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INVESTIGATING THE EFFECT OF POLYMERIZATION CURRENT DENSITY OF CONDUCTING POLYMER CATHODE ON THE PERFORMANCE OF Cu BASED RECHARGEABLE CELLS

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ABSTRACT

Conducting polymers have been identified as a promising candidate as cathode material in rechargeable cells. It has been clearly identified that current density (j) used to polymerize thecathode has a great influence on the performance of polymer rechargeable cells. In this study, it is reported that preliminary work done on investigating the effect of polymerization current density on the performance of Cu based rechargeable cells. The cathode is a conducting polymer, polypyrrole (PPy). The gel polymer electrolyte was made with polymethylmethacrylate (PMMA), ethylene carbonate(EC), propylene carbonate (PC) and Copper trifluoromethanesulfonate (CuTF) as the salt. PPy films were galvanostatically polymerized on to a stainless-steel electrode. Then copper (Cu) rechargeable cells were assembled using a brass sample holder in the array of Cu/ Gel polymer electrolyte (GPE) / PPy. The effects of polymerization current density on the performance of rechargeable cells were investigated using cyclic voltammetry and continuous charge/discharge tests.

Keywords: Polypyrrole, Conducting Polymers, Cyclic Voltammetry.

1. INTRODUCTION

There has been a lot of interests on research and development of conducting polymer as a promising candidate for cathode material in rechargeable cells due to their favorable qualities such as wide range of electrical conductivity, mechanical flexibility and high thermal stability[1].

When preparing conducting polymer cathode, factors such as cathode thickness, charge density and current density should be considered[2]. Out of them current density is utmost important since it will directly effects for the cell characteristics such as open circuit voltage, capacity of the cell. To have high cycle life (charging – discharging time) and open circuit voltage simultaneously, selecting the most appropriate current density is vital in designing a polymer rechargeable cell. As the material for conducting polymer cathode, Lithium (Li) has been dominated in real world applications for a long period of time[3]. But Li batteries have severe health and safety problems and Li is highly reactive and disposal of batteries are not ecofriendly[4]. Copper (Cu) has been identified as a better material for the conducting polymer cathode since it is much ecofriendly while having favorable characteristics including excellent electrical conductivity, strength, hardness, ductility, low magnetic permeability and higher melting point(1083°C)[5]. In this study, the effect of polymerization current density of conducting polymer cathode on the performance of Cu based rechargeable cells is reported.

2. EXPERIMENTAL

2.1 Polymerization of conducting polymer film:

Sodium Dodecyl Benzene Sulphonate (SDBS, ALDRICH) and monomer-Pyrrole (ALDRICH) were used for polymerizations. The polymerization electrolyte was an aqueous solution of 0.05M SDBS and 0.1 M pyrrole monomer.

Three electrode configuration was used to polymerize the PPy film on to a stainless steel dies galvanostatically. In three electrode configuration, Ag/AgCl and Platinum (Pt) electrodes were served as reference and counter electrodes respectively.Stainless steel dice was used as the working electrode.

2.2 Preparation of the gel polymer electrolyte:

Polymethylmethacrylate (PMMA, ALDRICH), ethylene carbonate (EC, ALDRICH), propylene carbonate (PC, ALDRICH), copper trifluoromethanesulfonate (CuTF, ALDRICH) and Acetone (ALDRICH) were used as the materials for preparing gel polymer electrolyte. PMMA and acetone was initially taken into a weighing bottle and solution was magnetically stirred well 45 minutes. After removing the excess acetone, EC, PC and CuTF were added to the mixture and heated at 80 °C for 1 hour. The hot mixture was pressed in between two well cleaned glass plates and a bubble free thin film was obtained. Composition of the GPE was chosen as 22.5% PMMA: 30% EC: 30% PC: 17.5% CuTF by weights.

2.3 Fabrication of the cells:

Cells were fabricated using a brass sample holder. A copper (Cu) plate that was fit with thesample holder was used as the anode of the cell. PPy film deposited on the stainless steel dicewas used as the cathode. A circular shape membrane from the electrolyte was used as theseparator. Then cell was assembled in the structure of Cu / PMMA:EC:PC:CuTF / PPyDBS.

2.4 Characterizations of the cells:

First, open circuit voltages of the cells were measured. Then linear sweep voltammetry was applied to the cell from open circuit voltage to the -0.01V. Thereafter,full cycles were performed within the potential window 0.7V to -0.02V. Scan rate was kept at 0.5mV/s while step potential was at 0.5mV. This procedure was repeated for all current densities. Thereafter these cells were tested for their ability to withstand continuous charge and discharge cycles. When following the charge – discharge test charging cutoff voltage was held at 0.5V and discharging cutoff voltage was held at 0V while the charging – discharging current was kept at 0.025mA.

3. RESULTS AND DISCUSSION

The observed open circuit voltages (OCVs) with respect to current densities are shown in table 1 below.

Table 1: Open circuit voltages with respect to current densities used to polymerize PPy film

Current density (j/mAcm^{-2})	Open circuit voltage (mV)
1.00	182.0
0.75	139.0
0.50	101.5
0.25	98.0

It can be clearly notice that with the current density, open circuit voltage has been increased. This result proposes to choose higher current densities for conduction polymer cathode to obtain higher voltage output from the batteries.

When the oxidation and reduction processes of the conducting polymer electrode are being carried out, electrochemical reactions will take place on the conducting polymer electrodedue to ion movements.During charging and discharging of the cell, ion incorporation or emission occurs in PPy film[6, 7]. In this study PPy was doped with a large anion. It has been reported that when PPy is doped with large anions, cations are responsible for electrochemical reactions.[8]. Therefore,cations in the electrolyte of the cell fabricated in the configuration Cu/GPE/PPy are supposed to participate in the oxidation and reduction process of the PPy cathode. Electrochemical reactions on the cathode can be formulated as follows,

$$PPy^{+}DBS^{-} + Cu^{1+} \Leftrightarrow PPy^{0} + Cu(DBS)$$

$$2PPy^{+}DBS^{-} + Cu^{2+} \Leftrightarrow 2PPy^{0} + Cu(DBS)_2$$

At the same time, electrochemical reactions mentioned below will occur at anode.

$$Cu \Leftrightarrow Cu^{1+} + e^{-}$$

$$2Cu \Leftrightarrow Cu^{2+} + 2e^{-}$$

Cyclic voltammograms obtained for experimented current densities is shown in figure 1.

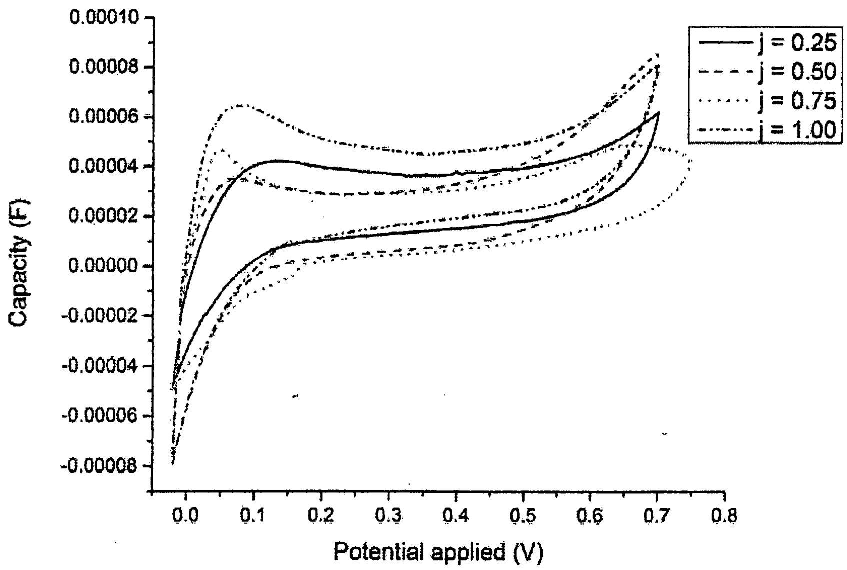

Figure 1: Cyclic voltammograms obtained for PPy films prepared with different current densities

The amount of average charge available during the cell reactions for different curre densities were calculated fromthearea of the cyclic voltammograms and shown in table 2.

Table 2: Amount of average charge available in the cells during cyclingwith respect topolymerization current densities of PPy film.

Current density (j/mAcm^{-2})	Capacity x10^{-5} (C/F)
1.0	4.51768
0.75	4.44080
0.50	4.14946
0.25	3.99661

Charging-discharging curves relevant to different current densities are shown figure 2.

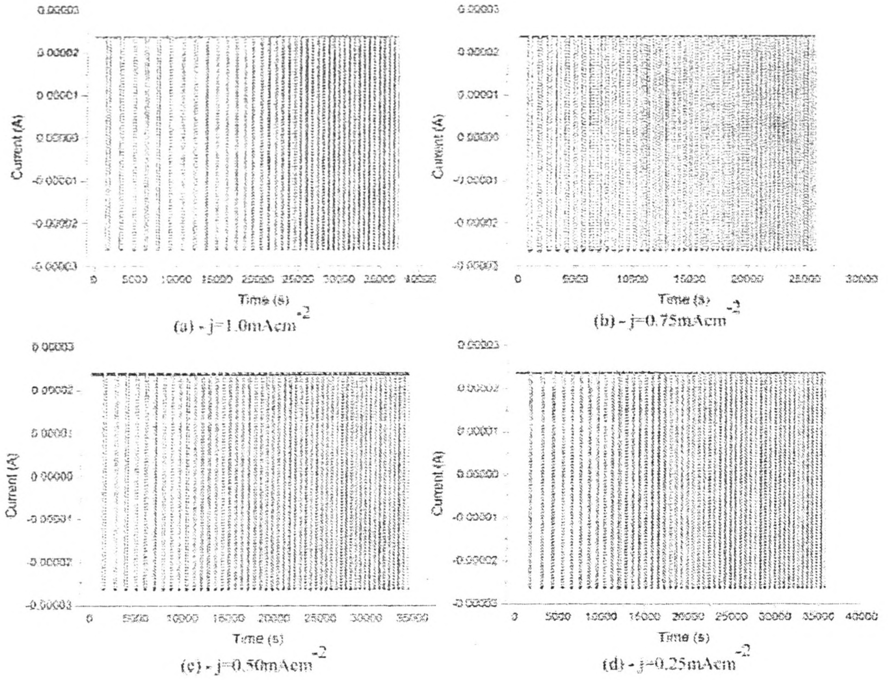

Figure 2: Charging-discharging curves relevant to cathodes prepared with different current densities

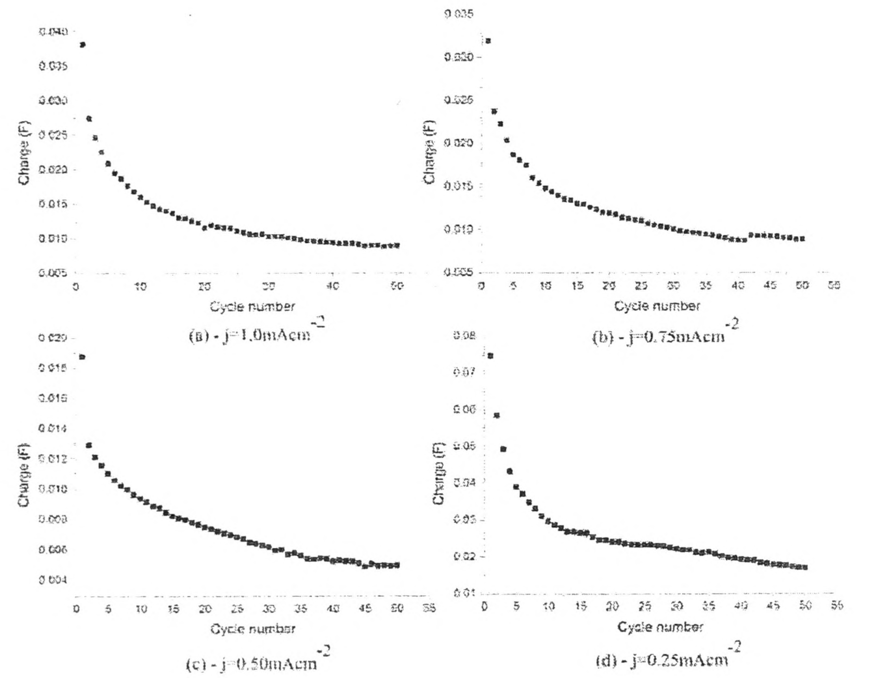

Figure 3: Variation of charge during discharging of the cells having cathodes prepared at different current densities

Available charge seems to be increased with the current density. This may be due to polymerization at high current density results morphology which helps the fast movement ions.Charging-discharging curves in figure 2 depicts that the cell assembled in Cu/GPE/PPy configuration seems to be almost stable for a longer period of time. Variations of charge with cycle number for the cells having cathodes prepared at different current densities are shown figure 3. With the cycle number, capacity of the cells has been reduced. This may be due to the formation of a passive layer on the surface of the Cu electrode[9].

4. CONCLUSION

Even though the open circuit voltages of the Cu based cells were not very high, it is clear that current density of conducting polymer cathode affects the performances of the rechargeable cells. In this preliminary study, it has been found that amounts of average charge available of the cells can be optimized by selecting a high current density during the polymerization of the conducting polymer cathode.

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