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CHARACTERIZATION OF RECHARGEABLE CELLS BASED ON CONDUCTING POLYMER/DODECYL SULPHONATE CATHODES OF DIFFERENT THICKNESS

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ABSTRACT

Currently there is a high demand for rechargeable cells due to flooding of consumer electronics. Among many materials which can use as cathodes in rechargeable cells, conducting polymers (CP) takes a prominent place. At present, there are many research works going on applying CPs as cathode materials. This study reports on the influence of the cathode thickness on the performance of CPs Polypyrrole (PPy) based rechargeable cells. Most of the reported CP base rechargeable cells are based on Lithium (Li). In this study attempts were made to apply Zinc (Zn) instead of Li as the anode. The PPy cathode doped with Sodium Dodecylsulfate (SDS) was synthesis on a stainless-steel (SS) electrode using galvanostatic method. Cells were assembled using Zn as the anode, gel polymer electrolyte as the separator, and PPy/DS as cathode. Cells were fabricated for four different thicknesses of PPy. Cyclic Voltammetry, Electrochemical Impedance Spectroscopy (EIS) and Continuous Charge Discharge tests were used to characterize the cells. The Open Circuit Voltage (OCV) measured was in between 0.951 V and 1.035 V and the highest capacity was 0.0536 F for the thicker film which is 1.5 μm. From the characterization of the cells it was reveled that better performance of Zn/GPE/PPy:DS cells can be obtain when thicker cathodes are engaged for the cell fabrication.

Keywords: Polypyyrrole, Cyclic voltammetry, Open circuit voltage, Electrochemical impedance spectroscopy.

1. INTRODUCTION

CPs have been tested as cathode materials in rechargeable cells[1,2,3]. Mostly tested polymer rechargeable cells were lithium (Li) based[1,2,3]. Although Li based cells are mostly used, they

have some drawbacks due to high reactivity of Li and difficulty in disposing. Therefore, alternative materials like Mg, Zn, Cu are being tested as positive electrode. CP PPy has being identified as a promising candidate as cathode materials in rechargeable cells due to its easy propagation, high conductivity and resistive to chemical reaction etc[1,2,3]. When PPy doped with different type of anions it behave differently. It has been reported that when PPy doped with surfactant anions the anion still dropped inside the polymer structure and redox process[4]. In this study, the effect of the thickness of PPy cathode doped with SDS was investigated on the performance of rechargeable cells fabricated with a gel polymer electrolyte.

2. EXPERIMENTAL

2.1 Preparation of Cathode

The monomer pyrrol (Aldrich) and SDS (Aldrich) were used for polymerization. The polymerization electrolyte solution was consists of 0.01 M pyrrole monomer and 0.05 M SDS. The solution was taken in to the glass flask of the three electrode configuration. Standard Ag^{+}/AgCl electrode was used as the reference electrode and a Platinum (Pt) wire was used as the counter electrode. PPy / DS film was prepared on a well cleaned SS which was used as the working electrode. Polymerization was carried out using galvanostatic method using current density of 1.0 $mAcm^{-2}$. Thickness of the PPy film was varied 0.5 to 1.5 μm.

2.2 Preparation of the gel polymer electrolyte

Polyvinylidenefluoride (PVDF, Aldrich), Zn trifluoromethanesulfate (ZnTF) (Aldrich), Ethylene Carbonate (EC) (Aldrich), Propylene Carbonate (PC) (Aldrich) were used for the preparation of gel polymer electrolyte. Required amounts of EC, PC were weighed. They were mixed and stirred until the EC dissolved in PC. The required amount of PVDF was measured and added to the above solution. The new solution was stirred magnetically about 30 minutes until the PVDF get dissolved. Finally the required amount of ZnTF was added to the above solution and stirred magnetically about 10 minutes. The complete solution was heated at 130 ^{0}C for 15 minutes. The hot mixer was pressed in between two glass plates. There by it was possible to obtain a bubble free thin film.

2.3 Fabrication of cells

The rechargeable cell was fabricated in a circular brass sample holder. The anode of the cell was a well cleaned Zn plate that matches with the size of sample holder and SS electrode. First a circular shape membrane was cut from the gel polymer electrolyte to the size of the SS electrode. A well cleaned doctor blade was used to cut and separate the membrane from the gel polymer electrolyte. Then it was smoothly laid on the PPy / DS film as the separator of the cell. Thereafter the well cleaned Zn anode was placed on the gel polymer separator. Next, the remaining SS electrode was placed carefully on the Zn anode and finally the cell was enclosed by the brass sample holder. The cells were characterized, first by measuring OCV then by cyclic voltammetry in a potential window of 1.0 V to 0.2 V, EIS measurements were obtained in the frequency range 400 kHz to 10 mHz in different time intervals during 6 hours. Continuous Charge Discharge tests were done in the range of 2.0 V and 0.5 V while keeping current at 7.5×10^{-5} A. This procedure was repeated for cells having different cathode thickness.

3. RESULTS AND DISCUSSION

The OCV measured for the Zn/GPE/PPy:DS cells fabricated with different PPy thickness are given in table 1.

Table 1: OCV variation of the cells with the thickness of PPy cathode

Thickness (μm)	OCV (V)
0.50	0.951
0.75	0.995
1.00	1.000
1.50	1.035

As shown in above table 1 the highest voltage was observe as 1.035 V for the thickness of 1.5 μm as well as the lowest voltage was observed as 0.951 V for the thickness of 0.5 μm. When the thickness was increase from 0.5 to 1.5 μm the voltage had increased by 0.084 V. Here all the cathodes in the cells were prepared using galvanostatic polymerization.

Figure 1 shows the cyclic voltermmograms (CVs) obtained for cells will different PPy thicknesses. According to that for the same thickness, peak position shift to more negative potentials with the cycle number. This may be due to change in the polymer structure with the cycling. Also it is visible that there is a shift in peak positions towards more positive

potentials when the film thickness is increased. This may be due to change in the diffusion length with the increase in the film thickness[5].

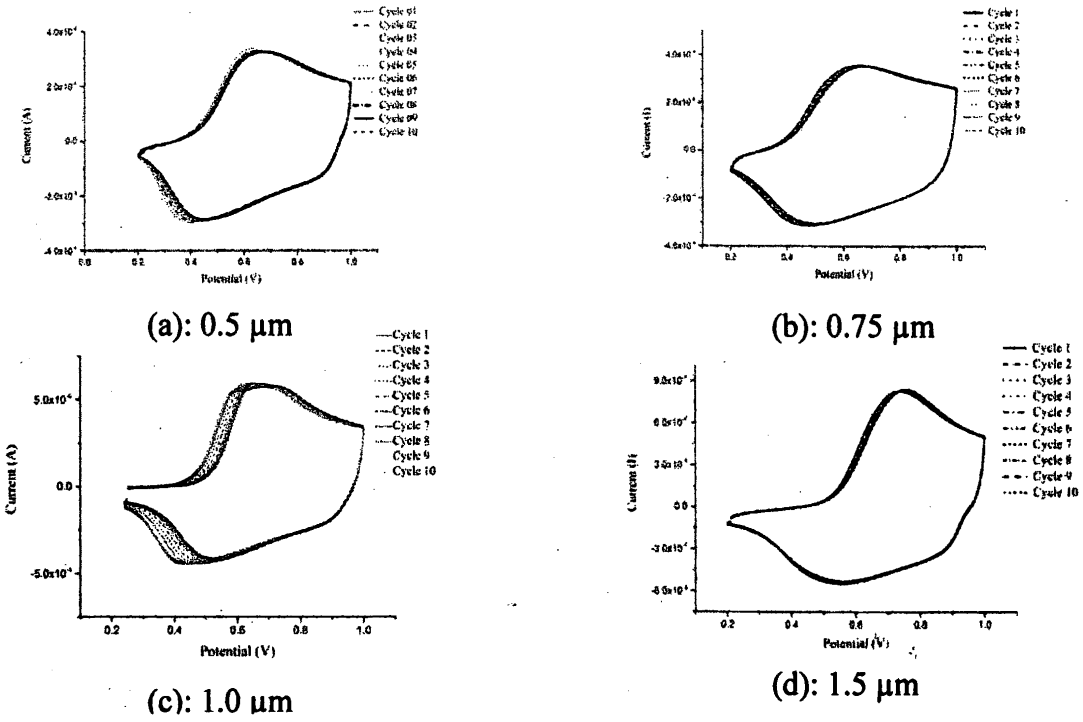

Figure 1: Cyclic Voltammograms of the cells according to cathode thickness. Scan rate $0.01 Vs^{-1}$

Figure 2 shows the CVs obtained for each cell at the 10^{th} cycle. Table 2 indicates the differential capacities of the cells for each thickness. It seems that differential capacity almost follow the thickness as in figure 2.

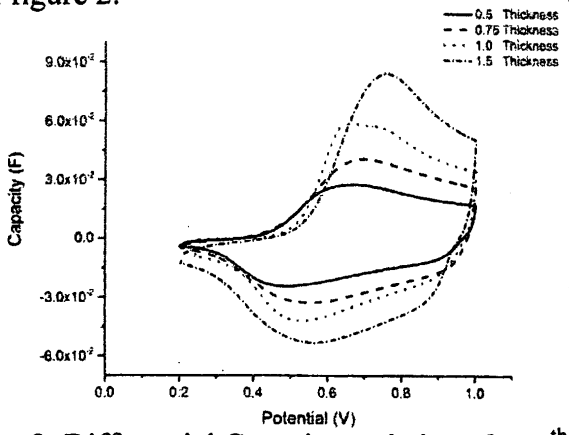

Figure 2: Differential Capacity variations for10^{th} CV

Table 2: Differential capacities of the cells obtain by figure 2

Thickness (μm)	Diff. Capacity (F)
0.5	0.0228
0.75	0.0325
1.0	0.0404
1.5	0.0536

Figure 3 shows the impedance plots obtained in different time intervals for cells having PPy cathode of different thickness

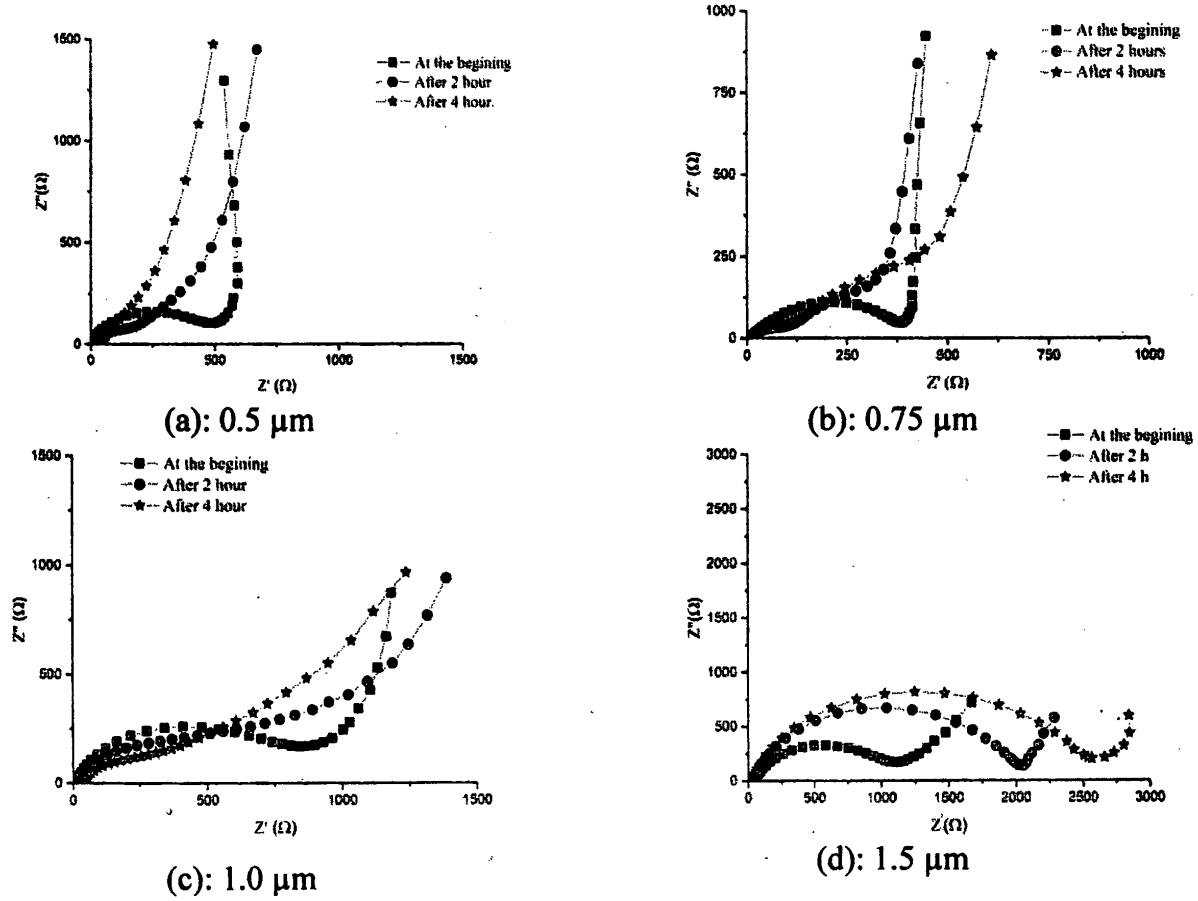

Figure 3: Impedance plot of Zn/GPE/PPy:DS for cathode in different thickness

According to theory, this type of system should have two semi circles and a spike. First semi circle at high frequency represent the bulk electrolyte resistance the second semicircle at middle frequency corresponds to the charge transfer resistance of electrolyte electrode interface and spike at low frequency is responsible for the diffusion process that take place in the electrodes[5]. The plot of 1.5 μm film follows the theory that with the time, value of the

charge transfer resistance increases due to formation of passivation layer as a result of unwanted reactions. At lower thickness this is not visible, it may occur due to mismatch of thickness at lower frequency. With the time, the cathodes with lower thickness have diffusion controlled kinetics, this may be a reason for the different of impedance plots at lower thickness.

Figure 4 shows the results of charging and discharging test for all thickness of cathode. According to that, charging time and discharging time for the thicker film take more time than other films. This is because of thicker films have more charges than thinner films. As shown in figure 5, discharging rate for thicker films is smaller than the other films. When the thickness is smaller, discharging rate has high values. This may occur due to short ion diffusion of thin films.

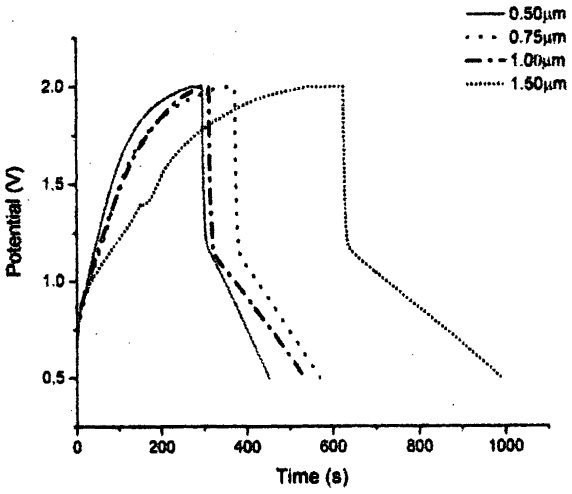

Figure 4: Charging Discharging curves of Zn/GPE/PP:DS cells having different cathode thicknesses

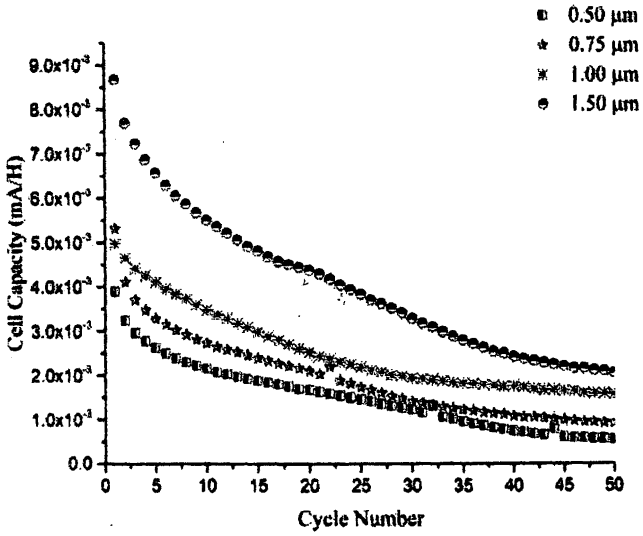

Figure 5: Discharging Capacity variation with the cycle number of Zn/GPE/PPy:DS cells having different cathode thicknesses

4. CONCLUTION

Rechargeable cells were fabricated using PPy with different thickness having GPE and Zn as the anode. It was found that for Zn/GPE/PPy:DS cells better performance can be obtained when they are fabricated with thicker PPy cathodes.

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