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Influence of NH₄F in Dextran Based Biopolymer Electrolytes: Conductivity and Electrical Analysis

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Abstract

Dextran polymer host was doped with different concentrations of ammonium fluoride (NH₄F) via casting technique. In this present work, dextran-NH₄F film has been employed to investigate the ionic conductivity using electrochemical impedance spectroscopy from 50 to 5 MHz. The highest room temperature conductivity is achieved at $(2.33 \pm 0.76) \times 10^{-3} \text{ S cm}^{-1}$ with 40 wt.% NH₄F. The electrolyte is found to obey Arrhenius rule at high temperature with activation energy of 0.21 eV. Dielectric analysis has been performed to obtain better understanding on the conductivity pattern. The dielectric parameters e.g. ϵ_{real} , ϵ_{imag} , M_{real} , and M_{imag} have been tested as a function of frequency at various temperature. The potential stability obtained for the highest electrolyte in this study is 1.58 V.

Abstract

Pengaruh NH₄F di dalam Elektrolit Biopolimer Berbasis Dextran: Kajian Kekonduksian dan Kelistrikan. Polimer dextran yang didoping dengan kepekatan amonium florida yang berbeza melalui penuangan larutan. Dalam kerja ini, dextran-NH₄F telah digunakan untuk menginvestigasi kekonduksian ionik melalui spektroskopi impedansi listrik. Kekonduksian tertinggi di suhu bilik yang diperoleh adalah $(2.33 \pm 0.76) \times 10^{-3} \text{ S cm}^{-1}$ dengan 40% berat NH₄F. Elektrolit didapati mengikut peraturan Arrhenius pada suhu tinggi dengan tenaga pengaktifan 0.21 eV. Analisis dielektrik telah dilaksanakan bagi memperoleh pemahaman tentang corak kekonduksian. Ciri-ciri dielektrik seperti ϵ_{real} , ϵ_{imag} , M_{real} , dan M_{imag} telah diuji dengan pelbagai frekuensi dan suhu. Kestabilan pontensi yang diperoleh untuk elektrolit yang mempunyai kekonduksian tertinggi adalah 1.58 V.

Keywords: dextran, ammonium fluoride, dielectric, Arrhenius, ionic conductivity

1. Introduction

Due to the concern regarding the global crisis, sustainable biomaterials have become interesting topics to work on. Synthetic polymers like polystyrene, polymethyl methacrylate and polyamide are expensive and non-biodegradable. The employment of non-biodegradable polymers can increase the number of plastic waste pollution. Biopolymer have been employed by researchers in the electrolyte studies as the polymer host due to

easy selection of solvent, biodegradable, good film forming properties and inexpensive [1]. Wide range of natural resources can be used to extract biopolymers thus provides safer materials for environment and human health [2].

Dextran is a biopolymer that is extracted from bacteria called *Leuconostoc mesenteroides* where glucansucrases enzyme is used in the extraction process. Most biopolymers have lone pair electron at the functional group

of the polymeric network which aids in ionic conduction [3]. The linear backbone of dextran is consisted of ,6- α -D-glucopyranosidic linkages [4]. Dextran has been used in medical field as drug conductor, blood alternative, plasma modification and bone curing [5].

Ammonium salts are known to have high ionic conductivity, compatible with various solvent as well as thermally stable. The expensive electrode materials in lithium batteries can be avoided with the use of ammonium salt [6]. Various types of ammonium salt have been used such as ammonium nitrate (NH_4NO_3), ammonium chloride (NH_4Cl), ammonium bromide (NH_4Br) and ammonium fluoride (NH_4F) [7-9]. The aim of this work is to prepare a high ionic conductivity biopolymer electrolyte using a biodegradable polymer host. Dextran has been chosen as the polymer host. The ionic conductivity and dielectric behaviour of the electrolyte has been monitored with various concentration of ammonium fluoride (NH_4F).

2. Experimental

Preparation of the electrolytes. An amount of 50 mL distilled water was used to dissolve 2g of dextran (Sigma-Aldrich). Upon dissolution, 10, 20, 30 and 40 wt.% NH_4F (R&M chemicals) were added into the dextran solution. The dissolved solution was poured in different plastic Petri dishes and left at room temperature for 4-6 days for drying process. The films formed were placed in desiccators.

Characterization of the electrolytes. HIOKI 3532-50 LCR HiTESTER was employed to perform electrochemical impedance spectroscopy (EIS) for 50 to 5 MHz. The range of temperature that will be used in this study is from 298 to 343 K. The electrolyte was placed in between two stainless steel which then placed in a teflon casing. The conductivity (σ) can be obtained from the following equation:

$$\sigma = d / AR_b \quad (1)$$

$$\sigma = \sigma_{pre} \exp\left(-\frac{E}{kT}\right) \quad (2)$$

here d stands for the electrolyte's thickness. The area and the bulk resistance of the electrolyte was denoted as A and R_b , respectively. σ_{pre} corresponds to factor of pre-exponential while E is the activation energy. k and T are Boltzmann constant and absolute temperature. From EIS results, dielectric constant (ϵ_{real}) and loss (ϵ_{imag}) can be expressed as:

$$\epsilon_{real} = \frac{Z_{imag}}{\omega C_o \left((Z_{real})^2 + (Z_{imag})^2 \right)} \quad (3)$$

$$\epsilon_{imag} = \frac{Z_{real}}{\omega C_o \left((Z_{real})^2 + (Z_{imag})^2 \right)} \quad (4)$$

While the real and imaginary part of impedance is called as Z_{real} and Z_{imag} , respectively. ω and C_o are denote as radiul frequency and vacuum capacitance. The real (M_{real}) and Imaginary (M_{imag}) parts of electrical modulus can be expressed as:

$$M_{real} = \frac{\epsilon_{real}}{\left((\epsilon_{real})^2 + (\epsilon_{imag})^2 \right)} \quad (5)$$

$$M_{imag} = \frac{\epsilon_{imag}}{\left((\epsilon_{real})^2 + (\epsilon_{imag})^2 \right)} \quad (6)$$

while DY2300 potentiostat was used in linear sweep voltammetry (LSV) analysis to study the potential stability of the electrolyte at 50 mV s^{-1} .

3. Results and Discussion

Conductivity study. The influence of NH_4F on the ionic conductivity at room temperature can be observed in Figure 1. Pure dextran film possesses room temperature conductivity of $(2.00 \pm 0.70) \times 10^{-9} \text{ S cm}^{-1}$. The addition of 10 and 20 wt.% NH_4F have increased the conductivity to $(2.65 \pm 0.13) \times 10^{-6}$ and $(2.70 \pm 1.21) \times 10^{-4} \text{ S cm}^{-1}$, respectively. The electrolyte achieves a maximum value at $(2.33 \pm 0.76) \times 10^{-3} \text{ S cm}^{-1}$ with 40 wt.% NH_4F . This value is comparable with report by Ahmad and Isa [8] where the conductivity value of $\sim 10^{-3} \text{ S cm}^{-1}$ is achieved with ammonium salt-based biopolymer. NH_4F dissolves in polymeric network of dextran providing free ions such cations (NH_4^+ or H^+) and anions (F^-). More ions are available for ionic migration as more salt is added, thus improve the ionic conductivity [10].

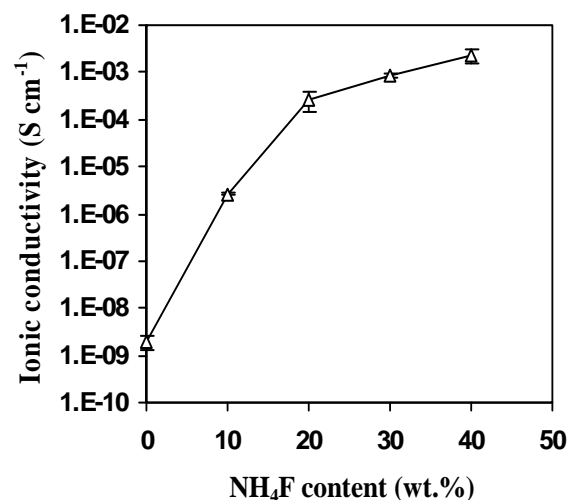


Figure 1. NH_4F Content Against the Ionic Conductivity at Room Temperature

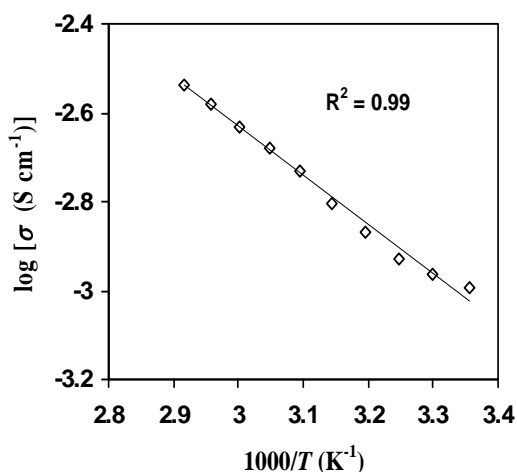


Figure 2. Conductivity at Elevated Temperature for Electrolyte with 40 wt.% NH₄F

Temperature dependence conductivity. The highest conducting electrolyte (40 wt.% NH₄F) has been used to study the conductivity at elevated temperature which can be observed in Figure 2.

The conductivity is observed to increase as the temperature increases. The dissociation of ion has been improved at high temperature. Thus, more ions are involved in the migration process [11]. It is noticeable that the conductivity has linear relation with temperature where regression (R_2) value is ~ 0.99 . This is an indicator of Arrhenius behaviour where the ionic conduction is theorized as thermally activated rather than the segmental motion of the polymeric network [12]. From equation (2), the value of activation energy (E) for the electrolyte with 40 wt.% NH₄F is 0.21 eV. Yusof et al. [13] reported a value of 0.20 eV for starch/chitosan-40 wt.% NH₄I based biopolymer electrolyte.

Dielectric analysis. Figure 3 shows the changes of ϵ_{real} and ϵ_{imag} as the NH₄F is included. ϵ_{real} corresponds to the energy stored in the electrolyte while ϵ_{imag} is loss of energy to migrate ions at the presence of electrical field. It can be seen that as the frequency is increased, both ϵ_{real} and ϵ_{imag} reduced. At high frequency, the periodic reversal of the electric field occurs so fast that charge carriers is prevented from orienting themselves in the field direction, resulting in the decrement of dielectric. [14].

The addition of NH₄F enhances both values of ϵ_{real} and ϵ_{imag} as observed in Figure 3. This is also a proof of increment in charge carriers with addition of more salt. According to Chandra [15], the inclusion of salt improves the flexibility of the polymer matrix, thus it is easier for ions to be conducted. The patterns of ϵ_{real} and ϵ_{imag} are harmonized with the trend of the conductivity.

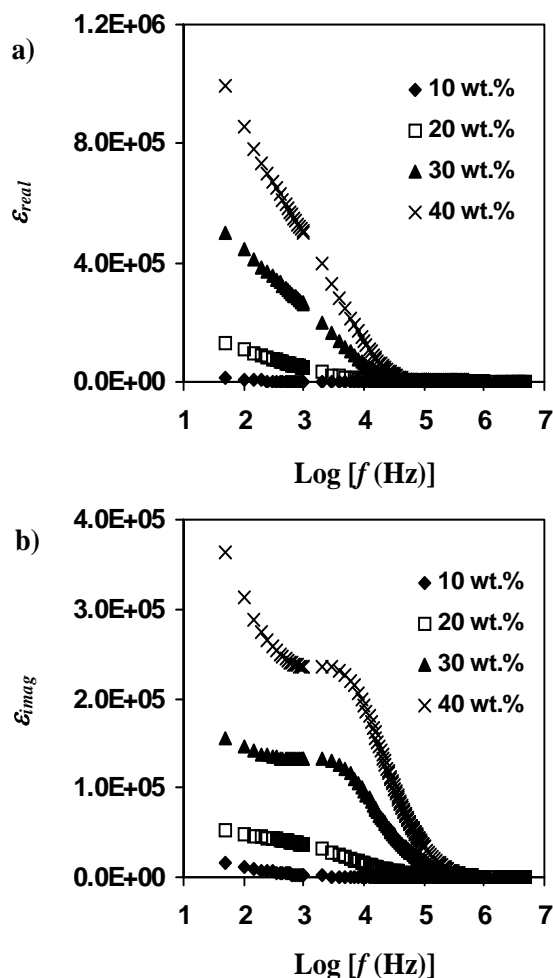


Figure 3. The Value ϵ_{real} and ϵ_{imag} as a Function of NH₄F at Room Temperature

Aziz et al. [16] also stated that the highest conducting electrolyte possesses the highest value of dielectric constant which is comparable to the results in this work.

Figure 4 illustrates the effect of temperature of ϵ_{real} and ϵ_{imag} for electrolyte with 40 wt.% NH₄F. The values of ϵ_{real} and ϵ_{imag} increase with temperature. The ionic dissociation is maximized at higher temperature thus provides more free ions [17]. This phenomenon enhances the ϵ_{real} and ϵ_{imag} which is harmonized with conductivity at high temperature.

Electrical modulus analysis. Figure 5(a) depicts the value of M_{real} as the function of NH₄F content at various frequencies. At low frequency region M_{real} is appeared to approach zero value where its increases at higher frequency region. This is because electrode polarization is dominant at low frequency. The movement of ions is considered chaotic at high frequency thus lessen the polarization effect [18]. It is obvious that the value of M_{real} reduces as NH₄F is added. The addition of salt promotes charge carriers to undergo more polarization

process at the presence of electric field. A peak can be seen for electrolyte with 10 wt.% NH₄F in Figure 5(a). This peak corresponds to the ionic conductivity relaxation which usually appears at high frequency region [19]. The absence of peak for the electrolyte with 20, 30 and 40 wt.% NH₄F is due to limitation of experimental frequency by the impedance analyzer.

Figure 5(b) shows the effect of temperature on the value of M_{real} for 40 wt.% NH₄F. The value of M_{real} is observed to decrease at elevated temperature. The polymeric network has become more flexibility and more ions are created at high temperature thus reducing the value of M_{real} [20]. This phenomenon tallies with the result of conductivity at elevated temperature.

Figure 6(a) portrays the effect of NH₄F addition on the value of M_{imag} at room temperature. There is a peak observed in the plot of 10 wt.% NH₄F. This peak divides the plot into two regions. These two regions are namely conduction and relaxation respectively. The presence of

peak also can be an indicator of ionic conductor [21]. The disappearance of peak for other electrolyte is due to frequency limitation. The decrease in M_{imag} value with the increase in temperature as shown in Figure 6(b) is attributed to the improvement of salt dissociation and polymeric segmental motion [22].

Linear sweep voltammetry. Potential stability is a significant parameter for an electrolyte to be discovered. Thus, LSV analysis is employed to check the voltage where the electrolyte started to decompose. Highest conducting electrolyte (40 wt.% NH₄F) has been used sandwiched in between two stainless steel electrodes. Figure 7 shows the LSV plot with scan rate of 50 mV s⁻¹. No obvious increment of current is observed up to 1.58 V. The current drastically increased after 1.58 V which indicates that the biopolymer electrolyte decompose at 1.58 V. Mishra et al. [23] reported a potential stability of 1.60 V for ammonium salt-based polymer electrolyte. The minimum requirement for an electrolyte to be used in proton-based electrical energy storage technologies is ~ 1 V [24]. Hence this electrolyte in this study can be used as a separator in device applications.

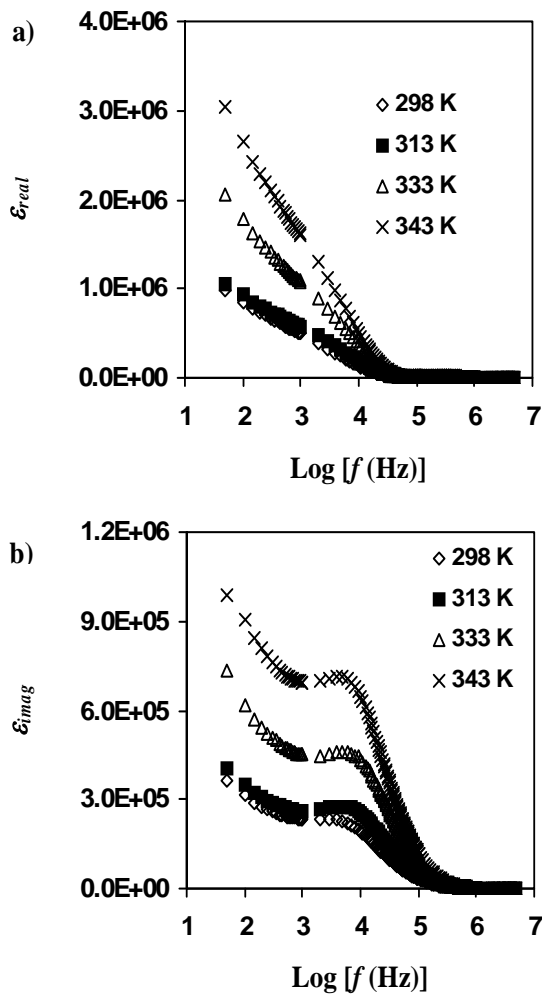


Figure 4. The Value ϵ_{real} and ϵ_{imag} as a Function of Temperature for Electrolyte with 40 wt.% NH₄F

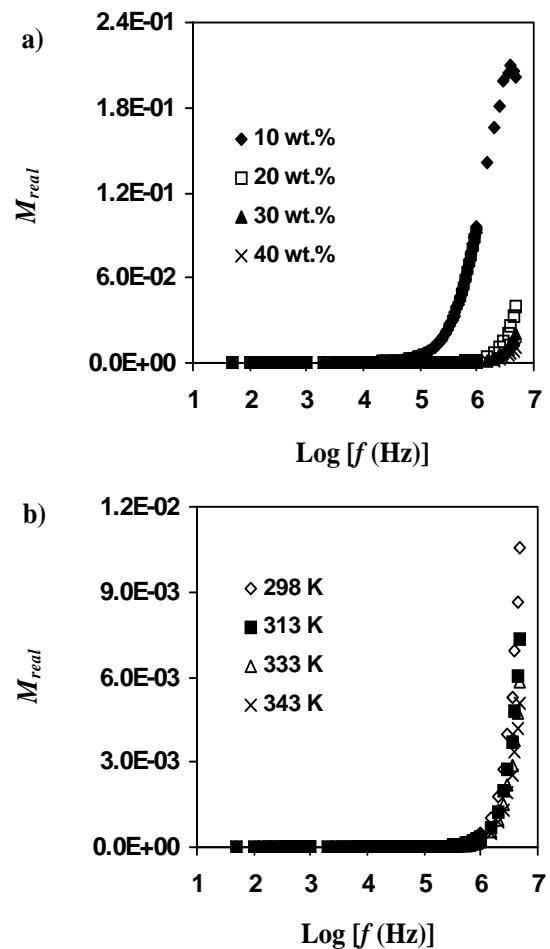


Figure 5. The Value of M_{real} (a) as a Function of NH₄F at Room Temperature and (b) for 40 wt.% NH₄F at Elevated Temperature

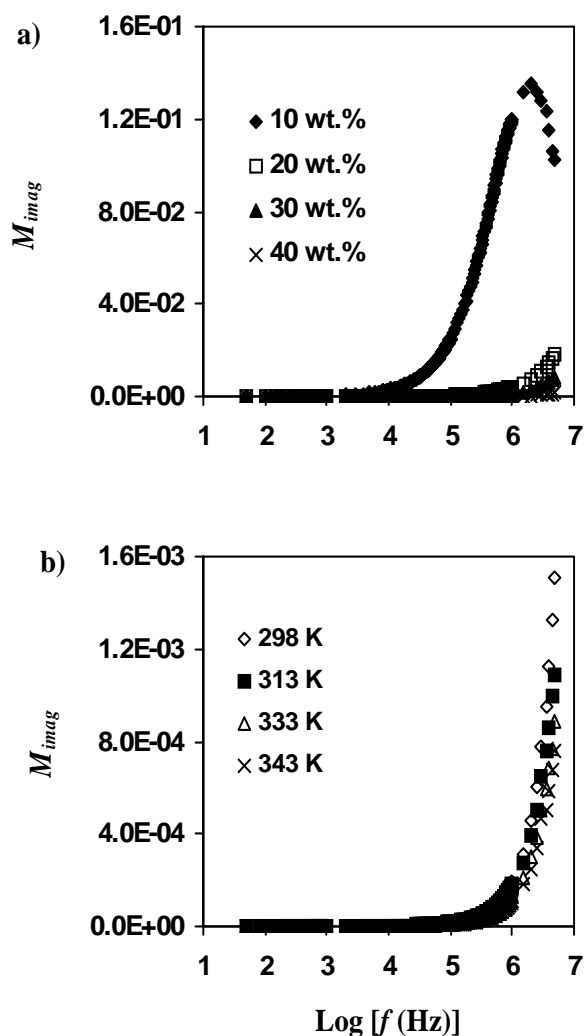


Figure 6. The Value of M_{imag} (a) as a Function of NH_4F at Room Temperature and (b) for 40 wt.% NH_4F at Elevated Temperature

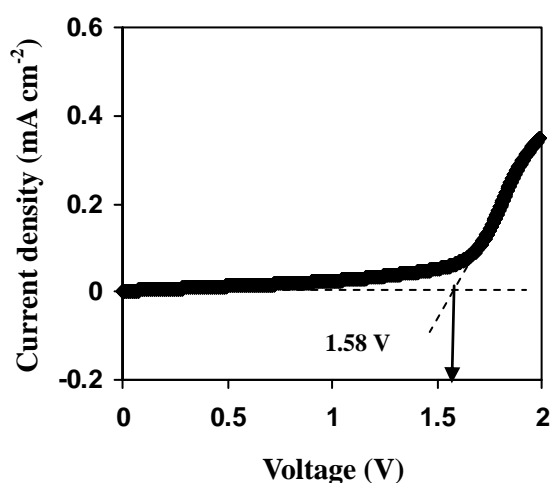


Figure 7. LSV Plot for Electrolyte with 40 wt.% NH_4F at 50 mV s^{-1}

4. Conclusions

Casting technique has been successfully employed to prepare electrolyte films with dextran and ammonium fluoride (NH_4F) as the polymer matrix and ionic source, respectively. Pure dextran film's conductivity at $(2.00 \pm 0.70) \times 10^{-9} \text{ S cm}^{-1}$ has discovered to increase up to $(2.33 \pm 0.76) \times 10^{-3} \text{ S cm}^{-1}$ with 40 wt.% NH_4F . It has been confirmed that the electrolyte is thermally activated at elevated temperature as the electrolyte obeys the Arrhenius conduction theory. Activation energy for the highest conducting electrolyte has found to be 0.21 eV. The increment in ionic conductivity has been verified via the pattern of dielectric constant and electrical modulus. From dielectric study, the electrolytes are observed to follow non-Debye behaviour. It is identified via LSV analysis that the highest conducting electrolyte is electrically stable up to 1.58 V. Hence dextran- NH_4F based electrolyte can be used as separator in electrochemical devices such as proton batteries and electrical double-layer capacitors (EDLC) in the future.

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