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Ionic Conductivity and Electrochemical Properties of Alginate– NH_4NO_3 -Based Biopolymer Electrolytes for EDLC Application

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Abstract

In this work, alginate doped with various contents of ammonium nitrate (NH_4NO_3) as a solid biopolymer electrolyte (SBE) was prepared via casting by using distilled water as a solvent. Impedance studies on alginate– NH_4NO_3 SBE films were conducted via impedance spectroscopy. The lowest bulk resistance (R_b) showed that the maximum ionic conductivity of the sample containing 25 wt.% NH_4NO_3 at ambient temperature (303 K) was $5.56 \times 10^{-5} \text{ S cm}^{-1}$. The temperature dependence of ionic conductivity was evaluated, and results confirmed that electrolytes followed an Arrhenius behavior. The highest conducting sample was fabricated into an electrical double-layer capacitor and characterized in terms of its electrochemical properties through cyclic voltammetry (CV) and galvanostatic charge–discharge (GCD) measurement. CV analysis indicated that specific capacitance decreased as the scan rate increased. Conversely, GCD analysis showed that specific capacitance almost remained unchanged for up to 5000 cycles.

Abstrak

Konduktivitas Ionik dan Sifat Elektrokimia dari Elektrolit Biopolimer Berbasis Alginate – NH_4NO_3 untuk Aplikasi EDLC. Dalam penelitian ini, alginate yang didoping dengan variasi konsentrasi dari amonium nitrat (NH_4NO_3) sebagai elektrolit biopolimer padat (SBE) di-casting dengan menggunakan air sebagai pelarutnya. Studi impedansi pada lapisan tipis SBE alginate- NH_4NO_3 dilakukan melalui spektroskopi impedansi. Hambatan limbak terendah (*Bulk Resistance*, R_b) menunjukkan bahwa konduktivitas ionik maksimum sampel yang mengandung 25% NH_4NO_3 pada suhu ambient (303 K) adalah $5,56 \times 10^{-5} \text{ S cm}^{-1}$. Hubungan antara suhu dan konduktivitas ionik dievaluasi dan hasilnya menunjukkan bahwa elektrolit mengikuti aturan *Arrhenius*. Sampel konduktor tertinggi difabrikasi menjadi kapasitor listrik *double-layer* dan dikarakterisasi sifat elektrokimianya dengan pengukuran *cyclic voltammetry* (CV) dan *galvanostatic charge-discharge* (GCD). Analisis CV menunjukkan bahwa kapasitansi spesifik menurun ketika laju pemindaian (*scan rate*) meningkat. Sebaliknya, analisis GCD menunjukkan bahwa kapasitansi spesifik hampir tidak berubah hingga 5000 siklus.

Keywords: alginate, ionic conductivity, EDLC, specific capacitance, CD profile

1. Introduction

Solid biopolymer electrolytes (SBEs) have gained technological importance as electrolyte materials for modern systems that generate and store energy because of their advantages over liquid electrolytes; some of these advantages are nonleakage property, flexibility, lightweight, good electrode/electrolyte contact, and low self-discharge [1],[2]. Biopolymer electrolytes made

from natural polymers have also been widely explored because of high demands for a green environment and limitations of synthetic polymer sources [3],[4]. Natural polymers, including starch [5], cellulose derivatives (e.g., hydroxyethyl cellulose [6], methyl cellulose [7], and carboxyl methylcellulose [8]), chitosan [9], agar-agar [10], pectin [11], gelatin [12], and alginate [13], have been commonly used as host polymers in SBE system development. Among them, alginate may be

utilized as a host in SBEs because of its superior ability to form an edible film, good mechanical properties, and anionic group suitable for forming complexes with ionic dopants. In the present work, alginate is chosen to obtain a green environment in the future. One of the main objectives of using SBE systems is to achieve favorable ionic conductivity for energy device applications. Studies have demonstrated the use of polymer electrolytes to fabricate energy devices, including electrical double-layer capacitors (EDLCs), because of their suitability for low-energy density devices [14]-[16]. An EDLC is also known as a supercapacitor that contains electrolytes and two carbon electrodes as alternative power sources to rechargeable batteries at the development stage [17].

In this work, alginate was developed as a host polymer and doped with ammonium nitrate (NH_4NO_3)-based SBEs. The performance of alginate- NH_4NO_3 in EDLC application was also studied. The prepared SBEs were characterized through impedance spectroscopy and fabricated into an EDLC. The electrochemical properties of the EDLC were determined via cyclic voltammetry (CV) and galvanostatic charge-discharge measurement.

2. Experimental Method

Sample preparation. Biopolymer electrolytes were prepared with alginate and doped with various NH_4NO_3 contents by using distilled water as a solvent via solution casting. Alginate was dissolved in distilled water until a homogeneous solution was obtained. Then, 0 wt.% to 35 wt.% NH_4NO_3 was added to the alginate solution and continuously stirred until it completely dissolved. The mixtures were cast into different Petri dishes and left in a desiccator at ambient temperature to further dry until a film was formed. The designation of alginate- NH_4NO_3 SBEs is presented in Table 1.

Characterization. In the present system, the prepared alginate- NH_4NO_3 biopolymer electrolytes were characterized via electrical impedance spectroscopy to determine their ionic conduction properties. Impedance was obtained using a HIOKI 3532-50 LCR Hi-tester interfaced to a computer in a frequency range of 50 Hz to 1 MHz. Bulk resistance (R_b) was measured from the imaginary impedance (Z_i) versus real impedance (Z_r) plot, and ionic conductivity (σ) was calculated using Equation (1):

$$\sigma = \frac{t}{R_b A} \quad (1)$$

where t is the thickness of the sample, and A (cm^2) is the cross-sectional area of the biopolymer electrolyte film. Activated carbon (AC BP20): super P: poly(vinylidene fluoride) at a ratio of 80:10:10 and N-methyl-2-pyrrolidone as a solvent were used to prepare the electrode for the development of an EDLC device. The

Table 1. Designation of Alginate- NH_4NO_3 Solid Biopolymer Electrolyte System

Designation	NH_4NO_3 content (wt.%)
S0	0
S1	5
S2	10
S3	15
S4	20
S5	25
S6	30
S7	35

mixture was stirred until it became homogeneous and formed a slurry. The slurry was spread on aluminum foil by using a doctor blade technique and baked in a vacuum oven for 24 h or until it dried. The EDLC was assembled by sandwiching the highest conducting sample with two electrodes in a coin cell (2032) and characterized through cyclic voltammetry and galvanostatic charge-discharge measurement.

3. Result and Discussion

Impedance studies. Figure 1 illustrates the Nyquist plot of the alginate biopolymer electrolyte doped with various amounts of NH_4NO_3 at room temperature. The Nyquist plot has two patterns: a semicircle with a spike and only a title spike. The semicircle at a high frequency is attributed to the bulk effect of the biopolymer electrolytes, whereas the spike at a low frequency is due to the migration of ions through the free volume of the polymer matrix in the SBE system [18]. In impedance analysis, the stainless steel blocking electrode is used, and the electrode/electrolyte interface can be viewed as capacitance. The semicircle at a high frequency represents the parallel combination of R_b and bulk capacitance, whereas spike can be fitted in a series by another bulk capacitance, as illustrated in Scheme 1 [19],[20]. The complex impedance plot reveals that R_b can be obtained with the intercept between imaginary and real parts.

Upon the addition of 25 wt.%, the semicircle starts to disappear possibly because of the enhancement of the mobility of ions via dissociation when a huge amount of dopant is introduced [21]. The appearance of the title spike at a high NH_4NO_3 content is attributed to a combination in a series of R_b and bulk capacitance [22]. Ramya *et al.* [23] reported that R_b decreases because of an increase in mobile charge carrier. The biopolymer electrolytes containing 25 wt.% of NH_4NO_3 (S5) shows the lowest R_b , indicating that S5 exhibits the highest ionic conductivity of $5.56 \times 10^{-5} \text{ S cm}^{-1}$. However, the semicircle re-appeared beyond S5, that is, S7. This phenomenon is due to a decrease in the number of mobile ions, thereby increasing R_b and decreasing ionic conductivity.

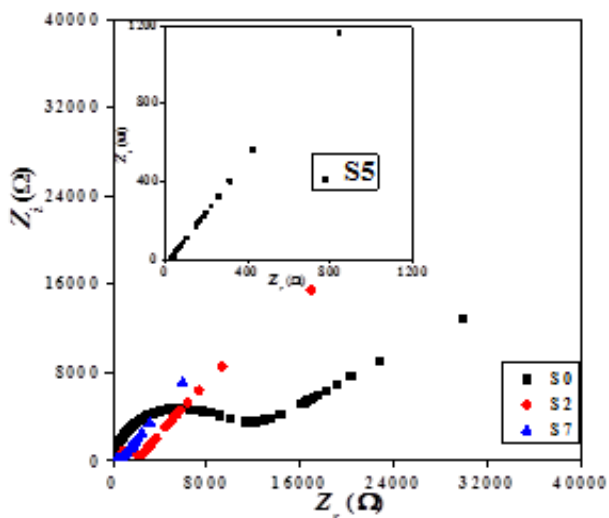
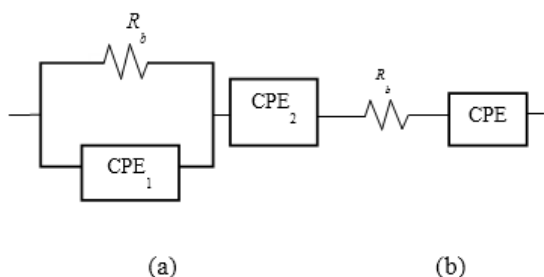


Figure 1. Nyquist Plot of Biopolymer Electrolytes with Different NH₄NO₃ Contents



Scheme 1. Equivalent Circuit of (a) The Semicircle with a Spike and (b) The Spike Only

Temperature dependence studies. Figure 2 shows the temperature dependence of the alginate biopolymer electrolyte system in the selected sample at different temperatures (303 K to 343 K). Ionic conductivity increases linearly upon the addition of NH₄NO₃ to the biopolymer complexes. No sudden decrease or increase in ionic conductivity is observed, indicating that SBEs exhibit an amorphous nature, which suggests the existence of a favorable charge carrier-based ionic dopant [24]. An increase in ionic conductivity with temperature improves ion mobility and induces ions to hop from one site to another in a biopolymer host matrix. As a result, ionic conductivity increases. Regression (R^2) is found to be almost unity ($R^2 \sim 1$), suggesting that all SBE systems follow the Arrhenius behavior and are thermally activated as described below:

$$\sigma = \sigma_0 \exp\left(\frac{-E_a}{kT}\right) \tag{2}$$

where σ_0 is the pre-exponential factor, E_a is the activation energy, and k is the Boltzmann constant. Sample S5 shows the lowest E_a (Table 2), which indicates that a lower E_a is required by ions to migrate

from one site to another in a polymer matrix because of a faster ion migration rate. Hence, ionic conductivity improves and reaches the maximum value.

Analysis of the electrochemical properties of EDLC. CV was carried out to study the performance of the SBE system in EDLC application. The cyclic voltammogram of the EDLC containing sample S5 is recorded (Figure 3). The voltammograms are determined in the potential range of 0–1 V, different scan rates of 2–10 mV s⁻¹, and room temperature.

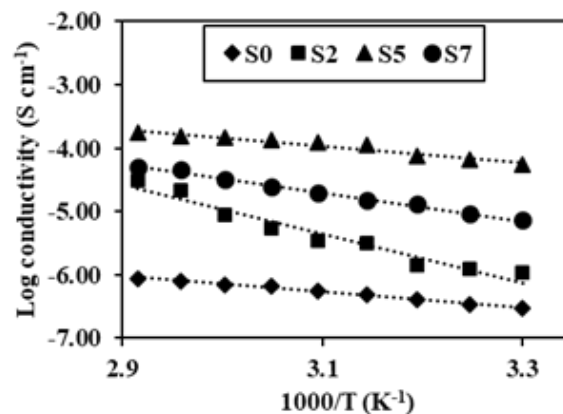


Figure 2. Temperature Dependence of Alginate–NH₄NO₃ SBEs

Table 2. Regression and Activation of SBEs at the Selected NH₄NO₃ Contents

Sample	R^2	E_a (eV)
S0	0.95	0.26
S2	0.98	0.23
S5	0.98	0.11
S7	0.96	0.16

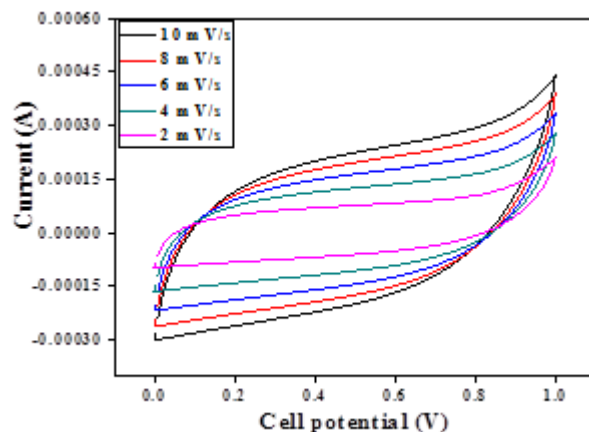


Figure 3. Cyclic Voltammogram of EDLC at Different Scan Rates

In Figure 3, the CV profiles display a leaf-like shape and become smaller as the scan rate decreases. This finding can be attributed to the decrease in the stored charge on the surface of the electrode, thereby increasing energy loss [25]. The CV curve almost appears rectangular at a scan rate of 2 mV s^{-1} . Good CV shapes correspond to the rapid current response to voltage reversal at each end potential. Conversely, no distinct peaks are observed in the CV curve at the given scan rates, indicating the absence of redox reactions or electron transfer in the fabricated EDLC coin cells [26]. The specific capacitance in our work is calculated, and a high value of 118.32 F/g is obtained at a scan rate of 2 mV s^{-1} . In Table 3, specific capacitance decreases as the scan rate increases possibly because the inaccessible ion portion diffuses at the electrode/electrolyte interface [27].

Table 3. Specific Capacitance of CV Analysis at Different Scan Rates

Scan rate (mV s^{-1})	Specific capacitance (F/g)
2	118.32
4	97.66
6	84.96
8	75.69
10	68.35

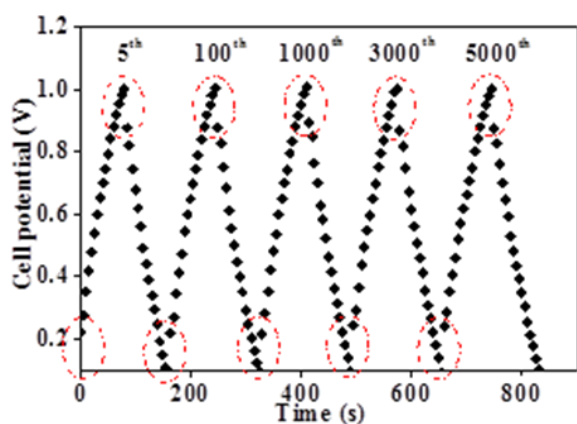


Figure 4. Galvanostatic Charge-discharge Curves of Alginate Electrolyte at the Selected Cycles

Figure 4 reveals the charge-discharge profile of the EDLC device in various cycles for up to 5000 cycles of the biopolymer alginate doped with 25 wt.% NH_4NO_3 with a current density of 0.3 mA cm^{-2} . However, the voltage in the present work ranges from 0.1 V to 1 V during charging; this value suggests that the internal resistance (I_R) of the cell increases from the electrode/electrolyte and polymer electrolyte interface [28,29]. The discharge curves are linear, which confirms the capacitive behavior of the fabricated EDLC [30]. Specific capacitance is dependent on ionic conductivity [31-33] because ionic mobility plays an important role in transport properties, which can influence the performance of the EDLC. The sudden voltage drop detected in the initial discharge curves is attributed to the effect of I_R that appears in the fabricated EDLC. I_R is observed because of interfacial resistances between electrodes and electrolytes and between the current collector and the active material used in the present device [15,34].

Figure 5 shows the ESR value, and the inset presents the specific capacitance and coulombic efficiency of the EDLC for over 5000 cycles. The ESR calculated from the voltage drop is $\sim 0.39 \text{ k}\Omega$, which is almost consistent; this result suggests that the nature of cations in biopolymer electrolytes containing different salts does not significantly affect I_R of EDLC [35]. Moreover, the lowest ESR favors the highest C_{sp} , indicating that the biopolymer electrolyte has an intimate contact with the electrode that facilitates the transport of ions toward the electrode pore. The inset in Figure 5 illustrates that the specific capacitance is almost constant, confirming the capacitive behavior of the fabricated EDLC [35,36]. The coulombic efficiency of EDLC is stable at above 90% for over 5000 cycles and reveal that the present SBEs have potential for EDLC application. Table 4 summarizes previous studies on polymer electrolytes in EDLC devices. The performance of the present SBEs in EDLC application is comparable with that reported in other studies, which have shown that they are stable for charge-discharge with the longest cycle. Thus, the proposed SBEs may be used for electrochemical devices.

Table 4. Previous Studies on Polymer Electrolytes EDLC Applications

Materials	σ (S cm^{-1})	Specific capacitance (F/g)	Cycles	References
PVA-Chitosan- NH_4NO_3 -EC	1.60×10^{-3}	27.1	100	[37]
PVA- $\text{CH}_3\text{COONH}_4$ -BmImI	9.63×10^{-3}	56.16	500	[15]
Starch-LiOAc-glycerol	1.04×10^{-3}	~ 33.00	1000	[34]
Chitosan/iota(t)-carrageenan- H_3PO_4	6.29×10^{-4}	35	30	[38]
Alginate- NH_4NO_3	5.56×10^{-5}	~ 52.22	5000	Present work

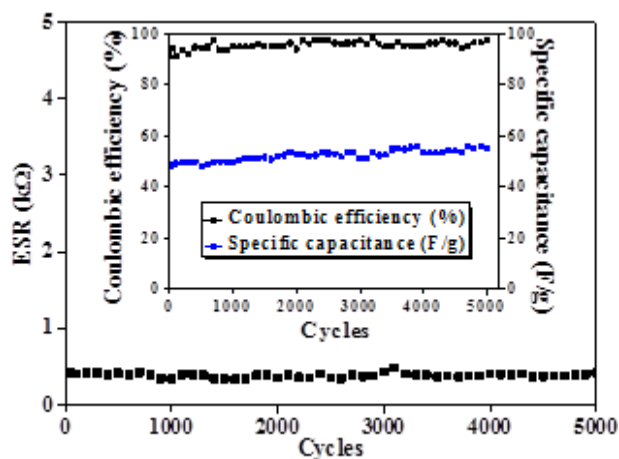


Figure 4. ESR Plot of 5000 Cycles. Inset: Coulombic Efficiency and Specific Capacitance Versus Cycles

4. Conclusion

SBEs based on alginate doped with various amounts of NH_4NO_3 are successfully prepared via casting. The biopolymer electrolyte containing 25 wt.% of NH_4NO_3 exhibits an optimum ionic conductivity at $5.56 \times 10^{-5} \text{ S cm}^{-1}$. The temperature dependence of ionic conductivity obeys an Arrhenius behavior and becomes thermally activated. CV and galvanostatic charge–discharge measurement are carried out to understand the performance of an EDLC consisting of an alginate electrolyte. The size of the rectangle obtained from CV analysis decreases as the scan rate decreases. As a result, specific capacitance increases. The charge–discharge profile of the EDLC device is in good condition and stable up to 5000 cycles.

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