

## CHAPTER 7

### FABRICATION AND CHARACTERIZATION OF PROTON BATTERIES AND EDLC

#### 7.1 Introduction

Proton conducting polymer electrolytes based on PVA-chitosan-NH<sub>4</sub>NO<sub>3</sub>-EC have been successfully obtained. From the literature, for application of polymer electrolytes in any electrochemical devices, the conductivity of the electrolyte should at least  $10^{-4}$  S cm<sup>-1</sup>. The highest conducting sample in the plasticized system as studied earlier in Chapter 6, is the sample with 70 wt. % EC concentration, (30[60C4P6-40AN]-70EC) with the conductivity value of  $1.60 \times 10^{-3}$  S cm<sup>-1</sup> and is suitable for electrochemical devices applications.

In this chapter, the sample (30[60C4P6-40AN]-70EC) is chosen to become the electrolyte or separator in an electrochemical devices which is primary proton battery, secondary proton battery and electric double layer capacitor (EDLC).

#### 7.2 Solid-State Proton Batteries

In the present work, two types of batteries have been fabricated:

1. Zn + ZnSO<sub>4</sub>·7H<sub>2</sub>O/30[60C4P6-40AN]-70EC/MnO<sub>2</sub> (Primary Proton Battery)
2. Zn + ZnSO<sub>4</sub>·7H<sub>2</sub>O/30[60C4P6-40AN]-70EC/MnO<sub>2</sub> + liquid electrolyte (Secondary Proton Battery)

### 7.2.1 Electrochemical Window Stability

The study of electrochemical window stability was carried out using linear sweep voltammetry as depicted in Figure 7.1. From the figure, current onset at room temperature was detected at 1.70 V as pointed by the arrow. The current onset is assumed to be the polymer electrolyte breakdown voltage.

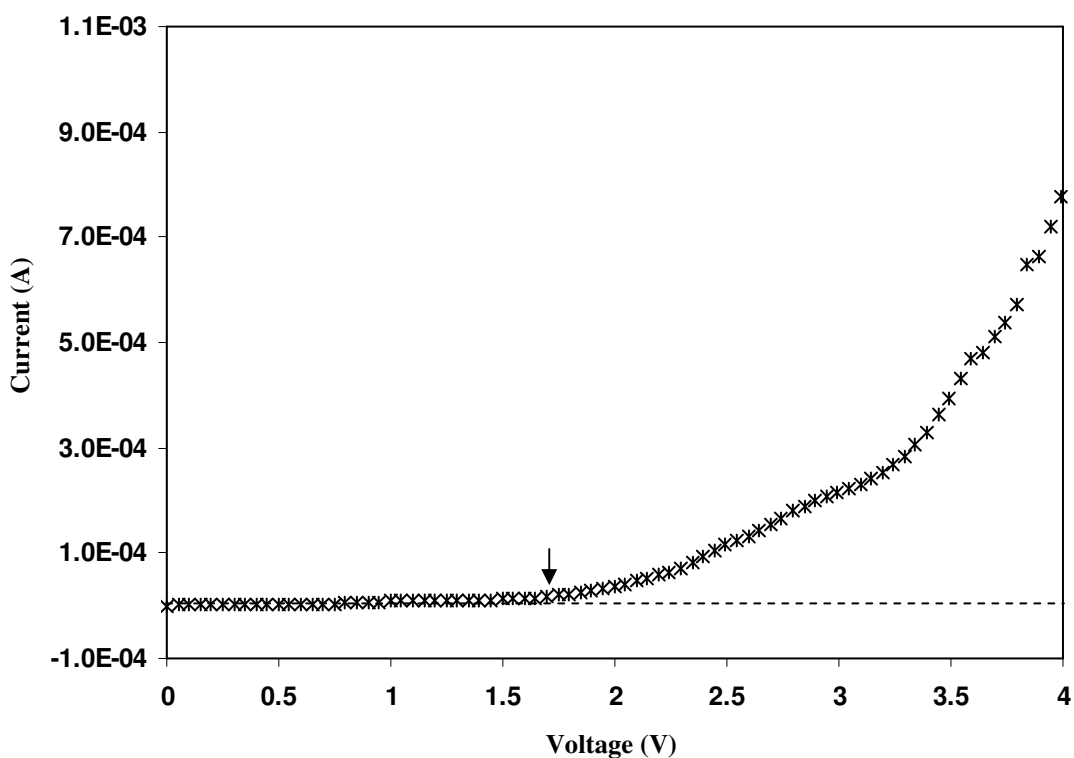


Figure 7.1: Linear sweep voltammogram at 10 mV s<sup>-1</sup>.

Pratap *et al.*, (2006) have reported that the standard electrochemical window for proton batteries is  $\sim 1$  V and therefore for the present work, the breakdown voltage is high enough to allow safe use of the PVA-chitosan blend polymer electrolyte in the application of any protonic devices. Ng and Mohamad, (2008) have reported that for chitosan-NH<sub>4</sub>NO<sub>3</sub>-EC the breakdown voltage at room temperature was about 1.80 V for the sample with conductivity of  $\sim 10^{-3}$  S cm<sup>-1</sup>. Their results are comparable with the present work.

## 7.2.2 Battery Chemistry

The chemical reaction that probably takes place in the cell is:

At the anode:



At the cathode:



Overall reaction:



The standard reduction potentials for reaction at the anode and cathode were obtained from West *et al.*, (1985). The overall reaction should provide the cell with  $E_0 = 1.986 \text{ V}$ . However in this work the cell  $\text{Zn} + \text{ZnSO}_4 \cdot 7\text{H}_2\text{O} / 30[60\text{C4P6-40AN}]-70\text{EC} / \text{MnO}_2$  gave a voltage of  $E = 1.63 \text{ V}$ , which is about 20 % lower than the expected cell potential.

For the secondary cell,  $\text{Zn} + \text{ZnSO}_4 \cdot 7\text{H}_2\text{O} / 30[60\text{C4P6-40AN}]-70\text{EC} / \text{MnO}_2 +$  liquid electrolyte the open circuit potential (OCP) is 1.66 V suggesting the plausible chemistry mentioned above is possible.

## 7.2.3 Primary Proton Battery Characterization

### 7.2.3.1 Open Circuit Potential (OCP) Studies for Primary Proton Batteries

Figure 7.2 represents the average open circuit potential during 24 hours storage time for the cells with configuration  $\text{Zn} + \text{ZnSO}_4 \cdot 7\text{H}_2\text{O} / 30[60\text{C4P6-40AN}]-70\text{EC} / \text{MnO}_2$ . The potential of the three cells is quite constant and stabilized from the

beginning of storage until 24 hours of storage and the average value of the OCP is 1.63 V.

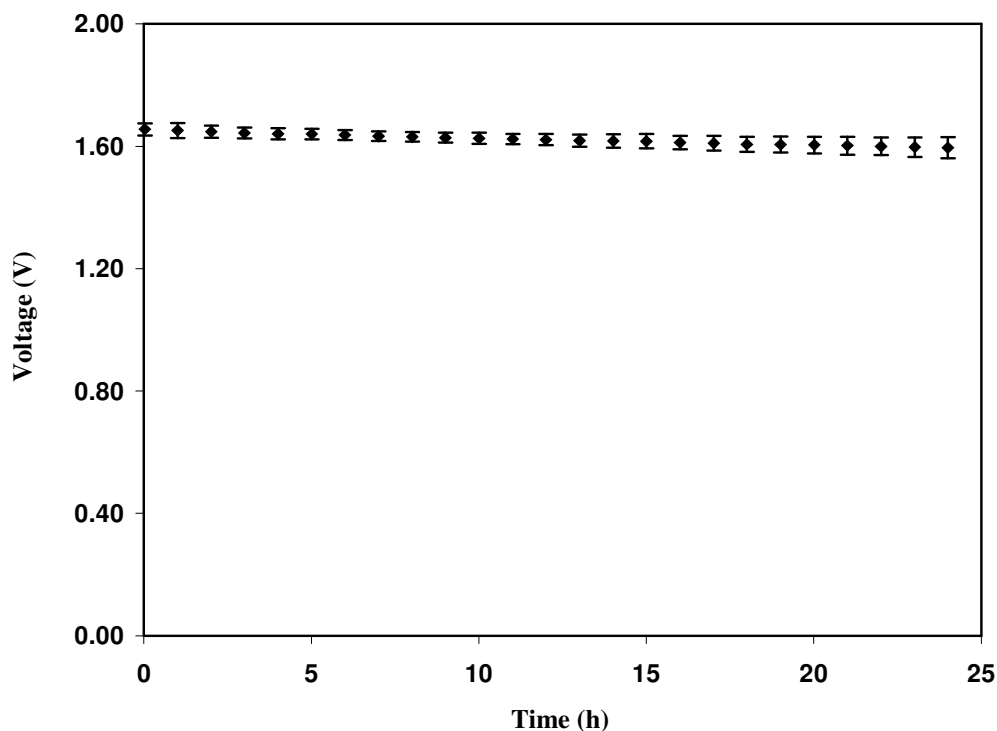


Figure 7.2: OCP of Zn + ZnSO<sub>4</sub>·7H<sub>2</sub>O/ 30[60C4P6-40AN]-70EC /MnO<sub>2</sub> cells during 24 hours of storage.

### 7.2.3.2 Discharge Characteristics of Primary Proton Batteries

The discharge characteristics of three cells with configuration Zn + ZnSO<sub>4</sub>·7H<sub>2</sub>O/30[60C4P6-40AN]-70EC/MnO<sub>2</sub> at a constant current drain of 2 mA is shown in Figure 7.3. The batteries experience a drop in voltage upon discharge before exhibiting an almost flat discharge plateau at  $(1.40 \pm 0.02)$  V. The discharge of the cells was continued until the cut off voltage of 0.30 V. The discharge capacity for the batteries was  $(38.86 \pm 4.12)$  mAh. The discharge characteristics of the three cells were found to be longer than what has been reported by Ng and Mohamad, (2006). In their report, the Zn + ZnSO<sub>4</sub>·7H<sub>2</sub>O/chitosan-NH<sub>4</sub>NO<sub>3</sub>-EC/MnO<sub>2</sub> cell was discharged at 1 mA and the discharge capacity of the batteries was  $(17.0 \pm 2.6)$  mAh.

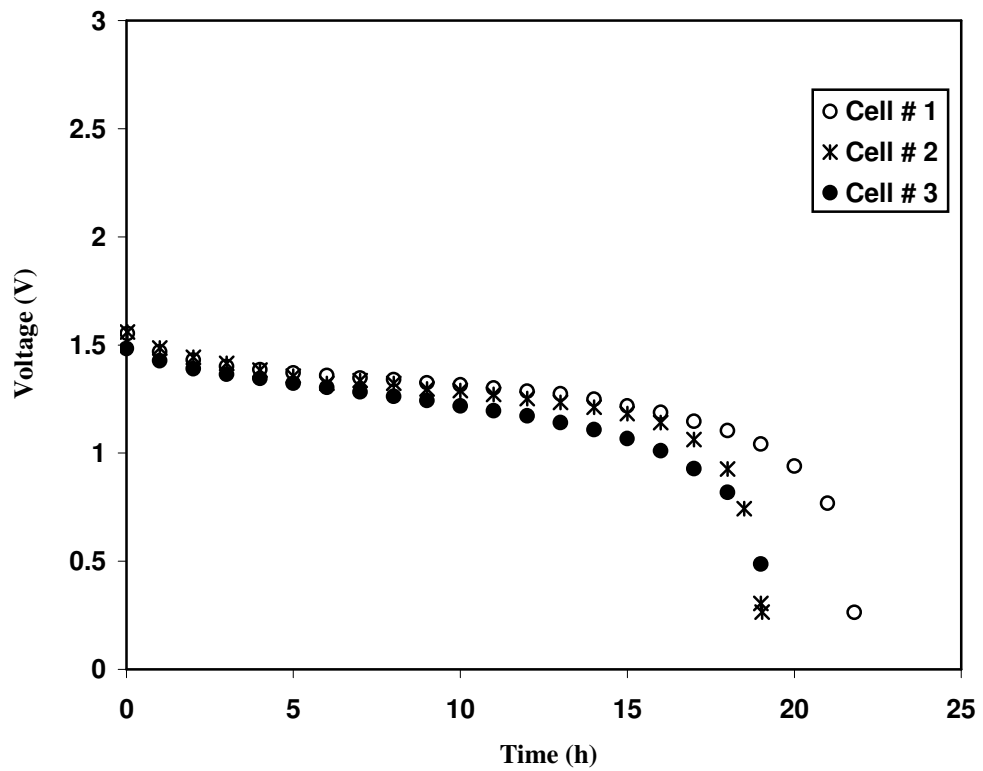


Figure 7.3: Discharge curves of primary proton batteries at 2 mA constant current.

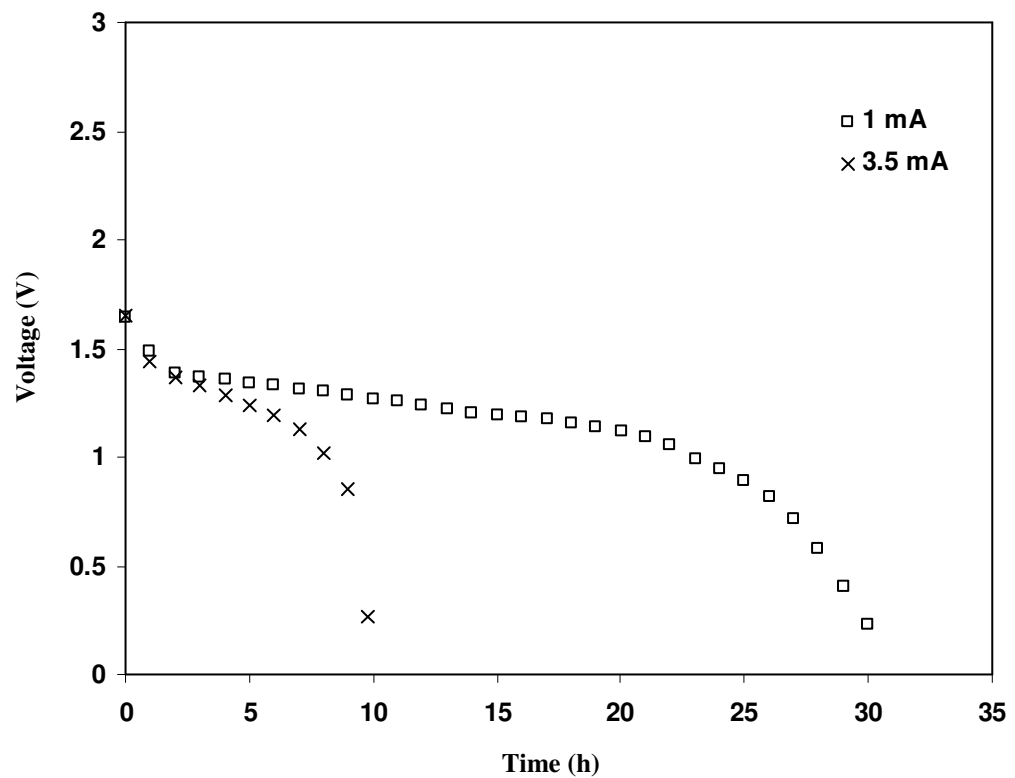


Figure 7.4: Discharge curves of primary proton batteries at 1 mA and 3.5 mA current.

Figure 7.4 shows the discharge of the primary proton battery at different current. It is found that the discharge period at 1 mA current drain is longer compared to that 3.5 mA and 2 mA in (Figure 7.3) current drains. At 1 and 3.5 mA current drained from the battery, the discharge process took about 30 and 10 hours respectively. The discharge capacity for the 1 mA current drain was found to be 30 mAh and for the 3.5 mA current applied was about 34 mAh. Value of discharge capacity for the current applied is still in the same range with 2 mA current applied which is 30 to 40 mAh. This shows that the amount of charge contained in the battery is consistent for the compositions in the electrodes content.

### 7.2.3.3 Voltage-Current-Power Characteristics of Primary Proton Batteries

The voltage-current-power characteristics for the battery with electrolyte plasticized with 70 wt.% EC at room temperature is shown in Figure 7.5. The V-I characteristic is a straight line that can be represented by the equation,

$$V = E - Ir \quad (7.4)$$

Here V is the voltage at particular current I, E is the OCP and r is the internal resistance. From Figure 7.4,  $E = (1.66 \pm 0.01)$  V and r is  $(33.0 \pm 4.0)$   $\Omega$ . The OCPs from the V-I graph for the two sets of batteries are almost the same as measured experimentally. The calculated short circuit current value of the cells is around 32 mA. The maximum power density is  $(9.47 \pm 0.26)$  mW cm<sup>-2</sup> and higher compared to the work of Ng and Mohamad (2006).

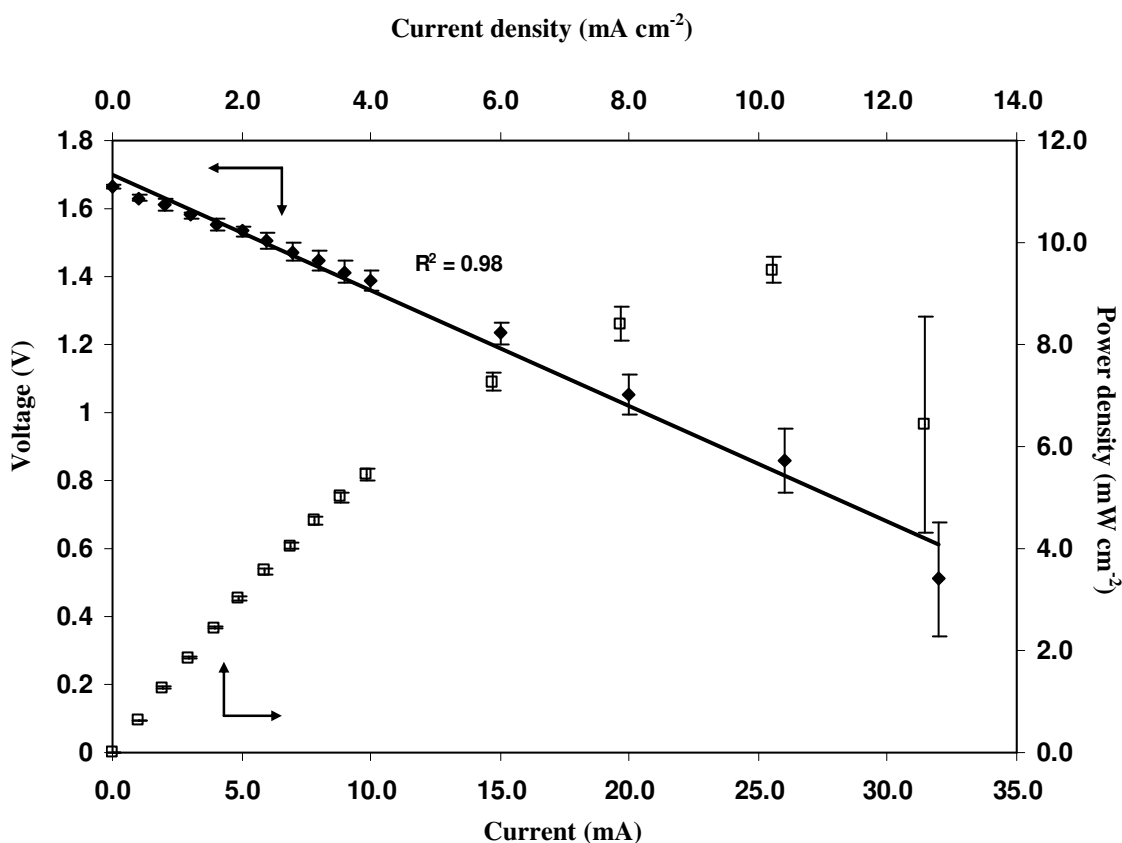


Figure 7.5: Voltage-Current-Power characteristic of primary proton batteries.

## 7.2.4 Secondary Proton Battery (Rechargeable Proton Battery)

### 7.2.4.1 Open Circuit Potential (OCP) Studies for Secondary Proton Battery

Figure 7.6 represents the average open circuit potential during 24 hours storage time of the cells with configuration  $\text{Zn} + \text{ZnSO}_4 \cdot 7\text{H}_2\text{O}/30[60\text{C}4\text{P}6-40\text{AN}]-70\text{EC}/\text{MnO}_2 + (30[60\text{C}4\text{P}6-40\text{AN}]-70\text{EC}$  in liquid phase). The cell gives a slightly higher potential as plotted in Figure 7.6 with the value of 1.66 V. It can be seen that the cell potential is quite stable during the storage period.

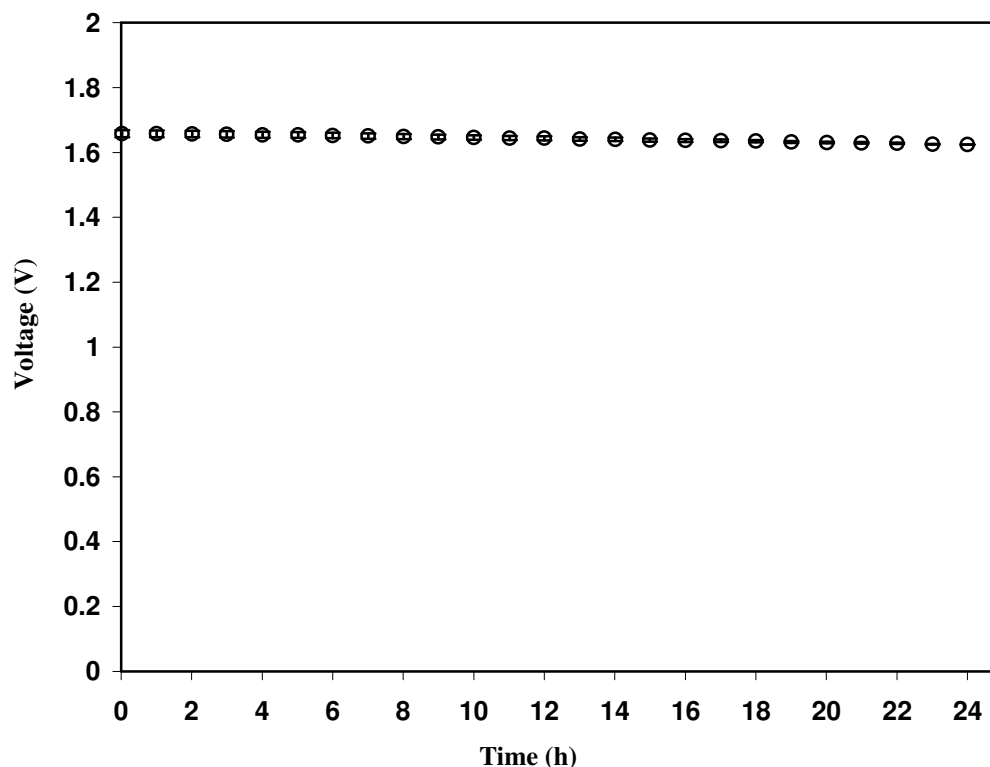


Figure 7.6: OCP of Zn + ZnSO<sub>4</sub>·7H<sub>2</sub>O / 30[60C4P6-40AN]-70EC/MnO<sub>2</sub> + liquid electrolyte cells during 24 hours of storage.

#### 7.2.4.2 Discharge-Charge Characteristics for Secondary Proton Battery

Rechargeability of the cell is shown in Figure 7.7. The addition of (30[60C4P6-40AN]-70EC) electrolyte in the liquid phase is thought to enable the intercalated H<sup>+</sup> to deintercalate from MnO<sub>2</sub> and enter the anode through the solid electrolyte. Thus, a rechargeable battery system may be obtained. The cell was charged and discharged using a constant current at 0.3 mA. From Figure 7.7 it can be seen that the voltage of the cell immediately dropped to 1.55 V upon discharge. The cell was observed to regain to its initial potential value after recharging.



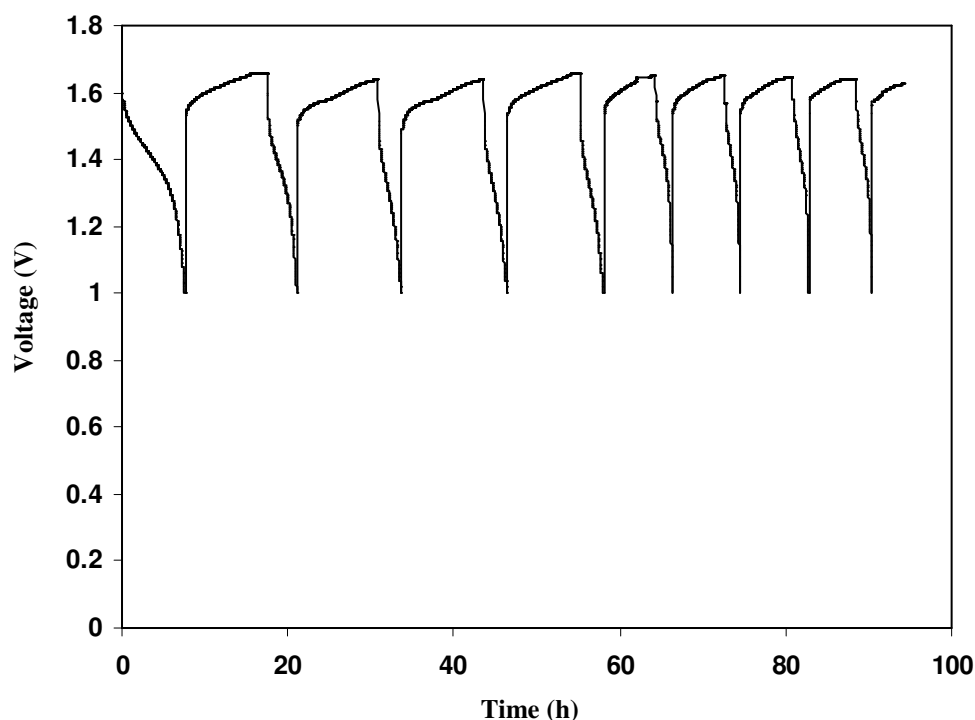


Figure 7.7: Discharge-charge characteristic of secondary proton battery.

It is known that the rechargeability of the battery is due to the presence of hydrogen supply [Pandey *et al.*, 1998] and in this work the hydrogen source came from the  $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$ . Pandey *et al.*, (1998) also claimed that battery rechargeability is closely associated to the proton intercalation in the cathode. The battery potential dropped to less than 20 % of the initial value after the 9<sup>th</sup> cycle. The charge and discharge processes of the battery lasted for almost 90 hours at 0.3 mA charge-discharge current. The charge and discharge currents applied in this work are larger than that used in [Pandey *et al.*, 1998; Lakshmi and Chandra 2002; Pratap, *et al.*, 2006]. Lakshmi and Chandra (2002) reported a proton battery that performed several charge and discharge cycles. The battery cycles lasted for 36 hours after which the voltage could not be charged back to its initial value. Pratap *et al.*, (2006) fabricated a rechargeable solid state battery that lasted 9 cycles before the voltage dropped to more than 20 % of its initial value. The charge and discharge cycles under a constant load regained its initial

voltage until the 9<sup>th</sup> cycle for ~ 34 hours [Pratap *et al.*, 2006]. The performance of the secondary battery in the present work is better than that reported.

### 7.2.4.3 Discharge Capacity for Secondary Proton Battery

Discharge curve for the secondary proton battery at cycles 1, 4 and 9 is shown in Figure 7.8. The battery experiences a drop in voltage upon discharge before exhibiting an almost flat discharge plateau at 1.5 V. The discharge of the cells was continued until the cut off voltage of 1 V.

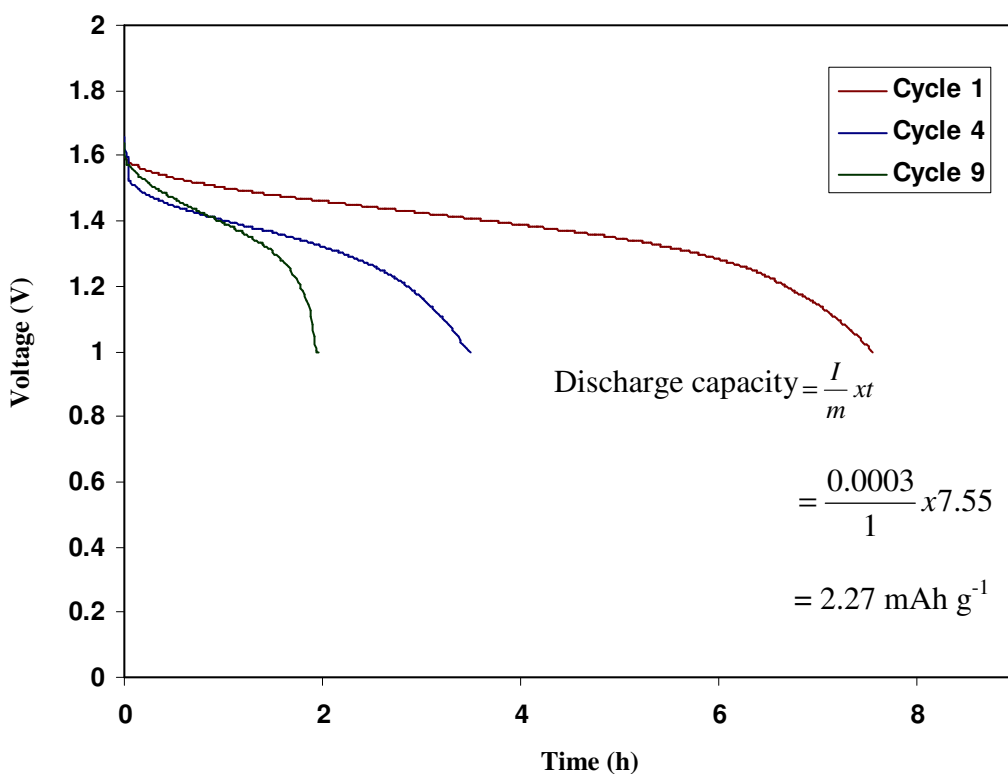


Figure 7.8: Discharge curve for secondary proton battery at cycle 1, 4 and 9.

It can be observed that at cycle 1, the discharge period is around 7.55 hours. The discharge period has become shorter after cycle 1 and this can be observed at cycle 4 and cycle 9. Inset of Figure 7.8 is the calculation of the discharge capacity of the cycle 1 and the value was obtained at 2.27 mAh g<sup>-1</sup>. The discharge capacity for the rechargeable

battery is shown in Figure 7.9 and the value has been calculated using the Equation 3.9 from the literature. Here, the current applied is 0.3 mA and mass,  $m$  of the cathode material is 1 g.

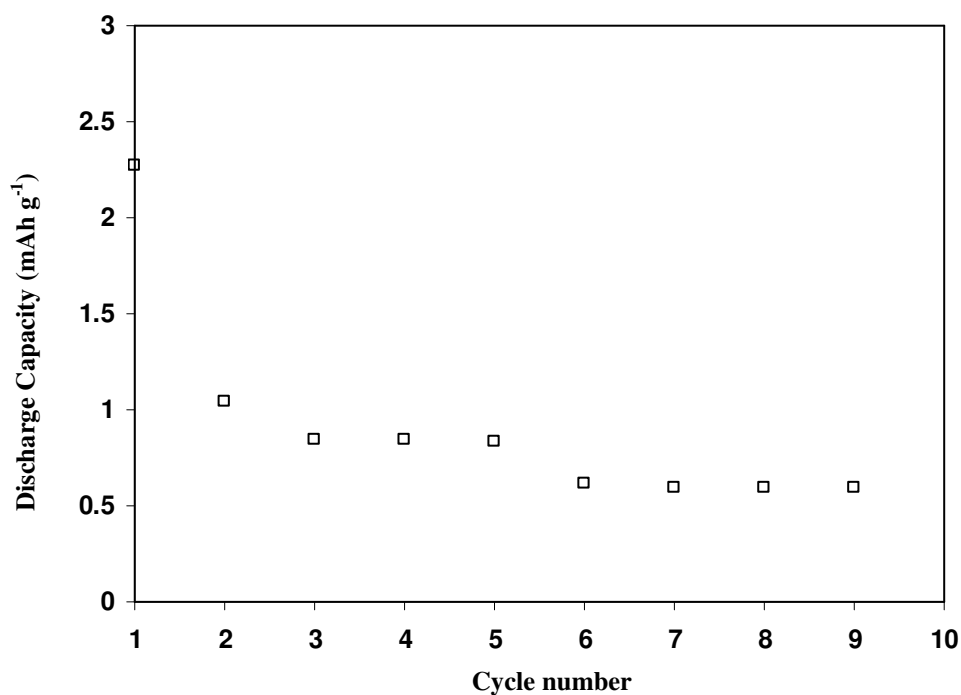


Figure 7.9: Discharge capacity of secondary proton battery.

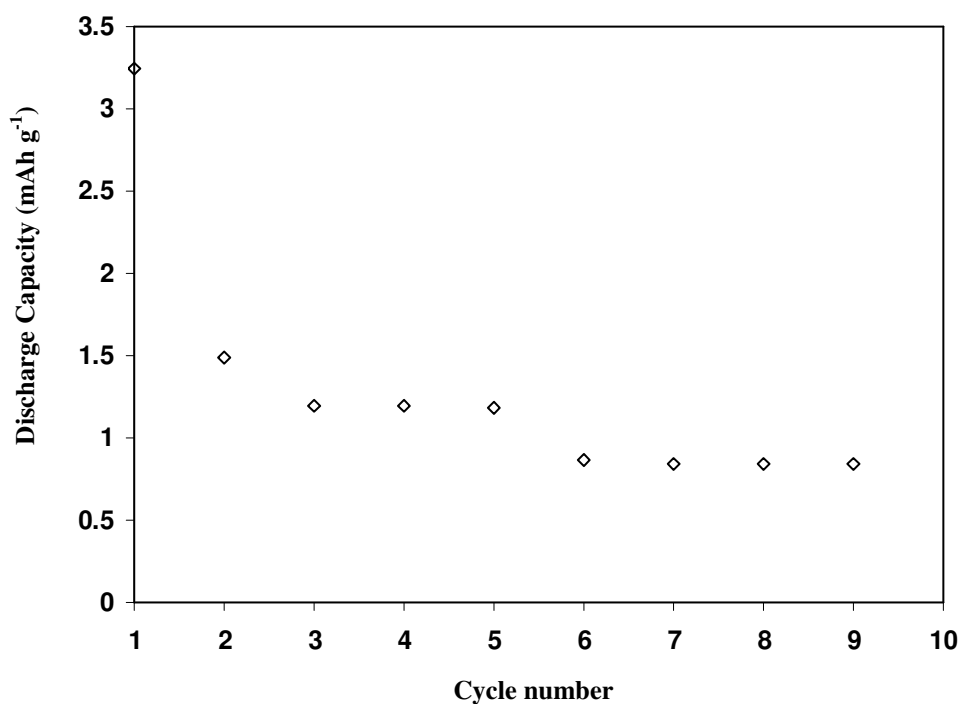


Figure 7.10: Discharge capacity of secondary proton battery considering the active material ( $\text{MnO}_2$ ) in the cathode.

Figure 7.10 shows the discharge capacity versus the cycle number using the same formula from Equation 3.9, only that the mass of active material in the cathode is taken into consideration which is the  $\text{MnO}_2$ . It is observed that the discharge capacity is higher in Figure 7.10 as compared to the value in Figure 7.9.

### 7.3 Electric Double Layer Capacitor (EDLC)

#### 7.3.1 Charge and Discharge Characteristics of EDLC

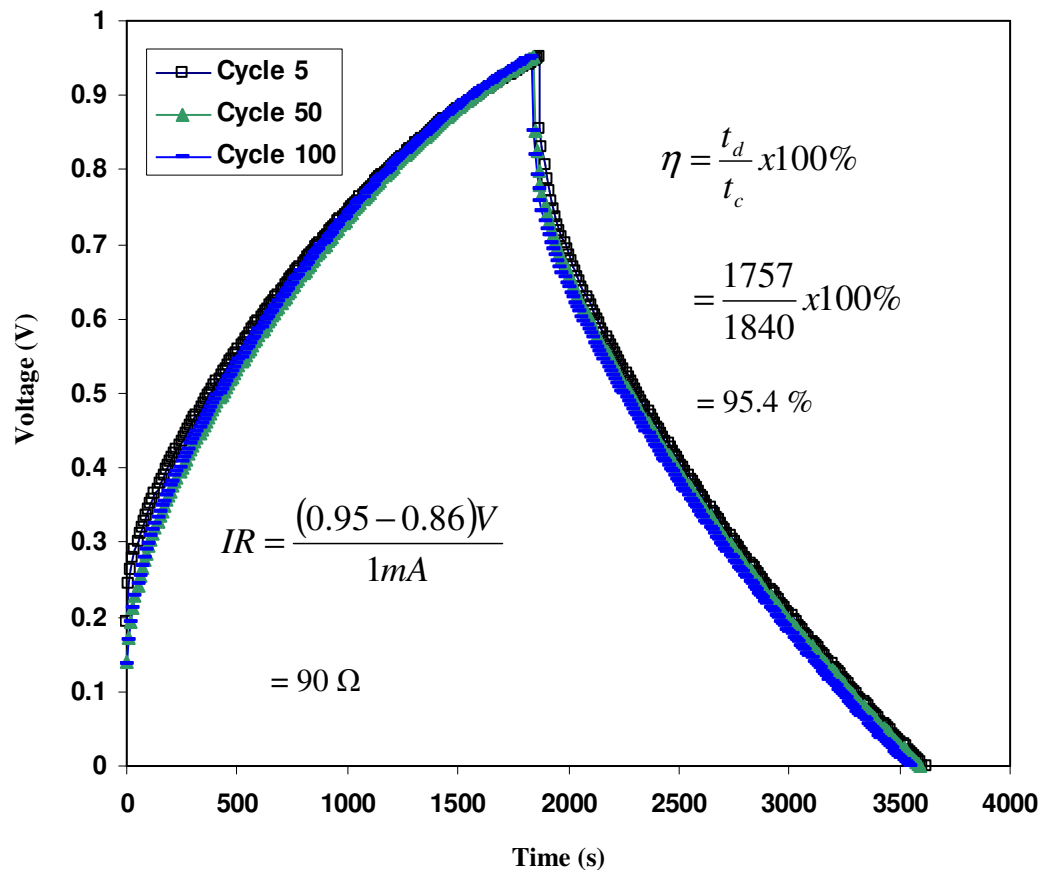


Figure 7.11: Charged and discharged curves for the EDLC at  $0.095 \text{ mA cm}^{-2}$  current density.

Figure 7.11 represents the profile of charge and discharge for the EDLC at  $0.095 \text{ mA cm}^{-2}$  current density with  $0.95 \text{ V}$  working voltage. The inverse V shape pattern is not perfectly observed. The instantaneous voltage between  $0.1$  to  $0.2 \text{ V}$  was observed within  $20 \text{ ms}$  of charging onset and the increase in voltage during charge is almost

linear with time until the voltage of 0.95 V was obtained. The voltage of the EDLC has dropped to 0.86 V at the onset of discharge. The EDLC was found to perform until 100 cycles. Inset of Figure 7.11 shows an example to calculate the efficiency and internal resistance of the EDLC.

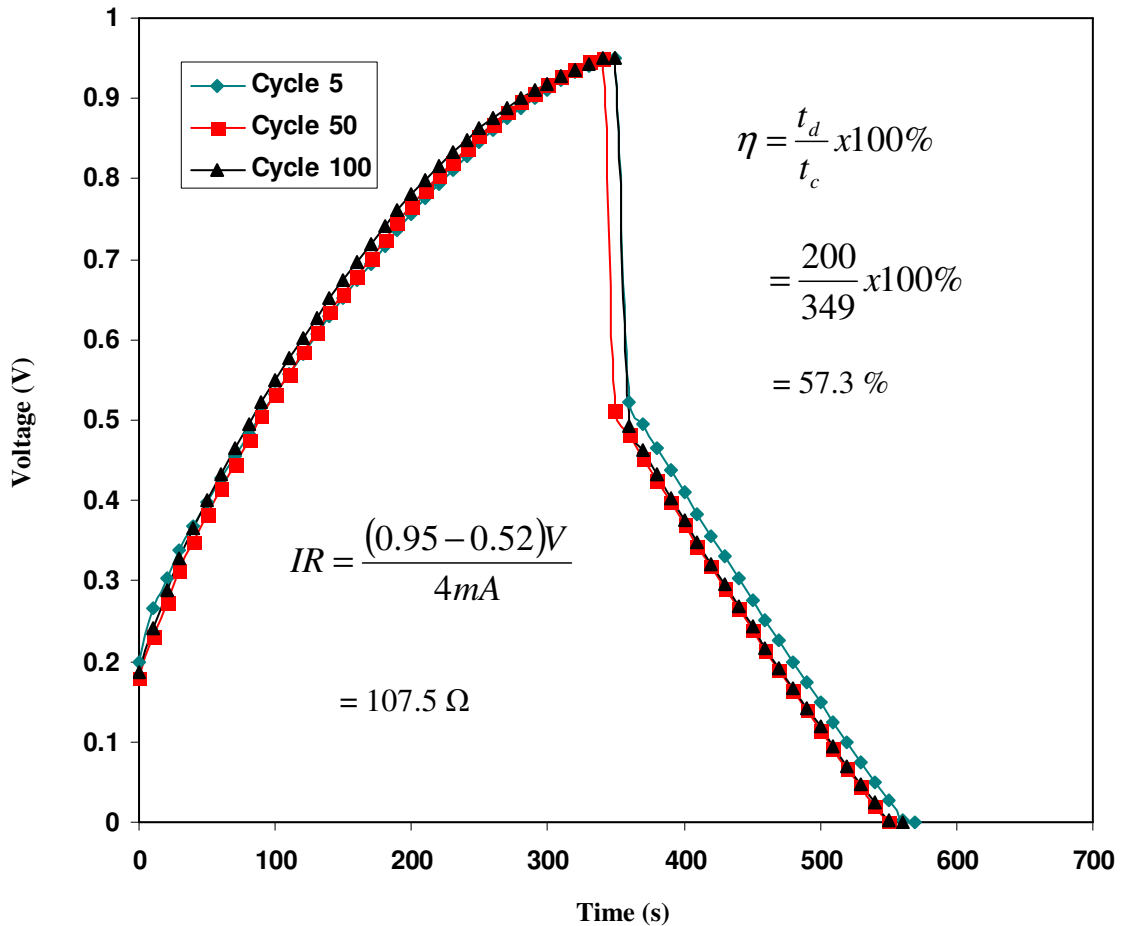


Figure 7.12: Charged and discharged curves for the EDLC at  $0.381 \text{ mA cm}^{-2}$  constant current density.

Figure 7.12 represents the profile of charge and discharge at  $0.381 \text{ mA cm}^{-2}$  current with 0.95 V working voltage. The instantaneous voltage between 0.1 to 0.2V was observed within 20 ms and the increase in voltage during charge is almost linear with time until the voltage of 0.95 V was obtained. The EDLC was found to perform until 100 cycles. The voltage of the EDLC dropped to nearly 0.52 V before onset of discharge.

## 7.3.2 Discharge Capacitance of EDLC

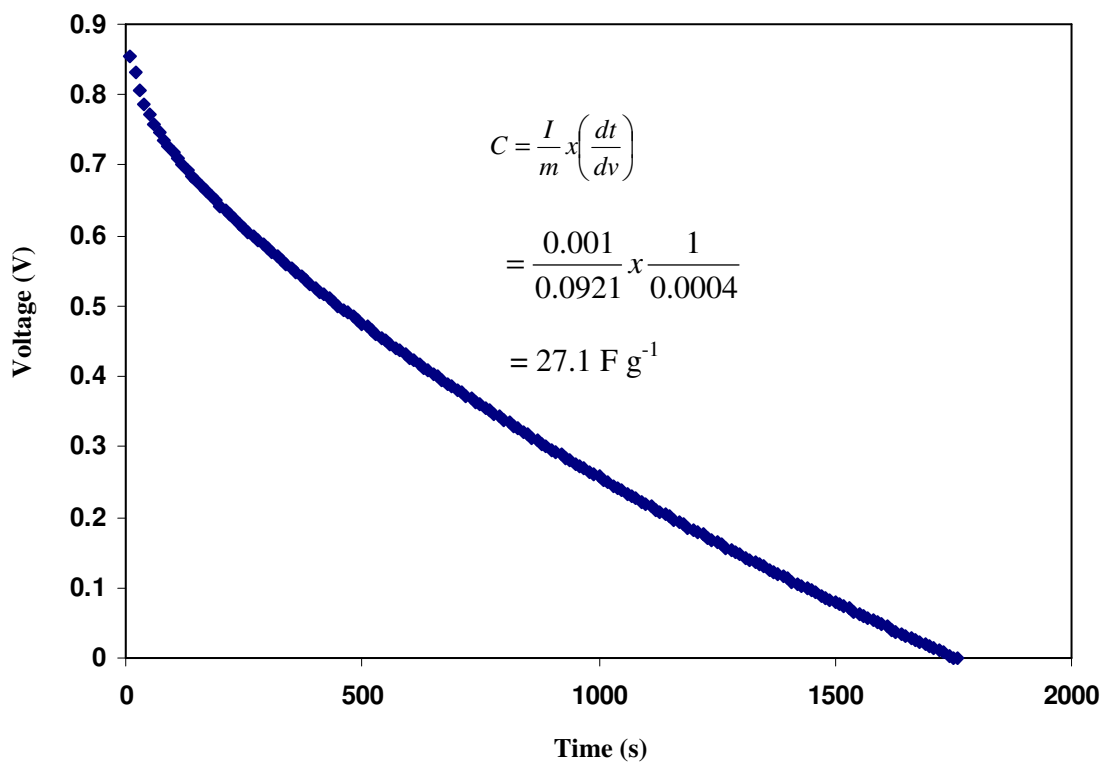
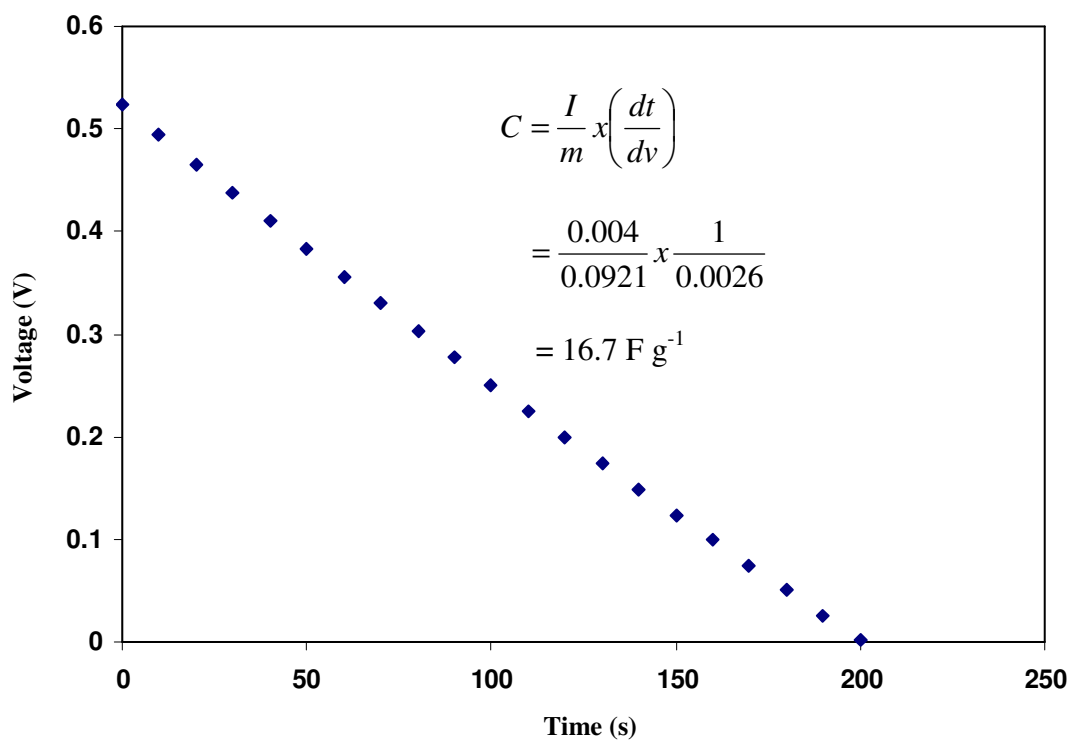
Figure 7.13: Discharged curves for the EDLC at  $0.095 \text{ mA cm}^{-2}$  constant current density.Figure 7.14: Discharged curves for the EDLC at  $0.381 \text{ mA cm}^{-2}$  constant current density.

Figure 7.13 and 7.14 shows discharge curve of the EDLC with applied current density of 0.095 and 0.381 mA cm<sup>-2</sup> respectively. For the EDLC performed at current drains of 1 and 4 mA, the voltage drops from 0.95 to 0.86 V and 0.95 to 0.52 V respectively before EDLC continues to further discharge and this was due to the internal resistance of the EDLC. The discharge curve is observed to lie on almost a straight line. Inset of the Figure 7.13 and 7.14 shows the calculation of the discharge capacitance. The discharge capacitance for the EDLC performed at 0.095 mA cm<sup>-2</sup> was calculated to be higher than that with 0.381 mA cm<sup>-2</sup> current density applied. The decrease in capacitance and energy stored at higher discharge rate could be due to the leakage in the double layer that results in dissipation and lost of the energy stored [Morita *et al.*, 2004; Mitra *et al.*, 2001; Shuhaimi *et al.*, 2008]. Figures 7.15 and 7.16 represents the discharge capacitance and the specific energy stored as a function of the cycle number.

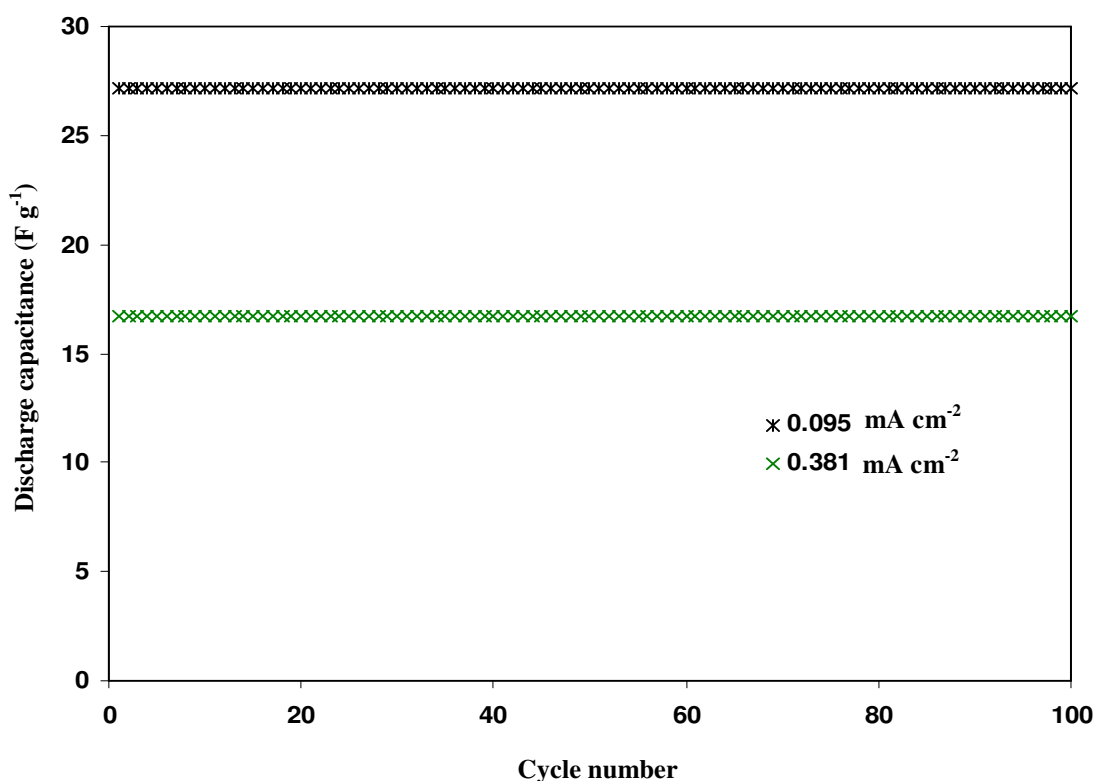


Figure 7.15: Discharged capacitance versus cycle number for the EDLC at different current density.

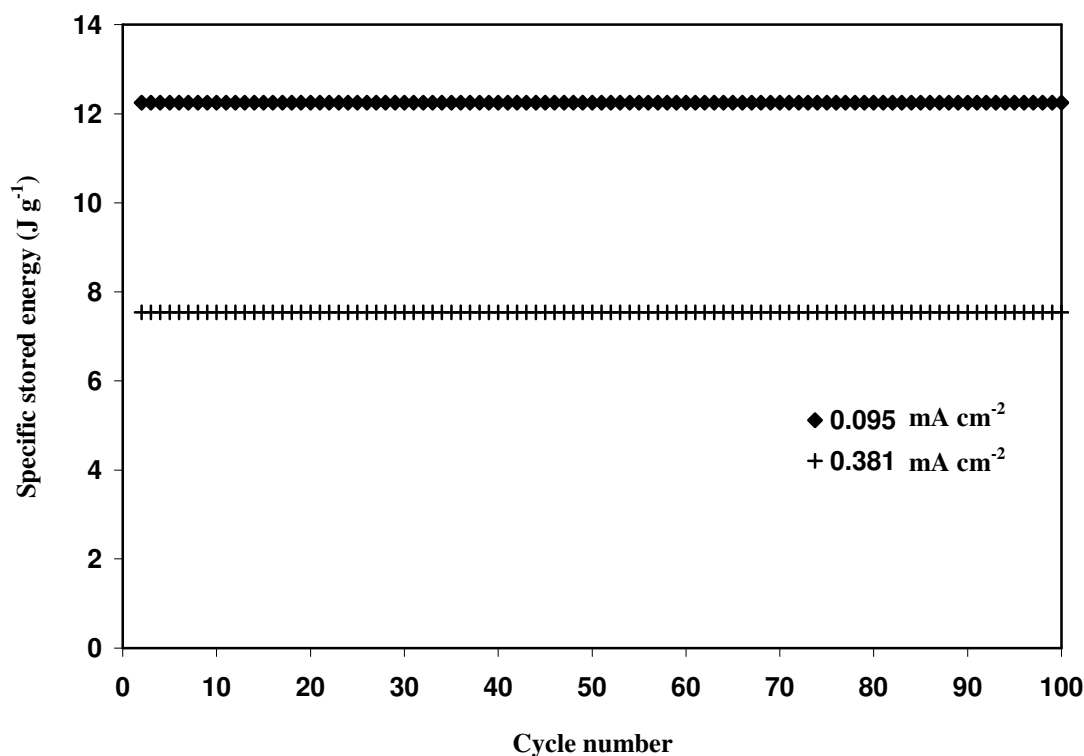


Figure 7.16: Specific stored energy versus cycle number for the EDLC at different current density.

#### 7.4 Summary

A primary and secondary proton batteries have been successfully fabricated using 30[60C4P6-40AN]-70EC solid polymer electrolyte. The OCP of the primary proton battery is around 1.63 V and for the secondary battery is slightly higher with 1.66 V. Hence the battery chemistry proposed in (equation 7.3) could be accepted and applicable. The primary battery can discharge with 2 mA constant current and the maximum power density is  $(9.47 \pm 0.26)$  mW cm<sup>-2</sup>. With the addition of 30[60C4P6-40AN]-70EC electrolyte in liquid phase to the cathode, the battery can perform as a rechargeable battery for 9 cycles. The EDLC can perform for 100 cycles at 0.095 and 0.381 mA cm<sup>-2</sup> current density. The capacitance of the EDLC was obtained to be 27.1 and 16.7 F g<sup>-1</sup> for the current density applied at 0.095 and 0.381 mA cm<sup>-2</sup> respectively.