

Biopolymeric electrolyte based on glycerolized methyl cellulose with NH_4Br as proton source and potential application in EDLC

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Abstract In the present work, biopolymer electrolyte films based on MC doped with NH_4Br salt and plasticized with glycerol were prepared by solution casting method. Fourier transform infrared (FTIR) spectroscopy analysis confirms the interaction between MC, NH_4Br , and glycerol. X-ray diffraction (XRD) explains that the enhancement of conductivity is affected by the degree of crystallinity. This result is verified by field emission scanning electron microscopy (FESEM). For unplasticized system, sample containing 25 wt% of NH_4Br possesses the highest ionic conductivity of $(1.89 \pm 0.05) \times 10^{-4} \text{ S cm}^{-1}$. The addition of 30 wt% glycerol increases the conductivity value up to $(1.67 \pm 0.04) \times 10^{-3} \text{ S cm}^{-1}$. The conduction mechanism was best presented by the correlated barrier hopping (CBH) model. The linear sweep voltammetry (LSV) and cyclic voltammetry (CV) result confirms the suitability of the highest conducting electrolyte to be employed in the fabrication of electrochemical double layer capacitor (EDLC).

Keywords Methyl cellulose · Biopolymer electrolytes · Conductivity · Conduction mechanism · EDLC

Introduction

Biopolymer electrolytes (BPEs) obtained from natural polymers such as starch, cellulose, and chitosan have attracted attention in recent years because of their good mechanical and electrical properties. Natural polymers have a natural tendency to decay compared to synthetic polymer which is indestructible [1–3]. Methyl cellulose (MC) is a biodegradable polymer which is a modified type of cellulose being the most abundant biopolymer in nature [4]. It is well known and of interest to be used as environmental friendly products, especially as coating or mulching film, because of its large availability, cheap, and easy processes ability. However, due to a biodegradable behavior of MC, it can be used only in limited applications [5]. MC has lone pair electrons at its oxygen atoms which can act as electron donor. The presence of lone pair electrons is a criterion for a polymer to play host for ionic conduction [6]. Besides, MC has good film forming property, high mechanical strength and can form a transparent film. In addition, MC is water-soluble polymer and consists of hydroxyl group in its chemical structure [7, 8]. It is reported that MC-ammonium nitrate (NH_4NO_3) obtained a room temperature conductivity of $(2.10 \pm 0.37) \times 10^{-6} \text{ S cm}^{-1}$ [9] and MC-ammonium iodide (NH_4I) obtained a room temperature conductivity of $(5.98 \pm 0.04) \times 10^{-4} \text{ S cm}^{-1}$ [10]. In this study, a new polymer electrolyte based on MC which is doped with NH_4Br was prepared. NH_4Br has been chosen as the proton source since ammonium salts are considered good proton donor to the polymer matrix [11].

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The addition of plasticizer into the polymer-salt complexes has been reported to enhance the conductivity of BPEs. This is because the incorporation of plasticizer can increase the amorphous content of polymer-salt complexes [12]. In this work, glycerol is chosen as the plasticizer agent. Glycerol has a dielectric constant of 42.5. Plasticizer with high dielectric constant value can assist the dissolution and dissociation of excess salt, hence increases the number density of ions [13, 14]. It is reported that the conductivity of starch-chitosan-ammonium chloride (NH_4Cl) electrolyte has been increased from $(6.47 \pm 1.30) \times 10^{-7}$ to $(5.11 \pm 1.60) \times 10^{-4} \text{ S cm}^{-1}$ on addition of glycerol [15].

Electrical energy storage technologies become increasingly important with the growth of portable consumer electronics and a promising technology for energy storage is the electrochemical double layer capacitor (EDLC) [16]. EDLC research has focused on improving energy density without compromising power density. Using biopolymer electrolytes, a high energy density application can be obtained because the characteristics of EDLC electrolytes are high conductivity, wide operating temperature range, large voltage window, and good stability during charge-discharge cycles [17]. This work reports the effect of glycerol on the characteristics of H^+

(proton) conducting biopolymer electrolytes based on methyl cellulose for EDLC application.

Experimental

Preparation of electrolytes

For the preparation of unplasticized electrolyte, 1 g of MC (132.14 g/mol) powder procured by Sigma Aldrich was dissolved in 100 ml of distilled water at room temperature for 24 h by using a magnetic bar stirrer. Different amount of NH_4Br (97.94 g/mol) (HmbG Chemicals) were then added to the solutions. The solutions were stirred continuously at room temperature for a few hours until a complete dissolution. For the preparation of plasticized electrolyte, different amounts of glycerol (92.09 g/mol) were added to the highest conducting unplasticized electrolyte solution. All homogeneous solutions were cast into plastic petri dishes and left to dry at room temperature in a drying oven to form films. Films obtained were then kept in desiccators with silica gel desiccants for further drying to discard any trace of moisture.

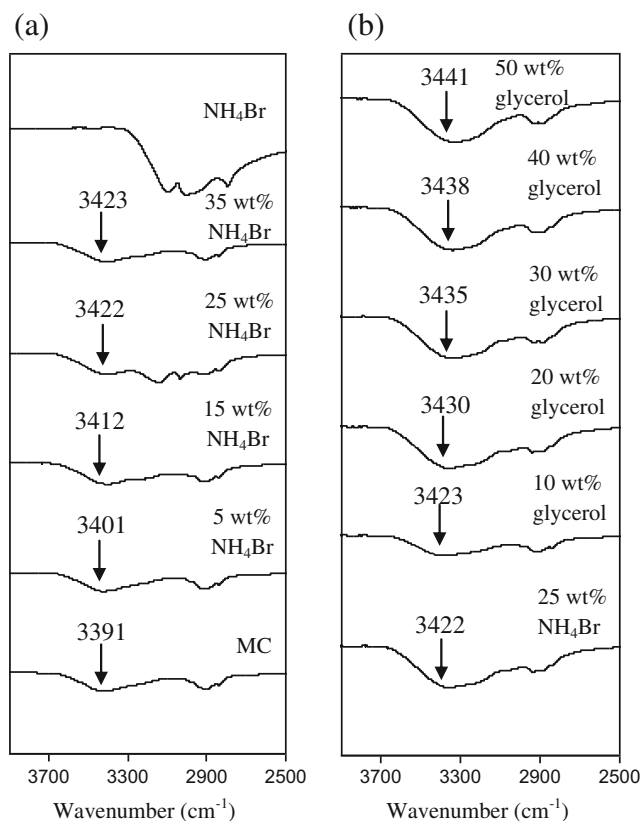


Fig. 1 **a** FTIR spectra for selected unplasticized electrolyte in the region of 2500–3700 cm^{-1} . **b** FTIR spectra for selected plasticized electrolyte in the region of 2500–3700 cm^{-1}

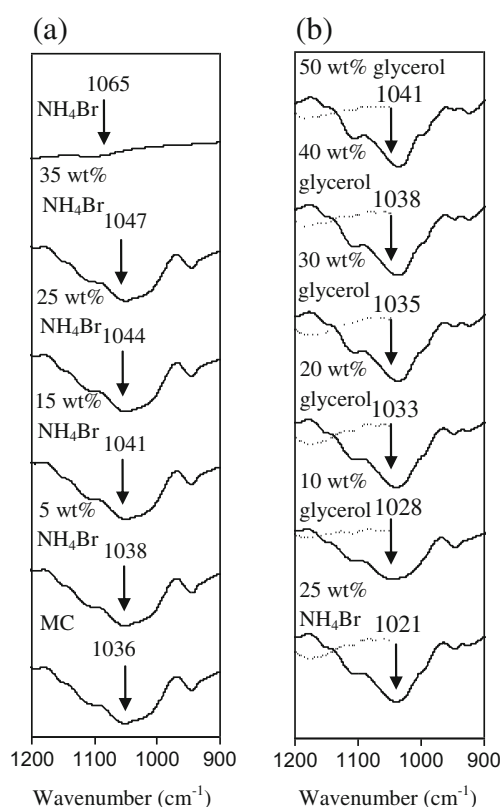


Fig. 2 **a** FTIR spectra for selected plasticizer free electrolyte in the region of 900–1200 cm^{-1} . **b** FTIR spectra for selected plasticized electrolyte in the region of 900–1200 cm^{-1}

Fourier transform infrared spectroscopy

Fourier transform infrared (FTIR) measurements were recorded using the Spotlight 400 Perkin-Elmer spectrometer in the wave-number range of 400–4000 cm^{-1} at a resolution of 1 cm^{-1} using ATR method. In this analysis, the interaction between polymer host conducting charge species will be the objective.

X-ray diffraction analysis

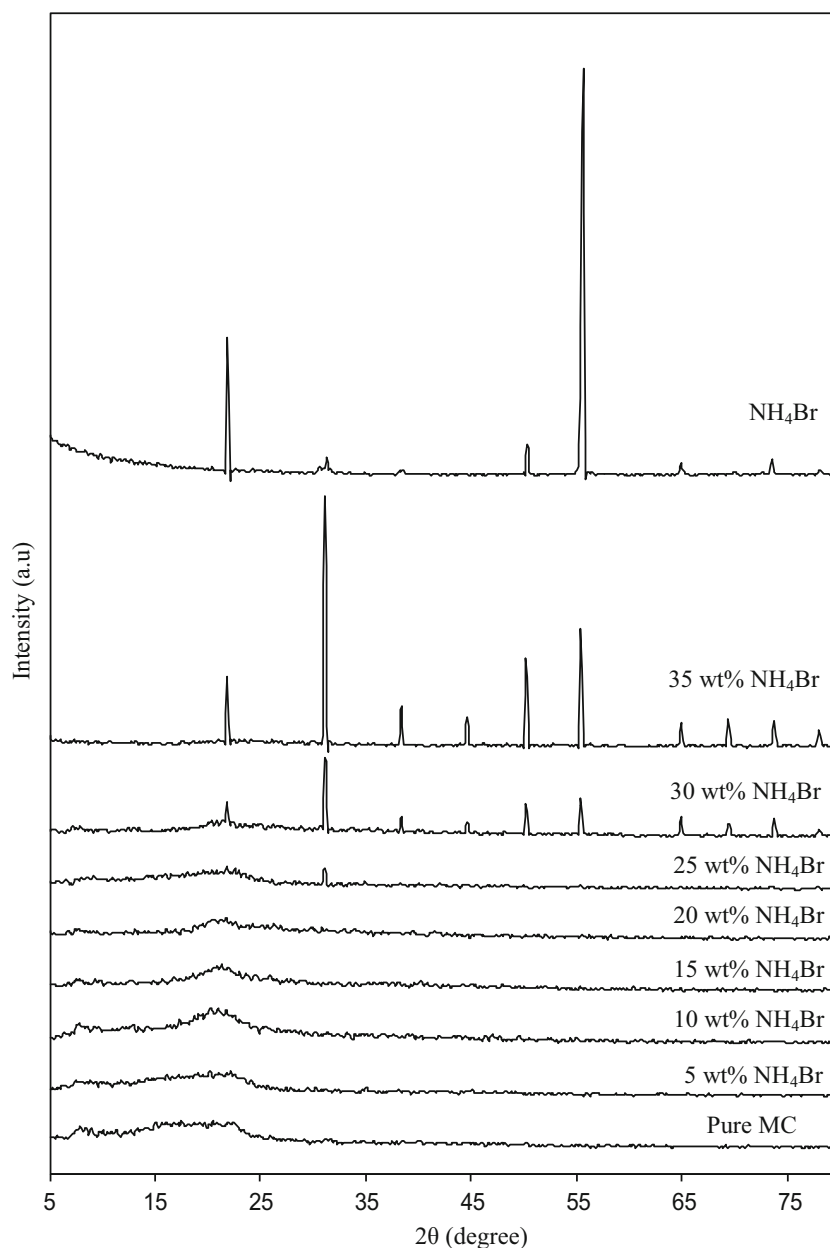
X-ray diffractograms were traced by Bruker Smart Apex II X-ray diffractometer. X-ray of 1.5406 Å wavelength was generated by a Cu K α source. The 2θ angle is ranged from

5° to 80° at a resolution of 0.1°. The degree of crystallinity (χ_c) of the electrolyte was determined via deconvolution method where individual amorphous and crystalline peaks were extracted by a curve-fitting process from the diffraction intensity profiles. The peaks fitting were done by Origin software, assuming Gaussian functions for each peak. χ_c is calculated from the ratio of the area of all crystalline peaks to the total area [18]:

$$\chi_c(\%) = \frac{A_C}{A_T} \quad (1)$$

where A_C and A_T are the areas of crystalline and total hump, respectively.

Fig. 3 XRD diffractogram of unplasticized electrolyte



Field emission scanning electron microscopy

The surface morphology of the electrolytes at room temperature was studied using a Hitachi SU8220 field emission scanning electron microscope. Before field emission scanning electron microscopy (FESEM) studies, the electrolytes were coated with a thin layer of gold using a SC7620 mini sputter coater to prevent electrostatic charging on the electrolytes. FESEM studies were done with $\times 400$ to $\times 8K$ magnification.

Electrochemical impedance spectroscopy measurements

The electrolytes were sandwiched between two stainless steel electrodes holder. Impedance measurements were evaluated using HIOKI 3532-50 LCR Hi-tester interfaced to a computer in a frequency range between 50 Hz and 5 MHz at room temperature of 298 to 353 K. The value of bulk resistance (R_b) was determined from the Nyquist

plots obtained from the impedance measurement. The conductivity of the electrolyte was calculated using the following equation [19]:

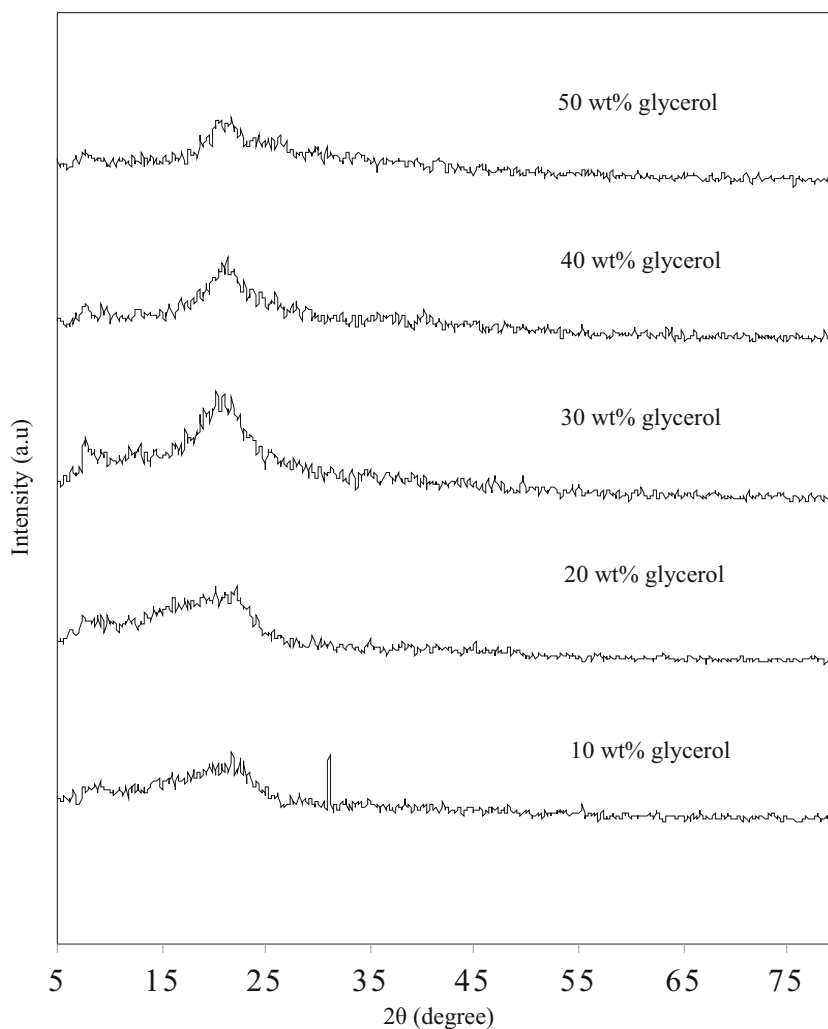
$$\sigma = \frac{y}{R_b A} \quad (2)$$

where y is the thickness of the electrolytes and A is the electrode-electrolyte contact area.

Linear sweep voltammetry

Linear sweep voltammetry (LSV) measurement was conducted by employing a three-electrode configuration where stainless steel electrodes were employed as working, counter, and reference electrodes. This electrochemical stability window was measured using Digi-Ivy DY2300 potentiostat at a scan rate of 1 mV s^{-1} in a potential range of 0 to 2.50 V at room temperature.

Fig. 4 XRD diffractogram of plasticizer electrolyte



Preparation of electrodes

The EDLC electrodes were prepared by mixing 13 g activated carbon (RP20, manufactured by Kuraray, Japan), 2 g poly(vinylidene fluoride) (PVdF), and 1 g carbon black (Super P) in 60 ml N-methylpyrrolidone (NMP) (EMPLURA). The mixture was stirred until a homogeneous slurry solution was obtained. The slurry was then spread on an aluminum foil using the doctor blade technique and heated at 60 °C in an oven. The dry electrodes were kept in a desiccators filled with silica gel desiccants for further drying.

EDLC fabrication and characterization

The performance of EDLC was characterized using cyclic voltammetry (CV) and charge-discharge cycling at constant current, 0.5 mA cm^{-2} . The highest conducting sample was sandwiched between two carbon electrodes using Perspex plates. CV was carried out at room temperature using a Digi-IVY DY2300 potentiostat between 0 and 0.85 V at different scan rates, 2, 5, 10, and 20 mV s^{-1} . The galvanostatic charge-discharge characteristics of the EDLC were carried out using Neware battery cycler in a voltage range between 0 and 0.85 V at a constant current density of 0.04 mA cm^{-2} .

Result and discussion

FTIR studies

FTIR is a direct method to distinguish molecular interactions by monitoring the band shifts of certain functional groups. According to Hema et al. [20], the cations of salt are expected to coordinate with the polar groups in the polymer matrix resulting in the polymer-salt complexation. Figure 1a, b depicts the FTIR spectra of unplasticized electrolytes and plasticized electrolytes in the hydroxyl band region of 2500 to 3700 cm^{-1} , respectively. The hydroxyl band in the spectrum of pure MC appears at 3391 cm^{-1} which is comparable with the reports in literature [21]. This peak has shifted to the higher wavenumbers as more NH_4Br were added. The oxygen atom of O–H carries lone pairs of electron [22]. From the FTIR results in Fig. 1, it can be inferred that the interaction has occurred between the H^+ ion and the oxygen atom.

Apparently, the higher the concentration of NH_4Br added to MC, the higher the concentration of H^+ , thus more electrons are withdrawn toward MC via C–O to form hydrogen bonding. Samsudin et al. [23] has shown that in the polymer–ammonium salt system, the conducting species is H^+ ion which originates from the ammonium ion.

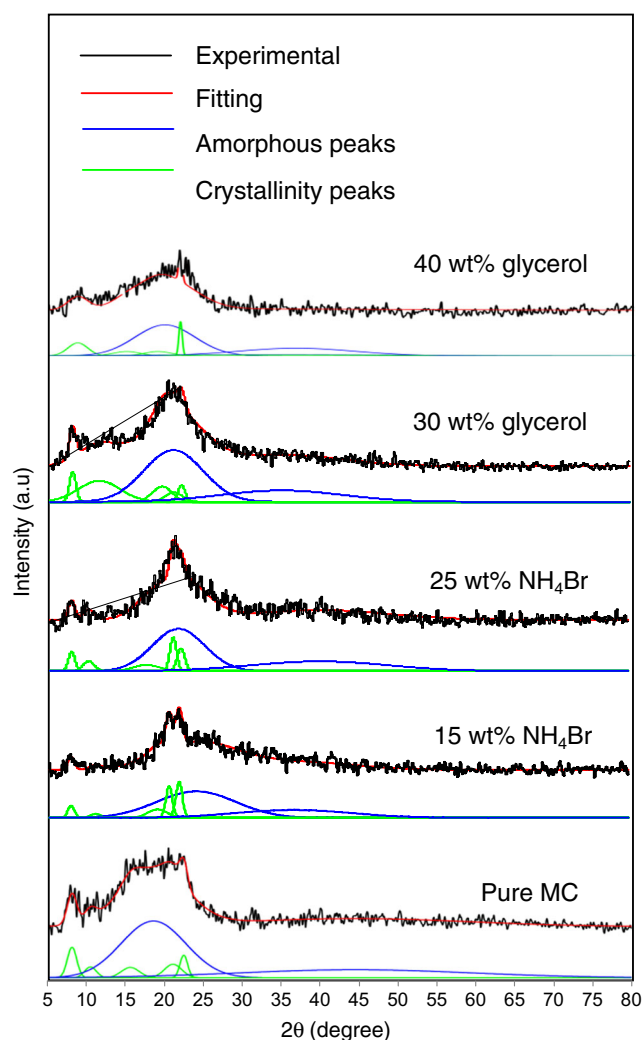


Fig. 5 XRD diffractogram of selected deconvolute electrolyte

This interaction causes an increase in the number of mobile ions which will lead to an increase in the conductivity of the unplasticized electrolytes. With addition of glycerol, it creates more pathways for the proton mobility which lead to an increasing number of mobile ion and thus give rise to the conductivity [24].

Figure 2 shows the FTIR spectrum of selected sample for unplasticized and plasticized electrolyte in the range of 900 – 1200 cm^{-1} . The peak observed at 1036 cm^{-1} for pure MC has shifted to higher wavenumbers with the increment of NH_4Br

Table 1 Degree of crystallinity of selected electrolytes in salted system

Sample	Degree of crystallinity (°)
Pure MC	15.5
15 wt% NH_4Br	14.2
25 wt% NH_4Br	13.6
30 wt% glycerol	11.8
40 wt% glycerol	10.1

and glycerol content. The addition of plasticizer promotes ion dissociation to occur hence more ions are available to interact with polymer's functional group [25]. All these changes in FTIR spectra were clear indications for the complexation of MC, NH_4Br , and glycerol.

XRD studies

The conductivity trend of electrolytes was verified by the XRD analysis. The XRD patterns for unplasticized and plasticized electrolyte systems are shown in Figs. 3 and 4, respectively. In order to study the XRD patterns of these biopolymer electrolytes, the XRD diffractograms were deconvoluted using Origin software to separate the crystalline peaks from the continuous scattering background. Fitting of multi-peaks using Gaussian distribution was done after carrying out the baseline correction for a particular diffractogram. The deconvoluted XRD patterns for unplasticized and plasticized system are shown in Fig. 5. It can be seen that the intensity of the diffraction peaks of electrolyte decreases and becomes broader with the increasing of salt concentration and glycerol. This may be due to the interaction of salt and glycerol with the polymer resulting in the increment of amorphousness in the electrolyte system where the degree of crystallinity decreases

with the increasing amount of salt and glycerol as shown in Table 1. These results suggest that the complexation between MC, NH_4Br , and glycerol takes place in the amorphous region of the polymer matrix which contributes to the increment of proton and transport in the amorphous phase. Thus, prove that the amorphous nature of the electrolyte give rise to the higher conductivity by providing greater ionic diffusivity that has been further discussed in the next section.

FESEM studies

Figures 6 and 7 depict the FESEM micrographs of the surfaces of the selected unplasticized electrolyte and plasticized electrolyte, respectively. Figure 6a shows the smooth and homogeneous surface of pure MC without any phase of separation. When 15 wt% of NH_4Br is added to the polymer host, links which act as the channels for ion conduction through the electrolyte are observed as shown in the micrograph in Fig. 6b. The links are more visible and clear when 25 wt% of NH_4Br is added and diminished as the particles agglomerated when more salt is added. The same result is observed for the FESEM micrographs of the surfaces of the selected plasticized electrolyte as shown in Fig. 7. When more than 20 wt% of glycerol is added, the links are observed clearly on the surface

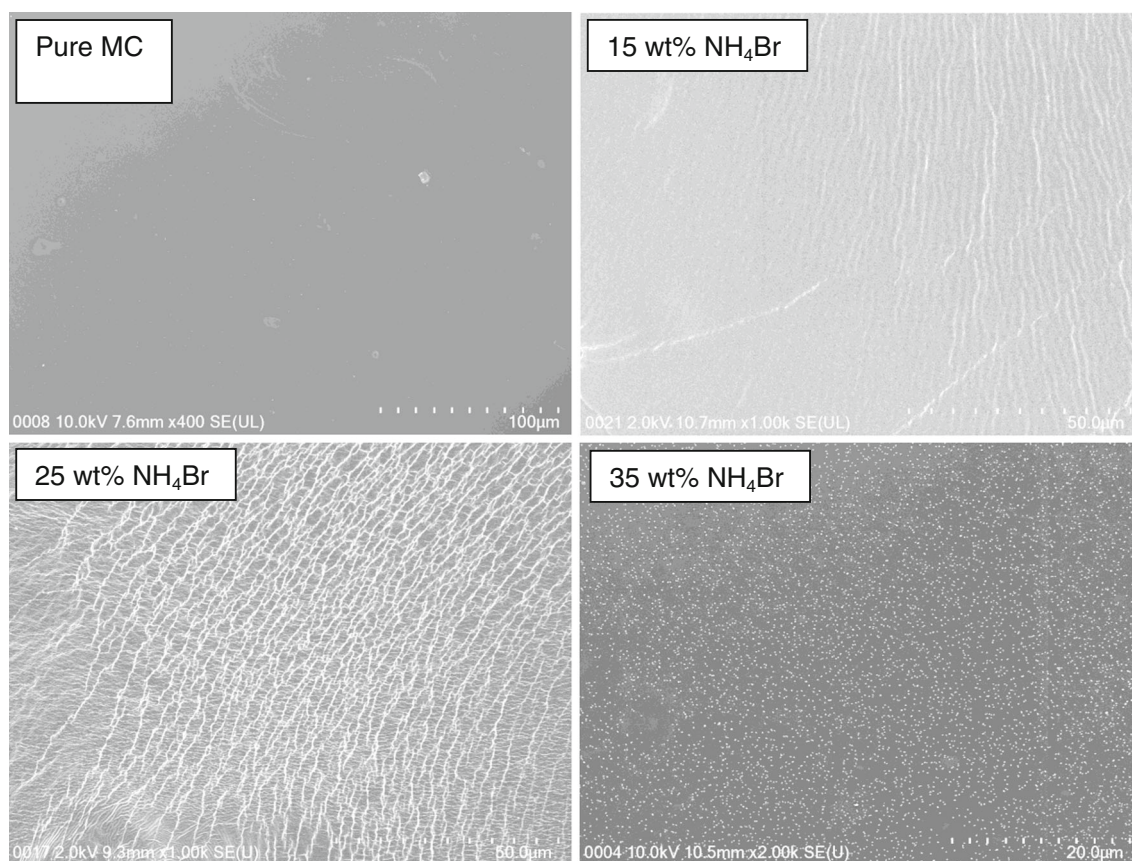


Fig. 6 Surface micrograph of selected unplasticized electrolyte

of the electrolyte but diminished when more glycerol is added due to the agglomeration of the particles which lead toward the ion pair's formation that do not contribute to the ionic conduction and decreases the number density of ions [15, 26].

Ionic conductivity at room temperature

The conductivity of electrolytes in unplasticized system is illustrated in Fig. 8a. The ionic conductivity was optimized at $(1.89 \pm 0.29) \times 10^{-4} \text{ S cm}^{-1}$ with addition of 25 wt% NH_4Br . The increase in conductivity can be attributed to the increase in number density of mobile charge carriers [27]. The interaction between the salt and the polymer hosts has led to the dispersion of H^+ ion resulting in an increase in conductivity [28]. On addition of more than 25 wt% NH_4Br , the conductivity decreases which can be attributed to the formation of ion aggregates. When too much salt was added to the polymer host, the anions and cations can become close to each other that they can form salt aggregates which hindered the free ions to move as well as reducing the number density of free mobile ions [29]. Samsudin et al. [30] reported that the highest conductivity of carboxyl methyl cellulose (CMC)- NH_4Br electrolyte system is $1.12 \times 10^{-4} \text{ S cm}^{-1}$ which is comparable with the present result.

In order to enhance the conductivity, different amounts of glycerol have been added to the highest conducting electrolyte in unplasticized electrolyte system. From Fig. 8b, the conductivity increases to $(1.67 \pm 0.19) \times 10^{-3} \text{ S cm}^{-1}$ with addition of 30 wt% glycerol. The presence of glycerol has created alternative pathways for ions to move which contribute to the conductivity enhancement [31]. Besides, the presence of glycerol as plasticizer has reduced the Coulombic force between cations and anions. Thus, more salts have been dissociated into a free mobile ion which increases the number density of ions [32]. This phenomenon leads to the increase in conductivity. However, the addition of more than 30 wt% glycerol decreases the conductivity. This is due to the displacement of the host polymer by plasticizer molecules within the salt complexes that causes the salt to recrystallize, hence resulting in the decrement of conductivity [34].

Ionic conductivity at elevated temperature

The temperature dependence of conductivity for unplasticized and plasticized electrolyte are shown in Fig. 9a, b, respectively. Both plots show that the conductivity of all NH_4Br and glycerol content is thermally assisted and the

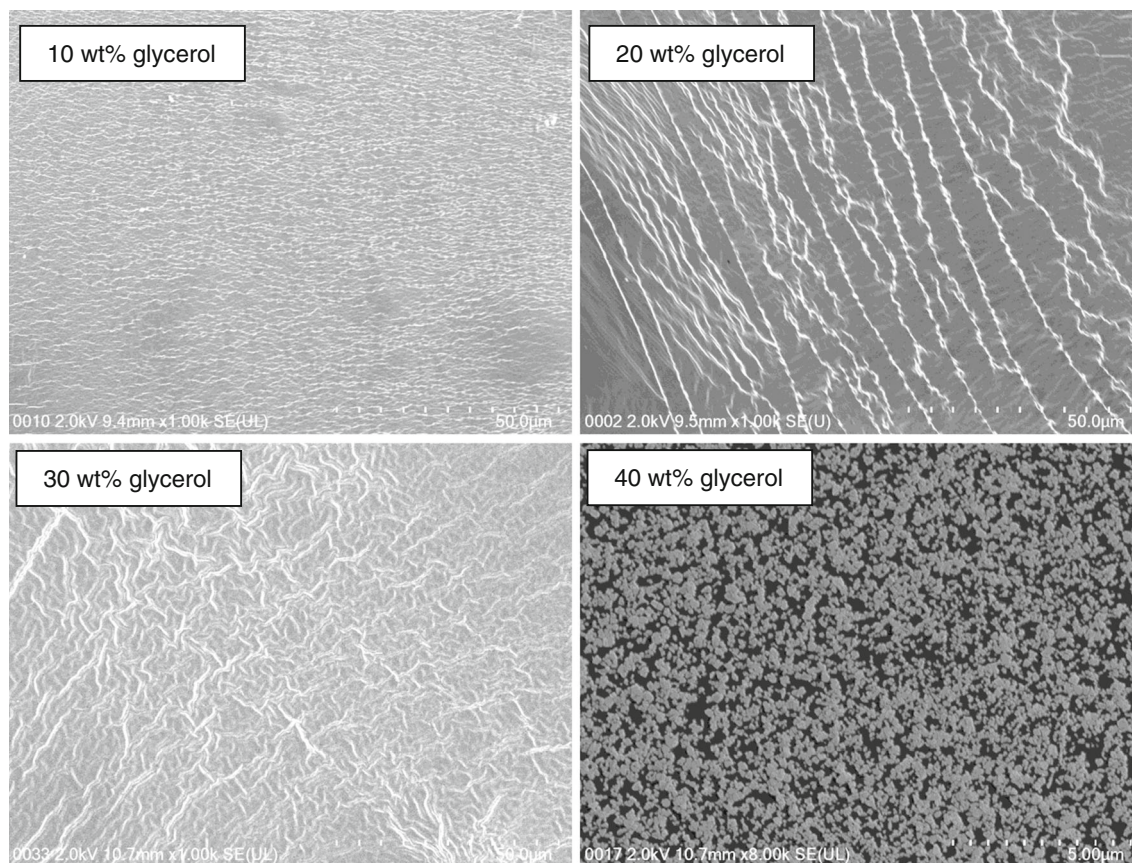


Fig. 7 Surface micrograph of selected plasticized electrolyte

conductivity-temperature relationship of the polymer electrolytes characteristically obeys the Arrhenius behavior. The ionic conductivity of biopolymer electrolytes is enhanced with increase of temperature. When the temperature is increased, the mobility of biopolymer chain is enhanced and the fraction of free volume in the biopolymer electrolyte system increases accordingly, which facilitates the translational motion of ions. It can be inferred that the nature of the cations transport in the biopolymer electrolytes occurred where ions jump into neighboring vacant sites, hence increases the conductivity [33].

The increase in temperature assist the segmental motion which allows faster ionic movement or provide pathways for ion to move, hence boosts the conductivity [34]. From the relationship between conductivity and temperature, the activation energy, E_a can be determined using the equation [35]:

$$\sigma = \sigma_0 \exp\left(\frac{E_a}{kT}\right) \quad (3)$$

Where σ_0 is the pre exponential factor, k is the Boltzmann constant, and T is temperature.

The regression value, R^2 , for the temperature dependence is in the range of 0.95 to 0.99. The linear relationships observed imply that no phase transition occurs in the polymer matrix or domains are formed by the addition of salt [36].

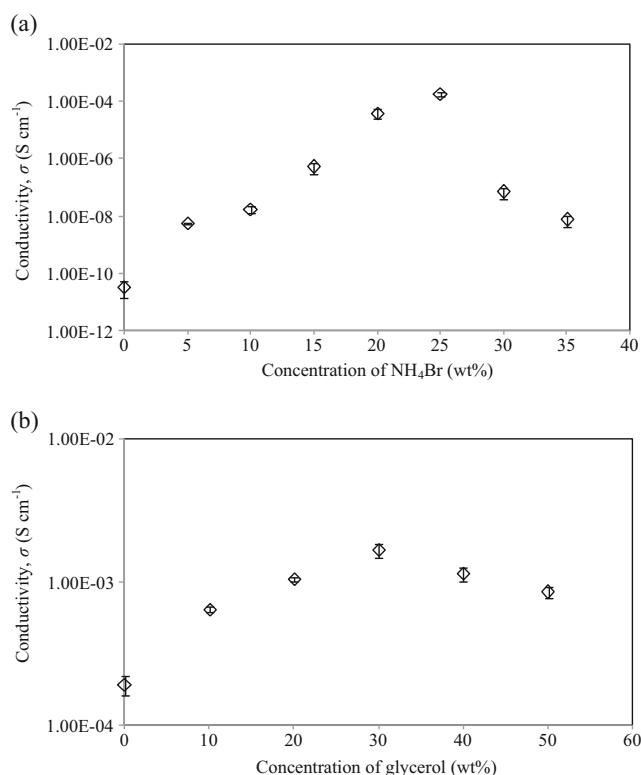


Fig. 8 Room temperature conductivity for **a** unplasticized electrolyte and **b** plasticized electrolyte

Conduction mechanism

Ionic conduction mechanism of an electrolyte can be determined by employing Jonscher's universal power law:

$$\sigma(\omega) = A\omega^s + \sigma_{dc} \quad (4)$$

Where $\sigma(\omega)$ is the total conductivity, σ_{dc} is frequency independent dc conductivity, A is a temperature-dependent parameter, and s is the power law exponent. Since $\sigma_{ac} = A\omega^s$, the value of s can be evaluated from the following relation [37]:

$$\ln \varepsilon_i = \ln \frac{A}{\varepsilon_0} + (s-1) \ln \omega \quad (5)$$

The value of exponent s is obtained from the slope of plots of $\ln \varepsilon_i$ against $\ln \omega$ in Fig. 10.

There are various reports which suggest that the acceptable frequency range is at the high frequency region due to the no or minimum rate of electrode polarization which occurs at this region [38]. At the higher frequency region, the direction of the electric field changes at a faster rate causing most of the ions in static state, thus decreasing the electrode polarization [39]. In this work, the acceptable frequency range for both unplasticized and plasticized electrolyte is $15.4 < \ln \omega < 15.7$.

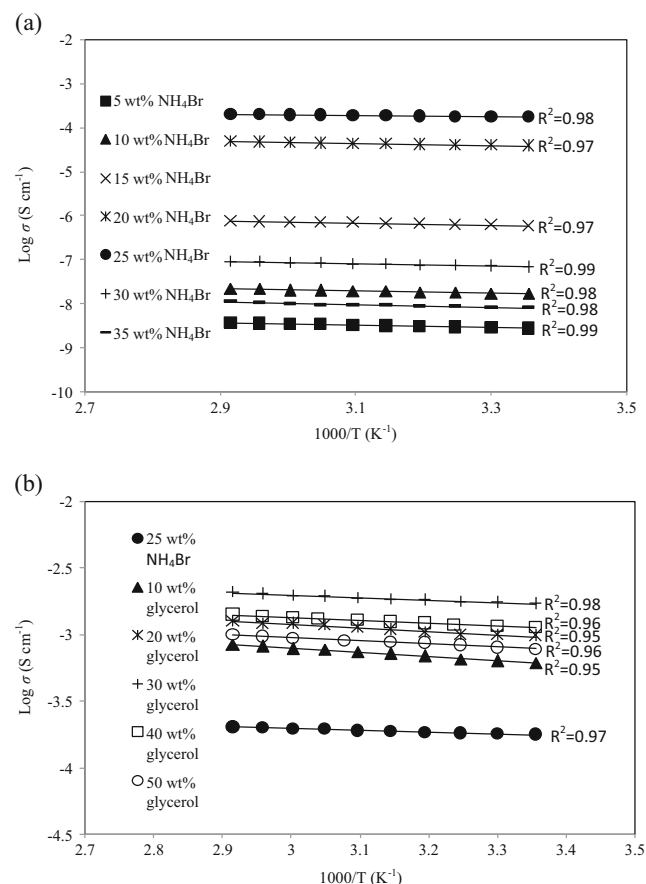
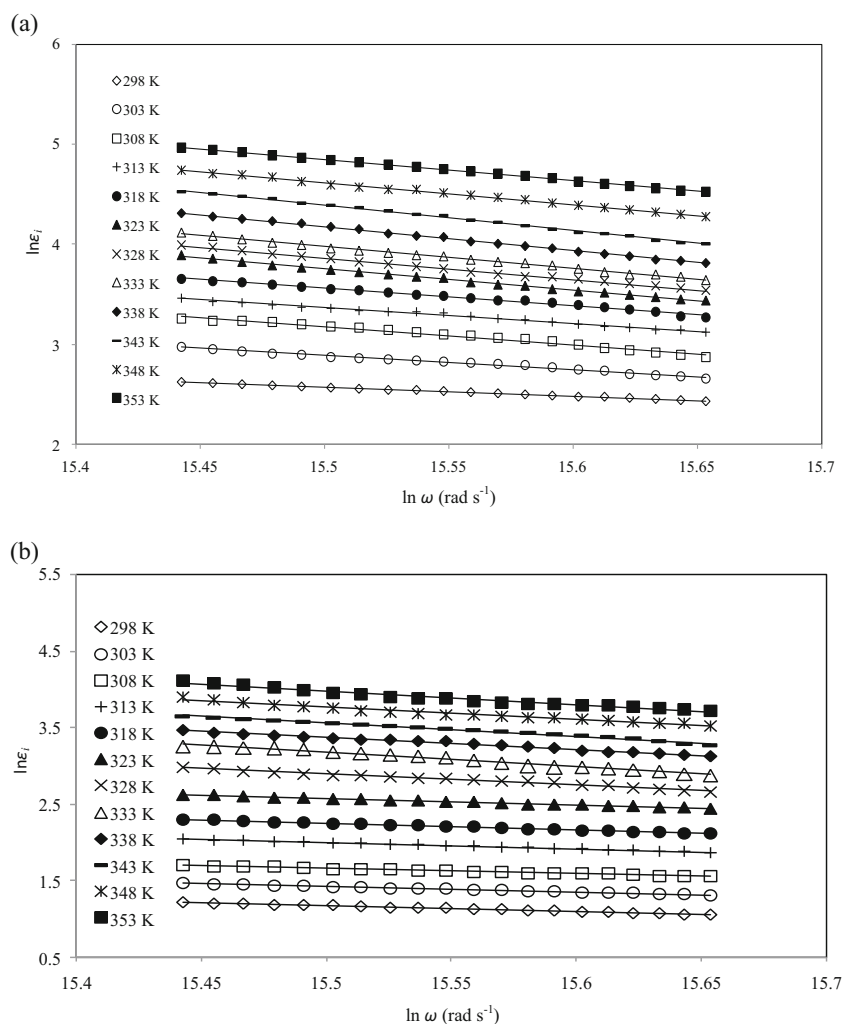


Fig. 9 Temperature dependence conductivity for **a** unplasticized electrolyte and **b** plasticized electrolyte

Fig. 10 Variation of $\ln \varepsilon_i$ with frequency at different temperature of **a** unplasticized electrolyte and **b** plasticized electrolyte



In the correlated barrier hopping (CBH) model, the exponent or index s value increases toward unity as $T \rightarrow 0$ K [40]. From the observations on the behavior of index s for both unplasticized and plasticized electrolyte shown in Fig. 11, it can be inferred that CBH model is applicable in explaining the conduction mechanism of these polymer electrolytes. For the unplasticized electrolyte, the plot can be fitted by the equation $s = -0.003 T + 1.349$, and for the plasticized electrolyte, the plot is fitted by the equation $s = -0.002 T + 1.298$. In this model, the ions reside in a potential well and are surrounded by several potentials such as Coulombic repulsive potential between the ions and the potential well [41]. The ions can hop from one site to another and may hop back to the initial site after they acquired enough energy. However, the ions will continue to move in the forward direction due to the formation of a new absolute potential which increases the back-hop barrier height [42]. Previously, we have reported that the conduction mechanism for MC-NH₄I occurs by way of a CBH model in which the plot of exponent s against T is fitted to the equation $s = -0.003 T + 1.187$ [10]. The present result is comparable with the previous work.

Linear sweep voltammetry

The electrochemical stability and the ability of membranes to endure the operating voltage of the fabricated device are important parameters for the prepared polymer electrolyte before being utilized in electrochemical device [43]. The electrochemical stability of the BPE system for the sample containing 30 wt% glycerol has been studied using LSV technique and the corresponding voltammogram is shown in Fig. 12. In this work, it can be observed that the decomposition voltage of the polymer electrolyte is around 1.53 V, where there is no obvious current through the working electrode from open circuit potential to the decomposition voltage. When the electrode potential is higher than the decomposition voltage, the current increases gradually. It is reported that the decomposition voltage of BPE electrolyte containing starch/chitosan doped with ammonium iodide and plasticized with glycerol has the decomposition voltage of 1.90 V which is higher than the result obtained in this present work [44]. However, MC-NH₄Br-glycerol BPE system is proved to be

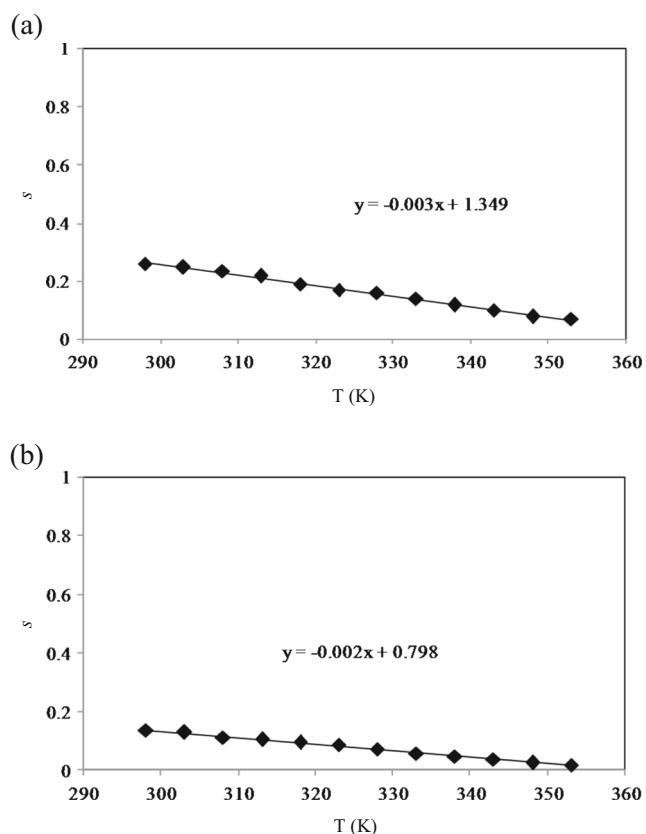


Fig. 11 Variation of exponent s with temperature for **a** unplasticized electrolyte and **b** plasticized electrolyte

Fig. 12 Linear sweep voltammetry curve for plasticized electrolyte containing 30 wt% glycerol at room temperature

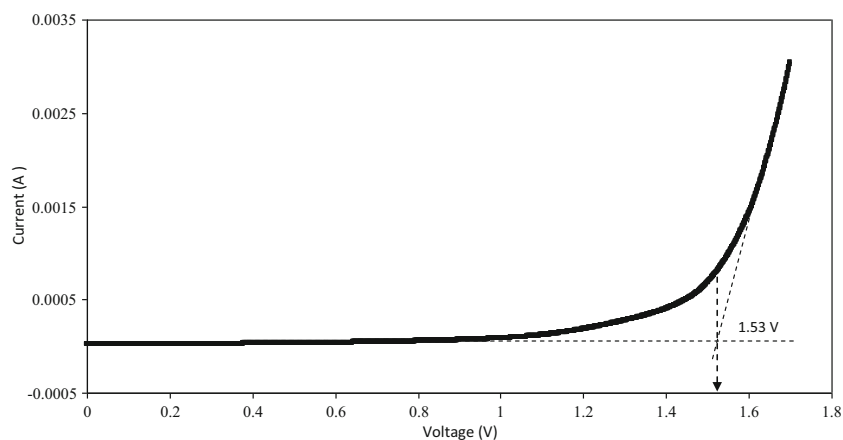
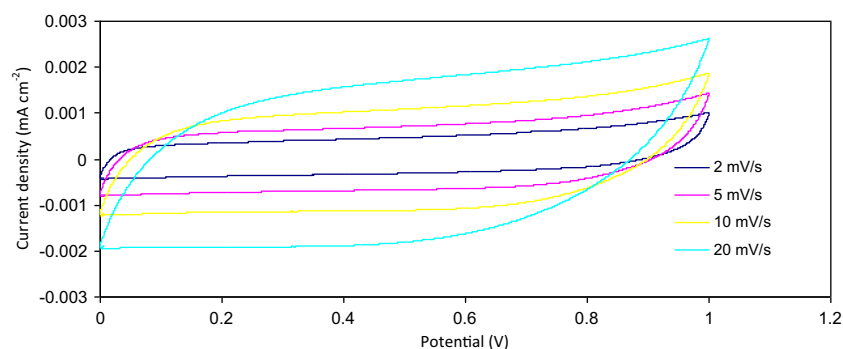


Fig. 13 Plots of cyclic voltammogram of EDLC at various scan rates



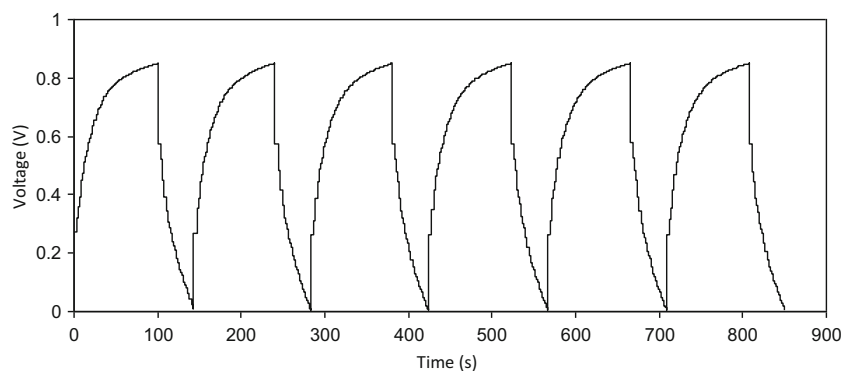
compatible for application in EDLC, based on the characterization of EDLC conducted as being explained in the next part.

Characterization of EDLC

The highest conducting polymer electrolyte has been optimized into EDLC. The CV of the EDLC was studied at various scan rates as shown in Fig. 13. The curves shown are almost rectangular without any visible peaks caused by redox reactions or electron transfer process which explains that the charge and discharge process occur reversibly at the electrode-electrolyte interfaces [45]. At higher scan rate, a slight deviation from the rectangular shape of the curve was observed and this is attributed to the internal resistance and carbon porosity [46]. It is reported that at higher scan rate, the current was delayed in reaching a constant value on reversible potential sweep which explains the characteristic of capacitor cells and the EDLC is a scan rate dependent [47].

Figure 14 shows the charge-discharge curves of EDLC at selected cycles using the highest conducting electrolyte. The EDLC was charged at room temperature from 0 to 0.85 V at a current density of 0.04 mA cm⁻². The curves are almost linear and further confirm the capacitive behavior of the EDLC [48].

Fig. 14 Charge-discharge profile of EDLC



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