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Original Article

Fabrication of high performance energy storage EDLC device from proton conducting methylcellulose: dextran polymer blend electrolytes

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ABSTRACT

This paper reports Methylcellulose:Dextran (MC:Dex) polymer blend based electrolyte system with NH4I salt for electrical double layer capacitor (EDLC) application. The structural and electrochemical properties of the electrolyte systems were investigated using X-ray diffraction (XRD), Fourier transformed infra-red (FTIR) spectroscopy, Field emission scanning electron microscope (FESEM), impedance spectroscopy, transference number measurement (TNM) and linear sweep voltammetry (LSV). The FTIR studies revealed the complexation between MC:Dex polymer blend and NH_4I salt. The reduction in the crystallinity of MC:Dex polymer blend with the increasing salt concentration was observed in XRD analysis. The electrolyte system was observed to be predominantly ionic in nature. The electrolyte composition with 40 wt.% of NH_4I showed the maximum ionic conductivity as 1.12×10^{-3} S/cm with electrochemical stability window of 1.27 V. The highest conducting composition of the electrolyte system was used to prepare EDLC with activated carbon electrodes. The EDLC exhibited initial specific capacitance as 79 F/g, energy density as 8.81 Wh/kg and power density as 1111.1 W/kg at a current density of 0.2 mA/cm^2.

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1. Introduction

Capacitors are electrical energy storage devices that have been used in a wide range of applications, such as our daily use electronic devices, transportation means, medical utilities and defense related systems [1]. Nowadays, electrical double layer capacitors (EDLCs), also referred to as supercapacitors, ultracapacitors and pseudocapacitors utilize different choices of electrolyte materials and carbon electrodes. These devices are in competition with other types of power sources, especially rechargeable batteries [2]. When choosing a desirable EDLC device, several parameters are needed to be taken into consideration, such as specific energy/power, charge-discharge cycle life and satisfactory safety [1]. The performance of EDLC can be improved either by the modification of the electrodes or materials mediated between the electrodes. Recent studies have revealed that polymer electrolytes (SPEs) are considered as the best promising candidates in the electrochemical devices, owing to their common benefits, such as solvent free, leakage-free, transparency, lightweight, elasticity, easy handling, easily forming thin films, good conductivity, and wide electrochemical windows in comparison to commercial liquid electrolyte counterparts [3,4]. To the best of our knowledge, the polymers that used in polymer electrolytes of energy storage devices as host materials are categorized into two main types; natural and synthetic polymers [5]. On one hand, most of the synthetic polymers are non-biodegradable, such as polyethylene oxide, polymethyl metacrylate, polyvinyl chloride, polycarbonate and polyacrylonitrile [6]. However, there is an existence of non-biodegradable synthetic polymers causing the depletion of petroleum resources and increase the disposal problems [7]. On the other hand, biopolymers can be used as the host polymer in energy storage devices, which minimize plastic waste pollution on the environment. It is apparent that the biopolymers are obtained from natural resources and offering unique characteristics, such as cheapness, compatibility with various solvents, abundance and ease of film forming [8–11]. For instance, starch, cellulose, chitosan, dextran and carrageenan are the most common biopolymers used in polymer electrolyte explorations [12–16]. Natural biopolymers tend to decay naturally, whereas synthetic polymers are relatively indestructible [7,17]. The most abundant organic polymer in nature is cellulose. It is accordingly regarded as an absolutely favorable renewable resource [18]. Recently, cellulose materials as a natural polymer are considered as alternatives to organic materials and may replace the petrochemical polymers [19]. Among these natural polymer materials, methyl cellulose (MC) is an abundant, cheap, and environmentally friendly class. As a cellulose derivative, MC is obtained from methylation of alkali cellulose and characterized by its biodegradability and satisfactory film forming properties, such as transparency and superior mechanical and electrical properties [7]. Modification of biopolymer, for example, methylcellulose with-1,4 glycosidic bond has been carried out via the introduction of methyl chloride or dimethyl sulfate to alkali based cellulose [20]. As it is known, certain ions can form a complex with oxygen containing functional groups of the polymer host by dative bond. MC contains functional groups, for instance hydroxyl, glycosidic bond and mexthoxy groups possess lone pair electrons, which are responsible for the ionic conduction [21,22]. This natural polymer has plausible solubility mechanical, thermal, and chemical stabilities as well as the excellent film-forming character, making the MC suitable for exceptional purposes [23]. Moreover, it is an amorphous polymer that has a relatively high glass transition temperature (T_g), ranging from 184 to 200 °C [22]. Likewise, dextran is another non-toxic and biodegradable polysaccharide. It can be obtained from the reproduction of bacteria *Leuconostoc mesenteroides*. This polysaccharide enriches in lone pair electron on heteroatoms, such as oxygen, which is necessary for dissolving inorganic salts [16]. It is well reported that polymer blend methodology provides more sites for ionic conduction [24]. It is emphasized that polymer blending methodology is a proper way for lowering the degree of crystallinity and thus increasing glass transition [25,26].

The downsizing trend of electronic device has motivated researchers to spend much effort towards EDLC devices [3]. EDLC can be used as an alternative to conventional batteries. Various materials can be employed as electrodes in these electrochemical devices [27,28]. The energy storage mechanism of EDLC involves non-Faradaic reaction, where ions form double-layer on its carbon-based electrodes [29]. Many advantages can be acquired from such device, such as higher power density, better thermal stability, longer life cycle, higher reversibility, cost-effective, fast charge-discharge rate, safe and simple fabrication techniques than Faradaic capacitor or pseudocapacitor [30–32]. Nowadays, activated carbon has been studied to be compatible with polymer electrolyte [33,34]. There are several favorable properties that make activated carbon preferable to be used in EDLC, such as high electrical conductivity, cost-effectiveness and excellent chemical stability as well as large surface area [35]. In addition to the device configuration, the electrode and electrolyte materials have a significant effect on the EDLC device performance. Although, there has been a great deal of work on manipulation of electrode materials, there has been little research on the electrolytes in supercapacitors. The key concepts of using electrolytes in supercapacitors are factors of determining electrochemical potential window, cycle life and safety [36].

In this work, firstly the electrical properties of methylcellulose:Dextran (MC:Dex) blend doped with ammonium iodide (NH_4I) are analyzed. Later on, a relatively highest conducting electrolyte sample is used in EDLC device. The results showed that polymer blending based on natural resources can be used for EDLC device fabrication with a high performance.

2. Experimental method

2.1. Materials and sample preparation

Methyl cellulose (MC) and dextran (Dex) powders were used as raw materials, which are provided by Sigma Aldrich (Sigma-Aldrich, Kuala Lumpur, Malaysia). For the preparation of the MC:Dex blended polymer, 70 wt.% of MC and 30 wt.% of Dex were dissolved separately, each in 50 mL of distilled water at room temperature for 180 min. Subsequently, the solution was mixed and stirred for 4 h to obtain a homogeneous blending solution. Then, different amounts of ammonium iodide (NH_4I)

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[CAS Number 12027-06-4, Molecular Weight = 144.94 g/mol] from 10 to 40 wt.% in steps of 10 were added separately to the MC:Dex blended solution with continuous stirring to obtain MC:Dex:NH_4I electrolytes. The polymer blend electrolytes were coded as MCD0, MCD1, MCD2, MCD3, and MCD4 for MC:Dex incorporated with 0, 10, 20, 30, and 40 wt% of NH_4I, respectively. After casting the solutions of constituents in the labeled Petri dishes (90 mm × 15 mm, Sigma-Aldrich, Kuala Lumpur, Malaysia), the solvent was allowed to evaporate at room temperature. Additional drying was induced by transferring the films to a desiccator. In this way, solvent-free electrolyte films were obtained.

2.2. *Structural, impedance and morphological characterizations*

X-ray diffraction (XRD) patterns were obtained for the samples using Empyrean X-ray diffractometer (PANalytical, Netherland) with operating voltage and current of 40 kV and 40 mA, respectively. A beam of monochromatic CuK_α X-ray of wavelength 1.5406 Å was used to irradiate the samples, where the glancing angles was in the range of $5^\circ \leqslant 2\theta \leqslant 80^\circ$ with a step size of 0.1°. Fourier transforms Infrared (FTIR) spectroscopy measurements were performed using Spotlight 400 Perkin-Elmer spectrometer with a resolution of 1 cm^{-1} (450–4000 cm^{-1}). A Hitachi SU8220 FESEM (Tokyo, Japan) was utilized to investigate the surface morphology of the blend electrolyte films at 500× magnification. HIOKI 3532-50 LCR HiTESTER was employed to analyze electrical impedance spectroscopy (EIS) measurements of the samples (50 Hz to 5 MHz).

2.3. *Transference number measurement (TNM) and linear sweep voltammetry (LSV)*

V&A Instrument DP3003 digital DC power supply was employed to analyze ionic (t_{ion}) and electronic (t_{el}) transference number. The largest conducting electrolyte was located in a teflon holder with similar stainless steel electrodes. The cell was subjected to 0.20 V at room temperature. To investigate the electrolyte electrochemical stability, linear sweep voltammetry (LSV) method was employed as a measurement technique via Digi-IVY DY2300 potentiostat. The applied scan rate was 100 mV s^{-1}. For this purpose, the electrolyte was located between two stainless steel of a teflon holder. Fig. 1 shows a schematic illustration of the stainless steel electrodes for both TNM and LSV analyses.

2.4. *EDLC preparation*

An amount of 0.25 g carbon black was combined with 3.25 g activated carbon with planetary ball miller before the mixture was poured in solution of 15 ml N-methyl pyrrolidone (NMP) and 0.50 g of polyvinylidene fluoride (PVdF). Black and thick solution was emerged upon dissolution. An aluminum foil was cleaned by acetone and flattened on glass surface. The solution was poured and spread on the foil by doctorblade technique. The electrodes were left in the oven for drying at 60 °C. The dried electrodes were then placed in a desiccator for further drying. The electrode was cut into a small circle shape with area of 2.01 cm^2. Electrolyte with the largest conductivity was located between two activated carbon electrodes and packed in a CR2032 coin cell. The EDLC characteristic was verified by cyclic voltammetry (CV) analysis at a scan rate of 10 mV s^{-1}. The EDLC charge-discharge profiles were tested by Neware battery cycler with a current density of 0.2 mA cm^{-2}. Fig. 2 shows schematic illustration of the EDLC cell for the charge-discharge measurements.

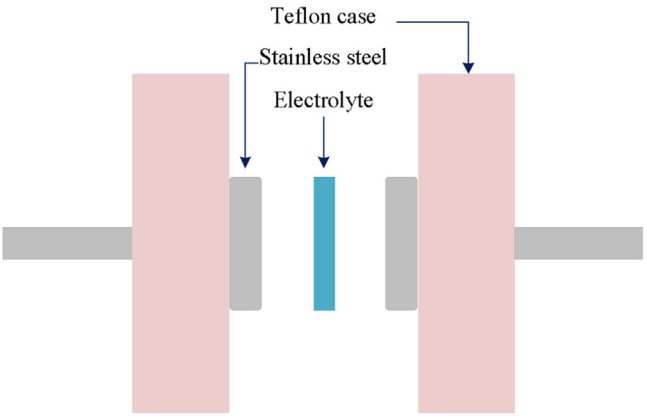

Fig. 1 – Schematic illustration of the stainless steel electrodes for TNM and LSV study.

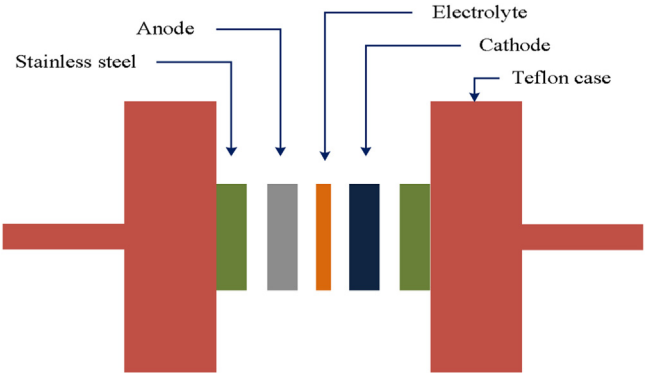

Fig. 2 – Schematic illustration of the EDLC cell for charge-discharge measurement.

3. Results and discussion

3.1. *Structural and morphological study*

Fig. 3(a–c) shows the X-ray patterns for the prepared MC:Dext films. It is well reported that MC host polymer has a unique peak at $2\theta = 19–21^\circ$, resulting from the intermolecular hydrogen bonding coupled with a short-distance order in the MC polymer chains [37–39]. Dextran is also known to have two broad peaks at $2\theta = 18$ and 23° [16]. More interesting observation is that the XRD pattern of the MC:Dext system has only exhibited one concave peak [see Fig. 3(b)] in addition to some small peaks. These broad hollows indicate the domination of a certain feature of the MC:Dext blend composite, which is the complete amorphous structure [4,40]. Therefore, a great opportunity for decreasing crystallinity and subsequently enhancing conductivity can be the implementation of

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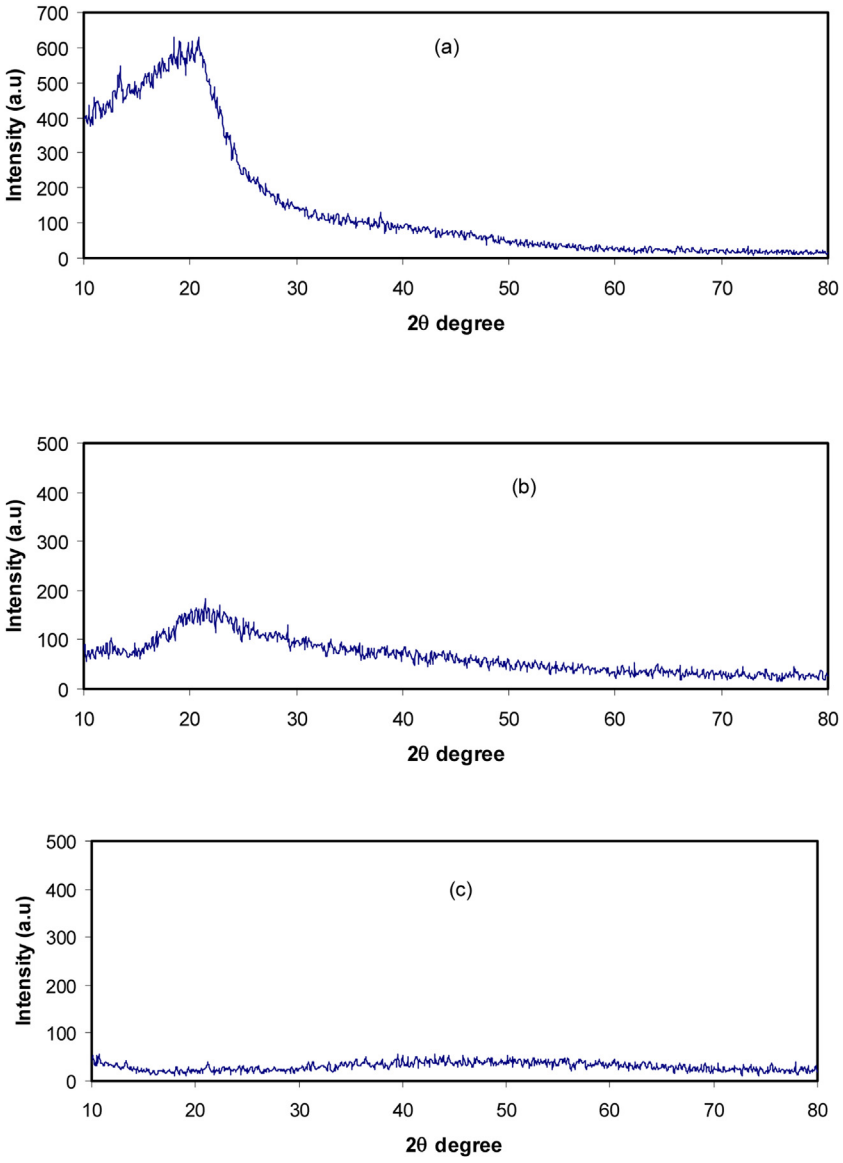

Fig. 3 – XRD pattern for (a) MCD0, (b) MCD2 and (c) MCD4 polymer electrolyte films.

polymer blending strategy. This approach involves mixing at least two structurally different kinds of polymers via interact through secondary forces with non-covalent bonding [41]. The XRD patterns for chosen blend electrolyte samples are shown in Fig. 3(b,c). It is obvious that with the addition of 20 wt.% of inorganic NH_4I salt into MC:Dext matrix, the hollow intensity of the MC:Dext was drastically lowered as shown in Fig. 3(b). This is an indication of lowering of crystalline region of the polymer blend and thus enhancing the amorphous phase [42]. From Fig. 3(c), it is clearly seen that an addition of 40 wt.% of NH_4I salt resulted in more broadened hollow. This finding shows that both peak widening and peak intensity lowering in diffractogram are reasonable evidence of the dominance of the amorphous region within the polymer system as anticipated.

It is documented that one can investigate the trend of conductivity of the electrolytes through the analysis of XRD pattern [43]. Upon the addition of the inorganic salt into the MC:Dext system, the degree of crystallinity has been reduced, which can be related to the complex formation between polar groups of the polymer and the salt cations (NH_4^+) through electrostatic interactions. Consequently, it caused to retard the ordering of the crystalline regions inside the polymer electrolyte through disrupting hydrogen bonding [44]. From Hodge et al.'s criterion, there is a correlation between the peak intensity and the degree of crystallinity, in which the change in intensity and particularly the peak broadening in the XRD pattern are considered to be indicators for the amorphous feature of the sample [45].

3.2. *FTIR analysis*

Fig. 4(a and b) exhibits the FTIR spectra of the pure MC:Dext and doped MC:Dext films in the regions of (a) 400 cm^{-1} to 2400 cm^{-1} and (b) 2400 cm^{-1} to 4000 cm^{-1}. It is known that to confirm the hydrogen bond formation within the polymer electrolytes based on MC:Dex films, one can use FTIR

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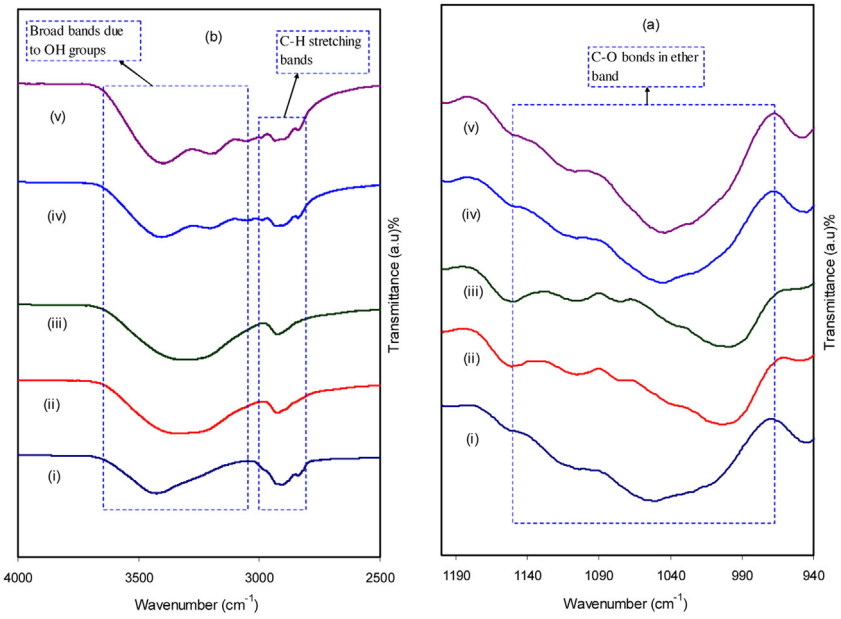

Fig. 4 – FTIR spectra of (i) MC:Dext (pure film, MCD0), (ii) MCD1, (iii) MCD2, (iv) MCD3, and (v) MCD4 in the region (a) 940 cm^{-1} to 1190 cm^{-1}, and (b) 2500 cm^{-1} to 4000 cm^{-1}.

spectroscopy. The principle of such technique is based on stretching vibration frequencies of the bonds, where each bond has a characteristic frequency [46]. As an example, the hydroxyl band observed for the pure MC:Dext system can be attributed to the wavenumber region 3447–3458 cm^{-1}, though each band needs to be at 1066 cm^{-1} and 1110 cm^{-1} [47]. It is well-known that FTIR spectroscopy has been widely used in dealing with the formation of polymer blends. It provides insight into intermolecular interaction through the FTIR spectra analysis in terms of stretching and bending vibrations of bonds. In this report, FTIR analysis is used for the MC:Dext polymer blend electrolyte, wherein the presence of OH groups is shown from the appearance of broad band with a maximum at 3351 cm^{-1} [48,49]. It is apparent that absorption bands centered at 3458 cm^{-1} in both pure MC:Dext and doped MC:Dext electrolyte films can ascribed to the O—H stretching [50,51] and the band peaked at 2906 cm^{-1} was attributed to C—H stretching in dextran [48,49]. More interesting observation was that the incorporation of NH_4I salt into MC:Dext caused a significant change in the bands intensity. This change in intensity is resulted strongly from the alterations in the macromolecular order. These bands in the spectra of the complexes may result from the extent of ordered structures [52]. It is evident from Fig. 4b that the hydroxyl band for the pure MC:Dext film has appeared in the form of a symmetric and homogeneous shoulder. On the other hand, for the blend electrolyte samples, a broad and asymmetric shoulder was seen. The wavenumber region from 950 to 1250 cm^{-1} can be very informative, where complicated strong absorption band profile of methylcellulose could be seen. This is mainly attributable to the C—O bonds' stretching vibrations in the cellulose and its ethers [53]. Another observation is that a reduction in the intensity of C—O bonds is seen in the doped samples. This confirms that there exists a strong interaction between the MC:Dext host blend polymer and incorporated salt. This apparent reduction of transmittance intensity and bands' shifting imply the process of complex formation between the salt cations and functional groups of the polymer blend matrix. Following the electrostatic interaction between salt cations and the functional groups of the host polymer, vibration of the polar groups can be reduced [11,39,54].

3.3. *Morphological study*

Acquiring images via scanning electron microscope (SEM) enables researchers to ensure the compatibility between different components of blend polymer electrolytes and determine phase separations, i.e., interfaces [41]. Furthermore, surface investigation provides benefits of understanding the structural and electrical properties changes under a number of processes. Previous studies have confirmed too much insight into changes over surfaces through the morphology views in polymers [8,55–57]. On the basis of crystallinity of polymer family, there is two extremes; crystalline and amorphous polymers. On one hand, the crystalline polymer features are compact assembly of stereo-regular chains; thereby, show high modulus and hardness but weak toughness. On the other hand, amorphous polymers are characterized by rubbery and glassy behavior [58]. In earlier work, the study the compatibility of salts with polar polymers was conducted via SEM [59–61]. Fig. 5(a–d) shows FESEM images for a number of MC:Dext systems doped with various weight percentages of NH_4I salt. The surface morphologies of the blend electrolyte samples revealed almost smooth surfaces and found no sign of protruded particles on them. This was, however, confirmed to be different in an earlier work, whereas more particles protruded out of the surface as more salts were added. Accordingly, polymer matrix capacity is limited to accommodate excess salt, which in turn led to salt recrystallization [62]. It is obvious that

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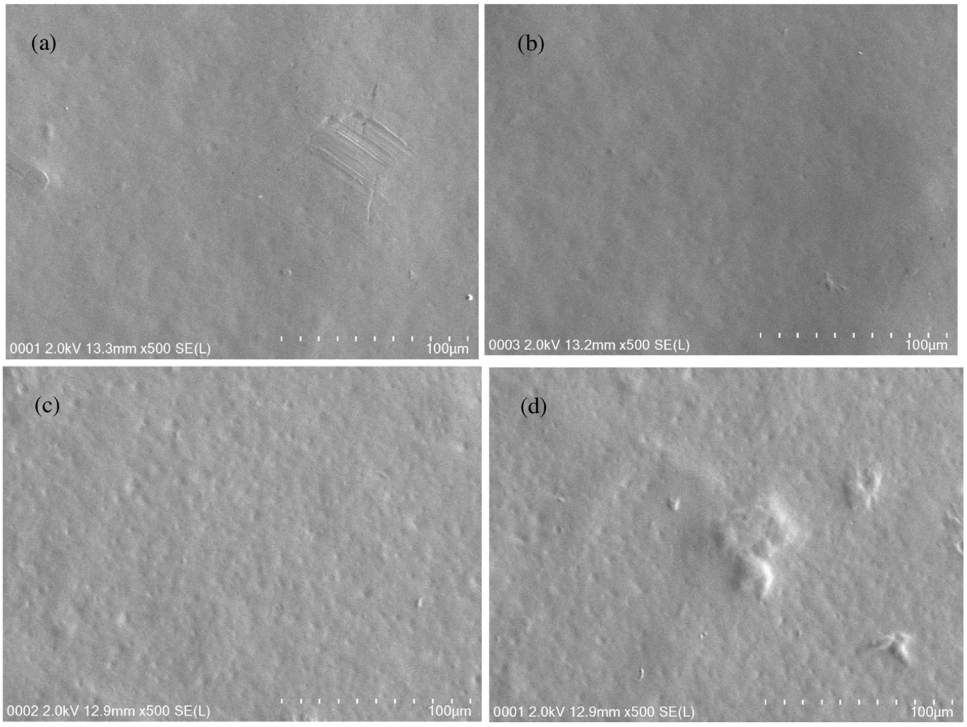

Fig. 5 – FESEM images for (a) MCD1, (b) MCD2, (c) MCD3, and (e) MCD4 blend films.

as re-crystallization proceeds, the amount of free ions lowers; in consequence, conductivity decreases [63].

There are various strategies that were applied in the attempt of overcoming several challenges. All these can be performed to gain deep understanding morphology thereby improves ion transport properties in polymer electrolytes. It is thought that in order to achieve high ion conductivity, the surface has to be smooth and having homogenous pores. In other words, it is correlated to the amorphous nature of the samples [33]. In fact, the complexation between the polymer blends and the incorporated NH_4I salt is evidenced by the smooth surface of the samples. In this work, the results show that there is a novelty of polymer blend fabrication as a new approach and an easy methodology to obtain relatively high DC conductivity. From the FTIR study, the complexation of the dopant salt and MC:Dext has been demonstrated. It is evidenced that the surface morphology of samples was found to be almost smooth without seen any noticeable protruded particles in the high rate incorporated NH_4I salt. From these findings, the synthesized polymer blending was defined by amorphous behavior even at high salt concentration.

3.4. *Impedance study*

In bulk materials, electrical charge displacements are carried out via two distinct physical phenomena; firstly, a polarization phenomenon, which occurs if the charge motion is strictly confined in a localized volume of the matter; secondly, collectively diffusion phenomenon, which is responsible for the electrical charges to be displaced over long distances in the materials and subsequently a dc conductivity (σ_{dc}) is established [64]. It is self-evident that four different types of polarization occur, once ac electric field is applied to a parallel plate capacitor separated by polymeric materials. These are electronic, atomic, dipolar and migrating charge polarization [65]. Firstly, ions are often regarded as impurities in the raw materials. Secondly, dipoles in atoms will occur with different electro negativities, which are bonded to each other on the backbone of polymeric materials [66].

From complex impedance spectroscopy (CIS) technique, one can take advantages of determination of relaxation frequency and distance between the opposite electrodes (low frequency spike) and bulk effects (high frequency semicircular region). The output of this technique comprises real (Z') and imaginary (Z") parts of impedance over a wide range of frequency. To the best of our knowledge, this technique has been successfully used for evaluation of the DC ionic conductivity and activation energy of ionic conductors [67]. The principle of CIS measurements is based on application of an alternating voltage on an electrochemical sample holder over a broad range of frequencies [68]. One of the outputs of electrical impedance spectroscopy (EIS) is a plot of the imaginary part of the impedance versus the real part. From this perturbation, the impedance plot is represented by the parallel combination of a resistor and a capacitor, and thereby $Z_{R\text{-}C}$ has semicircular shape on the complex impedance plane as presented in Fig. 6(a,b) at high frequency regions. In this electrochemical cell perturbation, ion accumulation occurs at the electrode/electrolyte interfacial region, yielding the low frequency inclined data from electrode polarization. It is interesting to note that at the end of low frequency of the impedance plots, an incomplete semicircular shape is exhibited. This is qualitatively interpreted that the impedance of the capacitor is very large at that region. The majority of

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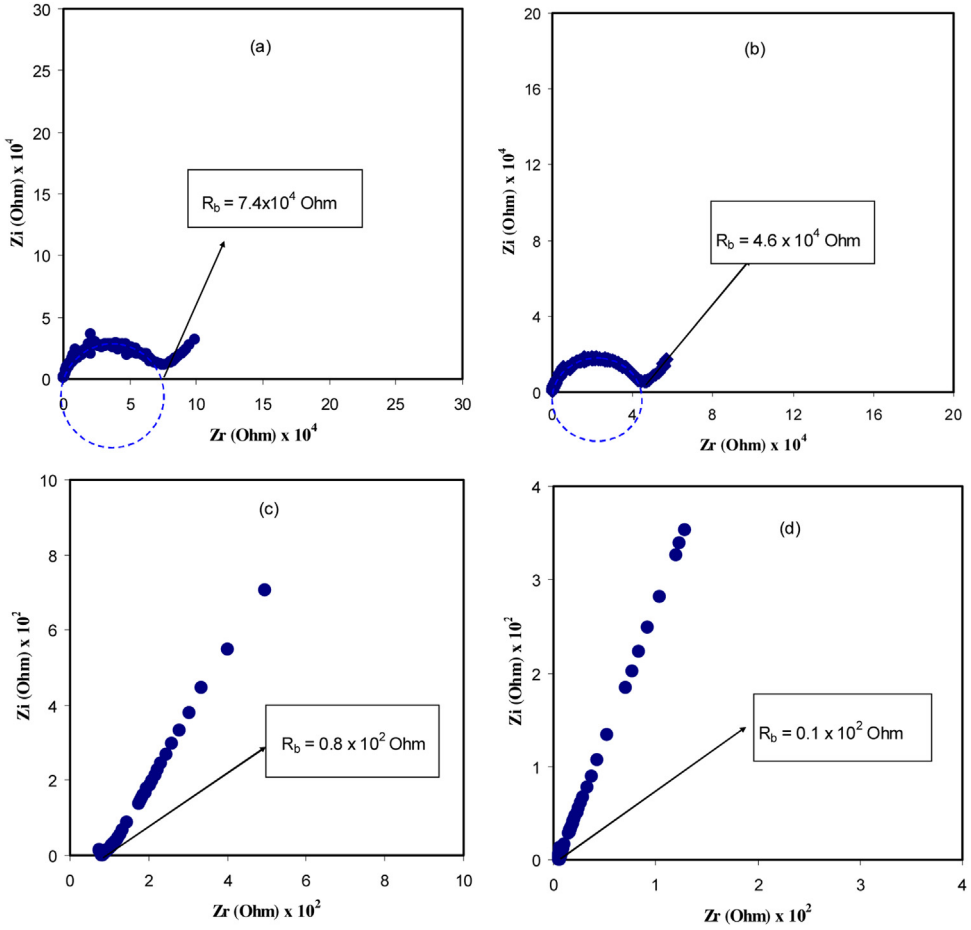

Fig. 6 – Impedance plots for (a) MCD1, (b) MCD2, (c) MCD3, and (d) MCD4 electrolyte films.

the current is, therefore, allowed to pass through the resistor, which dominates the behavior. However, the impedance of the capacitor is very small at very high frequency. It, thus, effectively shorts out the resistor, tending the total impedance toward zero [69]. It is shown in Fig. 6 that with an increase of salt concentration, there is a decrease in the bulk resistance (see the insets). In the analysis of the data point, the value of R_b is determined from the point, where the semicircle intersects the real axis (Zr). The sample conductivity has been determined based on the R_b value and the sample dimensions, using the following equation:

$$\sigma_{dc} = \left(\frac{1}{R_b}\right) \times \left(\frac{t}{A}\right) \quad (1)$$

where t and A are the thickness and surface area of the films, respectively.

The DC conductivity of systems is increasing with increasing salt concentrations (Table 1). This conductivity behavior of the electrolyte system is associated with increasing concentration of ions in the electrolytes coupled with high faster segmental motion of polymer blend chains in amorphous MC:Dex:NH_4I electrolytes. The high DC conductivity of blend electrolytes is a guarantee for the application of the blend samples in EDLC devices.

Table 1 – DC conductivity for pure MC:Dext and blend electrolyte films at ambient temperature.

Sample designation	DC conductivity (S/cm)
MCD0	6.5×10^{-10}
MCD1	1.49×10^{-7}
MCD2	2.41×10^{-7}
MCD3	1.38×10^{-4}
MCD4	1.12×10^{-3}

3.5. *Energy storage EDLC study*

3.5.1. *Transference number measurement (TNM)*

TNM analysis is used to determine the main or dominant charge carrier species in the polymer electrolyte. The recorded current showed saturation at 0.20 V. The graph of polarization current versus time for the highest conducting electrolyte (MCD4) was obtained (see Fig. 7). The large value of the initial current is assigned to the participation of both ion and electron conductions at the initial stage. Fig. 7 revealed that the current has decayed drastically prior to reach the steady state. In the steady state, the cell is polarized to large extent and the remaining current flow is due to electron. This is due to the ionic blocking effect by stainless steel electrodes, where electron is a unique entity pass through [70]. The cell was sub-

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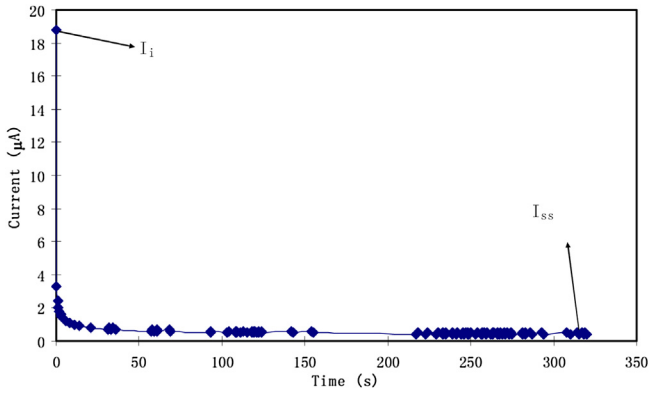

Fig. 7 – Polarization current versus time for the highest conducting (MCD4) electrolyte film.

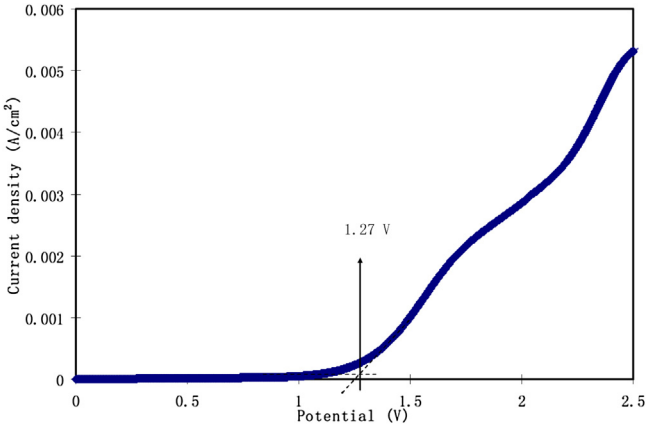

Fig. 8 – Linear sweep voltammetry (LSV) plot for the highest conducting (MCD4) blend electrolyte.

jected to 0.20 V at room temperature. t_i was identified using the following equation [71]:

$$t_i = \frac{I_i - I_{ss}}{I_i} \quad (2)$$

$$t_i = 1 - t_e \quad (3)$$

where I_{ss} and I_i are the steady state and initial current, respectively.

The values of t_i and t_e are obtained from both Eqs. (2 and 3) and the values of I_i and I_{ss} were extracted and found to be 18.8 μA and 0.4 μA, respectively. The t_i value was 0.98 and found to be of vital interest because of very closeness to its ideal value of unity. As a consequence, in MC:Dext:NH_4I system, ions are found to be responsible the migration process of the charge carriers. This finding is comparable to the system of Potato starch (PS)-methyl cellulose (MC) blend solid biopolymer electrolytes mixed with ammonium nitrate (NH_4NO_3) and glycerol as plasticizer (PS-MC-NH_4NO_3-glycerol-based electrolytes), which is documented by Hamsan et al. [72]. In comparison, the ionic transference number obtained in the current work is quite similar to earlier studies. Polu et al. [73,74] have studied the ionic transference numbers of PVA-$Mg(CH_3COO)_2$ and PVA-$Mg(NO_3)_2$ and found to be 0.96 and 0.98, respectively. Wang et al. [75] have examined that the ionic transference numbers of PVA-LiTFSI-EMITFSI is 0.995.

3.5.2. *Electrochemical stability study*

In this section, the LSV method is used to determine the electrochemical stability of the highest conducting MC:Dext:NH_4I system. Fig. 8 shows the LSV plot of the sample. The voltage was swept over a potential range of 0 V to 2.5 V at a scan rate of 100 mV s^{-1}, a large current is observed at certain potentials. This was cut-off current resulted from the decomposition of electrolyte at the inert electrode [76]. In MC:Dext:NH_4I system, it is found to be stable up to 1.27 V, which is appropriate at the sufficient range for proton based energy device applications. Pratap et al. [77] have studied the standard electrochemical window of proton batteries, which was recorded to be ~1 V. In the present work, the recorded breakdown voltage of methylcellulose-dextran blend polymer electrolyte was found to be relatively high enough in order to be used safely in the application of any protic electrolyte devices. Therefore, based on this finding, it can be concluded that the highest conducting MC:Dext:NH_4I SPE film is electrochemically durable to be applied in electrochemical devices, for instance, in proton battery application. An incredible interest in this study is comparability with the results obtained in ammonium salt based polymer electrolytes. Kadir et al. [33] have examined a plasticized system of methyl cellulose (MC) incorporated with NH_4Br, in which the electrochemical stability was obtained up to 1.53 V. In another study conducted by Woo et al. [78], poly (ϵ-caprolactone) (PCL)-based polymer electrolytes was found to electrochemically durable up to 1.4 V.

In the present study, the decomposition voltage of the polymer electrolyte was around 1.27 V. In a comparison, it is well-reported that the decomposition voltage of blend biopolymer electrolyte containing starch/chitosan incorporated with ammonium iodide and plasticized with glycerol has the decomposition voltage of 1.90 V, which is larger than the outcome achieved in our work [79]. However, MC:Dext:NH_4I system is verified to be more compatible for application in EDLC, based on the EDLC characterizations performed as being explained in the next sections.

3.5.3. *Cyclic voltammetry (CV) study*

The nature of charge storage at the electrode-electrolyte interfaces in EDLCs can be deeply conducted through the cyclic voltammetric. The analysis of the nature of charge storage at the interfacial region in the anodic and cathodic regions can be obtained from CV of the EDLC cells [2]. Fig. 9 exhibits the CV of the assembled cell at room temperature. Firstly, there is no peak in the polarization curve, indicating that no redox reaction takes place in the potential range of 0–0.90 V. This phenomenon strongly proves the existence of electrical double layer capacitors [80]. The charge storage mechanism in EDLC is based on the ion accumulation at the electrode-electrolyte interfaces under an electric potential perturbation [81]. The figure shows a nearly rectangular shape of CV, which shows a capacitor behavior. Compared to those reported in the literature, which are quite close to leaf-like shape [78,81]. An ideal EDLC has a perfect rectangular shape CV. The high scan rate causes a discrepancy of

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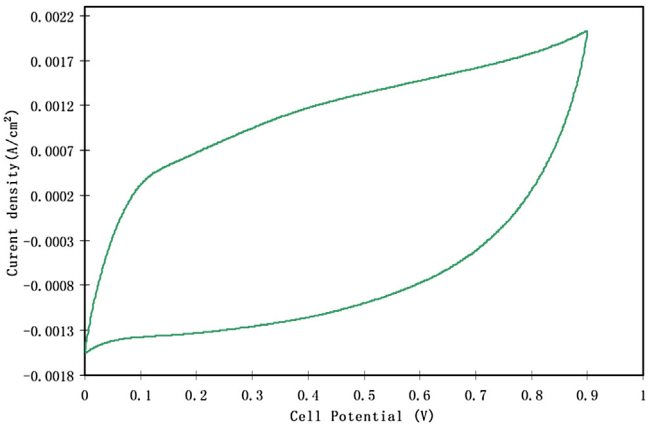

Fig. 9 – Cyclic voltammetry (CV) plot of the fabricated electrical double layer capacitor (EDLC) for MCD4 film in the potential range of 0 V–0.90 V.

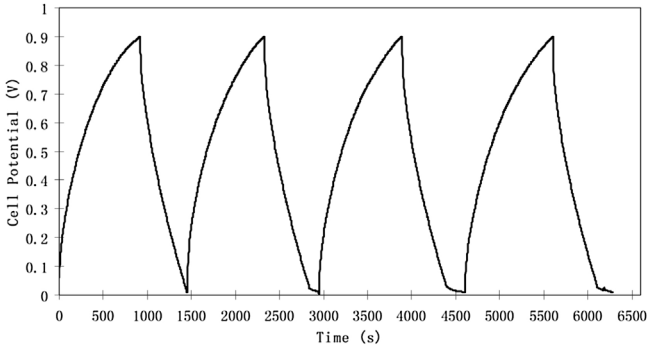

Fig. 10 – Charge-discharge profiles for the fabricated EDLC at 0.5 mA cm^{-2}.

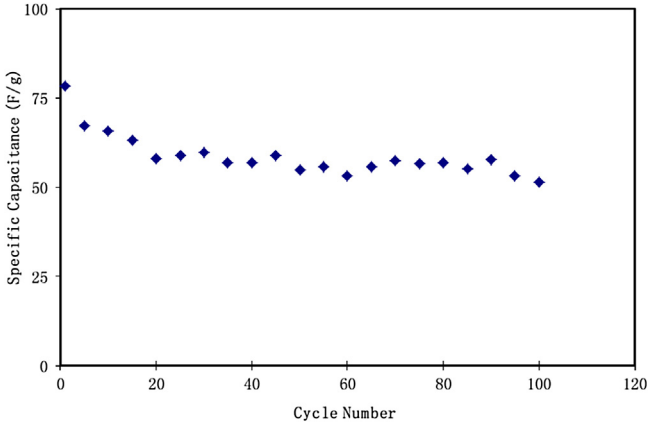

Fig. 11 – Specific capacitance of the fabricated EDLC for 100 cycles.

the cyclic voltammogram shape from a perfect rectangular shape, which might be ascribed to both carbon porosity and the internal resistance, thereby creating a current dependence of voltage [82]. The mechanism of charge storage in EDLC device is still a subject of debate. Dealing with the mechanism of energy storage, microporous materials can be crucial for both fundamental and industrial aspects. The great advance in designing super-capacitors with a relatively high performance has enabled researchers to develop such technology for industrial applications in very close future. It is also considered as a breakthrough to some extent in the field of super-capacitor fabrication. Moreover, researchers have been encouraged to verify that the mechanism of charge storing—in terms of experimentation and theory—is necessary [83]. Eftekhari [84] has, however, shown a review, where the energy storage mechanism is based on housing of ions inside microporous and mesoporoes somewhat than the formation of a double layer capacitor. Consequently, this mechanism is dissimilar to some level from the classical model, in which the ions aid the charge separation and storage in energy storage devices. On the other hand, the classical models are based on the inner layer, which is formed due to the electrostatic forces; thereby the charged species are accumulated on the surface of the electrode without any real chemical interaction. Therefore, the double layer charging on the electrode surface should be ideally polarizable [85].

3.5.4. *Charge-discharge characterization*

Fig. 10 shows galvanostatic charge–discharge characteristics of the fabricated EDLC. The gradient of the discharge parts are almost linear, suggesting the presence of charge double-layer and capacitive characteristics [86]. The specific capacitance (C_{sp}) of the EDLC,

$$C_{sp} = \frac{i}{gm} \tag{4}$$

where, i is the operating current, g is the gradient of discharge curve and m is the active material's mass. From the gradient of discharge curve, the value of C_{sp} is calculated, using Eq. (4).

Fig. 11 shows the plot of C_{sp} against cycle number for the fabricated EDLC. The value of C_{sp} acquired for the 1st cycle was found to be 79 F g^{-1}, whereas it dropped to 55 F g^{-1} at the 20th cycle. The value of C_{sp} has remained almost constant over the cycles beyond the 20th cycle till it completed 100 cycles. The relatively high in the capacitance value for the first cycle in EDLCs/supercapacitors is ascribed to the fast build-up of the double layers as well as the contribution of both ion and electron at the initial stage. After the first cycle, the initial decrease in the C_{sp} values toward the 20th cycle is noticed in Fig. 11, which is due to the current decayed before reaching the steady state. In earlier reports large reduction of C_{sp} was noticed with increasing the number of cycles. It is believed the reduction of these electrochemical properties of EDLC belongs to the formation of ion aggregation. Indeed, the mobile ions prefer to be paired up or aggregated beyond the rapid charge and discharge processes. These ion pairs can block the ionic transportation in the polymer electrolyte and consequently influence ion adsorption into the pores of carbon, which decreases the creation of ion adsorption at the electrode–electrolyte interface region. Therefore, the specific capacitance, energy density and power density of EDLC decrease with increasing the cycle number as a result, the electrochemical properties, such as the specific capacitance, energy density and power density of EDLC decrease as the number of cycle increases [87]. The obtained value of C_{sp} in the present work is greater than that

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Table 2 – Capacitance of EDLCs using different solid polymer electrolytes.

Polymer electrolytes	Electrode material	Cs(F g^{-1})	References
PEO-Mg(Tf)2 + EMITf	MWCNTs-AB-PVdF-HFP	2.6–3.0	[2]
Nafion/PTFE composite polymer	carbon	16	[88]
Chitosan-κ-carrageenan-NH_4NO_3	Activated carbon	18.5	[89]
Chitosan-PVA-NH_4NO_3-EC	Activated carbon	27.1	[82]
MC-PS-NH_4NO_3-glycerol	Activated carbon	31	[72]
MC-NH_4NO_3- PEG	PEG coated with activated carbon	38	[90]
Polyvinylalcohol–polystyrene sulphonic	carbon	40	[91]
Cellulose acetate-$LiClO_4$	p/p polypyrrole	90	[92]
Methylcellulose-dextran-NH_4I	**Activated carbon**	**79**	**Present work**

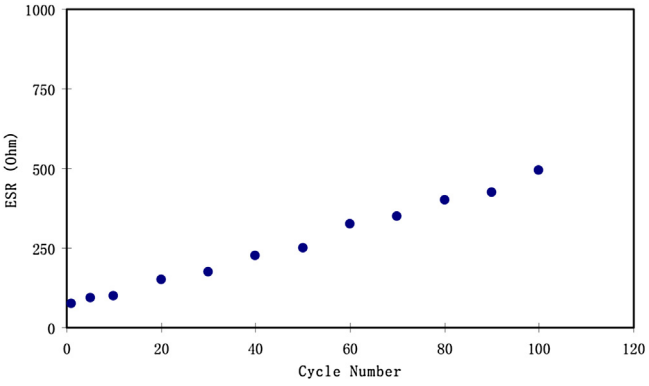

Fig. 12 – The pattern of the equivalent series resistance of the EDLC for 100 cycles.

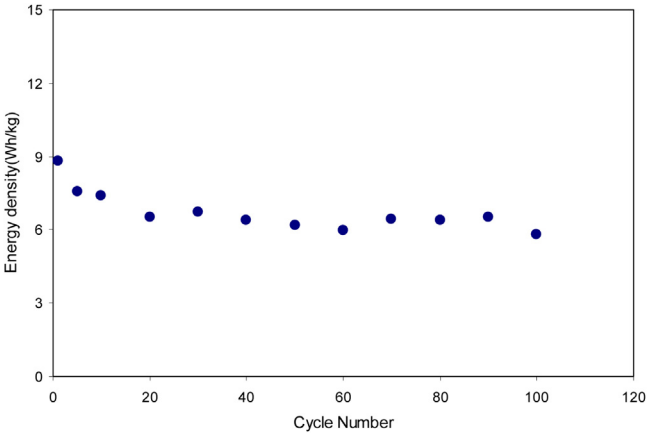

Fig. 13 – Energy density of the fabricated EDLC for 100 cycles.

reported in the literature. The value of C_{sp} of the fabricated EDLC is compared to other reports using various polymer electrolytes as listed in Table 2.

From Fig. 10, one can see a potential drop prior starting of every discharge process. This is associated to the presence of an internal resistance called equivalent series resistance (R_{es}). The EDLC parameters, such as R_{es}, energy density (E) and power density (P), can be calculated using the following equations [93]:

$$R_{es} = \frac{V_{drop}}{i} \quad (5)$$

$$E = \frac{C_s V}{2} \quad (6)$$

$$P = \frac{V^2}{4mR_{es}} \quad (7)$$

where V_{drop} stands for voltage drop before discharging process and V is the voltage applied.

From Fig. 12, the value of R_{es} was found to be varied from 75 to 493 Ω. The logical explanation of the existence of R_{es} in the EDLC is mainly due to three resistances; current collector, the bulk of the electrolyte as well as the interfacial region between electrolyte and electrodes [94]. Kumar and Bhat [91] have examined such increase in voltage drop throughout the charge-discharge cycle, which led to an increase in ESR as a result of the degradation of the solid polymer electrolytes in the EDLC. In the present work, the ESR of the EDLC is quite low if it compared to that (1300 Ω) documented for ionic liquid incorporated with Poly(ethylene oxide) (PEO) based polymer electrolyte [2].

The value of E_d calculated from Eq. (6) can be seen in Fig. 13. From the figure, the value of E_d at the 1 st cycle is 8.81 Wh/kg. The E_d value then decreases for few cycles and then nearly constant at 6.3 Wh/kg in average from the 20th cycle to the 100th cycle. Hence, it can be assumed that the ion migration possesses nearly similar energy barrier in this cycle range [21]. In fact, this decreasing in E_d value throughout the cycle number is mainly owing to an increase in the internal resistance, leading to the increment of energy loss during the process of charging and discharging cycle [82,95].

The achieved energy density for the EDLC cell is large enough compared to that reported (0.3 Wh/kg) for ionic liquid incorporated with PEO based polymer electrolyte [2]. The energy density obtained in the current work is of the large interest compared to the energy density values of 2.2 Wh/kg which obtained for EDLC of the system of methycellulose (MC)-starch-NH_4NO_3 [72]. Moreover; the energy density of the present work (6.3 Wh/kg) is of great interest compared to the values reported (1.4 Wh/kg and 0.86 Wh · kg^{-1}) in our previous works for Chitosan:Dextran incorporated with NH_4F and $LiClO_4$ salts, respectively [96,97]. While, it is lower to that obtained (8.63 Wh kg^{-1}) for biopolymer blend electrolytes inserted with NH_4SCN [98]. These results indicate that the type of salts and designing of polymer blends based on natural resources has great effects on the performance of EDLC devices.

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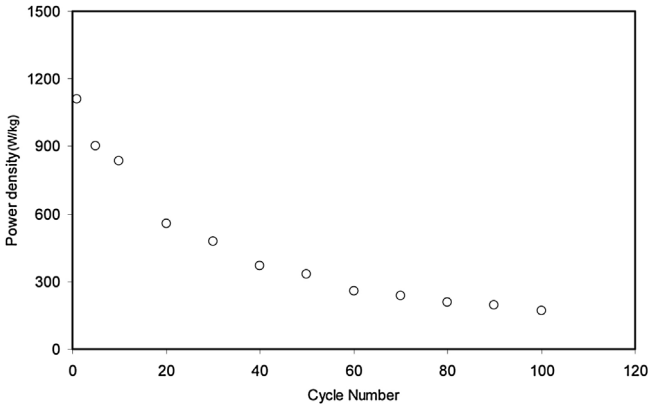

Fig. 14 – Power density of the fabricated EDLC for 100 cycles.

The calculated value of power density (P_d) from Eq. (7) is seen in Fig. 14. Upon charge-discharging over 100 cycles, the P_d of the EDLC shows a drastic drop from 1111.1–170.0 W/kg. The outcome of the current study is comparable with that reported by Shukur et al. [93]. The value of P_d is lowered as the cycle number increased. This decline trend harmonized with the raising trend of Res in Fig. 12. The increment of internal resistance is caused by the depletions of the electrolyte and aggregation of ions regarding a fast charge and discharge mechanism; therefore, it provides lower power density at large cycle number [99]. The decrease of specific power density, energy density, and capacitance is owing to the electrolyte depletion. Ion agglomeration after the fast charged and discharged processes will block the ionic movements toward the surface of the electrodes which cause a decrease of ion adsorption at the electrode–electrolyte interface [87].

4. Conclusions

In conclusion, polymer blend electrolyte films comprising methylcellulose:dextran (MC:Dex) blend doped with various amounts of ammonium iodide (NH_4I) are crucial for EDLC application. The shifting in the band positions and relative decrease in their intensities observed in the FTIR studies corroborate the complexation between the MC:Dex and NH_4I. The XRD studies reveal the enhancement in the amorphous nature of electrolyte systems with increasing salt concentration. The DC conductivity is found to be increasing with increasing the salt concentration and maximum conductivity is found to be 1.12×10^{-3} S/cm for composition with 40 wt% of NH_4I. The electrolyte system is predominantly ionic in nature. From LSV analysis, MC:Dex:NH_4I electrolyte is found to be electrochemically stable up to 1.27 V. The DC conductivity value, TNM and LSV results reveal the availability of the samples for electrical double layer capacitor (EDLC) application. The existence of charges double-layer in the fabricated EDLC is proven from cyclic voltammetry (CV). The fabricated EDLC offers an initial specific capacitance as 79 F/g, energy density as 8.81 Wh/kg and power density as 1111.0 W/kg at a current density of 0.2 mA/cm^2. Fading is observed in the EDLC performance in prolonged cyclic tests. The results shown in the present work indicate that the above electrolyte system comprising polymers obtained from natural resources have potential to be used in EDLC devices.

Conflicts of interest

The authors declare no conflicts of interest.

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