

Performance of Zn rechargeable cells having Polypyrrole cathodes doped with surfactant anion

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Abstract. Currently there exists a very high demand for electrochemical energy storage devices such as rechargeable cells and super capacitors due to massive increase in the use of portable electronics. At the moment this demand is mainly supplied by Li based cells. However, due to high cost, rapid reactivity and issues in disposal of Li, attention has been diverted on non Li based cells. Zn has been identified as a good candidate to replace Li. Even though several Zn based rechargeable cells were reported, not much work has been carried out on cells with conducting polymer cathode based Zn cells. In this study, performance of Zn rechargeable cells fabricated with conducting polymer polypyrrole (PPy) doped with a surfactant anion is reported. PPy films were galvanostatically electro polymerized on to stainless steel disc and cells were assembled with a polyvinylidene fluoride based gel polymer electrolyte having zinc-trifluoromethanesulfonate as the salt. Cells having different cathode thicknesses were fabricated and were characterized using cyclic voltammetry, electrochemical impedance spectroscopy and continuous charge-discharge tests. Cells exhibited open circuit voltages between 0.9 -1.0 V. Cycling testes showed that cycleable capacity almost follows the thickness variation of the cathode. Continuous charge-discharge tests revealed that the capacity decrease with the cycle number was higher in thinner films.

Keywords. Gel polymer electrolyte, Polypyrrole, Rechargeable cell, Surfactant.

1 Introduction

Currently there exists a very high demand for electrochemical energy storage devices such as rechargeable cells and super capacitors due to massive increase in the use of portable electronics (Chalamala 2007). At the moment this market is mainly covered by Li based cells. However, Li is expensive, highly reactive and it becomes problematic in the disposal of the cell.

Therefore, attention has been focused on developing low cost non-Li based rechargeable cells. There are several substitutes such as Zn, Cu and Mg to replace Li.

Conducting polymers (CPs) have been identified as one of the most promising candidates for cathode material due to their interesting features such as appreciable electronic conductivity, low cost, easy handling and environment friendliness (Cheng *et al.* 2006; Huang 2006; Wang *et al.* 2006; Green *et al.* 2010). Several conducting polymers have been tested for use as cathode materials. Among them polypyrrole (PPy), polyaniline (Pani), polythiophene (Pth) are widely reported polymers (Ghanbari *et al.* 2007; Li *et al.* 2013; Trinh *et al.* 2013). Out of the three polymers mentioned above, PPy has been mostly studied as the cathode material due to some special features such as longer cycle life, lower self discharge rate, endurance to over discharging, low manufacturing cost and shape flexibility. During the synthesis of the CPs, different anions are incorporated to the polymer backbone and it has been found that the properties of such polymer electrodes depend on the type of anions used (Skaarup *et al.* 2000, 2003). In one of our early studies on Li based cells, we have reported that better performance of CP could be obtained when it is doped with large anions and even more electro activity with surfactant based anions (Vidanapathirana *et al.* 2000).

In this study, the performance of a Zn rechargeable cell with a PPy based cathode doped with sodium dodecylsulphonate (SDS) is reported. A gel polymer electrolyte based on polyvinylidene fluoride (PVdF), ethylene carbonate (EC), propylene carbonate (PC) and zinc trifluoromethanesulfonate (ZnTF) was used as the separator.

2 Materials and Methods

2.1 Preparation of the cathode

The monomer pyrrole (Aldrich) was distilled and stored under refrigeration prior to use. polypyrrole (PPy) films were galvanostatically electro-polymerized on to stainless steel discs using a three electrode set up. A Ag/AgCl and Pt electrodes were used as the reference and the counter electrodes respectively. Monomer concentration was 0.1 M. The salt used was 0.05 M sodium dodecylsulfonate (SDS) (Aldrich). It has been reported that a charge density of 240 mC/cm^2 gives rise to a film of thickness $1 \mu\text{m}$ (Diaz *et al.*, 1980). Based on that, the thickness of the PPy films was varied from 0.5 to $1.0 \mu\text{m}$.

2.2 Preparation of the gel polymer electrolyte (GPE)

Polyvinylidene fluoride (PVdF) (Aldrich), zinc trifluoromethanesulfonate ($\text{Zn}(\text{CF}_3\text{SO}_3)_2 - \text{ZnTF}$) (Aldrich), ethylene carbonate (EC) (Aldrich) and propylene carbonate (PC) (Aldrich) were used as received. Appropriate amounts were weighed and magnetically stirred well and heated at 120°C for 30 minutes. The hot mixture was pressed in between two glass plates. Thereby, it was possible to obtain a bubble free thin film. Composition of the GPE was chosen as 0.5 PVdF: 1 EC: 1 PC: 0.7 ZnTF (by weight). Conductivity of the electrolyte was found to be in the range 10^{-3} Scm^{-1} .

2.3 Fabrication of cells

First, open circuit voltages (OCV) of the cells were measured using a digital multimeter. Subsequently, cyclic voltammetry tests were carried out for the cells in the potential range 0.2 - 1.0 V using a computer controlled potentiostat/ galvanostat (Metrohm-AUTOLAB M101) where PPy electrode was used as the working electrode and Zn was used as both the counter and reference electrodes. Cells were cycled at the scan rate of 10 mVs^{-1} .

Electrochemical impedance spectroscopy (EIS) measurements of the cells were carried out for the frequencies ranging from 400 kHz to 0.01 Hz using Metrohm Frequency Response Analyzer. Impedance data were analyzed using Non-Linear Least Square fitting programme. Measurements were taken at time intervals of 15, 30, 60 and 90 minutes.

Thereafter these cells were tested for their ability to withstand continuous charge and discharge cycling. For this, the cells were first 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 (20% of maximum charge current) was reached and then discharged using a computer controlled charge-discharge setup. The maximum charge and discharge currents were set to $75 \mu\text{A}$.

3 Results

The open circuit voltages of the cells fabricated by varying the thickness of PPy/DS cathode are given in Table 1.

Table 1. Open Circuit Voltage values (OCV) of the cells with the variation of PPy thickness.

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

Cyclic voltammograms obtained for cells fabricated with different cathode thicknesses are shown in Figure 1. Figure 1(a) shows the capacity variation of the cells in 1st cycles while Figure 1(b) shows the same in the 10th cycle.

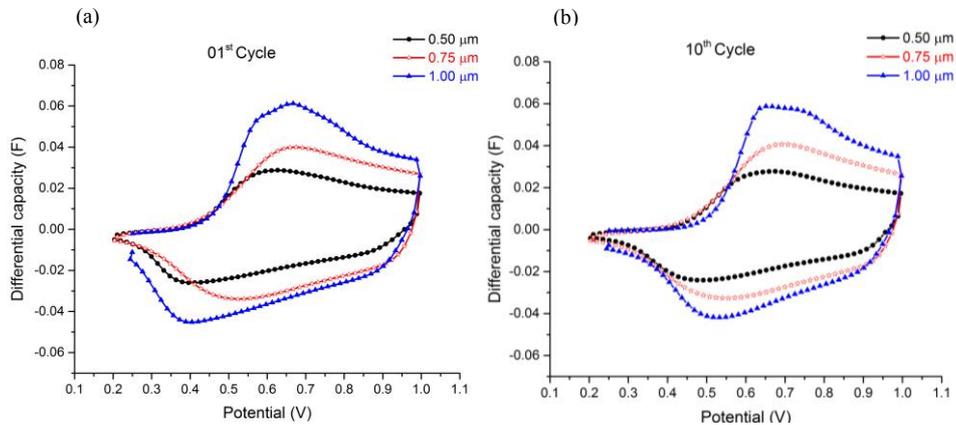


Fig. 1. Cyclic voltammograms with the capacity variations according to the PPy film thickness. Scan rate 10 mVs^{-1} . (a) 1st cycle, (b) 10th cycle.

The impedance plots obtained for the cells at different time intervals are given in Figure 2. Cells were subjected to continuous charge-discharge tests and the discharging capacity variation with the cycle number for the three cells is given in Figure 3.

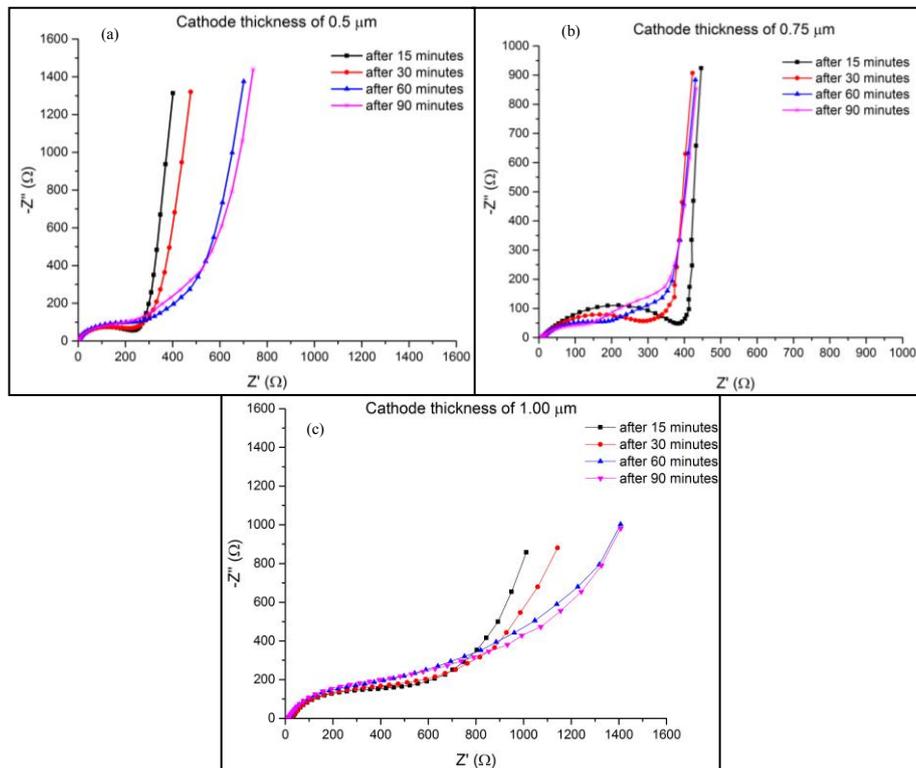


Fig. 2. Impedance plots taken at different time intervals for cells having three PPy film thicknesses. (a) 0.5 μm , (b) 0.75 μm , (c) 1.0 μm .

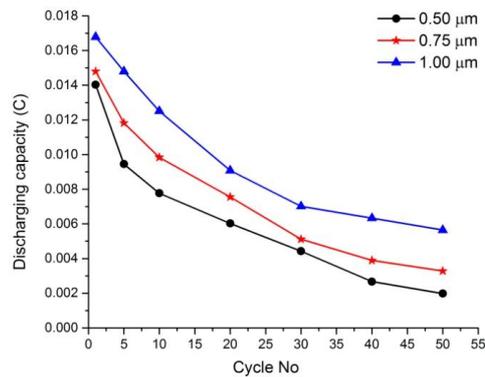


Fig. 3. Discharging capacity variation with the cycle number for the cells having different PPy film thicknesses.

4 Discussion

Open circuit voltages (OCV) of the cells showed an increasing trend from 0.9 V to 1.0 V when the thickness of the cathode was varied from 0.5 to 1.0 μm . This indicates that there is no significant effect on the OCV with the thickness of the cathode. However this OCV is very much comparable with the results reported in early studies. Zhang *et al.* have obtained only 1.15 V for Zn-polyaniline cells even with a liquid electrolyte (Zhang *et al.* 2006).

Cyclic voltammograms (CVs) in Figure 1 exhibit anodic peaks in the potential range 0.6 to 0.65 V and cathodic peaks in the range 0.4 to 0.55 V. The peaks at CVs appear at potentials on which redox reactions of the cells take place. The anodic peak is assigned to the oxidation of the PPy electrode while the cathodic peak to the reduction process (Tang *et al.* 2010). These oxidation and reduction peaks can be assigned to the cation (Zn^{2+}) insertion and deinsertion because one of our early studies has reported that when PPy is doped with a large anion, it tends to trap in the polymer chain and cation in the cycling electrolyte move in and out during the redox process (Vidanapathirana *et al.* 2002).

If the reactions are fully reversible, the peaks should appear at identical potentials resulting zero peak separation. However, the CVs obtained show a peak separation which may be due to difference in the rate of reactions during oxidation and reduction. Furthermore, it is seen that the thickness of the cathode is also affecting the peak separation. As the thickness increased, peak positions shift towards higher potentials. This is because for thicker films, more energy is needed to obtain the maximum cycleable capacity and hence peak positions move to higher potentials (Vidanapathirana *et al.* 2006). This shift in the peak position could also be due to the slower diffusion of ions in the thicker films as suggested by Osaka *et al.* (Osaka *et al.* 1987).

In the 1st cycle as well as in the 10th cycle, when the cathode thickness is increased, the corresponding capacity has increased. This is because when thickness is high, more charges can be retained giving rise to high capacity. When the capacity variation with cycle number is considered, it is seen that between 1st and 10th cycle, (Fig 1(b)), there is no significant loss in the cycling capacity. This proves that there exist good interfacial contacts between the electrodes and electrolyte without any side reaction.

EIS results on three different cells taken at 15, 30, 60, 90 minutes are given in Figure 2. Theoretically, high frequency intercept of the plot gives the bulk electrolyte resistance (R_b). Semi-circle arc at intermediate frequencies represents the Zn anode resistance. Low frequency part corresponds to the diffusion process and charge accumulation in PPy cathode. R_b of all cells at each time period has not changed. This confirmed the stability of the gel polymer electrolyte.

In cells based on conducting polymers, at low frequencies, two spikes are possible. One at about $\pi/4$ inclination representing Warburg behavior and the other portion has an inclination close to $\pi/2$. Warburg behaviour represents diffusion controlled kinetics. The portion with $\pi/2$ shows capacitive behavior indicating polymer electrode behaves like a capacitor at very low frequencies.

From the three impedance plots, a special feature in Figure 2(c) is that no charge accumulation has taken place in the cathode. Always, diffusion controlled kinetics are present. Probably this may be due to the mismatch of thickness of the cathode and the low frequency range. If the frequency was lowered too much, charge accumulation would have initiated. In the cell having the thin cathode, soon after fabrication, charges may accumulate on the cathode but as time goes on, diffusion controlled kinetics also take place. Because of this effect, at 60 minutes and 90 minutes time periods, low frequency region shows two spikes having two different inclinations. Similar results have been observed with the cell having the cathode with intermediate thickness.

Results obtained from continuous charge-discharge tests, (Figure 3), show that discharge rate of thin films are higher than that of thicker films. This can be attributed to the fact that thin films have short ion diffusion and migration lengths compared to thicker films (Wang *et al.* 2009; Valaski *et al.* 2002). This phenomena has been observed in a previous study on PPy films deposited on stainless steel mesh (Wang *et al.* 2005).

In conclusion, Zn rechargeable cells with conducting polymer cathode and gel polymer electrolyte were successfully fabricated with reasonable open circuit voltage and cycling capacity. It was evident that discharge rate of the cells with thinner cathodes are higher than that of thicker electrodes.

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