Properties of Bacterial Cellulose/Polyvinyl Composite Membrane for Polymer Electrolyte Li ion Battery

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Received 13 June 2022; Accepted 5 April 2023

ABSTRACT

High ionic conductivity and porous properties of material play important role as a solid polymer electrolyte in Li ion battery application. In this study, a bacterial cellulose (BC) based polymer was modified with polyvinyl pyrrolidone (PVP) and polyvinyl alcohol (PVA). Blending the polymer host is one more approach to work on the morphology pore and electrochemical properties of polymer electrolytes. The slurry of BC is rich of fibers that contribute to forming of the pore template for solid electrolyte membrane. Polyvinyl act as material to creating pore and increases the polymer segmental ion lithium mobility. Pore morphology of BC-PVA and -PVP composite membrane homogeneously distributed by SEM observations. The presence of many pores makes the tensile strength of the BC PVA membrane lower. For solid electrolytes purposes, it does not affect battery performance but has a greater possibility for battery lifetime. The presence of pores contributes to the absorption of electrolytes membranes. In addition, enhancement of the conductivity upon addition of salt is correlated to the enhancement of pores from solid polymer electrolyte. The conductivity of BC-PVA composite is reported 8.7 x 10⁻³ Scm⁻¹, and this ion conductivity is slightly higher than conductivity in BC-PVP 8.4 x 10⁻⁷ Scm⁻¹ at room temperature. In the future, BC-PVA can be applied for solid electrolyte membranes material based on cellulose.

Keywords: bacterial-cellulose, polyvinyl pyrrolidone, polyvinyl alcohol, solid polymer electrolyte

INTRODUCTION

The electrolyte is an important part of an ion transfer medium from the anode to the cathode. It plays during the charging and discharging interactions. However, lithium based ion batteries use the liquid electrolytes suffer from inherent drawbacks, such as flammability, leaking, and environmental toxicity. These issues become important consideration for application to electric vehicles (EVs) or high energy density energy storage devices [1]. Solid polymer electrolyte (SPE) plays a role and as important alternative in eliminating leakage because no liquid electrolyte is applied. However, still remain research challenge to prepare materials with a high electrochemical performance [2]. In some references reported that a solid polymer electrolytes also give a comparable ionic conductivity and suit to enhance the safety in battery applications [3].
The role of solid polyelectrolyte matrices based on various groups of respect in this field has been studied. One of them is bacterial cellulose (BC). BC is a natural and inexpensive biopolymer. BC application as a gel polymer electrolyte for lithium based ion batteries displays astounding layered dependability, excellent ionic conductivity ($\sim 10^{-5}$ Scm$^{-1}$) and competitiveness battery performance [4-5]. BC is super hydrophilic material due to the large number of hydroxyl groups on its surface. This groups are vital for the utilization of polymer electrolyte membrane. Wang and coworker reported, when a thin film was made from cellulose fibers using polyvinyl alcohol (PVA) as composite addition, after swelling with a standard liquid electrolyte, the ionic conductivity of the membrane reached to $6.7 \times 10^{-5}$ Scm$^{-1}$ [6]. The PVA is water-dissolvable polymer and containing with hydroxyl (-OH) groups. This functional groups become the domain sites for hydrogen bonding interaction during composite arrangement with bacterial cellulose and PVA. Thus, this sites create a large volume or space for lithium ions movements [7]. Meanwhile, the polyvinyl alcohol (PVA) as the polymer host indicate versatility for forming various SPE complexes electrolyte salts and additives [8]. In addition to that, another material such as polyvinyl pyrrolidone (PVP) has been reported as an alternative to improve the dimensional stability of the electrolyte [9]. It has ionic conductivity up to $1.1 \times 10^{-5}$ Scm$^{-1}$ at room temperature [10].

The physical characteristic of PVP are amorphous solid and constructed by cyclic hetero-hydrocarbon chain contain of carbonyl (C=O) and amino (-NH) groups in their lateral bonds [11]. It has also easily dissolved in several polar solvents, and the capability to crosslink with inter- and intra- molecule provide thermal and mechanical stability [3]. In addition, both material of PVP and PVA can be applied as a pore shaping agent, by adding as suspension [12]. Therefore, combination of both with bacterial cellulose (BC) improve the performance, low cost, and environmentally friendly for solid electrolyte materials-based lithium ions.

**EXPERIMENT**

**Chemicals**

Bacterial cellulose (BC) was purchased from a local of coconut farmers. Polyvinyl pyrrolidone (PVP), polyvinyl alcohol (PVA) (MW = 89,000) was used as the polymer host. Lithium bis(trifluoromethanesulfonyl)imide (LiTFSI) has analytical grade [13], sodium hydroxide, ethyl carbonate (EC), and ethyl methyl carbonate (EMC) from Sigma Aldrich.

**Bacterial cellulose pretreatment**

Bacterial cellulose membrane was pretreated by soaking in 0.1 M solution of sodium hydroxide at 90 °C. It was to eliminate bacterial cell residue and cleaning the membrane. It was further washed and rinsed with deionized water until neutral pH. The blending was repeated to produce a smooth bacterial cellulose.

**Tensile strength measurement**

The tensile strength of bacterial cellulose membrane was measured at 25 °C using the Yasuda 216-10k. Universal material tester and performed following ASTM D882 procedure for thin film with stretchable test pace 5 mm/min. The sample length and width was 10 and 5 mm. Sample was connected with throw on two closure. The elasticity was applied to the heap cell until the membrane film broken.

**Morphology observation**

Bacterial cellulose membrane was characterized by using FESEM JEOL JIB 4160F, and the fibre diameter was measure and analysis using ImageJ software.
Measurement membrane ionic uptake

Membrane electrolyte uptake is a major factor affecting ionic conductivity [14]. A dry bacterial cellulose was placed under argon gas in the glove box for 1.5 hour. Then, the electrolyte retention in the membrane measured. Measurement based on the weight of bacterial cellulose before (W₀) and after (W₁) absorption. And the electrolyte uptake (η) of the liquid electrolyte was calculated following equation (1).

\[
\eta (\%) = \frac{W_1 - W_0}{W_0} \times 100\%
\]  

(1)

The ion conductivity for lithium-ion transfer on bacterial cellulose was measured using the EIS HIOKI-9263 SMD test component LCR with frequency 0.6-20 kHz.

Viscosity measurement

Viscosity of the sample or liquid was measured at room temperature by ViscoQC.

Reaction procedure

To develop solid polymer electrolyte (SPE) membrane, solution casting technique was employed. BC pulp, PVA and PVP powder was mixed in deionized water at 90 °C. It was stirred for 3 hours until a clear solution was obtained. The mixture was poured in petri dish. A slow evaporation method was applied to dry the samples at room temperature. After 48 hours, membranes were effectively peeled off from the petri dishes. The self-supporting membrane, BC with a diameter of 19 mm and thick about 100 μm was moved in glove box under argon atmosphere. It was further immersed in a 50 μL solution of 1 M of lithium hexafluorophosphate (LiTFSi) with a molar ratio of ethylene carbonate (EC) to ethyl methyl carbonate (EMC) (1:1) at ambient temperature. The sample was dried again in a glove box to give a BC water free or dry solid polymer-electrolyte.

RESULT AND DISCUSSION

The addition of lithium-based ion electrolyte on composite bacterial cellulose membrane is observed with SEM (Figure 1). The combination of bacterial cellulose with polyvinyl alcohol (PVA), bacterial cellulose with polyvinyl pyrrolidinone (PVP), and original bacterial cellulose give a different feature on their surface morphology, including their pore size indicated. A tight fiber was observed in the surface of bacterial cellulose. Its composite with PVA and PVP indicate reducing tightness of the cellulose fiber. Thus, expanding the pore size of the composite. Analyzing pore size for bacterial cellulose give pore diameter about 103.16 nm. It enlarges to 212.87 nm and 143.20 nm for composite bacterial cellulose-PVA and PVP, respectively. Composite with PVA retain free hydroxyl groups (-OH) that straightforwardly interact by hydrogen bonding with water molecule or lithium ion. Compared to the composite bacterial cellulose with PVP, it structures possess carbonyl group (C=O) that water molecule and lithium ion not easily uploading from the surface of bacterial cellulose membrane. The PVP material retain in the polymer matrix, and water or electrolyte ion diffusion prevention occur entering the pore. That not only lesser the pore size, but also reducing electronic conductivity (Table 1).

The contact angle measurement of the bacterial cellulose, the composite of BC and PVA, and the composite BC-polyvinyl pyrrolidinone (PVP) with dropping of electrolyte is displayed in Figure 2. The wettability of the surface from pure bacterial cellulose gives 5.40°. Meanwhile the combination bacterial cellulose with polyvinyl alcohol increases the contact
angle to 13.69°. The immersion of composite bacterial cellulose and polyvinyl alcohol increase the contact angle become 38.81°.

**Figure 1.** SEM morphology pore of (a) pure BC, (b) BC-PVA, and (c) BC-PVP after immersion with LiTFSi electrolyte.

**Figure 2.** Contact angle membrane composite (a) pure BC, (b) BC-PVA and (c) BC-PVP after droplet electrolyte.

<table>
<thead>
<tr>
<th>Polymer blend composition</th>
<th>Electrolyte Uptake (%)</th>
<th>Contact Angle</th>
<th>Ion conductivity (Scm⁻¹) at 25 °C</th>
<th>Viscosity (mPas) at 25 °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pure BC</td>
<td>100</td>
<td>5.40°</td>
<td>5.5 x 10⁻⁵</td>
<td>6.18</td>
</tr>
<tr>
<td>BC PVA</td>
<td>100</td>
<td>13.69°</td>
<td>8.7 x 10⁻⁵</td>
<td>11.88</td>
</tr>
<tr>
<td>BC PVP</td>
<td>90.20</td>
<td>38.81°</td>
<td>8.4 x 10⁻⁷</td>
<td>27.35</td>
</tr>
</tbody>
</table>

**Table 1.** Characteristic of the membrane BC composite.

In general, the ion conductivity depends on the electrolyte viscosity. Based on the data displayed in Table 1, bacterial cellulose has the least viscosity. In addition, combination of bacterial cellulose with PVA (BC-PVA) gives lower viscosity than that in BC-PVP. Thus, inhibit the ion mobility. The electrolyte viscosity \( \eta \), is also strongly tied to physicochemical properties of the electrolyte solution. The electrolyte uptake indicate salt electrolyte content in solid polymer membrane [4-15]. And it correlates to the viscosity as well. The declining of conductivity possibly the effect of viscosity increments in the membrane. The effective mobility of ionic carriers decreases with increasing viscosity [16]. Due to the uniformity of the membrane, the viscosity dominates the permittivity of the plasticizer during the study of conductivity [3]. Ionic conductivity (\( \sigma \)) of the solid polymer electrolytes was resolved from the complex impedance spectrum using the equation, \( \sigma = \frac{L}{RA} \) (Table 1). Where L, R, and A are the thickness, resistivity, and area of the solid polymer electrolyte, respectively [17].
Volume resistivity was determined from the high frequency portion of the Nyquist diagram on the real impedance axis (Figure 3a). The increase in BC-PVA of ionic conductivity was steeper than BC-PVP when the diffusion coefficients of Li salt and Li\(^+\) ions were high.

Viscosity study is often used to characterize the interaction between two different polymers in a common solvent [18]. Due to the uniformity of the membrane, the viscosity dominates the permittivity of the plasticizer during the study of conductivity. The thickness of the membrane can be constrained by changing the viscosity (concentration) of the blend. Membrane thickness contribute to make membrane have high tensile strength Figure 3b. The focus of attention is the maximum ability of the BC membrane to withstand the load. Young's Modulus is a curve that expresses the relationship between strain and stress [19]. This curve (Figure 3) shows that pure BC membrane is more brittle than PVA and PVP composite membranes. Addition of PVA content tends to make the membrane more weak, resulting in a lower tensile strength, as salts can disturb intermolecular interactions inside the host polymer and form new interactions. And the break point elongation was extended [20].

![Figure 3.](image)

**Figure 3.** (a) Nyquist plot and (b) tensile strength of SPE BC composite.

**CONCLUSION**

It can be summarized that combination of PVA as an additive for bacterial cellulose composite for solid polymer electrolyte give a more porous structural morphology than it with PVP. As a result, it gives better ionic conductivity. This finding provides another insight for its conceivable solid polymer electrolyte application in energy storage frameworks.

**ACKNOWLEDGMENT**

The authors acknowledge for the research support from Research Center for Physic, National Research and Innovation Agency and Advanced Characterization Laboratory, Serpong through E-layanan sains, Badan Riset Inovasi Nasional.

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