

## **EFFECT OF DOPING ANION OF THE CATHODE ON THE PERFORMANCE OF Mg/PVdFMgTF/PPy RECHARGEABLE CELLS**

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### **ABSTRACT**

Today, Li rechargeable cells play a vital role in fulfilling low power requirements. However, some drawbacks of Li have lead finding alternatives for Li in rechargeable cells. Among many possible alternative metals that have been studied, Mg presences as a natural choice. However, it is required to find a better combination of electrodes and electrolyte for Mg rechargeable cells. Conducting polymers were identified as promising candidates for cathode materials in rechargeable cells due to their unique features. In this study, the effect of the anion used to dope PPy cathode on the performance of Mg rechargeable cells is reported. The cell structure was Mg as anode/PVdF:PC:EC:MgTF gel polymer electrolyte/PPy cathode doped with different anions. Cells were tested for their cycling ability at different scan rates using Cyclic Voltammetry and continuous charge-discharge tests at different voltages and currents. 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.

**Keywords:** Polypyrrole, Cyclic voltammogram, Continuous charge-discharge

### **1. INTRODUCTION**

The application of conducting polymers for both electrode and electrolyte materials in Li rechargeable cells has generated a lot of interest during the past few years<sup>1, 2</sup>. After many significant research studies, gel polymer electrolytes (GPEs) have been introduced as the electrolyte in Li rechargeable cells which have several advantages over liquid and solid electrolytes, including no shape restrictions, faster charging/discharging, and higher power density<sup>1, 3</sup>. Moreover, many different types of conducting polymers have been widely studied as cathode material for Li rechargeable cells and PPy has drawn more attention due to its

superior electroactivity, good electrical conductivity and chemical stability<sup>2,4</sup>. During the synthesis of PPy, different types of anions were introduced and it has been reported that the dopant anion plays an important role in the performance of Li rechargeable cells and PPy doped with larger anions are more suitable as cathode material<sup>4</sup>. However, the expensiveness, high reactivity, safety issues and environmental effect of disposing of Li has lead find alternatives for Li anode in rechargeable cells<sup>5</sup>. It has been reported that the thermodynamic properties of Mg make it a natural choice for use as an anode material in rechargeable batteries<sup>5</sup>. However, it is required to find a better combination of electrodes and electrolytes for Mg rechargeable cells. In this study, the effect of the doping anion used to dope PPy cathode on the performance of Mg rechargeable cells is reported. The cell structure was Mg as anode/PVdF/PC/EC/MgTF gel polymer electrolyte/PPy cathode doped with different anions.

## 2. EXPERIMENTAL

### 2.1. Preparation of Cathode:

The two anions Dedecylbenzenesulfonate (DBS<sup>-</sup>) and Trifluoromethanesulfonate (TF<sup>-</sup>) were used as dopants. To find the best suitable current density for each type of cathode, PPy/DBS and PPy/TF films were galvanostatically prepared on a Pt wire at current densities 0.25, 0.50, 0.75, 1 mA/cm<sup>2</sup> and characterized using Cyclic Voltammetry (CV) method. Most suitable current density for each type of doping anion was decided by analyzing the capacity of each cyclic voltammogram.

PPy/anion films for cathode electrodes were galvanostatically polymerized on a well-polished stainless steel dice with surface area of 1.095 cm<sup>2</sup>. Thickness of PPy films were maintained at 1 μm. The electrolyte was prepared with 0.1M Pyrrole monomer and 0.05M anion salt with deionized water. SDBS and MgTF were used as the anion salts for PPy/DBS and PPy/TF films respectively. An Ag/AgCl and a Pt electrode were used as reference and counter electrodes in three electrode setup. The current densities 1 mA/cm<sup>2</sup> and 0.25 mA/cm<sup>2</sup> were used for PPy/DBS and PPy/TF films respectively in accordance with the previous results.

### 2.2. Preparation of Electrolyte:

Gel polymer based on Polyvinylidene fluoride (PVdF), MgTF, Ethylene Carbonate (EC) and Propylene Carbonate (PC) was used as the electrolyte. Starting materials were 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: 1PC: 0.7 MgTF (by weight).

### 2.3. Fabrication of cells:

The PPy film deposited on the stainless steel dice with diameter 11.81mm 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 Mg strips were cut to the size of the same diameter served as the anode. The cell configuration was Mg as anode/PVdF: PC: EC: MgTF gel polymer electrolyte/PPy-anion cathode.

### 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 0.4 - 1.85 V using a computer controlled potentiostat / galvanostat. Here the PPy electrodes served as the working electrode, Mg was used as both the counter and reference electrodes. Cells were cycled at scan rate of 1mV/s. 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  $\mu$ A.

## 3. RESULTS AND DISCUSSION

### 3.1. PPy on Pt wire with the variation of current density

Cyclic voltammetry studies were done for the films made of PPy/DBS and PPy/TF in Pt wire at different current densities. Cyclic voltammograms obtained for PPy/DBS and PPy/TF films at scan rate 10 mV/s are given in Figure 1.

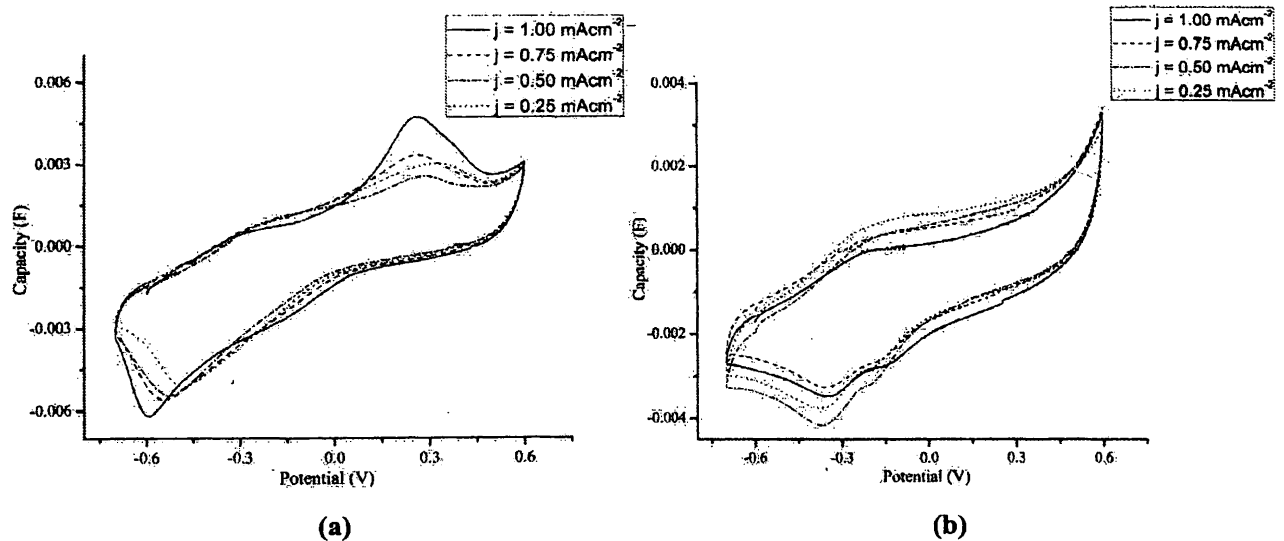


Figure 1: Cyclic voltammograms obtained for 0.25 $\mu$ m polymer films on Pt wire at different current densities. Scan rate 10mV/s (a) PPy/DBS, (b) PPy/TF

According to Figure.1 (a) PPy/DBS film prepared at current density 1mA/cm<sup>2</sup> exhibits the largest capacity of cyclic voltammogram. It was noted that the capacity of cyclic voltammogram reduces with the current density for films made of PPy/DBS. In contrast, according to Figure.1 (b) the capacity of the cyclic voltammogram grows when the current density reduces for PPy/TF films. Thus PPy/TF film prepared at current density 0.25mA/cm<sup>2</sup>exibhits the largest cyclic voltammogram capacity. However it was found that films made of PPy/DBS and PPy/TF exhibit the largest capacity of cyclic voltammogram at current densities 1.00mA/cm<sup>2</sup> and 0.75mA/cm<sup>2</sup> respectively.

### 3.2. Results of cells with the configuration of Mg/gel polymer electrolyte / PPy-anion

The open circuit voltages (OCV) of the two types of cells are shown in Table 1.

Table 1: OCV obtained for cells made of PPy/DBS and PPy/TF

Cell configuration	OCV / V	
	Cell 1	Cell 2
Mg/gel polymer/PPy:DBS	1.648	1.580
Mg/gel polymer/PPy:TF	1.814	1.791

The resulting cyclicvoltammograms for cells having PPy: X (DBS<sup>-</sup>/TF<sup>-</sup>) electrodes of 1  $\mu$ m thickness are shown in Figure.2.

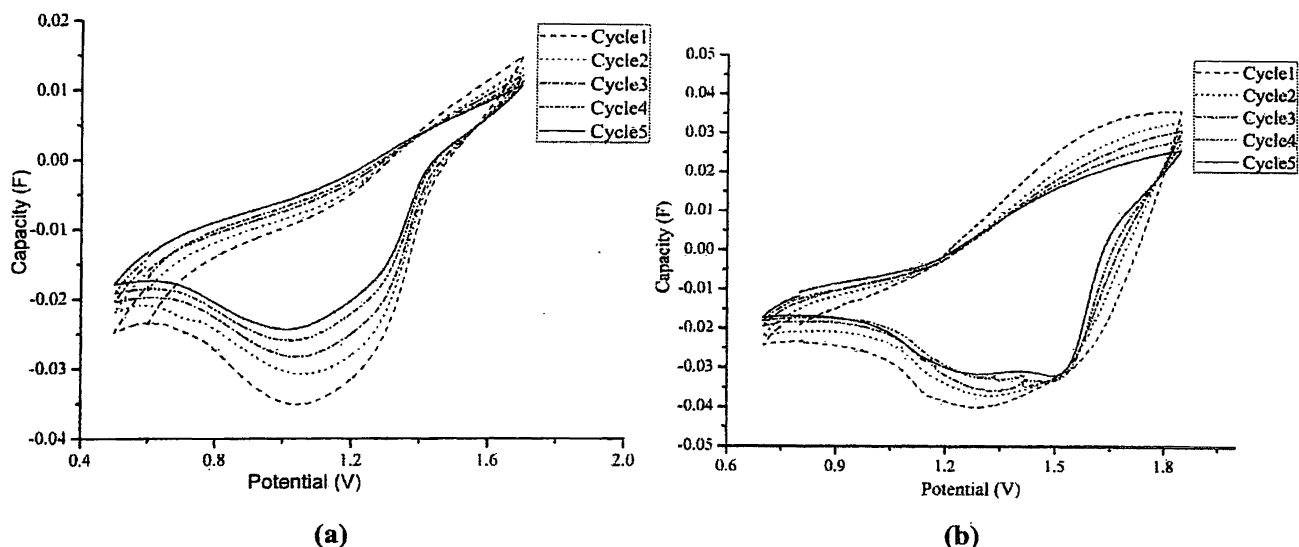


Figure 2: Cyclic voltammograms obtained for the cells with the configuration Mg / PVdF:EC:PC:MgTF / PPy:X. X: (a) DBS<sup>-</sup> ; (b) TF<sup>-</sup> varying the cycling number. Scan rate 1 mVs<sup>-1</sup>

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 at which redox reactions of the cells at charging (oxidation) and discharging (reduction) take place. If the reactions are fully reversible, the ion insertion and desorption to the cathode during charging and discharging occurs at identical potentials at each cycle. Hence, the corresponding peaks should appear at the same potential values resulting zero peak separation<sup>5</sup>. Here the cathodic peaks appeared well but anodic peaks were not very dominant. However, the peak separations in both cells are very smaller. The amount of charge available during the cell reactions exhibits from the area of the cyclic voltammograms<sup>4</sup>. Available charge seems to reduce upon cycling since the areas of the curves tend to decrease with increasing cycle number. It may be because upon cycling, the cell reactions may not complete fully, due to formation of passivation layers and corrosion of electrodes. The amount of charge available during the cell reactions were calculated from the area of the cyclic voltammograms. They are given in the Table 2 below.

Table 2: Charge associated in the cycling of the cells with respect to cycle number

Cycle Number	Charge / C	
	PPy/DBS	PPy/TF
1	0.017	0.036
2	0.015	0.031
3	0.014	0.028
4	0.013	0.026
5	0.012	0.025

Available charge seems to reduce upon cycling in both cells. Further, the amount of charging reduction seems to be getting reduced with the increasing cycle number. It was also noted that the charge of PPy/TF cell is about two times of PPy/DBS cell.

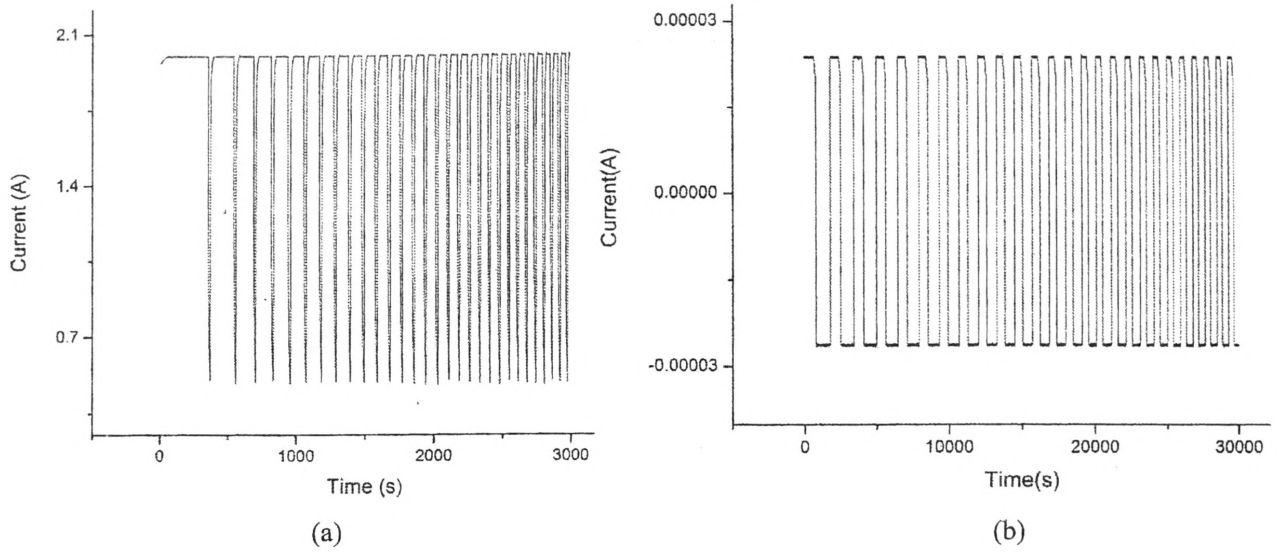


Figure 3: Continuous charge-discharge curve of the cell Mg/PVdF:EC:PC:MgTF/PPy:X with respect to time X: (a) DBS<sup>-</sup>, (b) TF<sup>-</sup>

Both cells could be continuously charge-discharge for over 60 cycles (it was limited because of the time constrain). Capacity variations with cycle no are shown in Figure 4.

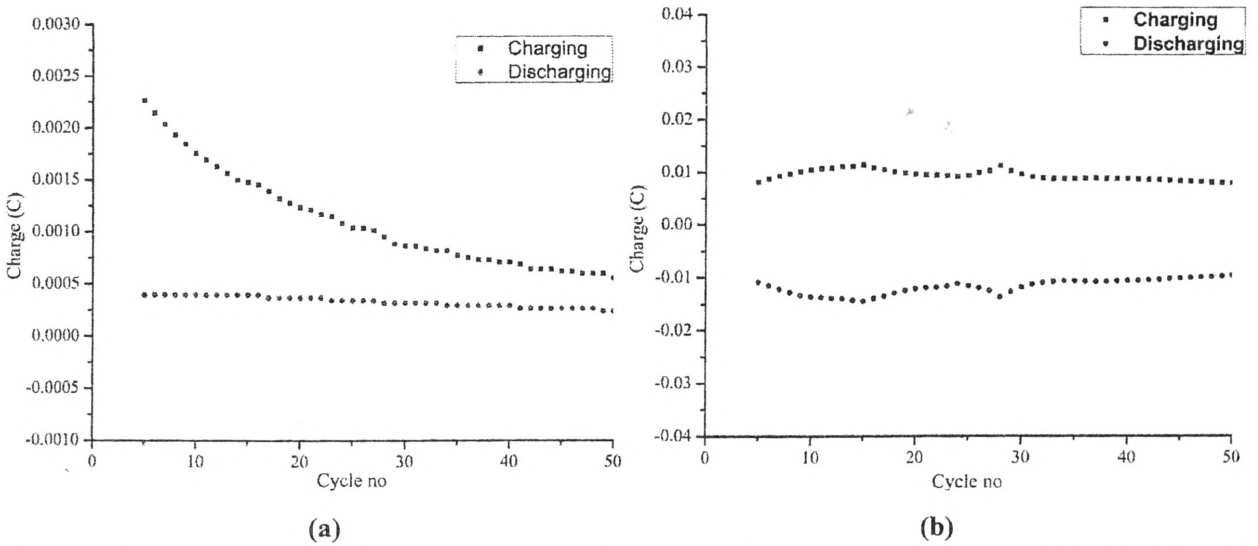


Figure 4: Capacity variation with cycle number for cells with PPy:X as cathode. X: (a) DBS<sup>-</sup>, (b) TF<sup>-</sup>

#### 4.0 CONCLUSION

Even though this is a preliminary study, the results predict the possibility of fabricating non Li cells for applications. Mg rechargeable cells with appreciable performances could be fabricated using PVdF:EC:PC:MgTF gel polymer electrolyte and PPy doped with DBS<sup>-</sup> or TF<sup>-</sup> as cathode materials with open circuit voltage around 1.6V and 1.8V respectively.

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