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RESEARCH

Performance study of sodium alginate (SA) with lithium chloride (LiCl)-based solid-state membrane as an electrolyte in electrochemical device application

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Abstract

In this article, we present a novel solid biopolymer-based membrane (BPM) with sodium alginate (SA) as host material incorporated with an ionic salt, lithium chloride (LiCl). Solid BPMs are prepared using the solution casting technique and used as an electrolyte in the fabrication of solid-state Li-ion conducting battery and coin cell. The X-ray diffraction (XRD) method has been carried out to analyze the crystalline/amorphous nature of the membrane. A Fourier transform infrared spectroscopy (FTIR) study is done to confirm the complex formation between the host biopolymer and salt. The ionic conductivity of all prepared BPMs is measured using AC impedance analysis, and the membrane with the composition of 15 mol% of SA:85 mol% of LiCl exhibits a high ionic conductivity of 3.06×10^{-2} S/cm. The glass transition temperature (T_g) of the prepared BPMs is examined using differential scanning calorimetry (DSC), and the membrane of 15 mol% of SA:85 mol% of LiCl exhibits a decreased T_g value of 54.33 °C. The thermal stability of the prepared membranes is studied using thermogravimetric analysis (TGA). Transference number measurement (TNM) is made to assure that the major charge carriers involved in transportation are ions. Using the highest ion conducting membrane as an electrolyte, a primary Li-ion conducting battery has been fabricated which results in an OCV of 1.91 V, and various loads are connected to observe the corresponding current drawn from the cell. A coin cell is constructed with the configuration of graphite (G) + tannic acid ‖ 15 mol% of SA:85 mol% of LiCl ‖ $LiFePO_4$ + G + pinch of highest ion conducting membrane, and the galvanostatic charge–discharge (GCD) analysis is carried out to analyze the rechargeable nature of the prepared membrane and the performance of the coin cell, whereas the cell has undergone charge/discharge process for 200 cycles and resulted with an energy density of 13.94 Wh/Kg, power density of 1111.11 W/Kg, and specific capacitance of 100.40 F/g, respectively.

Keywords Biopolymer · Sodium Alginate · Lithium Chloride · Li-ion conducting coin cell · Galvanostatic charge–discharge analysis

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Introduction

In this modern era, the world is facing many serious issues such as depletion of fossil fuels, lack of nonrenewable energy resources, and emission of CO_2 [1]. In order to overcome these issues, electrochemical energy storage and conversion devices such as batteries, supercapacitors, solar cells, and fuel cells have been introduced with advanced developments in this recent technological world. At present, batteries and supercapacitors composed of electrodes and electrolytes show sustainable growth with superior properties and extraordinary performance with lightweight and small-size construction. This makes the device user-friendly and easy to handle with portable nature [2, 3].

Among various types of batteries, lithium batteries [4] ascribe high performance and high energy storage capacity with better commercial application. The limited drawbacks faced by lithium batteries are their flammable nature and dendrite formation [4] which reduces the lifetime of the battery. In order to overcome these hurdles, Li-ion conducting batteries (lithium metal is replaced with graphite) [5] are utilized much in the research and commercial world of applications. In view of the charge storage mechanism, supercapacitors are categorized into three types: (1) electric double-layer capacitance (EDLC) that is non-faradaic/electrostatic charge storage at the electrode–electrolyte interfaces, (2) pseudocapacitance that is fast faradaic redox reaction at the electrode–electrolyte interfaces, and (3) hybrid capacitors [6]. Various approaches have been done to enhance the performance of the supercapacitors, particularly the energy density of the same. Few modifications in the structural design of liquid (or) solid-based EDLCs and pseudocapacitors have shown appreciable results. Further, the energy density can be improved by finding an alternative for one of the supercapacitor electrodes with a battery electrode without affecting the power density of the constructed device. This type of fabricated device is named as hybrid battery-supercapacitor (HBC), which has the configuration of both secondary battery and supercapacitors simultaneously [6].

In the performance of HBC, electrolyte also plays a vital role as it is responsible for good electrochemical stability, compatibility, and ionic conduction.

Electrolytes are of various forms based on their state as liquid [7], gel [8], and solid [9]. Though an aqueous form of electrolytes exhibits high ionic conductivity, it has a few drawbacks such as leakage issues, corrosion, short-circuiting, and flammable [7]. The replacement of solid-state electrolytes guarantees safety with a leakproof nature, ease of preparation, and convenience of handling [9]. The solid form of electrolytes can be prepared using various simple methods with ceramic [10] and polymer-based materials [11] as host materials. As ceramic material exhibits brittle nature and operates only at high temperature, polymers with diverse advantageous properties such as better flexible nature, low volatility, long life span, lightweight, and high binding capacity have been selected as host material in the preparation of an electrolyte.

Polymers utilized as a host material in many research works are categorized based on their nature as synthetic [11] and bio/natural polymers [12]. Tremendous works have been carried out using synthetic polymers because of their high mechanical stability and better outcomes with increased ionic conductivity. But, few petroleum/chemical-based synthetic polymers are environmentally hazardous. And so, biopolymers prepared using a fermentation process from bio-based naturally abundant materials have attracted the attention of many researchers as it is environment-friendly, cost-effective, and easily available when compared to synthetic polymers. Numerous works have been carried out using many biopolymers like chitosan [13], pectin [14], gellan gum [15], agar–agar [16], and cellulose acetate [17] and many as host material in the synthesis of an electrolyte. These biopolymers as an electrolyte resulted in notable ionic conductivity and good efficiency.

Based on this line of research, in the present work, sodium alginate (SA), a linear anionic polysaccharide has been selected as the host material in the preparation of an electrolyte. SA is a derivative of alginic acid which is comprised of two uronic acids such as 1, 4-β-D-mannuronic (M blocks) and α-L-guluronic (G blocks) acids and MG blocks which are connected together by glycoside linkages [18]. Figure 1 represents the chemical structure of sodium alginate (SA). SA is obtained from the cell walls of marine brown algae named *Phaeophyceae* and contains approximately 30 to 60% of alginic acid [19]. Due to its peculiar properties and non-toxic nature, this linear polysaccharide has been utilized in many fields of application such as food, pharmaceutical, and chemical industries as a gelling agent, thickener, and stabilizer. SA is chosen as host material in polymer-based electrolytes due to the presence of polar groups such as carboxyl ($-COOH$) and hydroxyl ($-OH$) which attract the cation of any ionic salts and may enhance the ionic conduction [20].

As ionic conductivity is a significant attribute in the performance of an electrolyte, in order to improve the ionic conduction, different methods such as the usage of organic plasticizers, inclusion of different ionic salts, blending polymers, and addition of nanofillers have been carried out. Based on this approach, lithium chloride (LiCl) which is an ionic salt with small sized cation (Li^+) when compared to other alkali salts and also shows better solubility in polar solvents with low lattice energy [21] has been chosen to be incorporated in the polymer matrix to attain an enhanced ionic conduction. Though SA holds a place in many industries such as food, chemical, pharmaceutical, and textile industries, its

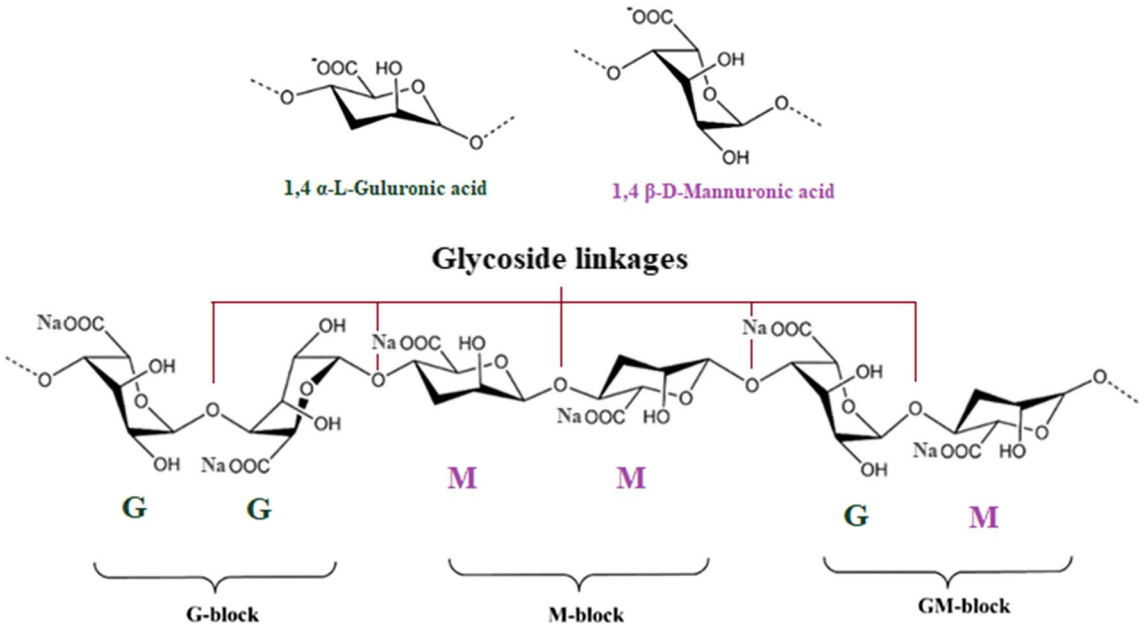

Fig. 1 Chemical structure of sodium alginate

role as an electrolyte in the electrochemical energy storage and conversion devices is countable.

Few works carried out using SA as a host material in the preparation of an electrolyte are reported by Vanitha et al. based on SA with ammonium formate (NH_4HCO_2) and ammonium thiocyanate (NH_4SCN) which resulted in the ionic conductivity of 2.77×10^{-3} S/cm and 8.72×10^{-3} S/cm at ambient temperature [22, 23], SA with 20 wt% of NH_4Br-based electrolytes are prepared by Fuzlin and Samsudin [24] and resulted with the ionic conductivity of 4.41×10^{-5} S/cm, and Fuzlin et al. reported the ionic conductivity of 5.32×10^{-5} S/cm for the membrane with the composition of SA with 20 wt% of glycolic acid [25].

Though notable works have been carried out using SA as host material in the preparation of electrolytes, no work is done yet with SA as host material incorporated with LiCl in the electrolyte to be synthesized.

The aim of the present work is to prepare an electrolyte with SA as host material incorporated with LiCl using a simple and easy method of preparation known as the solution casting method. The prepared biopolymer-based membranes (BPMs) are characterized using various characterization techniques such as the X-ray diffraction method (XRD), Fourier transform infrared spectroscopy (FTIR), differential scanning calorimetry (DSC), AC impedance spectroscopy, transference number measurement, and thermogravimetric analysis (TGA). Then, using highest Li-ion conducting membrane as an electrolyte, primary Li-ion conducting battery is constructed, and performance of the same is observed by connecting various loads. And also the Li-ion conducting coin cell is fabricated to analyze the nature of the membrane and it undergoes galvanostatic charge–discharge (GCD) analysis in order to analyze the performance of fabricated coin cell.

Materials purchased and used

Biopolymer, sodium alginate (SA) purchased from S D Fine-Chem Limited, and lithium chloride (LiCl) (anhydrous extra pure) purchased from Laboratory Reagent are used as raw materials, and distilled water is used as a solvent to prepare biopolymer-based electrolyte.

Synthesis process of an electrolyte

The biopolymer-based membranes used as an electrolyte in the application of energy storage devices are prepared using the solution casting method. In the present work, sodium alginate (SA) is used as a host material incorporated with lithium chloride (LiCl) in order to improve the ionic conductivity. The total estimated weight is determined as 1 g. The SA and LiCl are taken with various weight percentages as SA25, SA20, SA15, and SA10, respectively. Table 1 gives the list of concise designations for the composition of the sample. Initially, the measured mol% of SA is added pinch by pinch to the hot double-distilled water maintained at the temperature of about 85 °C and is allowed to stir well for an hour. Then, the calculated mol% of LiCl is taken and dissolved in warm double-distilled water and included drop

Table 1 List of concised designations for the composition of the sample

Composition of the sample	Concised designation
Pure SA (1 g)	SA100
25 mol% of SA:75 mol% of LiCl	SA25
20 mol% of SA:80 mol% of LiCl	SA20
15 mol% of SA:85 mol% of LiCl	SA15
10 mol% of SA:90 mol% of LiCl	SA10

by drop in the SA100 solution. The mixture is then stirred well for 2 h under a temperature of about 60 °C. Then, the obtained homogeneous solutions with different concentrations of SA and LiCl are poured into polypropylene petri dishes which are placed in the hot plate fixed at the temperature of 45 °C and allowed to evaporate for ~ 24 h. The resulting free-standing and flexible solid electrolyte ranges in thickness from 0.15 to 0.20 mm and is kept in a vacuum desiccator. The membranes are taken out whenever necessary for characterization.

Characterization techniques

The synthesized biopolymer-based membranes based on sodium alginate and LiCl have been characterized using various techniques in order to analyze their structural, vibrational, thermal, and transport properties.

Structural analysis (XRD)

X-ray diffraction (XRD) study is done using an X'Pert PRO diffractometer with Cu-Kα radiation operated under the condition of 40 kV/30 mA between the angle ranges 10 and 80° at the rate of 2°/min to understand the crystalline/amorphous nature of the prepared BPMs [16].

Vibrational study

Fourier transform infrared spectroscopy (FTIR)

Fourier transform infrared spectroscopy (FTIR) is carried out with a SHIMADZU IR Affinity-1 Spectrometer fixed within the spectral range of 500–4000 cm^{-1} under the resolution of 1 cm^{-1} in the transmission mode, and the spectra are obtained through ATR mode to assure the complex formation between the host biopolymer and salt [22].

NMR analysis (^{1}H NMR analysis and.^{7}Li NMR analysis)

^{1}H and ^{7}Li and NMR measurement was carried out using Bruker Avance 500 MHz NMR spectrometer operating at a frequency of 194.37 and 500.13 MHz, respectively. The samples were transferred into 5 mm glass tubes, and the measurements were made at ambient temperature. 1 M LiCl in D_2O solution and 2 vol% tetramethylsilane (TMS) in $CDCl_3$ were used as external standard for referencing ^{7}Li and ^{1}H NMR chemical shift ($\delta_{iso} = 0.0$ ppm).

AC impedance analysis

The impedance of the prepared BPMs is measured using the HIOKI 3532–50 Hi-Tester LCR meter under the fixed frequency range of 42 Hz–5 MHz at room temperature to calculate the ionic conductivity [16].

Thermal analysis

Differential scanning calorimetry (DSC)

The glass transition temperature of synthesized BPMs is examined by carrying out differential scanning calorimetry (DSC) with DSC Q20V4 under a nitrogen atmosphere maintained at the heating rate of 10 °C/min and flow rate of 50 ml/min [23].

Thermogravimetric analysis (TGA)

The thermal stability of the optimized BPMs is observed by monitoring the mass of a substance as a function of time or temperature using the DSC-TGA standard (SDT Q600 V20.9 Build 20) which is maintained under a nitrogen atmosphere at a flow rate of 200 ml/min. The prepared membranes are heated at the controlled temperature of 30 to 700 °C at a heating rate of 10 °C/min, and the weight of the membrane is around ~ 3 mg [26].

Transference number analysis

Wagner's polarization technique

The nature and transportation of the charge carriers in the optimized high ion conducting membrane are identified from Wagner's polarization method. The synthesized BPM is placed between stainless steel electrodes, and a small DC voltage is applied to the constructed setup in order to observe the variation in current with respect to time [16].

Evan's polarization technique

Evan's polarization method is done to analyze the contribution of cation towards the ionic conductivity of the highest ion-conducting membrane. This method is carried out by sandwiching the highest ion conducting membrane between two silver electrodes (silver electrode ‖ SA15 ‖ silver electrode) and supplying a DC voltage to the constructed