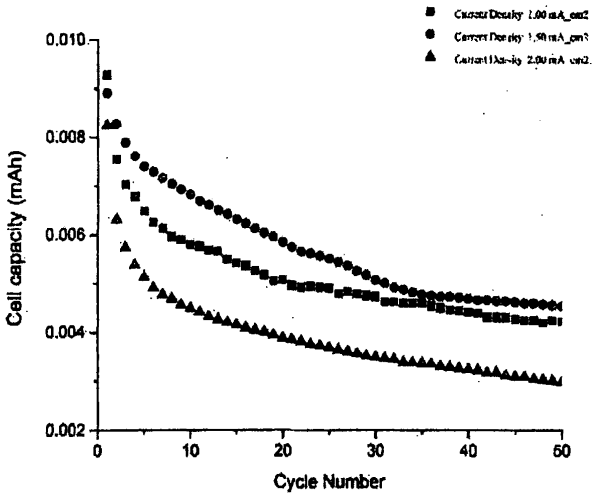

Figure 2: Cell capacity variation with the cycle number for the cells having cathodes prepared with different current densities

According to the figure 2, it is evident that when the polymerization current density increased from 1 to 2 mA cm^{-2}, the cell capacity has increased by 83%. Also after 50 cycles, the cell with 2.0 mA cm^{-2} retained 60% from its original capacity while other two having only 56% and 50% respectively. Impedance measurements obtained relevant to the different current densities are given in figure 3.

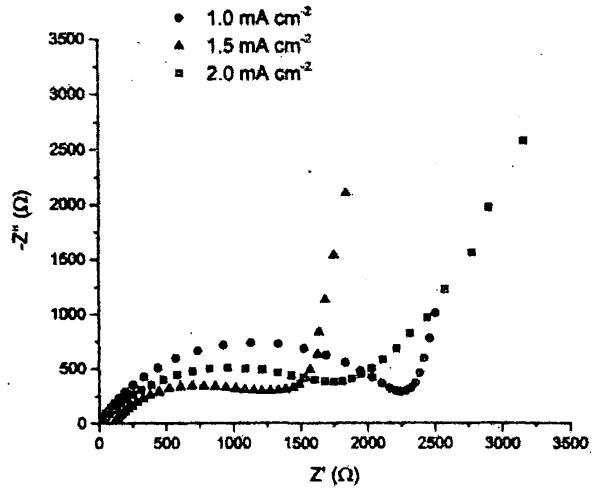

Figure 3: Impedance plots taken at 15 minutes after fabrication of the cells having PPy films prepared with different current densities

According to theory, semi-circle arc at intermediate frequencies represents charge transfer resistance. High frequency intercept of the plot gives the bulk electrolyte resistance. Low frequency part corresponds to the diffusion process and charge accumulation in PPy cathode. It seems that electrolyte resistance of all cells has not changed. This confirmed the stability of the gel polymer electrolyte. However the charge transfer resistance of the three cells differ very much. This may be due to unwanted reaction and forming passivation layers.

4.0 CONCLUSION

Even though this is a preliminary study, the results predict the possibility of fabricating non Li rechargeable cells for applications. Zn rechargeable cells with appreciable performances could be fabricated using PVdF:EC:PC:ZnTF gel polymer electrolyte and PPy doped with DBS as cathode materials with open circuit voltage around 1.00V. It has been found that the performance of the cells can be increased by selecting a high current density during the polymerization of the CP cathode.

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