CHAPTER 6

CHARACTERISTICS OF ELECTRICAL DOUBLE LAYER CAPACITOR

6.0   Introduction

Today, the energy storage technologies have received much attention. Electrical devices such as PDAs, Ipod players, laptops, digital cameras, cell phones, walkman and others require power to switch on. To power these devices without the conventional electricity, energy storage devices like batteries and capacitors are required. So as not to be in conflict with environmental conscious parties, researchers have attempted to produce energy storage devices using environment-friendly materials.

In this chapter, an attempt is made to fabricate electrical double layer capacitors (EDLC) using activated carbon electrodes and the highest conducting polymer electrolyte prepared in the present study. The characteristics of the EDLCs were studied using cyclic voltammetry and galvanostatic charge-discharge cycling to evaluate the capacitance value, maximum energy and power that can be delivered by the EDLC. Open circuit potential (OCP) and self-discharge characteristics were also determined.

6.1   Electrochemical stability of polymer electrolytes

The electrochemical stability of the polymer electrolyte must be determined before the EDLC can be fabricated and characterized. Electrochemical stability of polymer electrolytes was determined by linear sweep voltammetry (LSV). The measurements were carried out using the Autolab PGSTAT 12 potentiostat/galvanostat in conjunction with the General Purpose Electrochemical System (GPES) software Version 4.9.005. The voltage applied for this study was in the range from -2.5 to 2.5 V at sweep rate 1 mV s^{-1}. All experiments were done at room temperature. Figure 6.1 displays the linear sweep voltammogram of the highest conducting unplasticized MC-NH$_4$NO$_3$ (75MC25AN) polymer electrolyte system.
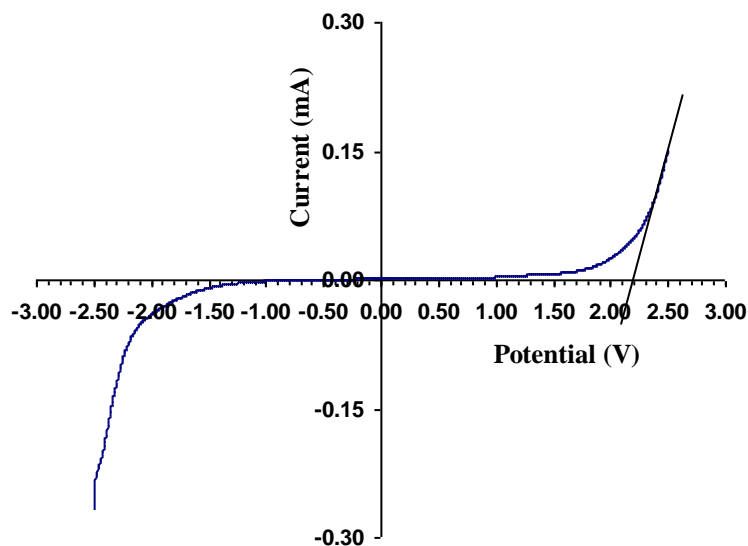

Figure 6.1: Linear sweep voltammetry (LSV) curves for 75MC25AN sample

From the figure, it can be seen that the current onset is detected at about 2.20 V. The current onset is assumed to be the polymer electrolyte film breakdown voltage [Baril *et al.*, 1997].

Figure 6.2 shows linear sweep voltammogram of the highest conducting plasticized MC-NH$_4$NO$_3$ (63.75MC21.5AN15PEG) polymer electrolyte.
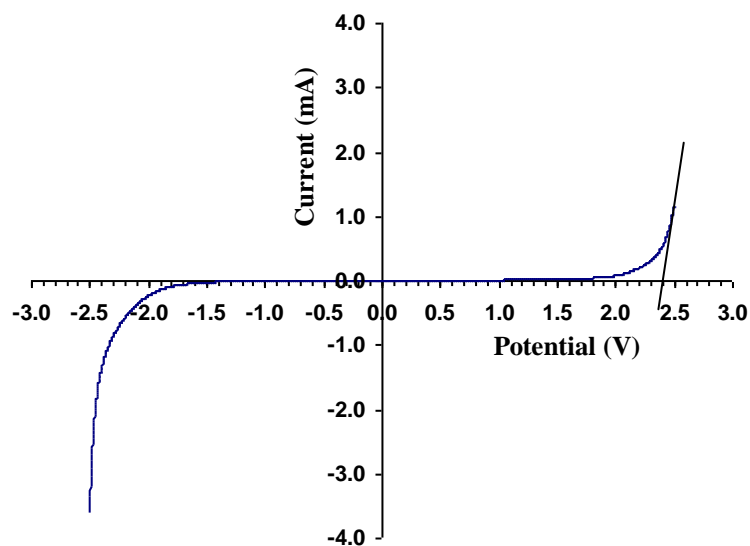

Figure 6.2: Linear sweep voltammetry (LSV) curve of the 63.75MC21.5AN15PEG sample

It can be observed that, for the highest conducting plasticized polymer electrolyte, the current onset is detected at about 2.40 V. To evaluate capacitor performance by charge-discharge cycling test, we must use a working voltage below this breakdown voltage to prevent the electrolyte from being destroyed. From these results, it may be inferred that conductivity influences decomposition voltage. The conductivity of the unplasticized sample is lower than that of the plasticized MC-NH$_4$NO$_3$ electrolyte system. No apparent difference is observed in both voltammograms except the decomposition voltage of the plasticized electrolyte is higher than that of the unplasticized electrolyte. The two electrolytes were electrochemically stable and should be safe to use in EDLCs that is to be charged to say, 0.85 V. The magnitude of current output from LSV is observed to be different for both systems where current output for the plasticized system is one order of magnitude higher than the unplasticized system. The conductivity of the plasticized system is $\sim 10^{-4}$ S cm^{-1}, two magnitude order higher than the unplasticized system ($\sim 10^{-6}$ S cm^{-1}).

6.2   EDLC configuration

The highest conducting plasticized polymer electrolyte, 63.75MC21.25AN15PEG, was used as a membrane in EDLC. Kaneko *et al*. (2005) pointed that power capability is influenced by conductivity of polymer electrolyte.

BP20 as the carbonaceous/active material, carbon black to reduce the internal resistance in electrode and methyl cellulose powder as binder were used to prepare the EDLC electrodes. From information obtained from the Kuraray website, BP20 was prepared from phenol resin. The properties are listed in Table 6.1.

Table 6.1: Properties of BP20 (From Kuraray website)

Test parameter	Units	BP (RP) 20
Iodine adsorption	mg/g	1700 ~ 1800
Benzene adsorption	wt.%	45 ~ 55
Total surface area	m^2/g	1600 ~ 1700
PH		5 ~ 8
Ash content	%	1.0 max
Diameter of particles	microns	3 ~ 20
*Capacitance with PC	F/g	23
**Volume capacitance with PC	F/cc	14

*Electrolye: tetrabutylammonium (nBu4N)>C104 1M/1 in PC (propylene carbonate) solvent
**Reference value (depends on the activated carbon density in electrode), electrolyte: nBu4N>C104 in PC

According to Staiti *et al*. (2002), the mechanical stability of the electrodes can also be increased by adding the polymer electrolyte in the electrode composition. Latham *et al*. (2002) pointed that the use of carbon black (CB) in the electrode material can improve electrolyte/electrode contact because CB also acts as binder in the electrode. The

percentage ratio BP20: MC powder: CB is 81.25:12.50:6.25. A small amount of 63.75MC21.25AN15PEG electrolyte solution was added to the electrode slurry.

The electrode slurry was applied onto the aluminum mesh current collector using dip-coating method. The polymer electrolyte was sandwiched between the activated carbon electrodes, which were clamped between rectangular Perspex plates to form the EDLC.

6.3   EDLC characteristics

6.3.1   Cyclic voltammetry test (CV)

Cyclic voltammetry is helpful to understand the electrochemical behavior of EDLC during charge-discharge processes [Tanahashi, 2005]. Cyclic voltammetry is almost similar to LSV. In this work, cyclic voltammetry tests were carried out using the AUTOLAB 12 potentiostat/galvanostat to evaluate the EDLC performance at scan rate 1 mV s^{-1} in a sweep region 0 to 0.85 V at room temperature.

Figure 6.3 displays the 5th scan of the cyclic voltammogram of an EDLC fabricated as described in section 6.2 with electrode size 0.8×0.9 and 1.5×3 cm^2. The capacitive current curve is in the range -0.27 to 0.51 mA for the smaller size EDLC and -0.51 to 1.11 mA for the larger EDLC. The large difference in the capacitive current observed indicates that the size of electrode gives an effect on the EDLC performance. For this experiment the discharge current was 1.0 mA.
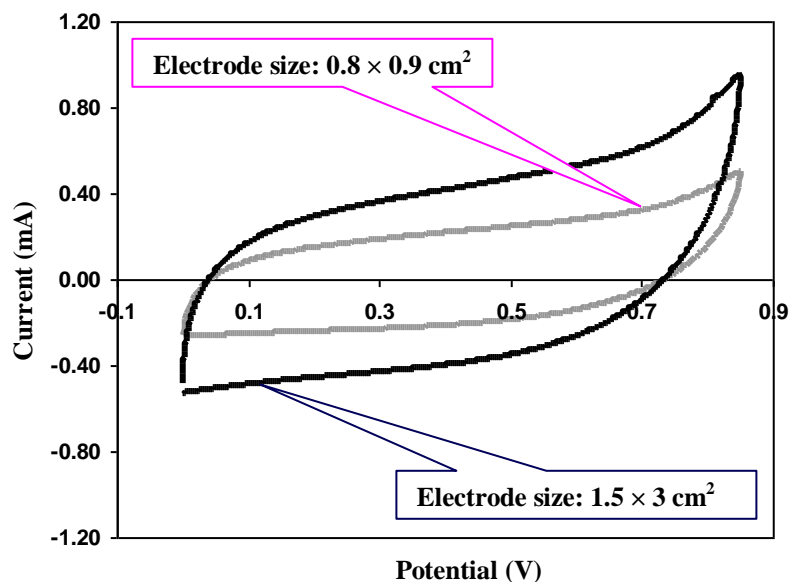
Figure 6.3: Cyclic voltammograms of the EDLC with electrode size 0.8×0.9 and 1.5×3 cm^2.

An ideal capacitor with no resistance would display a rectangular shape where non-Faradaic reactions take place over the potential range of operation [Frackowiak and Béguin, 2001]. This shape shows that electric charge is stored in the electric double layer at the interface between electrode and electrolyte [Matsuda *et al*., 1999] or in other words, reversible electrostatic reaction takes place and capacitance is independent of potential. Voltammograms in Figure 6.3 shows the non-ideal EDLC and takes a parallelogram-like shape. A parallelogram-like shape is attributed to the distributed capacity effect that occurs when the exterior surface of the porous electrode charges or discharges faster than the interior and when the electrode resistance is non-uniform [Tanahashi, 2005].

Another EDLC was fabricated according to the method described in section 6.2, but the electrodes were coated with a layer of PEG. Cyclic voltammetry test was carried out for freshly fabricated EDLC using uncoated electrodes and electrodes coated with PEG of the same size, Figure 6.4.

Figure 6.4 depicts the 5th scan of cyclic voltammogram of an EDLC fabricated using uncoated and coated electrodes with size 1.5×3 cm^2. The capacitive current curve is in range -0.88 to 1.84 mA for EDLC using electrode coated with PEG while for EDLC using uncoated electrode shows the capacitive current curves in range -0.51 to 1.11 mA.
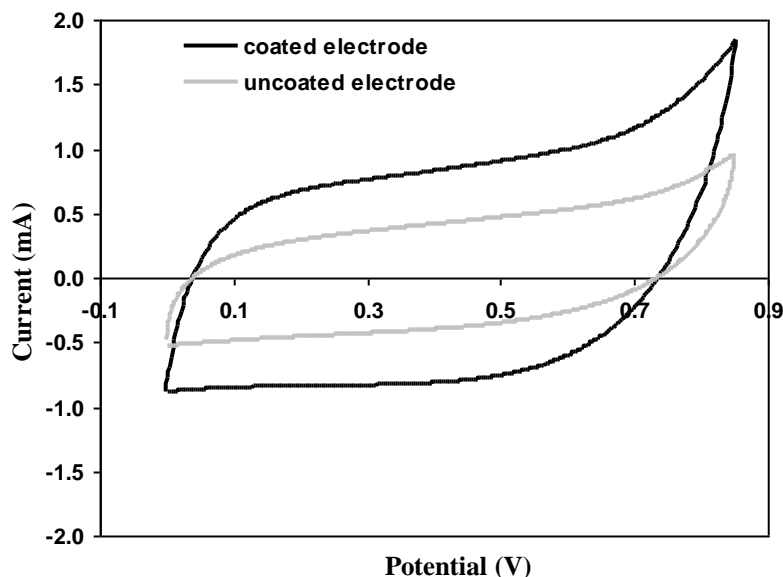

Figure 6.4: Cyclic voltammogram of the EDLC with electrode size 1.5×3 cm^2.

The two voltammograms in Figure 6.4 are of similar shape and still shows deviation from the rectangular shape or still parallelogram-like. The capacitive current does not exhibit large differences in both voltammograms. It indicates that electrodes coated with PEG on its surface do not give much effect on the capacitive behavior of EDLC. The voltammograms do not show redox and oxidation peaks, indicating that the charge and discharge occur at a constant rate over the complete cycle. The discharge current shows an almost plateau feature for the two voltammograms especially on the return path. This can be attributed to the formation of a homogeneous and ideally polarizable double layer formed at the interface [Ganesh *et al.*, 2008].

The voltammogram depicted in Figure 6.5 is recorded after 100th charge-discharge cycling test for EDLC using electrode with size 1.3×1.4 cm^2. It can be seen that no visible changes of voltammogram were detected when CV test was repeated after 100th charge-discharge cycling measurements.
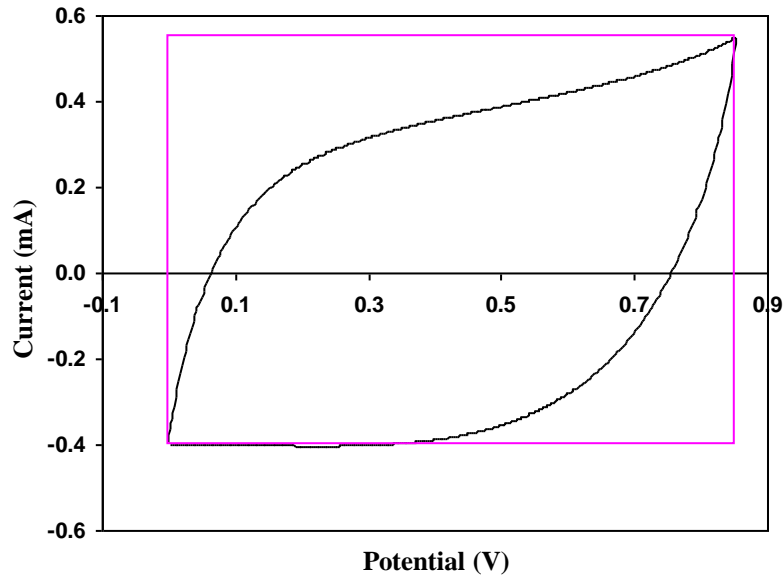

Figure 6.5: Cyclic voltammogram of the EDLC with electrode size 1.3×1.4 cm^2 after 100th cycle and electrode was coated with PEG on the surface.

Cyclic voltammograms can also be used to determine power loss. Power depends on current and voltage, $P = IV$. Here P is power in watts, I is the charge or discharge current in amperes and V is the EDLC working voltage in volts. If the voltammogram is perfectly in rectangular shape, the power could be obtained can also be inferred as listed in Table 6.2. The power is lost as heat during charge and discharge processes. The loss is caused by resistance in the electrodes, contact and in the electrolyte. Power loss in each voltammogram have been calculated and listed in Table 6.2. Each voltammogram displayed here is obtained after 5th cycle CV running.

Table 6.2: Lists of power loss from cyclic voltammogram

Figures	Electrodes	Sizes (cm $\times$ cm)	Power could be obtained (mW)	Power loss (mW)	
				Cathodic	Anodic
6.3	Uncoated	0.8×0.9	0.66	0.08	0.10
6.3/6.4	Uncoated	1.5×3.0	1.23	0.29	0.22
6.4	Coated	1.5×3.0	2.31	0.27	0.27
6.5	Coated	1.3×1.4	0.81	0.12	0.09

From the table above, differences in the cathodic and anodic power loss can be observced. For EDLC using uncoated electrodes with size 0.8×0.9 cm^2, the cathodic power loss is 0.08 mW while the anodic power loss is 0.10 mW. For EDLC using uncoated electrode with size 1.5×3.0 cm^2, the cathodic power loss is 0.29 mW while the anodic power loss is 0.22 mW. The voltammograms of these two EDLCs are parallelogram in shape. More rectangular voltammograms give smaller difference between cathodic and anodic power losses. For EDLC using coated electrode with size 1.5×3.0 cm^2, cathodic and anodic power loss is 0.27 mW. It shows zero difference between cathodic and anodic power losses. It is because of this, EDLC perform a voltammogram is more rectangular in shape. EDLC using coated electrodes with size 1.3×1.4 cm^2 shows a smaller difference between cathodic and anodic power losses, i.e. 0.03 mW. From Table 6.2 power losses seem to depend on size of EDLC. It can also be inferred that almost rectangular part gives smaller power loss.

From CV test, the voltammograms imply that, EDLC employed using 63.75MC21.25AN15PEG sample as electrolyte and activated carbon electrode depicts the capacitive behavior but the performance of the EDLC can still be improved to make the EDLC deliver more charge in a shorter time. The voltammograms obtained in the present

work are also similar in behavior to the voltammogram of EDLCs reported by Matsuda *et al*. (1999), Lewandowski *et al*. (2003) and Staiti *et al*. (2002). Voltammogram of EDLC fabricated by Matsuda *et al*. (1999) is quite rectangular in shape. From the voltammogram, the power that could be obtained by Matsuda *et al*. (1999) is 0.99 mW. The cathodic and anodic power losses for their EDLC are the same, i.e. 0.22 mW. In the work of Lewandowski *et al*. (2003), the power that could be obtained from the voltammogram is 4mW. The cathodic power loss is 0.73 mW and the anodic power loss is 0.36 mW. The difference is. 0.37 mW. Power could be achieved from Staiti *et al*. (2002) is 24 mW. Cathodic power loss for EDLC studied by Staiti *et al*. (2002) was calculated is 2.35 mW while anodic power loss is 6.39 mW. The larger difference is manifested by the shape of the voltammogram which shows distortion from rectangular shape during the anodic part of the cycle.

The percentages of power lost in this work are 27.27 and 41.46 % for EDLC fabricated using uncoated electrodes with size 0.8×0.9 and 1.5×3.0 cm^2 respectively. For same size but different electrode conditions, EDLC fabricated using coated electrode has lower percentage of power loss, 23.38 % compared to uncoated electrode, 41.46 %. The percentage power loss for EDLC after 100th cycle for coated electrode with size 1.3×1.4 cm^2 is much smaller, 25.92 % compared to uncoated electrode. As comparison with other reports, Matsuda *et al*. (1999) gets 42.42 % power loss in their work. Lewandowski *et al*. (2003) obtained 27.25 % power loss and Staiti *et al*. (2002) achieved 36.425 % power loss. It can be deduced the EDLC fabricated in this work gives reasonably good performance in power storing compared to those in the three reports mentioned before.

6.3.2   Charge-discharge characteristics

For EDLC performance, working voltage is largely dependent on the electrolyte breakdown voltage, while internal resistance and capacitance depends on the electrode and conductivity of electrolyte. In this work, the voltage limits were set between 0 to 0.85 V to avoid the decomposition of the polymer electrolytes and constant current of 1 mA was applied during charge and discharge. Charge-discharge characteristics were carried out to study the effect of current density on the EDLC performance.

6.3.2.1 The effect of current density on the EDLC performance using uncoated electrodes

Depicted in Figure 6.6 are the typical charge-discharge curves for two EDLCs after the 4th cycle at different current densities.
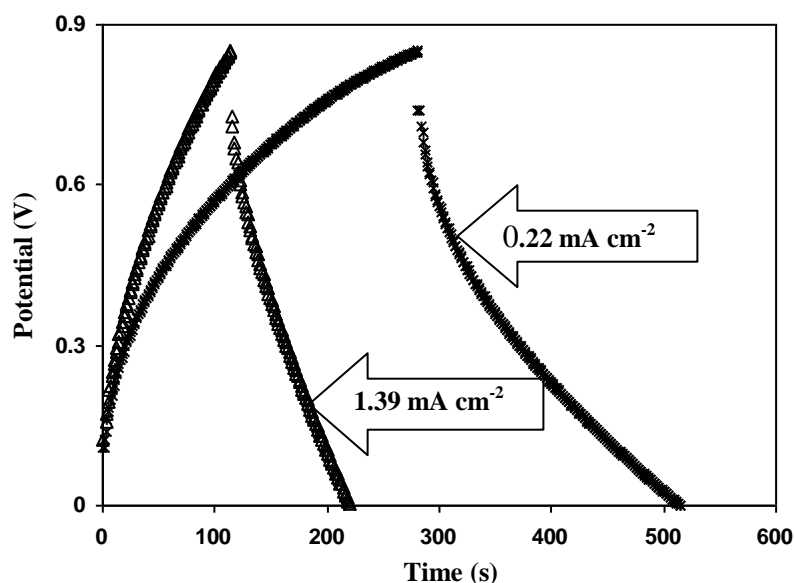

Figure 6.6: Charge-discharge curves of the EDLC at different current density. The surface of electrode was not coated with PEG.

These curves do not show the perfect "inverse V" shape for charging and discharging. An instantaneous voltage was observed when current was applied i.e. 0.12 V and 0.11 V for current density 1.39 and 0.22 mA cm^{-2} respectively. These voltages are almost the same to the amount of voltage drop at the beginning of discharge i.e. 0.12 V for 1.39 mA cm^{-2} discharge current density and 0.11 V for 0.22 mA cm^{-2} discharge current density. Charge and discharge current is 1.0 mA.

The value of ESR, charge and discharge capacitance, coulombic efficiency, maximum energy and power delivered from EDLCs studied are listed in Table 6.3.

Table 6.3: Characteristics of EDLC cells at different current density for 4th cycle

Characteristics	Current density at 1.39 mA cm^{-2}	Current density at 0.22 mA cm^{-2}
ESR (Ω)	122.40	109.10
Specific charge capacitance (F g^{-1})	15.23	44.99
Specific discharge capacitance(F g^{-1})	14.40	33.25
Coulombic efficiency (%)	94.55	73.91
Specific maximum energy (kJ kg^{-1})	5.50	16.25
Specific power delivered (kW kg^{-1})	0.12	0.13

A sudden potential increase while charging and sudden drop while discharging is normally seen for EDLCs [Hashmi *et al*., 2007; Pandey *et al*., 2010]. Hashmi *et al*. (2007) applied PMMA-EC:PC-NaClO$_4$ gel electrolyte to an EDLC based on activated charcoal powder electrode and charged the cell to 1.0 V. An EDLC consisting of EMITf/PVDF-HFP gel polymer electrolyte and multiwalled carbon nanotube electrodes was charged from 0 to 2.0 V by Pandey *et al*. (2010) and the initial sudden drop/jump in the voltage while charging and discharging is due to ohmic loss across the internal resistance. These voltages

are also known as IR drop or equivalent series resistance (ESR) [Tripathi *et al*., 2006]. It may be inferred that the larger EDLC gives higher discharge and charge capacitance.

The specific capacitance of EDLC obtained by Matsuda *et al*. (1999) is 10.3 F g^{-1} with R$_{IRdrop}$ ~ 56 Ω. Lewandowski *et al*. (2003) obtained specific capacitance ~ 33 F g^{-1} from EDLC using activated carbon powder (ACP) electrodes from CV and 34 F g^{-1} from galvanostatic charge discharge. 13.2 F g^{-1} capacitance was reported by Staiti *et al*. (2002) who used prepared Nafion 1100 solution by casting (NGR50) electrolyte in EDLC.

6.3.2.2 The effect of current density on the EDLC performance using coated electrodes

The EDLCs were fabricated in the same manner but the electrodes were coated with PEG. Figure 6.7 displays the charge-discharge curves for EDLC using electrodes coated with PEG at the 4th cycle.
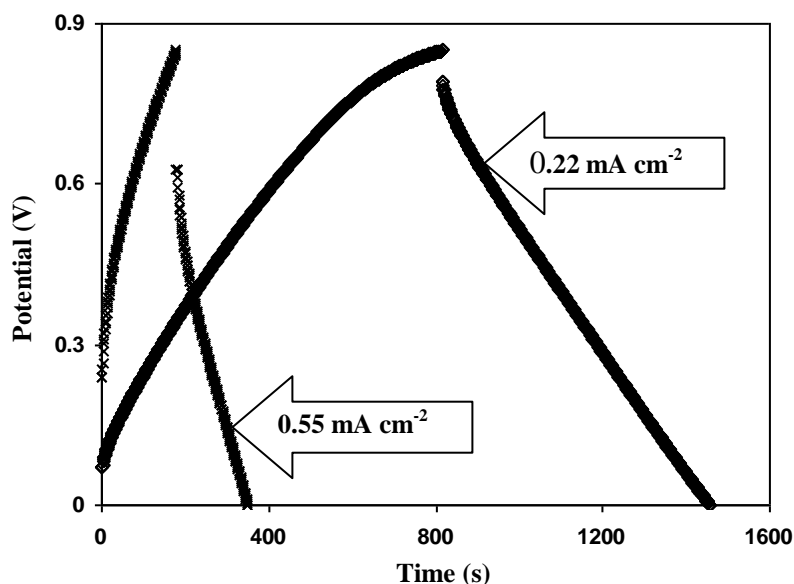

Figure 6.7: Charge-discharge curve of the EDLC at different current density for coated electrodes

The EDLC charged and discharged with low current density, 0.22 mA cm^{-2} illustrated almost perfect inverse V shape. According to Wada *et al*. (2004), the linear charge-discharge curve shows good electrode/electrolyte contact has formed in the EDLC cell and the cell worked quite successfully. The instantaneous voltages observed when current was applied are 0.23 V and 0.07 V for current density 0.55 and 0.22 mA cm^{-2} respectively. These voltages are almost of the same magnitude to the amount of voltage drop during discharge i.e. 0.22 V for 0.55 mA cm^{-2} current density and 0.06 V for 0.22 mA cm^{-2} current density. The value of internal resistance, charge and discharge capacitance, coulombic efficiency, maximum energy and power delivered from EDLCs are listed in Table 6.4.

Table 6.4: Characteristics of EDLC cells at different current density for 4th cycle

Characteristics	Current density at 0.55 mA cm^{-2}	Current density at 0.22 mA cm^{-2}
ESR (Ω)	220.00	60.10
Charge capacitance (F g^{-1})	41.67	41.94
Discharge capacitance(F g^{-1})	34.72	38.45
Coulombic efficiency (%)	83.33	91.67
Specific maximum energy (kJ kg^{-1})	15.05	15.15
Specific power delivered (kW kg^{-1})	0.09	0.14

It can be observed that on coating the electrode with PEG improves the characteristics of the EDLC.

6.4   Self-discharge characteristics

The self discharge characteristics are one of the most crucial factors to determine the performance of the EDLC. It can be determined by measuring the open circuit voltage of the EDLC as a function of time. The EDLC cell was charged, discharged and charged again at a constant current. When charging current is stopped, voltage decreased. This is self-discharge [Ricketts and That, 2000]. From self-discharge, we can know the period of stored energy in an EDLC.

Figure 6.8 demonstrates the voltage drop upon discharge at 1 mA compared to self-discharge (open circuit voltage) reading for 86 seconds. The fabricated EDLC has electrode size 1.5×3 cm^2 and aluminum mesh as current collector. It can be observed that the voltage initially drops to 0.67 when the EDLC was discharged at 1 mA and 0.77 V for self-discharge.
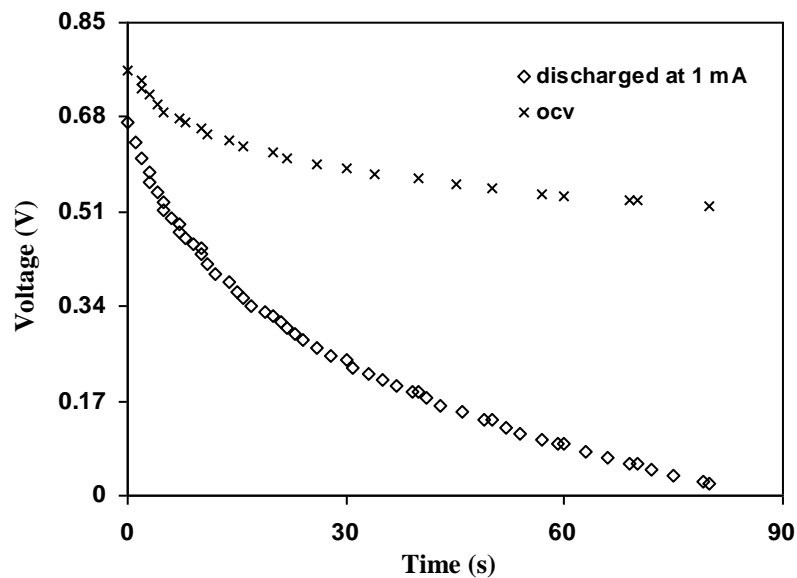
Figure 6.8: Self discharge profiles resulting from charging to 0.85 V of EDLC using uncoated electrode size 1.5×3 cm^2.

Depicted in Figure 6.9 is voltage drop upon discharge at 1 mA and OCV for EDLC cell fabricated using electrode with PEG coated on it surface.
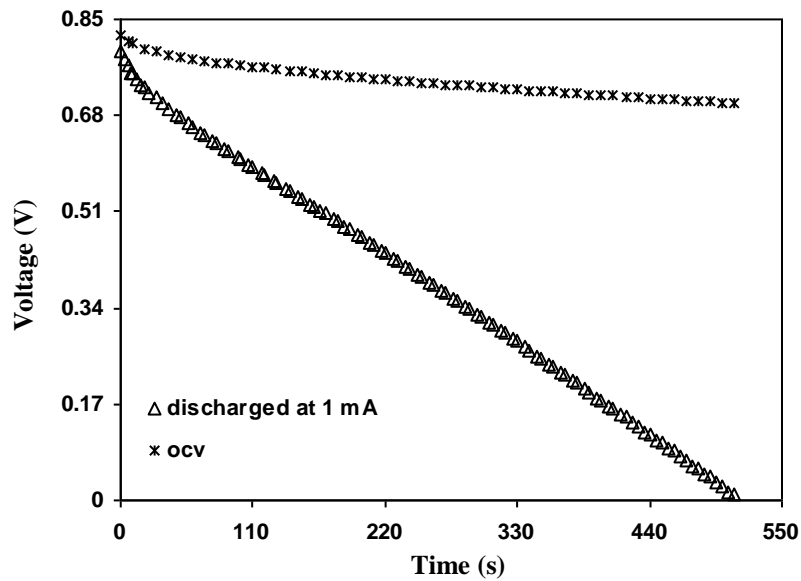

Figure 6.9: Self discharge profile resulting from charging to 0.85 V of EDLC using coated electrode with PEG; size 1.5×3 cm^2.

It can be observed that, the initial voltage drop for this cell when EDLC was discharged at 1 mA is 0.79 V and 0.82 V for self discharge. The instantaneous voltage drop is related to internal resistance in EDLC. The self-discharge is quite rapid for EDLC using uncoated electrodes and the value of voltage drop for EDLC using uncoated electrodes is higher compared to EDLCs with coated electrodes. This again shows that PEG can upgrade the EDLC performance.

Figure 6.10 displays a self-discharge curve (OCV) for EDLC using coated and uncoated electrodes measured for 2 hours. It can be observed that, the voltage decreased to 0.36 and 0.24 V for EDLC using coated and uncoated electrodes respectively after 2 hours self-discharge.
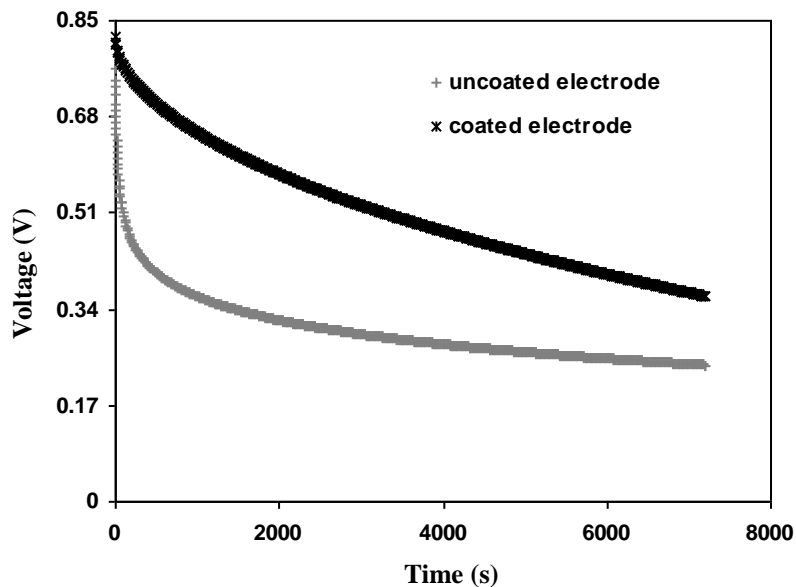
Figure 6.10: Self discharge profiles after charging with 0.85 V.

6.5   Cycle life of the EDLC

Cycle life is also a very important parameter in quantifying the EDLC performance. The advantage of EDLC compared to conventional batteries is its long cycle life [Kumar and Bhat, 2009]. This section represents the cycle life for EDLC using PEG coated electrodes and size 1.3×1.4 cm^2. The performance of an EDLC could be shown by the constant capacitance over a large cycle number. A longer cycle time shows that a higher amount of electric energy can be stored in the EDLC. Figure 6.11 represents the variation of charge and discharge capacitance with cycling number. It can be distinguished that the charge capacitance is not initially stable, but after 25 cycles it has become almost stable and continues to show stability up to 100 cycles. Discharge capacitance is very stable for 100 cycles. A high coulombic efficiency would be an advantage for EDLCs.
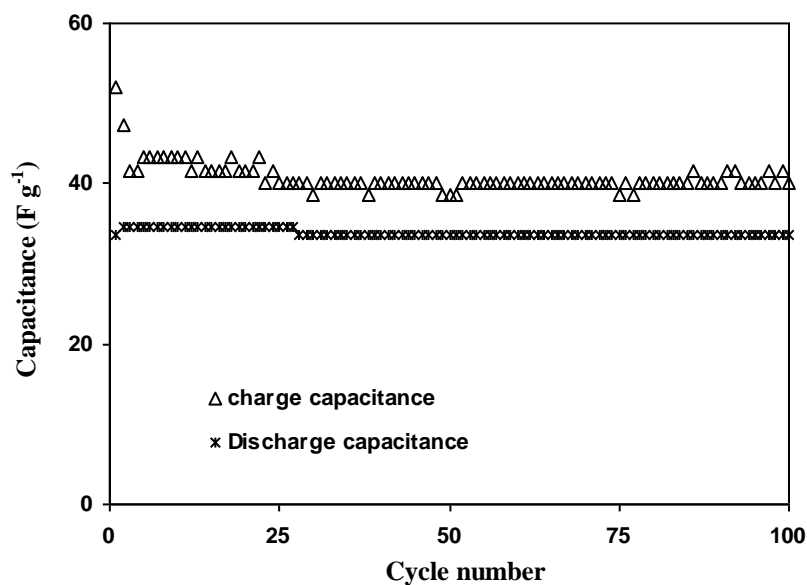
Figure 6.11: Charge/discharge capacitance of the EDLC using coated electrode with size 1.3 × 1.4 cm^2.

Figure 6.12 shows the coulombic efficiency versus cycling number. This coulombic efficiency is quite high (in the range 65 to 87 %) and almost constant. The coulombic efficiency is not 100 % indicating that the charge and discharge processes in the EDLC is not fully reversible.
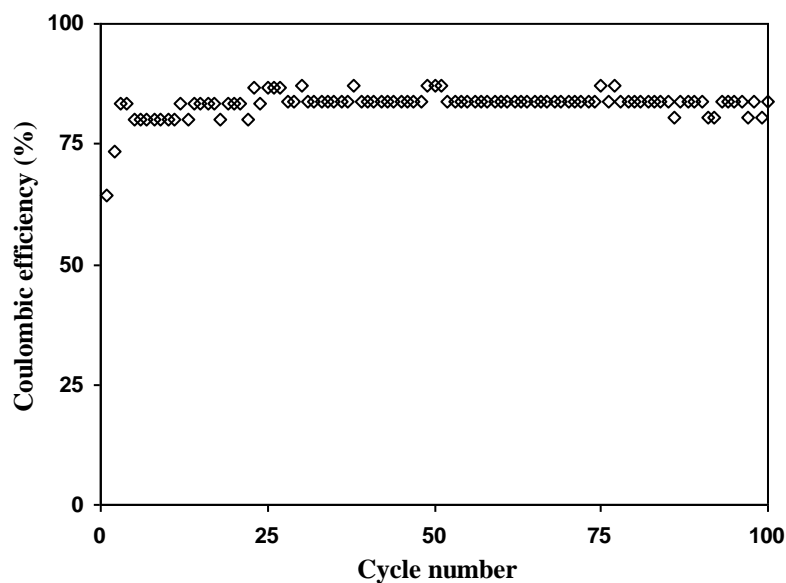

Figure 6.12: Coulombic efficiency of the EDLC using coated electrode with size 1.3 × 1.4 cm^2.

The internal resistance can also be considered as an important parameter to investigate EDLC characteristics because it gives a big effect on the EDLC performance. In this work, all EDLC fabricated have high internal resistance and a typical plot of internal resistance versus cycle number is as shown in Figure 6.13.
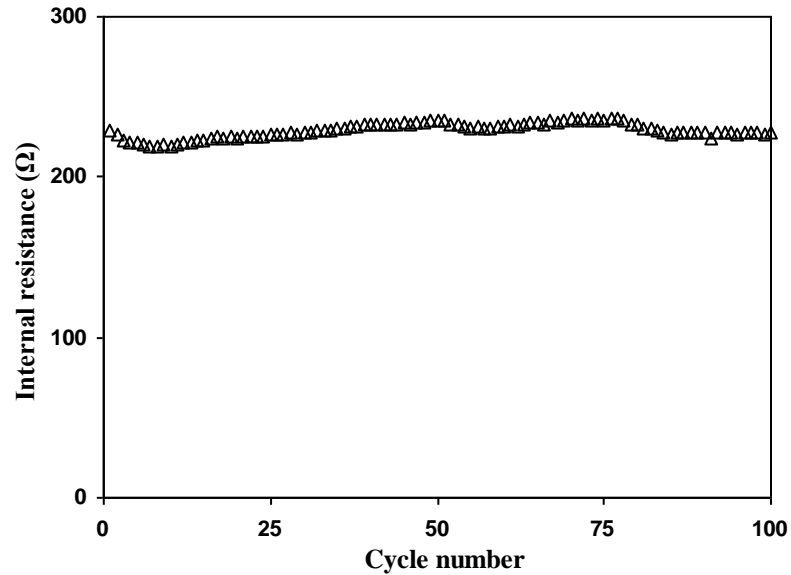
Figure 6.13: Internal resistance of the EDLC using coated electrode with size 1.3 ×1.4 cm^2.

Figure 6.14 displays the variation of specific maximum energy and specific power delivered from the EDLC against cycling numbers.
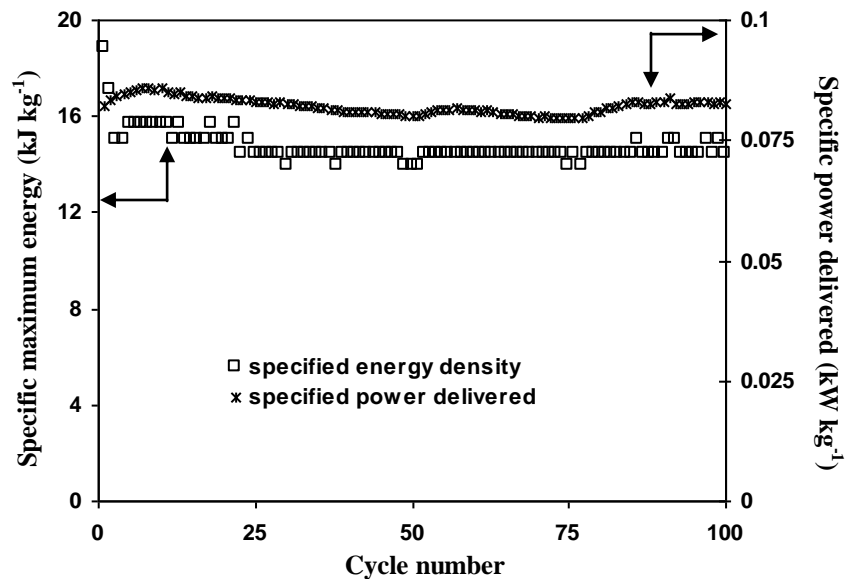
Figure 6.14: Specific maximum energy and specific power delivered of the EDLC using coated electrode with size 1.3 ×1.4 cm^2.

6.6 Summary

In this work, we have studied the electrochemical stability of the highest unplasticized and plasticized $MC-NH_4NO_3$ polymer electrolyte systems. The linear sweep voltammogram shows both samples have wide electrochemical stability. The polymer electrolyte 63.75MC21.25AN15PEG has been used in the fabrication of EDLCs. The EDLCs were fabricated in different sizes and different electrode conditions. Firstly, we observed the EDLC with larger electrode gives a better performance compared to smaller electrode. Secondly, we found that an EDLC, which the electrodes coated with PEG has excellent characteristics compared to EDLC using uncoated electrodes. It can be seen from the cyclic voltammogram test EDLC using coated electrodes exhibits voltammogram of a more rectangular shape and on the other hand, EDLC using uncoated electrodes only shows parallelogram-like shape. From charge-discharge characteristics, the EDLC using coated electrodes presents a higher discharge capacitance and low internal resistance compared to EDLC using uncoated electrode.