Characterization of Solid Polymer Electrolyte Membrane made of Methylcellulose and Ammonium Nitrate

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Abstract. Nowadays, the application of portable electronics devices such as smartphone, notebook and tablet playing important role in daily life. This portable electronic devices required portable powering sources such as battery. However, the current battery technology containing liquid electrolyte which is hazardous and harmful when leaking. Therefore, the major purpose of this study was to propose a new biodegradable, safe and low cost solid polymer electrolyte (SPEs) mainly from Methylcellulose (MC) doped Ammonium Nitrate (AN). The study was conducted by using casting method as it is the most appropriate technique due to its simplicity and low cost. Methylcellulose (MC) as the host was doped with different weight percent (wt%) of Ammonium Nitrate (AN) to fabricate SPEs. The result shows the adding of AN onto MC was significantly enhanced the physical properties of SPEs. The loading of 2g MC with 25% AN (MC2_25AN) yield the highest conductivity at 3.5 x10⁻⁷ Sm⁻¹ at room temperature. Furthermore, the MC2_25AN poses a good stability with the lowest swelling rate. Therefore, the use of low cost and biodegradable MC and AN have a great potential to replace the hazardous electrolyte in electrochemical powering sources.

1. Introduction

As the booming of internet and wireless technology communications, the application of portable electronics devices such as smartphone, notebook and tablet become essential in routine daily life. This portable electronic equipment is an electrochemical devices that required portable powering sources such as battery. Table 1 shows the current technology for portable powering sources. However, most of portable power source such as battery lithium ion made up from high cost fabrication and not ecologically friendly. The extensive use of electrochemical device has created many environmental worries, such as toxic metal pollution. Battery manufacture consumes resources and often involves hazardous chemicals which is mainly from the electrolyte used [1]. Eventhough, the electrolyte in electronic devices today are high in conductivity, but it is dangerous and non-recyclable, thus, it is risk to the environment and also human.

Even though, liquid electrolyte possesses high ion conductivity, it is also creating a few setbacks such as leakage, reaction with electrode, poor electrochemical stability, yet make it inappropriate for longer applications in electrochemical devices. Therefore, the solid polymer electrolytes (SPEs) research field was greatly booming due to its excellent mechanical and thermal stability and high ionic conductivity. The researchers [2][3][4] found SPEs have remarkable potential to replace the liquid electrolyte, especially in the applications of batteries, sensors, fuel cells and other electrochemical...
devices. Moreover, the installation of polymer electrolytes (PE) in devices take up smaller space, compact and lighter mass as well as on their physical.

Table 1  Current battery technology

| Type of battery   | Electrolyte          | Devices                                                                 |
|------------------|----------------------|-------------------------------------------------------------------------|
| Nickel Cadmium   | 30% solution of KOH  | Two-way radios, emergency medical equipment, professional video cameras and power tools |
| Nickel-Metal Hydride | Alkaline solution KOH | Digital cameras                                                           |
| Lead Acid        | Solution of Sulphuric acid KOH | Emergency lighting, large backup power supplies for telephone and computer centres, grid energy storage, and off-grid household electric power systems |
| Nickel Zinc      | Alkaline solution KOH | Power tool and high-drain devices                                         |
| Lithium Ion      | Lithium salts in an organic solvent KOH | smartphone, laptop, remote control, digital camera and watch |

Solid polymer electrolytes (SPEs) have a very limited or problem in leakage or pressure distortion [5]. Commonly, the matrix of SPEs were developed from synthetic polymers which are Polyethylene Oxide (PEO), Polyacrylic Acid and Polyvinyl Alcohol which are high cost polymers. However, methylcellulose (MC) is polysaccharide is considered as an almost inexhaustible source for environmentally friendly materials and cheap [6]. It is abundant, renewable, biodegradable as well as biocompatible and used in a wide range of applications, from paper, regenerated films and fibers to various medical applications. It can easily be chemically modified, which possess good film-forming properties such as transparency, flexibility and resistance to oil and fats a good solubility in aqueous solutions [7].

A new composite gel polymer electrolyte of nonwoven fabric (NWF) and MC were developed by Li et al, 2015. The result shows the highest ionic conductivity was obtained at 0.29 mS cm⁻¹ at ambient temperature. In order to improve membrane permeability and anti-fouling behavior, MC also were used additive in polysulfane membrane [9]. Liebeck et al. (2017) synthesized bio composite membrane using MC/keratin hydrolysate. They found the increasing of keratin hydrolysate loading will increase the mechanical properties of membrane. The researches has shown that potential of MC to enhanced the physical and mechanical properties of membranes. Therefore, this study is conducted to investigate the physical properties of new biodegradable and low cost solid polymer electrolytes (SPEs) using MC as matrix and Ammonium Nitrate (AN) will used as a dopant salt.

2. Methodology

Methylcellulose used as membrane material was supplied by Aldrich. Ammonium Nitrate (AN) was obtained from Merck. The SPEs were synthesized using simple solution casting technique. The solution of MC were prepared for 2 different weighs which 1g (MC1) and 2g (MC2) with different percentages of AN solution as shown in table 2. A solution of MC were added with different weight of AN and stirred for 24 hrs. There were 3 different percentage of AN (8%, 16.5%, 25%) were added into MC1 solution and MC 2 solution, namely MC1_8AN, MC1_16.5AN, MC1_25AN, MC2_8AN, MC_16.5AN, MC_25AN. The mixture were casted and dried at room temperature. The evaluation of physical characteristics of SPEs were evaluated for water uptake, swelling rate and conductivity. The water uptake and swelling rate were calculated as equation (1) and (2) respectively.
Water Uptake = \frac{W_{\text{wet}} - W_{\text{dry}}}{W_{\text{dry}}} \times 100\% \quad (1)

Where \( W_{\text{dry}} \) was the initial weight of SPEs, \( W_{\text{wet}} \) was the final weight of SPEs after soaked in water after 24 hours.

Swelling rate = \frac{D_i - D_f}{D_f} \quad (2)

Where \( D_i \) was the initial dimension of SPEs, \( D_f \) was the final weight of SPEs after soaked in water after 24 hours. The conductivity of SPEs were analyzed using EIS Autolab PGSTAT128N.

Table 2  Sample preparations of MC-AN

| Weight of MC | Percentage of AN |
|-------------|-----------------|
| 1 g         | 8               |
| 1 g         | 16.5            |
| 1 g         | 25              |
| 2 g         | 8               |
| 2 g         | 16.5            |
| 2 g         | 25              |

3. Results and Discussion

3.1. Water Uptake

Figure 1 shows the water uptake of the SPEs for different loadings of pure MC and MC-AN samples. The figure shows for the MC1, the highest water uptake is for pure MC (33%), followed by 1MC-8AN. The lowest water uptake is for 1MC-25AN. The similar trend was obtained for MC2 as shows in figure 1. The result clearly shows the addition loading of AN will decrease the water permeability. The MC polymer was intercalated into the layer structure of AN, resulting in a tortuous path for water transportation. Therefore, the water permeabilities of the MC-AN are lower than that of pure MC. This findings was similar to previous publications [11].

Figure 1: Water uptake for different loadings of AN at room temperature.
3.2. Swelling Rate

The swelling properties is the dimensional change of SPEs for Pure MC and MC-AN as depicted in figure 2. The ability to swell is an important property of SPEs. Understanding of swelling behavior is important on the thoughtful of ion transfer inside the membrane and microstructure of the SPEs. Figure 2 shows the highest swelling rate occurred in pure MC1 and pure MC2. The result shown the increasing of AN loading will decrease the swelling rate. The swelling properties result obviously correlated with the water uptake findings as the dimensional change of the SPEs depends on water sorption [12]. Whereas, the higher water uptake ability, resulting more dimensional change of SPEs.

![Figure 2: Swelling rate for different loading of AN at room temperature.](image)

3.3. Ionic Conductivity

Figure 3 illustrated the ionic conductivity of pure MC samples and MC-AN samples. Pure MC shows the lowest conductivity either for MC1 or MC2. These findings indicated that the dopant salt is significant to increase the ionic conductivity of cellulose membrane. The highest conductivity obtained for sample MC2-25AN was at value $3.5 \times 10^{-7}$ Sm$^{-1}$. The conductivity value of MC2-25AN almost double compared to the same loading of 25% AN onto MC1. The increasing amount of MC will increase the membrane porosity that enhance AN flux [9]. It apparently revealed the used of AN as dopant salt is significantly increased the ionic conductivity with seven magnitude order.

![Figure 3: Conductivity value for pure MC and different loadings of MC at room temperature.](image)
4. Conclusions
In this study, the SPEs were fabricated using Methylcellulose (MC) doped with Ammonium Nitrate (AN). The study found the sample with loading 2MC-25AN poses the best physical properties with the highest ionic conductivity value $3.50 \times 10^{-7} \text{Sm}^{-1}$. The MC2_25AN SPEs have a good stability as the swelling rate is very low. Therefore, the low cost MC-AN SPEs have great potential for further exploration to replace the commercial and existing electrolyte battery.

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