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ORIGINAL PAPER

Development and characterization of a biomaterial (Centella Asiatica Leaf)-based electrolyte for electrochemical devices

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Abstract

Biomaterial, Centella Asiatica Leaf (CAL), has been developed as a bio-membrane electrolyte with ammonium thiocyanate (NH_4SCN) by the solution casting method for proton conducting electrochemical devices. The amorphous/crystalline nature of the prepared bio-membranes has been analyzed using XRD. DSC measurement has been used to find the T_g of the membranes. AC impedance measurement shows 1 g CAL + 0.7 M. wt% NH_4SCN bio-membrane possesses a high proton conductivity value of $9.31 \pm 0.25 \times 10^{-3}$ S/cm at ambient temperature. Transport parameters have been calculated for the prepared bio-membranes. SEM and thermal stability (TGA) measurements have been made for pure CAL and the highest conducting bio-membranes. The tensile strength of the highest conducting bio-membrane has been estimated by mechanical strength analysis. The electrochemical stability of 2.05 V has been found for the highest proton-conducting bio-membrane using LSV. The primary proton battery and PEM fuel cell with the highest proton conducting bio-membrane show an OCV of 1.55 V and 448 mV, respectively.

Keywords Centella Asiatica Leaf · Solid bio-membrane electrolyte · Proton battery · PEM fuel cell

Introduction

The progress of the economic world is currently encouraged by the usage of green energy sources in electrochemical devices, which have enormous potential in day-to-day life [1–3]. In every electrochemical device, the electrolyte plays an important role in ion transportation [4]. For many years, polymer-based solid electrolyte research has received much attention because of its good flexibility, lightweight, film-forming capacity, good electrode–electrolyte contact, and ionic conductivity [5]. To enhance the features of solid polymer electrolytes, numerous techniques are applied, such as cross-linking two polymers, blending two polymers, and adding inorganic fillers or plasticizers into polymers [6].

Typically, polymers are classified as synthetic and natural (or) biopolymers. It is known that both types of polymers have a good number of polar groups in their chemical structures and have very good membrane-forming properties [7–9]. The available polar groups assist polymer chain molecules in membrane formation by interacting with solvents like water [10]. Theoretical studies predict the potentiality of hydrogen bonding in polymer membranes [11–13]. An analysis of relevant literature has exposed that the majority of electrolyte research has been processed with synthetic polymers and biopolymers [14–17]. Some synthetic polymers are quite expensive and not environment friendly and few biopolymers are expensive. Therefore, the researchers have introduced biomaterials to avoid the defects of synthetic and biopolymers [18, 19].

Biomaterials such as leaves, flowers, and seeds are derived from naturally occurring renewable sources [20]. These are eco-friendly, cost-effective, and solve many international issues, such as global warming, price fluctuations,

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and complicated extraction processes [21]. Any biomaterial having sufficient number of polar groups among its chemical constituents to which the cation of any salt can be attached could be used as an electrolyte [19]. Hence, it is a viable replacement for both synthetic and natural polymers. The primary goal of this study has been to develop electrolytes based on biomaterial to be used in electrochemical devices such as fuel cells and batteries. This is the novel aspect of the current work.

The biomaterial Centella Asiatica is a perennial herbaceous flowering plant also known as Gotu Kola, Indian pennywort, or Asiatic pennywort. It belongs to the Umbelliferae or Apiaceae family and is a traditional herbal remedy. It is indigenous to Asian wetlands [22]. It has a wide range of therapeutic qualities, like wound healing, anxiolytic, antidepression, antioxidant properties, anti-inflammatory, neuroprotective, and drug delivery systems [23]. It is grown all over the world because of its medicinal value and great potential. The leaves are eatable, yellowish green color, thin, and orbicular to reniform in shape [24, 25].

Phytochemical analysis of Centella Asiatica Leaf (CAL) shows polar dominant chemicals such as asiaticoside, asiatic acid, madecassic acid, madecassoside, kaempferol, quercetin**,** tannin, saponin, and rutin [24–28]. Figure 1 shows the chemical structures of the above-mentioned phytochemicals.

Table 1 Chemical element in Centella Asiatica Leaf (CAL) and their number of polar groups

S. No	Chemical constituents	Number of polar groups
1	Asiaticoside	13
2	Asiatic acid	5
3	Madecassic acid	6
4	Madecassoside	14
5	Kaempferol	5
6	Quercetin	6
7	Tannin	5
8	Saponin	9
9	Rutin	11

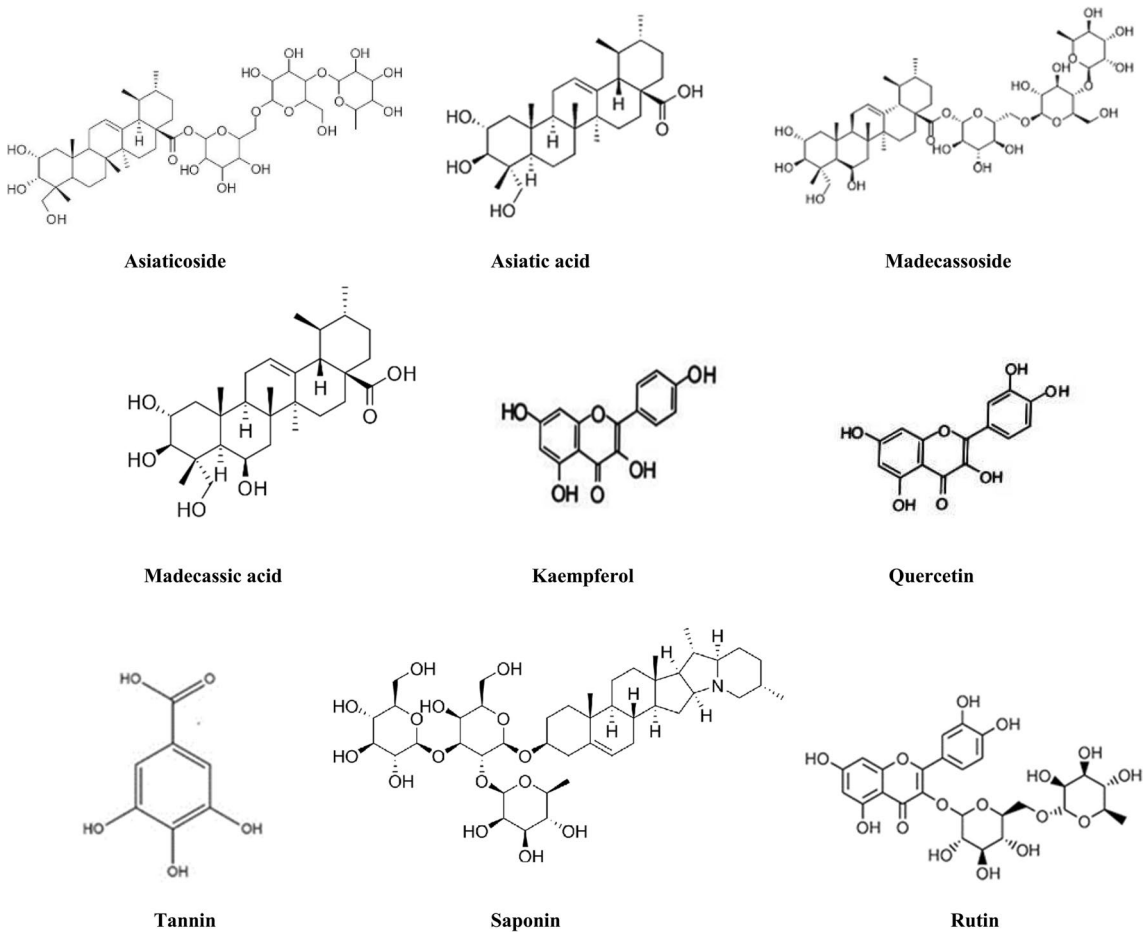

Fig. 1 Shows the polar dominant phytochemical structures of Centella Asiatica Leaf (CAL)

Table 1 provides the number of polar groups in each phytochemical. All the chemical structures contain polar groups such as OH. The polar group from the CAL assists the various organic molecules in film formation by interacting with the water (solvent) [10–13].

Due to the availability of large number of polar groups, the biomaterial Centella Asiatica Leaf is chosen as the host material for the development of a novel proton conducting electrolyte for electrochemical energy storage devices. The conductivity of biomaterial electrolytes can be improved by the addition of ionic salts. Ammonium salts are effective proton donors to the polymer matrix [29]. Because the ammonium ion is made up of four protons and one of the protons is loosely bound. Among ammonium salts, ammonium thiocyanate (NH_4SCN) has been chosen for this research work because of its low lattice energy (605 kJ/mol) [30]. Muniraj Vignesh et al. have studied the biomaterial solid electrolyte based on Moringa oleifera seed, tannic acid with ammonium thiocyanate (NH_4SCN) [19].

In this present work, a biomaterial CAL membrane with different concentrations of ammonium thiocyanate (NH_4SCN) has been prepared by using the solution casting technique. The prepared membranes have been characterized by different techniques such as X-ray diffraction analysis (XRD), differential scanning calorimetry (DSC), AC impedance, scanning electron microscopy (SEM), thermogravimetric analysis (TGA), mechanical strength analysis, and linear sweep voltammetry (LSV). The highest ion conducting membrane has been used as an electrolyte in the primary proton battery and single-stack proton exchange membrane fuel cell.

Experimental section

Materials

Centella Asiatica leaves are collected (local market, Madurai), thoroughly washed repeatedly with double-distilled water, and dried in the sunlight for 2 days. Then, using a kitchen blender, CA Leaves are turned into powder. In this research, CAL powder and ammonium thiocyanate (NH_4SCN) (Nice A15429, Orientallabs Retail Services Pvt. Ltd, India, purity: 97%, molecular weight: 76.12 g/mol) are used.

Preparation of bio-membrane

In this research, CAL-based bio-membranes are prepared by a simple solution-casting technique. One gram of CAL powder is mixed with 40 ml of double-distilled water and stirred for two consecutive days with a magnetic stirrer. After 2 days, 0.5 M. wt%, 0.6 M. wt%, 0.7 M. wt%, and 0.8 M. wt% of NH_4SCN have been dissolved in 10 ml of double-distilled water separately. Dissolved solutions of NH_4SCN are added to 1 g of CAL powder solution and stirred well for a day. Then, the mixed solution is cast on a hot plate at 40 °C using a polypropylene petri dish. A free-standing membrane is taken from a petri dish after

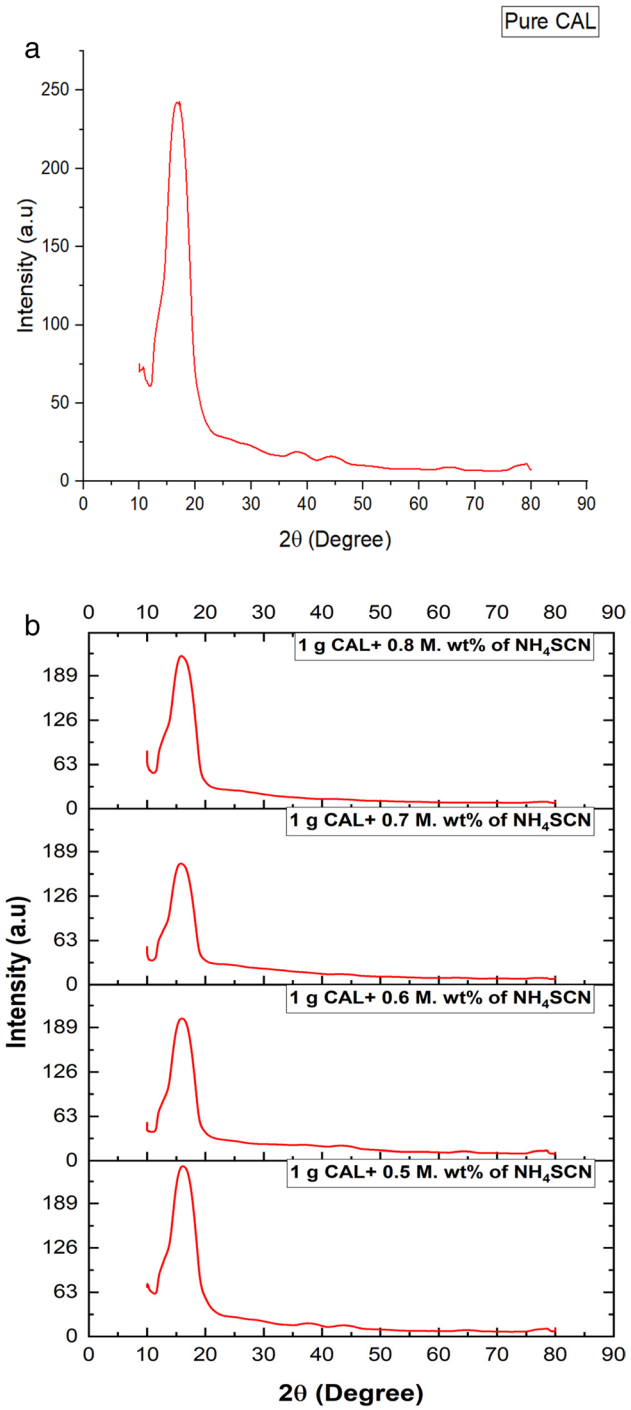

Fig. 2 XRD pattern of **a** pure CAL bio-membrane and **b** 0.5, 0.6, 0.7, and 0.8 M. wt% of NH_4SCN with 1 g CAL bio-membranes

24 h. Then the membrane is kept in a vacuum oven at ambient temperature and taken out of the oven whenever necessary for characterization.

Characterization techniques

XRD (X-ray diffraction)

To analyze the amorphous/crystalline nature of the prepared membrane, XRD has been taken by BRUKER ECO D8 ADVANCE X-ray diffractometer with Cu-Kα source in $5° \leq 2\theta \leq 80°$ range at ambient temperature.

Differential scanning calorimetry

The DSC measurement has been done to find the glass transition temperature (change from crystalline to rubbery state). The DSC Q20 V24.11 Build 124 has been used to carry out the DSC measurements in a nitrogen environment with a heating rate of 10 °C/min between 0 and 300 °C temperatures.

Impedance spectroscopy

The HIOKI-3532 Hi Tester LCR meter has been utilized to gage the AC impedance of the prepared bio-membrane in the frequency between 42 Hz and 5 MHz at ambient temperature.

SEM analysis

To examine the surface morphology of the prepared bio-membranes, SEM reports have been obtained using a JEOL JSM – 6390 Scanning Electron Microscope.

TGA analysis

Using the DSC-TGA standard (SDT Q600 V20.9 Build 20) in a nitrogen environment at a flow rate of 200 ml/min and a heating range of 30 to 700 °C at a rate of 10 °C/min, the thermal stability of bio-membranes has been studied.

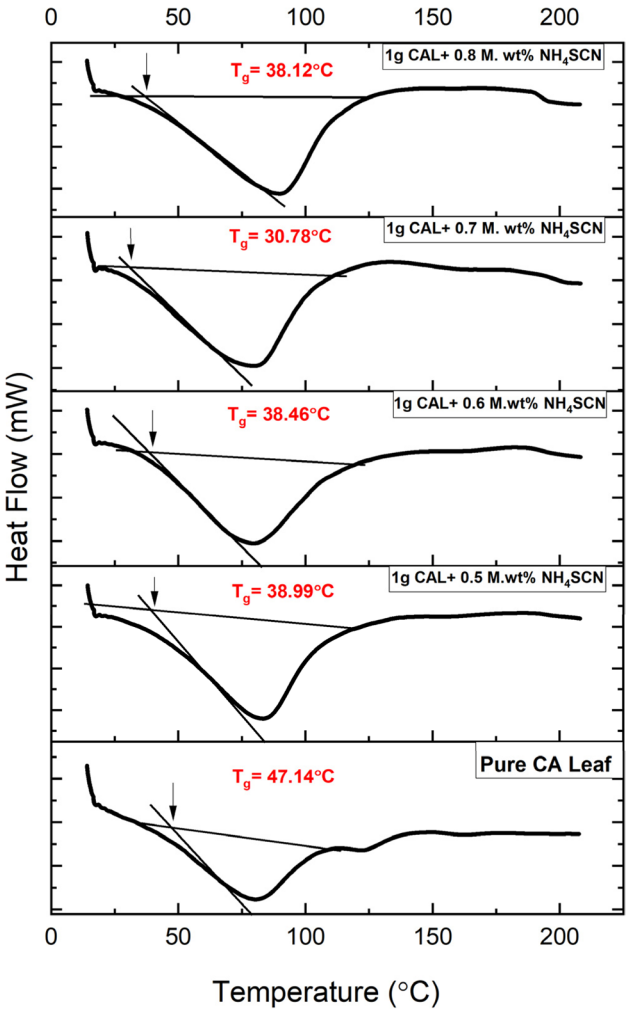

Fig. 3 DSC thermogram of pure CAL bio-membrane and 1 g CAL with varying salt concentrations (0.5, 0.6, 0.7, and 0.8 M. wt% of NH_4SCN) bio-membranes

Mechanical strength analysis

The mechanical strength of the highest proton conducting bio-membrane, with a dimension of 10×2 cm has been tested using an Instron 8801 (Dynamic Testing Machine) with a 0.025 kN at a displacement rate of 1.5 mm/min.

Table 2 XRD peak position, intensity, and the crystalline percentage of all the prepared bio-membranes

Sample compositions	Peak position 2θ (degree)	Intensity (a. u)	Crystalline (%)
Pure CAL	17.25	243.12	56.12
1 g CAL + 0.5 M. wt% of NH_4SCN	16.14	239.96	50.73
1 g CAL + 0.6 M. wt% of NH_4SCN	15.96	203.12	49.95
1 g CAL + 0.7 M. wt% of NH_4SCN	15.78	173.10	47.82
1 g CAL + 0.8 M. wt% of NH_4SCN	15.88	218.01	54.72