

Cycling performance of Mg rechargeable cells with Polypyrrole conducting polymer cathodes

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ABSTRACT

A big demand has arisen in the low power sources for the miniature consumer electronics. At present Li based cells are employed to provide that requirement. Due to the possible environment hazards in disposing such Li cells, studies have been carried out to replace Li with other metals. This study reports a preliminary work done on Mg rechargeable cells incorporating a gel polymer electrolyte and a Polypyrrole (PPy) based conducting polymer cathode. PPy was galvanostatically polymerized on stainless steel dice in the presence of a large anion and cells were fabricated in the array of Mg/Gel polymer electrolyte (GPE) / PPy inside a brass sample holder. Cells were initially tested for their cycling ability using Cyclic Voltammetry. Continuous charge-discharge tests were thereafter done. Open circuit voltages of the cells showed that they are suitable for low power requirements. Results also showed that cells can be cycled over a significant number of cycles without decaying much of the cycling capacity.

1. INTRODUCTION

Conducting polymers have been identified as promising candidates for cathode materials in rechargeable cells since they can be easily synthesized by using chemical or electrochemical methods and they show high redox reversibility, high electrical conductivity, highly stability in both air and aqueous mediums [1, 2].

Most of the studies reported were focused on application of conducting polymers in Li rechargeable cells [3-5]. However Li is expensive, highly reactive and it becomes problematic in the disposal of the cell. Therefore attention has been focused on developing non-Li based rechargeable cells. There are several options available to replace Li, such as with Zn, Cu and Mg. This study reports about cells fabricated with Mg as the anode, Polyvinilidene flouride based gel polymer as the electrolyte and PPy as the cathode.

2. EXPERIMENTAL

2.1 Preparation of the Cathode:

The monomer Pyrrole (Aldrich 99%) was distilled and stored under refrigeration prior to use. PPy film was electrochemically polymerized on to a stainless steel dies galvanostatically using a three electrode set up. A Ag/AgCl and Pt electrodes served as reference and counter electrodes respectively. Monomer concentrations was 0.1M. The

salt used was, Sodium Dedecylbenzenesulfonate (SDBS), (Aldrich) and its concentration was 0.05M. Thickness PPy film was maintained at 1 μ m.

2.2 Preparation of the Electrolyte:

Gel polymer based on Polyvinylidene fluoride (PVdF) (Aldrich), Magnesium trifluoromethanesulfonate ($\text{Mg}(\text{CF}_3\text{SO}_3)_2$ – MgTF) (Aldrich), Ethylene Carbonate (EC) (Aldrich) and Propylene Carbonate (PC) (Aldrich) was used as the electrolyte. Starting materials were magnetically stirred well and heated at 120 $^\circ\text{C}$ 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: 1PC: 0.7 MgTF (by weight)

2.3 Fabrication of Cells:

Cells were fabricated using a brass sample holder. PPy film deposited on the stainless steel dice was used as the cathode. A circular disc with same diameter as the cathode cut from the gel polymer electrolyte membrane was used as the electrolyte or the separator. Well cleaned Magnesium strips which were cut to the size the identical diameter as the electrolyte served as the anode. Cell structure was in the form of Mg / PVdF:EC:PC:MgTF / PPyDBS.

2.4 Characterization of Cells:

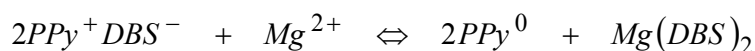
First, open circuit voltages of the cells were measured using a digital multimeter. Cyclic voltammetry tests were carried out for the cells in the potential range 0.5 - 1.8 V using a computer controlled potentiostat / galvanostat. While the PPy electrodes served as the working electrode, Mg was used as both the counter and reference electrodes. Cells were cycled at different scan rates. Thereafter these cells were tested for their ability to withstand continuous charge and discharge cycling. 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 25 μA .

3. RESULTS AND DISCUSSION

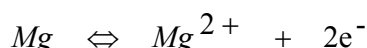
The average open circuit voltage was 1.8V. The electrochemical reactions of the cells based on conducting polymer cathodes are related to the oxidation and reduction of the conducting polymer electrode. Therefore for the cell fabricated in the configuration Mg/Polymer electrolyte/ PPy, during charging and discharging of the cell ion incorporation or ejection occurs in PPy film according to the oxidation and reduction of the polymer. This ion incorporation and ejection during oxidation and reduction depends on the type of the doping ion used during polymerization of PPy. It is reported that when

PPy is doped with small anions, they are responsible for electrochemical reactions [6]. Contrary to this, when PPy is doped with considerably large anions it is reported that instead of the anions, cations take the dominant role in electrochemical reactions [7].

In the system under study PPy was doped with a large surfactant anion and therefore it is expected that cation in the electrolyte take part in the oxidation and reduction process of the PPy cathode. As such, the following reaction is supposed to take place at cathode.



At the anode, the reaction given below may occur.



The cathodic peak (negative current) of the cyclic voltammogram is assigned to the reduction and the anodic peak (positive current) is assigned to the oxidation [8]. Hence cathodic peak shows the potential at which cathode undergoes reduction.

Cyclic voltammograms obtained for the cell fabricated in the form of Mg / PVdF: EC:PC: MgTF/ PPyDBS is shown in the Fig. 1.

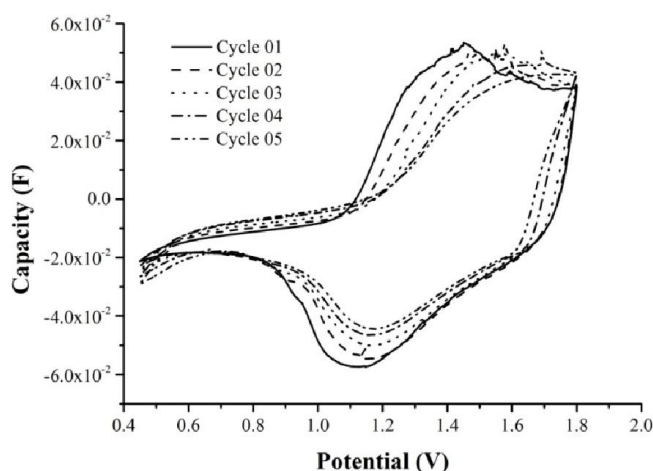


Fig. 1: Cyclic voltammograms obtained for the cells with the configuration Mg/PVdF:EC:PC:MgTF / PPyDBS varying the cycling number. Scan rate 1 mVs⁻¹

As per the oxidation and reduction processes shown by the graph, it seems that the cycling capacities of the cell during oxidation and reduction are almost same. Also the oxidation and reduction peaks occur at very near potentials indicate the reversibility of the reactions. There seems to be a shift in the peak potentials to higher potential with the cycle number. The reason for this may be due to stabling of the cell reactions that take place with cycling.

The amount of charge available during the cell reactions were calculated from the area of the cyclic voltammograms. They are given in the Table 1.

Table 1: Charge associated in the cycling of the cell with respect to cycle number

Cycle Number	Charge / C
1	0.029
2	0.027
3	0.025
4	0.023
5	0.021

Available charge seems to reduce upon cycling. It may be because upon cycling, the cell reactions may not complete fully.

After cyclic voltammetry studies, cells were subjected to continuous charge –discharge test. They were first galvanostatically discharged to 0.5 V, immediately followed by galvanostatic charged up to 2.0 V and maintained at that potential until the current drops by 20% of the discharge current and then subjected to discharge using a computer controlled charge-discharge setup. The maximum charge and discharge currents were set to 25 μA . Fig. 2 illustrates the charging and discharging curve of the cell with respect to time.

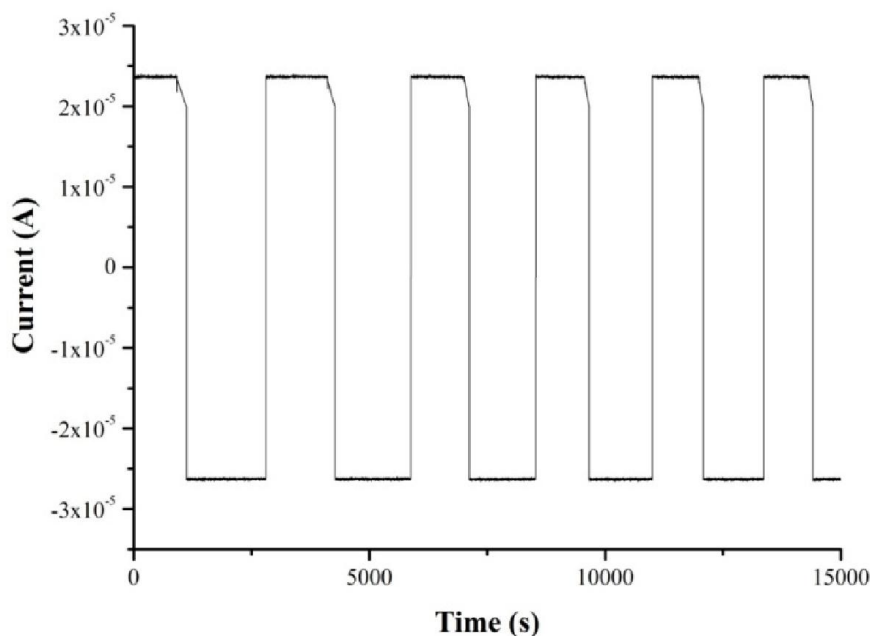


Fig. 2: Continuous charge-discharge curve of the cell Mg/PVdF:EC:PC:MgTF/PPyDBS with respect to time

Cycling charge variation with cycle number is given in Fig. 3.

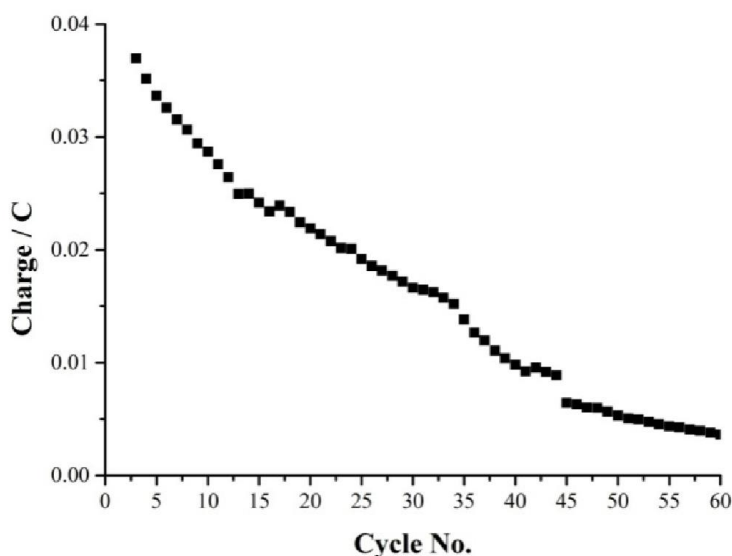


Fig. 3: Variation of charge during discharging of the cell Mg/PVdF:EC:PC:MgTF/PPyDBS with the cycle number

With the assumption that 0.33 anions are associated per monomer during polymerization, the calculated charge that incorporated in to the conducting polymer was found to be 0.042 C [9].

From the Fig. 3 it is evident that the initial discharging capacity is close to 0.040 C confirming that it is possible to achieve the charge associated in polymerization process during the cycling of the cell. However when the number of cycles increases, the capacity decreases gradually. Such occurrence can be reasonably attributed to decomposition of components mainly in the electrolyte.

It is also interesting to note that initial charge (during discharge) available at continuous charge-discharge test (0.036 C) is nearly equal to charge available at cyclic voltammetry study. Anyhow, upon cycling, the decay of available charge amount is faster than in continuous charge-discharge. It is because during cycling, cells are forced to cycle at a predetermined scan rate. Therefore all available charges do not involve in all reactions.

4. CONCLUSION

Rechargeable cells with appeasable performance could be fabricated in the form of Mg / PVdF:EC:PC:MGTF / PPyDBS having open circuit voltage of 1.8V. It was able to obtain almost the same charge used for polymerization of the conducting polymer during the charging/discharging the cell. Cell performance could be improved by fine tuning the compositions.

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