The present work deals with a new biodegradable biopolymer electrolyte-based carboxymethyl cellulose, CMC which was isolated from palm oil empty fruit bunch. Biopolymer electrolytes were developed with different ratios of sodium acetate (NaCH₃COO) via a solution casting technique, and their structural, electrical and electrochemical behaviours were investigated. The incorporation of 30 wt% sodium acetate yielded an optimized ionic conductivity of $1.83 \times 10^{-3}$ S cm$^{-1}$ at room temperature. Fourier transform infrared results suggested that interactions between components occurred in the biopolymer. The CMC-NaCH₃COO film with the highest conductivity had an electrochemical stability of 2.8 V, and transference number measurements confirmed that ions predominate in the conduction of electrolytes.

**Keywords:** Biopolymer electrolytes; sodium acetate; electrical studies; electrochemical stability

**1. INTRODUCTION**

Over four decades ago, in 1973 solid polymer electrolytes were reported as replacements for liquid electrolytes because of their high conductivity performance in addition to good thermal and mechanical stability. They were proposed to overcome the problems faced by liquid electrolytes such as leakage, reaction with electrodes and poor chemical stability [1, 2]. Many studies have been carried out for the development of solid polymer electrolytes by using materials such as synthetic polymers. Synthetic polymers based on petroleum resources such as polyethylene oxide, polyacrylic acid and polyvinyl alcohols have been widely used as host polymers even though these polymers are high in cost. Since petroleum resources are declining significantly, polysaccharides have become better alternatives because of their abundance, low cost and unique properties.
Biopolymers are chain-like molecules made up of repeating units and are covalently bonded to form a larger structure such as cellulose, carrageenan, chitin, starch, myoglobin and DNA. Based on past and recent studies performed by researchers, polysaccharides have been widely used in many chemical industries such as food, drugs, health and hygiene products, papers and textiles. In addition to these applications, polysaccharides such as carrageenan, starch, cellulose, chitosan, agar, and DNA are also used for electricity due to their functional groups that are rich in electrons. Their morphological properties can be altered from a crystalline structure to an amorphous structure based on the transition temperature. Due to the increase in amorphous properties, the polymeric chain in the amorphous phase becomes flexible, which results in the enhancement of the segmental motion of the polymer. These properties have attracted the attention of many researchers, especially in the electrical and electronic industries, since they can be applied in many applications, such as fuel cells and battery applications. Additionally, these polysaccharides are low cost, non-hazardous, and biodegradable and have been discarded as industrial waste around the world.

Today, Li⁺ ion batteries are the most promising concept for vehicular application and have attracted the attention of researchers due to the small ionic radii of Li⁺ ions which could be intercalated into the layers of the layered materials in electrodes. With the likelihood of enormous demands on available global lithium resources, concerns over lithium supply – but mostly its cost – have arisen. Many global lithium reserves are located in remote or politically sensitive areas. Even if extensive battery recycling programmes were established, it is possible that recycling could not prevent the depletion of this resource in time. Furthermore, increasing lithium utilization in medium-scale automotive batteries will ultimately increase the price of lithium compounds, thereby making large-scale storage prohibitively expensive. Therefore, the focus of extended study is investigating alternative sources of charge carriers to replace Li⁺. In a report by Moreno et al., it was observed that the incorporation of sodium bis(trifluoromethanesulfonate) imide (NaTFSI) increased the flexible and ionic conductivity of poly(ethylene oxide) (PEO). All films showed excellent ionic conductivities of 10⁻³ S cm⁻¹ above 70 °C. Isa et al., reported that the electrical and electrochemical properties of polyvinylidenefluoride-co-hexafluoropropylene (PVDF-HFP) were enhanced in the presence of sodium trifluoromethane sulfonate (NaCF₃SO₃). Sodium salts seem to be the best candidates due to the similarity of their properties to those of lithium salts and are impregnated in CMC from palm oil empty fruit bunch. Despite the many studies on biopolymer electrolytes (BEs), there is no work on the interaction of CMC synthesized from palm oil empty fruit bunch with sodium acetate BE systems. Henceforth, the scope of this article is to investigate the interactions, and electrical and electrochemical properties of CMC-NaCH₃COO BEs by means of various physical techniques namely Fourier transform infrared (FTIR) spectroscopy, scanning electron microscopy (SEM), electrical impedance spectroscopy (EIS), linear sweep voltammetry (LSV) and transference number measurement (TNM).
2. EXPERIMENTAL

2.1 Preparation of BE films

Palm oil empty fruit bunch (POEFB) was commercially obtained from Sabah Softwoods Sdn. Bhd., Malaysia while sodium acetate (99.99%), sodium hydroxide (99%), isopropanol (98%), sulfuric acid (98%), glacial acetic acid (99.5%), monochloroacetic acid and sodium chlorite (80%) were purchased from Sigma-Aldrich and Systerm-chemAR. All materials were used without further purification. Cellulose derived from palm oil empty fruit bunch was modified into CMC; following the method in our previous paper [11]. The degree of substitution (DS) value for the obtained CMC is 1.27 which is higher than commercial CMCs. A higher DS value for CMC means it has a higher number of oxygens therefore, more active sites for coordination with the cations of the doping salt will be provided, contributing a high conductivity value [11]. Conventional solution casting was conducted to form thick electrolyte films with varying concentration of NaCH$_3$COO (10, 20, 30 and 40 wt%) dissolved in 40 mL of aqueous acetic acid (1%) solution. A pure CMC (0 wt% NaCH$_3$COO) film was prepared as a reference sample. The homogeneous solution was then transferred into glass Petri dishes and left to dry to form thin films. All films were relocated to a desiccator for further drying.

2.2 Characterization of CMC-NaCH$_3$COO BEs

To investigate the interactions between CMC and NaCH$_3$COO, FTIR spectroscopy was performed by using a Perkin Elmer Frontier (FTIR) spectrometer equipped with attenuated total reflection (ATR). The sample was placed on top of a diamond surface. A pressure arm applied force on the sample, and infrared light passed through the sample. FTIR spectra were recorded in the spectral range of 4000-550 cm$^{-1}$ (±1.0 cm$^{-1}$) at a scan resolution of 2 cm$^{-1}$ at room temperature. The FTIR data were recorded in transmittance mode. A Zeiss EVO MA10 scanning electron microscope was used to observe the surface morphology of each BE film with 500×, 1000× and 2000× magnifications with a 10 kV electron beam. A Solartron 1260 impedance/gain phase analyser was used on the BE film to determine its impedance measurements with frequencies ranging from 10 to 4 MHz. Each BE sample was sandwiched between two stainless steel electrodes with a diameter of 2.0 cm (area = 3.142 cm$^2$). The impedance of the samples was measured at temperatures in the range of 303 K to 338 K. The electrochemical stability and ionic transference number measurement of BE films were determined by using a Wonatech ZIVE MP2 multichannel electrochemical workstation. In the measurement, the electrolyte was sandwiched between two stainless steel electrodes. For electrochemical stability window measurement, the BE film data were recorded at a scanning rate of 1 mVs$^{-1}$. The voltage was applied in the range of 0 to 4 V. Meanwhile, the ionic transference number ($t_{ion}$) was evaluated with a direct current polarization technique by monitoring the polarization current as a function of time. $t_{ion}$ was calculated using the following equation below:

$$t_{ion} = \frac{I_{initial} - I_{final}}{I_{initial}}$$

(1)
\[ t_{\text{electron}} = \frac{I_{\text{final}}}{I_{\text{initial}}} \]  

(2)

where \( I_{\text{initial}} \) and \( I_{\text{final}} \) denote the initial and steady state currents, respectively.

3. RESULTS AND DISCUSSION

3.1 Structural analysis

Figure 1 depicts the FTIR spectra in the region from 550 cm\(^{-1}\) to 4000 cm\(^{-1}\) for NaCH\(_3\)COO, pure CMC as a reference and CMC-NaCH\(_3\)COO (10-40 wt\%). The absorption band for O-H stretching which appears at 3347 cm\(^{-1}\) for pure CMC (Figure 1 (b)) shifted to lower wavenumbers as the NaCH\(_3\)COO concentration increased. This indicates that there was an interaction between the polymer and dopant salt. This is attributed to the interaction of the cation [Na\(^+\)] substructure of NaCH\(_3\)COO with oxygen atoms of the hydroxyl group of CMC [29]. Although the interaction between the polymer host and ionic salt normally occurs at the oxygen atom, other bands can also be affected [30]. In pure CMC, the carboxyl group (C=O) is the band of interest to be investigated, and the C=O band at 1597 cm\(^{-1}\) shifted to a lower wavenumber (1558 cm\(^{-1}\)) upon the incorporation of 30 wt% NaCH\(_3\)COO into the polymer matrix, indicating the occurrence of an interaction between the (C=O) moiety in CMC and Na\(^+\). The changes that occurred in the FTIR spectra provide clear indications of the formation of CMC-NaCH\(_3\)COO complexes.

![Figure 1. IR-spectra of (a) NaCH\(_3\)COO, (b) CMC powder, and the addition of (c) 10, (d) 20, (e) 30 and (f) 40 wt% NaCH\(_3\)COO in the spectral region between 4000 and 550 cm\(^{-1}\).](image)
3.2. Morphological study

The prepared films were flexible, free standing and transparent. Scanning electron microscopy (SEM) images of pure CMC and CMC-NaCH$_3$COO complexed films are shown in Figure 2. All BE films were in a solid, free-standing film form during characterization. The surface morphology in Figure 2 (a) clearly shows that the pure CMC film appeared to have a rough, uneven and dark surface. Moreover, a few cubic shapes of various sizes are visible in a certain area. Figure 2 (b) shows the SEM image of the highest-conducting film containing 30 wt% NaCH$_3$COO. The BE film surface was observed to have a smooth and bright morphology, which demonstrates that the film became amorphous and may have contributed to a greater region for fast ionic motion leading to conductivity enhancement [31]. The presence of the dark and bright regions in the SEM images represents an amorphous and dark surface according to study done by Monikoswa et al. [32]. Therefore, this supports that the increase in the smooth and bright region in the CMC-30 wt% NaCH$_3$COO BE film suggests an enhancement in the amorphous region.

![Figure 2. SEM micrographs of (a) pure CMC and (b) CMC complexed with 30 wt% NaCH$_3$COO films.](image)

3.3. Impedance study

The CMC doped NaCH$_3$COO BE films were analysed using EIS. EIS is a non-destructive and powerful technique to compute the electrical properties of electrolyte materials and their interfaces with electronically conducting electrodes. Figure 3 presents the complex impedance spectra for the CMC-30 wt% NaCH$_3$COO BE film at elevated temperatures. Normally, polymer electrolyte spectra show two distinct regions: a semicircle in the high frequency region and a spur in the low frequency region. However, the complex impedance plots in this present study only spikes, indicating that ion conduction is the main contributor to ionic conductivity [33]. $R_b$ of the films was calculated from the intercept of the tilted spike at the real impedance axis. With increasing salt concentration, the value of $R_b$ decreases.
Figure 3. Complex impedance spectra for CMC films with 30 wt% NaCH₃COO added at different temperatures.

The room temperature ionic conductivity of CMC-NaCH₃COO content is presented in Figure 4. It can be observed that the ionic conductivity increases with the addition of NaCH₃COO, which can be explained by the increase in the free charge carrier movement in the membrane. The optimized ionic conductivity of $1.83 \times 10^{-3}$ S cm⁻¹ was achieved for the film incorporated with 30 wt% NaCH₃COO. As seen in the surface morphology analysis, the film with 30 wt% NaCH₃COO is found to be the most amorphous film which supports the conductivity result. This finding is similar to what was previously reported in the literature [34]. The charge carriers became more densely packed with the addition of salt; thus, the attractive interactions between these free charge carriers increased [35]. After the system reached the maximum value; at 30 wt% NaCH₃COO, the conductivity decreased. This phenomenon is attributed to the host matrix which becomes packed with ions (overcrowding) impeding charge carrier mobility [36].
**Figure 4.** Ambient temperature ionic conductivity of CMC-NaCH$_3$COO.

A plot of log conductivity, $\sigma$ against $1000/T$, for CMC-NaCH$_3$COO (0–40 wt%) is depicted in Figure 5. The regression values, $R^2$ of all plots are between 0.996 and 0.999, suggesting that the temperature dependence for all BE films is linear, showing that the conductivity is thermally assisted [37-39].

**Figure 5.** Temperature dependence of the ionic conductivity of pure CMC (0 wt%) and CMC with 10-40 wt% NaCH$_3$COO.
Figure 6. Activation energy vs. concentration of NaCH$_3$COO salt.

Figure 6 shows the pattern of the activation energy, $E_a$ vs. concentration plot. The $E_a$ plot is the inverse of the conductivity plot as shown in Figure 4. The barrier (band gap) to Na$^+$ transport is reduced when the NaCH$_3$COO concentration increases. Hence, $E_a$ decreases [40, 41]. The lowest $E_a$ value was found at 0.101 eV for the highest conducting membrane (CMC-30 wt% NaCH$_3$COO), suggesting that ionic conduction is the most favourable considering that much less energy is required for ions to jump from one coordinate site to another coordinate site [38, 42]. However the slight increase in the activation energy for the system incorporated with 40 wt% NaCH$_3$COO is probably due to a decrease in the ionic mobility in the system [43].

3.4. Transference number study

Ions and/or electrons are the responsible species that contribute to the overall conductivity value. Herein, the contributions of the particular charge species in the BEs to the overall charge transport were investigated via transference number measurements. Figure 7 shows a plot of the normalized polarization current versus time for CMC-30 wt% NaCH$_3$COO. The depletion of the charge carriers or ionic species in the electrolyte caused the initial total current to decrease with time. In the completely depleted condition, the current becomes constant. The ionic transference number, $t_i$ for the CMC-30 wt% NaCH$_3$COO film is 0.98, while the electron transference number, $t_e$ in CMC-30 wt% NaCH$_3$COO is only 0.02 which can be neglected [44, 45]. This suggests that ions were predominantly responsible for the conduction of the CMC-30 wt% NaCH$_3$COO electrolyte film. The finding in this study are comparable with those for other sodium salt-based polymer electrolytes [46].
Figure 7. Normalized polarization current versus time for the CMC-30 wt% NaCH₂COO biopolymer film.

3.5. Linear sweep voltammetry (LSV) study

Analysis of linear sweep voltammetry (LSV) was conducted to determine the electrochemical stability window and decomposition voltage of the electrolyte [47]. Figure 8 illustrates the LSV curve of the CMC-30 wt% NaCH₂COO BE system. There were no obvious current changes below 2 V; however, a drastic change occurred as the potential increased. The electrochemical stability of this film reached up to 2.8 V. This voltage is the decomposition voltage of the studied sample. Ibrahim et al. [46] reported that castor-oil based polyurethane incorporated with sodium iodide showed a decomposition voltage of 1.8 V. In another study conducted by Isa et al. [28], a potential stability of 3.4 V was achieved with a polyvinyllidenefluoride-co-hexafluoropropylene (PVDF-HFP)-sodium trifluoromethane sulfonate (NaCF₃SO₃) system. Henceforth, it is concluded that the samples in this study are stable enough to be applied as biopolymer electrolytes in electrochemical devices.
4. CONCLUSION

Biopolymer electrolyte films of palm oil empty fruit bunch-based carboxymethyl cellulose were successfully prepared using sodium acetate by using a conventional solution casting technique. The highest ionic conductivity $1.83 \times 10^{-3}$ S cm$^{-1}$, was exhibited by the system containing 30 wt% sodium acetate. The temperature dependence of the conductivity showed that all biopolymer electrolyte-based CMC-NaCH$_3$COO films obeyed Arrhenius thermal activated model behaviour. FTIR analysis confirmed the interaction between the polymer host and NaCH$_3$COO. The results of transference number measurements demonstrated that the charge transport in the CMC-NaCH$_3$COO biopolymer film was mainly attributed to ions. The electrochemical stability of CMC-30 wt% NaCH$_3$COO reached up to ~2.8 V, as shown in the LSV results.

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