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RESEARCH

Study of biomaterial electrolyte based on *Peltophorum pterocarpum* incorporated with NH_4SCN for proton-conducting battery and PEM fuel cell applications

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Abstract

A novel development of biomaterial membrane based on *Peltophorum pterocarpum*—a flower with various concentrations of ammonium thiocyanate (NH_4SCN)—is prepared with distilled water as a solvent by using solution casting technique. The prepared membranes are subjected to different characterization techniques such as X-ray diffraction analysis, differential scanning calorimetry, AC impedance analysis, transference number measurement, and linear sweep voltammetry. The crystalline/amorphous nature of the prepared biomaterial membrane is studied by using XRD. The T_g values of the prepared membranes are analyzed using differential scanning calorimetry. The highest ionic conductivity is found to be 2.19×10^{-2} S/cm for 1 g PP with 0.7 M wt% NH_4SCN by AC impedance analysis. The highest ion-conducting biomaterial membrane of 1 g *Peltophorum pterocarpum* with 0.7 M wt% NH_4SCN is observed with an electrochemical stability of 2.00 V from LSV. Primary proton battery and proton exchange membrane (PEM) fuel cell are fabricated using the highest ion-conducting biomaterial membrane. The open-circuit voltage (OCV) of primary proton battery is observed to be 1.57 V, and its performance is studied. A single fuel cell is constructed, which exhibits a cell potential of 487 mV.

Keywords *Peltophorum pterocarpum* · AC impedance · Proton battery · NH_4SCN · PEM fuel cell

Introduction

In our day-to-day life, the demand for electrochemical devices has increased much. The electrochemical devices include batteries, supercapacitors, fuel cells, and sensors [1, 2]. An electrochemical device, such as a battery, consists of electrodes and an electrolyte. Considerable interest has been focused on the electrolyte. Electrolytes play a vital role in the performance of a battery. So far synthetic and biopolymers with addition of different salts have been used as electrolyte. Some synthetic polymers are non-biodegradable, and biopolymer-based electrolyte is costly due to processing procedure. To overcome the above drawbacks, cost-effective and biodegradable biomaterials such as flower, petals, and seeds are used to prepare electrolyte by adding appropriate salts. In this work, biomaterial *Peltophorum pterocarpum* has been used as host material. It contains many organic compounds as shown in Fig. 1. Organic molecules contain sufficient amount of polar groups, where the cation of any salt could be attached to increase the ionic conductivity [3–6].

Many batteries are made with liquid electrolyte because of its good ionic conductivity. However, a liquid electrolyte may cause internal short circuits, leakage problems, and corrosion in its further applications [7]. So, we require a solid electrolyte to overcome these drawbacks. The main advantages of solid membrane–based electrolytes are good stability, better ionic conductivity, proper interfacial contact with electrodes, and the ability to form membrane easier [8–10]. Synthetic polymer, biopolymer, and biomaterial are types of solid electrolytes.

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In solid polymer electrolytes (SPEs), the important synthetic polymers are PVA (poly vinyl alcohol) [11–14], poly(ethylene glycol) [15], poly(methyl methacrylate) [16, 17], PAN (poly acrylonitrile) [18, 19], PVC (polyvinyl chloride) [20, 21], etc. However, few synthetic polymers are of high cost and non-biodegradability in the environment, so the researchers started to focus on the naturally available polymers known as biopolymers to act as superior alternatives for synthetic polymers. Agar–agar [22, 23], gellan gum [24, 25], cellulose acetate [26, 27], k-carrageenan [28, 29], I- carrageenan [30], pectin [31, 32], chitosan [33], etc. have been studied extensively. Biopolymers have biodegradable and non-toxic nature, but some biopolymers are high in cost. The above difficulties have been solved by using biomaterial-based electrolytes. Due to the advantages of biomaterials, they are used instead of synthetic and biopolymers. The advantages include biodegradability, non-toxicity, eco-friendliness, cost-effectiveness, and the easy availability of materials [9].

The flower *Peltophorum pterocarpum* (PP), a member of the family Caesalpiniaceae, is a native to tropical southeastern Asia. PP flowerlets are yellow in color, 2.5 to 4 cm in diameter [34]. Figure 1(i) shows the chemical structure of PP flower and (ii) different parts of PP flower; many polyphenols and flavonoids are present in PP flower. The flowers are anti-inflammatory and antibacterial. It is used as astringent for gastrointestinal disorders and to relieve intestinal disorders after pain at childbirth [35]. Structural studies have revealed the presence of many polar groups, such as "– OH" in its structure. The major chemical constituents of PP flower are flavonoids, saponins, tannins, terpenoids, and alkaloids [36]. Membrane formation is due to the presence of various polar (organic) constituents [37]. The flower PP is chosen as a host material, because it contains numerous numbers of – OH polar groups. So, cation of any salt could be attached to it.

In this work, ammonium thiocyanate (NH_4SCN) is used as an additive to enhance the ionic conductivity. Ammonium salts are very good proton donors. In NH_4^+ ion, one H^+ ion is loosely bounded. It can easily escape and hop from one polar site to another in a membrane matrix to give better ionic conductivity. Though the flower PP has many medicinal properties such as to cure sprains, intestinal disorders after child birth, and muscular pain [35], this is the first-ever work done with

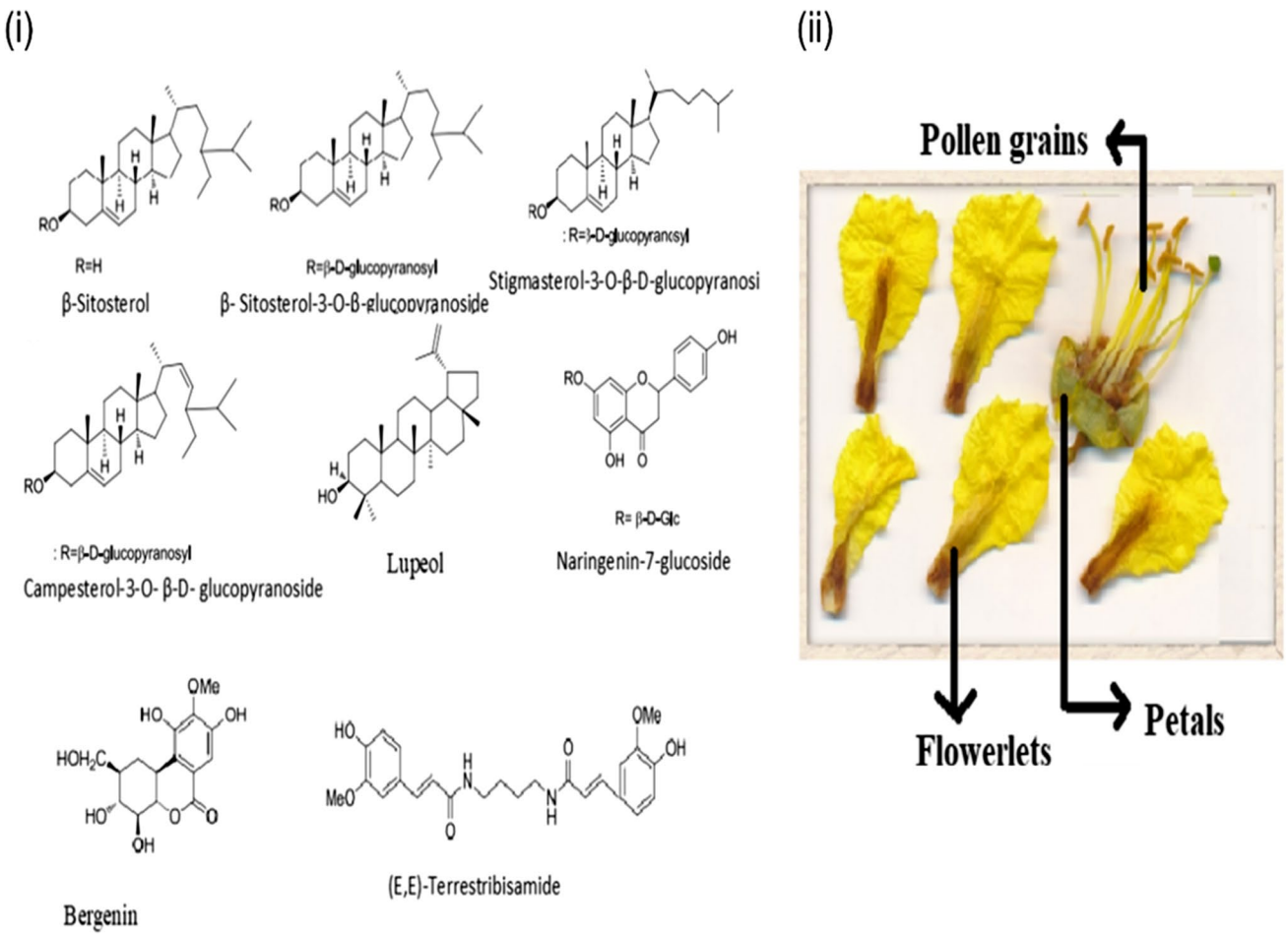

Fig. 1 (**i**) Structure of *Peltophorum pterocarpum* (PP) and (**ii**) parts of the Peltophorum pterocarpum (PP) flower

PP flower in the preparation of electrolyte for the application of electrochemical devices. As per literature survey, ammonium thiocyanate has been employed as ionic donor in various solid electrolyte systems. Moniha et al. have prepared a biopolymer solid electrolyte by using iota-carrageenan with ammonium thiocyanate [3]. Solid electrolyte based on dextran-PVA with ammonium thiocyanate was prepared by Maheshwari et al. [38]. Gellan gum with ammonium thiocyanate solid electrolyte has been fabricated by Meera Naachiyar et al. [39]. Agar–agar doped with ammonium thiocyanate–based electrolytes is prepared by Selvalakshmi et al. [40].

Due to the increasing demand for energy devices, fuel cells have received high attention for the last two decades. By comparing with other fuel cell such as solid oxide fuel cell, PEMFC (proton exchange membrane fuel cell) is a hydrogen fuel energy device which has various advantages such as low cost and low working temperature.

The main focus of this present work is to prepare a biomaterial-based membrane with different concentrations of NH_4SCN using the solution casting technique. The prepared membranes are characterized using various techniques such as X-ray diffraction analysis (XRD), differential scanning calorimetry (DSC), AC impedance analysis, and linear sweep voltammetry (LSV). Using the highest ion-conducting membrane as an electrolyte, a primary proton battery and PEMFC are constructed, and their performance is analyzed.

Materials and methods

The PP biomaterial membrane is prepared by using the simple technique, known as solution casting technique. PP flowers are collected and cleaned and then well-dried for 1 week. The dried PP flower was grinded by using kitchen blender, to obtain fine powder of PP.

Preparation of PP electrolyte

One gram of fine PP powder is mixed with a quantity of 40 ml double-distilled water and stirred for 24 h. Then, various molecular concentrations (0.5, 0.6, 0.7, 0.8 M wt%) of NH_4SCN salt are added to that solution and stirred for 2 days, by using a magnetic stirrer to attain a homogeneous solution. The prepared solution is poured into the petri dish and kept in the hot plate at 60 °C. After 12–24 h, a free-standing and flexible membrane is taken from the petri dish, and the membrane is kept in vacuum oven and the membrane is taken out whenever necessary for characterization. Figure 2 shows the prepared biomaterial membrane.

Fig. 2 The image of prepared biomaterial material membrane

Characterization techniques

XRD

XRD (X-ray diffraction method) is used to analyze the crystalline/amorphous nature of the prepared biomaterial electrolyte. X-ray diffraction patterns for the prepared membranes are obtained using the BRUKER ECO D8 ADVANCE X-ray diffractometer system with CuKα radiation. The XRD spectrum is recorded at room temperature in the various range of $5° \leq \theta \leq 80°$.

DSC

DSC (differential scanning calorimetry) measurements are obtained by using the DSC Q20 V24.11 Build 124 instrument. The temperature ranges from 0 to 300 °C under nitrogen atmosphere with the heating rate of 10 °C per minute.

AC impedance study

AC impedance studies for the prepared biomaterial membranes were done by using HIOKI 3532–50 Hi Tester LCR meter in the frequency range between 42 Hz and 5 MHz.

Transference number measurement

Using transference number measurement, the presence of ions (t_+) and electrons (t_-) was evaluated for the highest proton-conducting biomaterial electrolyte by using Wagner's dc polarization method.

Linear sweep voltammetry

The highest proton-conducting biomaterial membrane is subjected to LSV analysis, and the electrochemical stability was determined. The LSV curves of the membranes are obtained using a CHI-600 C instrument with the potential range of 0–5 V.

Fabrication of primary proton battery

The primary proton-conducting battery is fabricated by using the highest ion-conducting electrolyte by placing it between the anode and cathode. The anode and cathode mixtures are well-grained and compressed into pellets using hydraulic pressure machine.

Anode: The combination of zinc powder (Zn), zinc sulfate ($ZnSO_4.7H_2O$), and graphite (C) in the ratio of 3:1:0.5.
Cathode: The mixture of lead oxide (PbO_2), vanadium pentoxide (V_2O_5), and graphite (C) in the ratio of 4:1:0.5.

Result and discussion

XRD analysis

Figure 3 represents the XRD patterns of PP powder, pure PP, 1 g PP with different concentrations of NH_4SCN. The XRD of PP powder exhibits two intense peaks at $2\theta = 8.97°$ and 22.19°. XRD pattern, for 1 g of pure PP membrane, shows a peak at an angle of $2\theta = 21.59°$. Membranes of 1 g PP with different concentrations of NH_4SCN (0.5 to 0.8 M wt%) show only a broadened single peak. But the position of the single peaks is shifted for each concentration of NH_4SCN. The shifted peak positions are from 21.59 (pure PP) to 23.5°, 23.98°, 23.09°, and 23.69° for various concentrations. The intensity of the single peak observed in the biomaterial membranes with various concentrations has decreased up to 0.7 M wt% of NH_4SCN, and the broad nature has also increased. This obtained result is in correspondence with Hodge et al. criteria [41]. Maximum amorphous nature is observed for 1 g of PP with 0.7 M wt% of NH_4SCN. As the concentration is increased to 0.8 M wt%, the intensity increases and the broadness decreases.

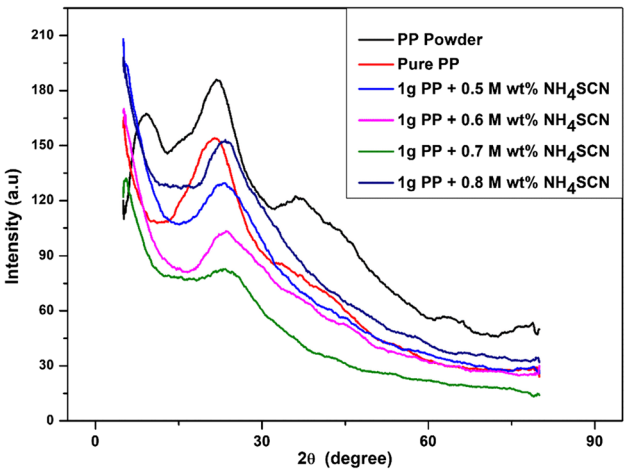

Fig. 3 XRD patterns of prepared biomaterial membranes

Crystallinity percentage of prepared biomaterial membranes is calculated by deconvoluting XRD pattern as shown in Fig. 4 by using the formula

$$Percentage\ of\ crystallinity = \frac{Area\ under\ crystalline\ region}{Total\ area\ of\ the\ peak} \times 100\% \quad (1)$$

Table 1 represents the crystallinity percentage values of the prepared membranes. From Table 1, it is noted that the crystallinity percentage of PP powder and 1 g of pure PP value are 62% and 56%. For salt-added membranes, crystallinity percentage decreases with increase in salt concentration. The membrane with composition of 1 g PP with 0.7 M wt% NH_4SCN obtained less crystallinity percentage of 37%; this confirms the high amorphous nature, compared to other salt-added membranes.

DSC analysis

Figure 5 shows (i) DSC thermograms of (a) pure PP, (b) 1 g PP with 0.5 M wt% NH_4SCN, (c) 1 g PP with 0.6 M wt% NH_4SCN, (d) 1 g PP with 0.7 M wt% NH_4SCN, (e) 1 g PP with 0.8 M wt% NH_4SCN and (ii) combined view of DSC thermograms. Table 2 shows the observed T_g values of prepared biomaterial membranes. From the DSC curve, the observed T_g value for pure PP is 34.99 °C. On addition of salt concentration, the T_g value increases. The membranes with the composition of 0.5 M wt% and 0.6 M wt% NH_4SCN with 1 g of PP give the T_g values of 36.89 °C and 46.15 °C, respectively. The increase in T_g value may be attributed to the strong transient cross-linkage between the proton and oxygen atoms in the membrane. Meera Naachiyar et al. and Muniraj et al. have also reported the same trend of increasing T_g value by adding NH_4SCN salt with gellan gum and *Moringa oleifera* seed [37, 39] Further, on addition of 1 g PP with 0.7 M wt% NH_4SCN, the T_g value decreases to 31.82 °C; this is due to reduction of transient cross-linkage between proton and oxygen atoms. For higher concentration, 1 g PP with 0.8 M wt% NH_4SCN, again the T_g value increases to 47.60 °C. This shows that the flexibility of the membrane decreases again. From the DSC data analysis, 1 g PP with 0.7 M wt% of NH_4SCN shows the lowest T_g value which indicates the plasticizing effect of the salt.