Bull. Mater. Sci. (2024) 47:194
https://doi.org/10.1007/s12034-024-03260-x

Natural polymer electrolyte based on guar gum doped with NaI for Na-ion batteries

K THRISHA* and **R SARATHA**
Department of Chemistry, Avinashilingam Institute for Home Science and Higher Education for Women, Coimbatore 641043, Tamil Nadu, India
*Author for correspondence (21phchf003@avinuty.ac.in)

MS received 5 July 2023; accepted 15 March 2024

Abstract. Solid polymer electrolytes play a vital role in energy storage devices, especially in the battery industry, to improve compatibility and portability. Natural polymers made from biowaste material are biodegradable and have been utilized for electrolyte preparation. Biopolymer-based electrolyte leads to sustainability due to their low cost, eco-friendly nature and non-toxicity. This work pertains to the preparation of one such natural polymer electrolyte based on guar gum as the host polymer, sodium iodide as an ionic dopant and 1,2 dimethoxy ethane as the plasticizer. Traditional Solution casting technique has been used for the preparation of electrolytes. The complexation between guar gum (GG) and NaI has been revealed by Fourier transform infrared spectra. The biopolymer electrolyte is stable up to 300–350°C and was assessed by thermogravimetric analysis. The surface roughness factor (R_a) was measured by 3D-optical profilometry. The transference number was determined by the chronoamperometry technique. AC impedance spectroscopy exhibited that the biopolymer electrolyte containing 0.4 g GG: 0.75 wt% NaI has the highest ionic conductivity of 7×10^{-3} S cm^{-1}. Hence with suitable electrodes, the prepared electrolyte may be used in the fabrication of coin cells.

Keywords. Biopolymer electrolyte; guar gum; NaI; 1,2 dimethoxy ethane; AC impedance spectroscopy; ionic conductivity.

1. Introduction

In this modern era, where everything is digitalized, there is a need for portable devices such as laptop, smartphones, etc., thus energy storage device plays a major role in day-to-day life. In this case, solid electrolytes are used more than liquid electrolytes due to their good electrode–electrolyte contact, ease of fabrication, good shelf-life, cyclability and processability [1]. At present, implementation of biopolymers in various fields has increased by researchers [2–5]. Biopolymers overtake synthetic polymers because of their enormous features such as eco-friendly nature, low cost, non-toxic, compatibility, abundant availability, good electrical and mechanical properties, and easy film-forming nature [6]. Polysaccharides are polymers composed of multiple monosaccharide units connected by glycosidic bond linkages and obtained by plant cell walls, plant seeds, seaweed extracts, bacterial cell walls, plant roots, tubers, and so on [7]. Several biopolymers such as chitosan [8], carboxy methyl cellulose [9], starch [1], corn silk starch [10], k-carrageenan [11], i-carrageenan [12], agar–agar [13], gelatin [14], pectin [15], sodium alginate [16], dextran [17], tamarind seed polysaccharide [18], *Moringa oleifera* gum [19], tragacanth gum [20] have been used to prepare electrolytes.

In the present study, guar gum (GG) is taken as the biopolymer. GG is the refined endosperm of *Cyamopsis tetragonoloba* (cluster beans) [5] and a member of the galactomannan family. GG consists primarily of a straight chain of D-mannose units coupled with (1 → 4) glycoside linkages, with one D-galactose unit in roughly every other mannose, joined by (1 → 6) glycoside links. GG has attractive properties, including hydrophilicity and biodegradability, and it is renewable [2, 5].

A literature review showed that a minimal number of works were carried out in GG-based biopolymer electrolytes for batteries. GG doped with LiTFSI was prepared and the ionic conductivity value of 2.041×10^{-3} S cm^{-1} was achieved by Abirami *et al* [21]. An ionic conductivity value of 1.59×10^{-3} S cm^{-1} for blended GG–pectin biopolymers doped with LiTFSI was prepared by Shilpa and Saratha [22]. Venkatesh *et al* [23] reported an ionic conductivity value of 4.91×10^{-3} S cm^{-1} for GG–NH_4SCN. Recently sodium salts have been mostly used with polymer complexation for sodium-ion batteries instead of lithium salts. NaI has a wide range of availability and is cheaper than lithium salts [22]. As of now, work on the biopolymer electrolyte of GG doped with NaI has not been reported.

Hence, the present work is based on the preparation of GG: NaI biopolymer electrolyte using 1,2 dimethoxy ethane (1,2 DME) as a plasticizer.

2. Experimental

2.1 *Materials*

Here, GG, sodium iodide (NaI) and 1,2 dimethoxy ethane (1,2 DME) were used. GG (mol. wt: 535 g mol^{-1}) was purchased from Loba Chemie Pvt. Ltd, Mumbai, India. NaI (mol. wt: 149 g mol^{-1}) was purchased from Spectrum Reagents and Chemicals Pvt. Ltd, Cochin, India. 1,2 DME was purchased from SRL Chemicals Pvt. Ltd, Mumbai, India. GG was taken as the host polymer, NaI was taken as the ionic dopant and 1,2 DME was taken as a plasticizer. Double-distilled water was used as the solvent.

2.2 *Method*

2.2a *Preparation of solid polymer electrolyte:* Biopolymer GG–NaI electrolytes were prepared using the Solution casting technique. A quantity of 0.4 g GG was doped with various compositions of NaI (1, 0.75, 0.50 wt%) in 40 ml double-distilled water and named as GS-1 (1 wt% of NaI), GS-2 (0.75 wt% of NaI) and GS-3 (0.50 wt% of NaI). Before adding the ionic dopant, 2 ml 1,2-DME was added to the solvent. The mixture was stirred using a magnetic stirrer for 24 h at room temperature. The obtained homogenous solution was transferred onto the polypropylene Petri dish and allowed to hot air oven at 40°C for 24 h. The dried samples were stored in a desiccator to avoid moisture absorbance. Then the prepared biopolymer electrolytes were characterized by Fourier transform infrared (FT-IR) spectroscopy, thermogravimetric analysis (TGA), 3D-Optical profilometry, AC impedance spectroscopy and chronoamperometry techniques.

2.3 *Characterization techniques*

FT-IR spectroscopy was recorded using MIRACLE 10 SHIMADZU instrument in the frequency range of 400–4000 cm^{-1} at room temperature. The TGA analysis was carried out from TG/DTA 6300 model instrument from EXSTAR. AC Impedance spectroscopy and chronoamperometry techniques were analysed by the electrochemical workstation of the Ametek PARSTAT ML-1000 instrument. The average roughness value of the sample was measured using ZETA-20 3D optical profilometer.

3. Result and Discussion

3.1 *FT-IR Spectroscopy*

The FT-IR spectrum of pure GG and GG–NaI-based electrolytes are depicted in figure 1. In pure GG, a broad and strong absorption at 3332 cm^{-1} was due to O–H stretching, and the major shifting was observed at 3410 cm^{-1} (GS-1), 3379 cm^{-1} (GS-2) and 3672 cm^{-1} (GS-3) because of the addition of the NaI salt in GG. The other peak is obtained at 2924 cm^{-1} (GG) corresponding to C–H stretching, which is shifted to 2905 cm^{-1} for both GS-1 and GS-2 samples [24].

The peak observed at 1635 cm^{-1} (GG) shifted to 1620 cm^{-1} (GS-1, GS-2, GS-3), which attributed to O–H bending vibration associated with the water molecule [23]. The peak obtained at 1419 cm^{-1} (GG) shifted to 1425 cm^{-1}(GS-1, GS-2), 1427 cm^{-1}(GS-3), which ascribed to the ring stretching. The peaks between 1200 and 800 cm^{-1} are observed for highly coupled C–C–O, C–OH and C–O–C stretching [21]. The peak at 771 cm^{-1} corresponds to (1,4)–(1,6) bond linkages of galactose and mannose in pure GG, which undergoes the shifting of 671 cm^{-1} (GS-1, GS-2), 663 cm^{-1} (GS-3) [24]. The shift obtained in the vibrational band confirms the interaction between the host polymer and ionic dopant.

3.2 *Thermogravimetry analysis*

The decomposition of GG–NaI-based electrolytes is a three-step process. Thermogravimetry analysis (TGA) curves of GG–NaI-based electrolytes such as GS-1, GS-2 and GS-3 are shown in figure 2. For pure GG, the 13% weight loss at 86°C is due to the degradation of moisture content [19]. While increasing the temperature, the major weight loss of 60% obtained at 250°C was attributed to the elimination of CO_2 in GG due to the cleavage of C–O–C bonds in

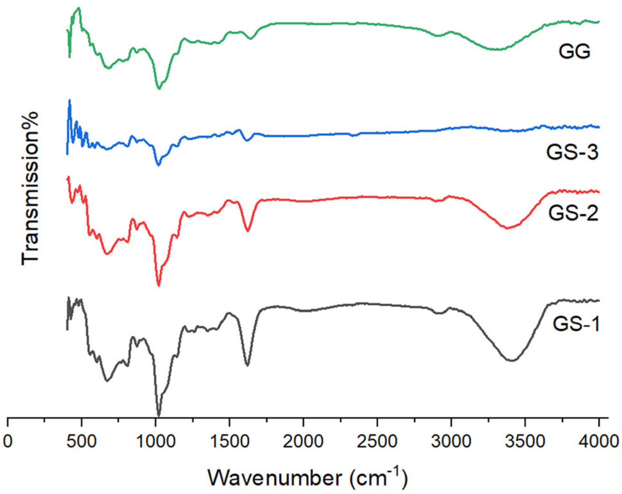

Figure 1. (i) Pure GG, (ii) GS-1 (0.4 g GG: 1 wt% NaI), (iii) GS-2 (0.4 g GG: 0.75 wt% NaI and (iv) GS-3 (0.4 g GG: 0.50 wt%).

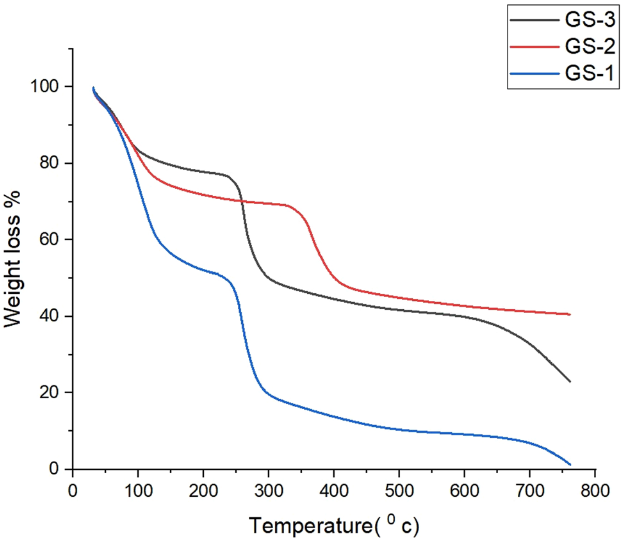

Figure 2. TGA curves of GG–NaI-based biopolymer electrolytes.

galactose and mannose backbone [22, 23]. The initial weight loss of 20% for GS-1, GS-2 and GS-3 was observed at 100°C due to the degradation of water. NaI is hydrophilic so it absorbs and restores the water content in the electrolyte [25, 26]. From 250 to 350°C, the weight loss of 60% takes place for GS-1, GS-2 and GS-3 electrolytes due to the interaction of the sodium salt with GG, which was confirmed by the FT-IR spectroscopy. The 15–20% leftover residues may be due to the grafted products of electrolytes. There is no significant change until 760°C, so the prepared electrolytes were thermally stable up to 300 to 350°C.

3.3 *3D-optical profilometry*

The surface properties and surface topography of the prepared electrolyte are studied by 3D-optical profilometry. Figure 3 shows the 3D-images and roughness factor (R_a) of the prepared samples. An increase in the R_a value indicates the increase in the roughness of the samples [14, 19].

Table 1 shows R_a values for the three sets of electrolytes such as GS-1, GS-2 and GS-3. GS-1 and GS-2 have R_a values of 3.456 and 1.95%, which are smoother than GS-3, which has a R_a value of 8.44%. The surface roughness factor (R_a) reveals the proper blending of the sample. The ionic conductivity of the films is related to the smoothness of the film; as the smoothness increased, the conductivity of the film also increased, which is evidenced from the impedance spectroscopy study.

3.4 *AC impedance spectroscopy*

Electrochemical impedance spectroscopy (EIS) is used to characterize the electrical properties of the material and analyse its electrolyte and electrode interfaces. Nyquist plot for GG–NaI-based biopolymer electrolytes is shown in figure 4.

The ionic conductivity for the GS-1, GS-2 and GS-3 samples was measured between 1 Hz and 1 MHz frequency range at 303 K. In the Nyquist plot, semicircle specifies the higher frequency region and the spike line specifies the lower frequency region. From figure 4, GS-3 shows the semicircle with spike, meanwhile GS-2 and GS-1 show the spike alone due to the absence of the semicircle. It indicates that increasing the concentration of salt, decreases the diameter of the semicircle and disappears later, so this disappearance of the semicircle shows the movement of ions across the electrode–electrolyte interface, which is the major reason for the ionic conductivity [19, 25–28]. The ionic conductivity of the prepared samples was determined by using equation (1),

$$\sigma = 1/R_b A, \tag{1}$$

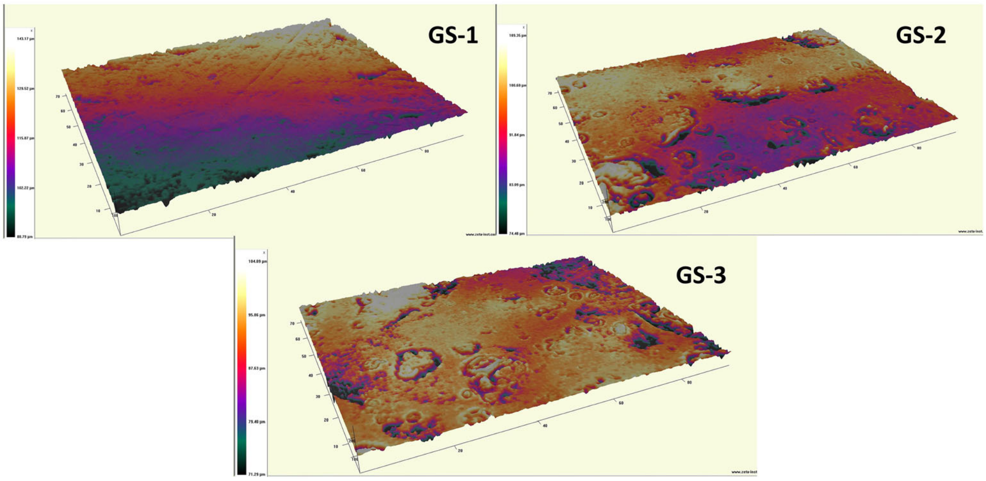

Figure 3. 3D images of GG–NaI-based electrolytes.

Table 1. R_a values for GG–NaI polymer electrolyte.

Composition of GG–NaI polymer electrolyte	R_a values (%)
GS-1 0.4 g GG: 1 wt%	3.45
GS-2 0.4 g GG: 0.75 wt%	1.95
GS-3 0.4 g GG: 50 wt%	8.44

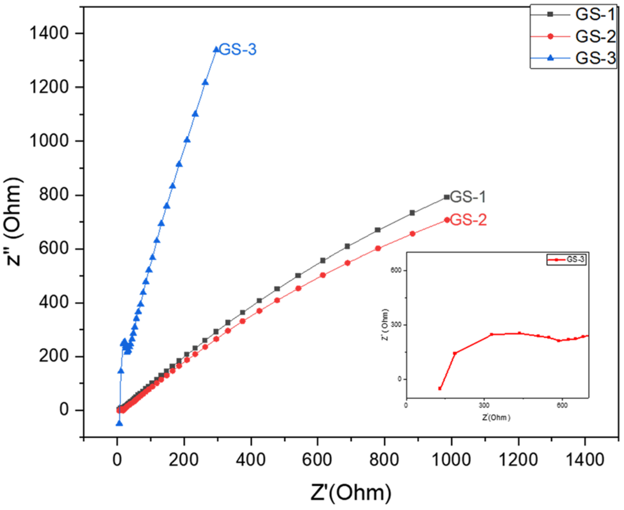

Figure 4. Nyquist plot for GG–NaI-based biopolymer electrolytes.

where R_b is bulk resistance (intercept of the semicircle and spike), l is thickness of the film, A is the surface area of the polymer film.

From table 2, the highest ionic conductivity value of 7×10^{-3} S cm^{-1} was obtained for the polymer electrolyte containing the 0.4 g GG: 0.75 wt% of NaI. In this case, increasing the salt concentration (1 wt% of NaI) decreases the conductivity (3×10^{-3} S cm^{-1}) due to the aggregation of ions, which may be due to aggregation of ion which reduces the ionic mobility [29, 30].

3.5 *Chronoamperometry*

Transference number was measured by the chronoamperometric technique using Wagner's polarization method. Transference number measurement (TNM) has been employed to determine the main charge carrier at the working voltage of 0.1 V. Figure 5 shows the polarization curve of the highest conducting electrolyte of 0.4 g GG: 0.75 wt% NaI. The drop in the initial total current *vs.* time is mainly due to decreased ionic charge carrier species in the electrolyte systems [31].

Table 2. Ionic conductivity values of GG–NaI polymer electrolyte.

Composition of GG–NaI polymer electrolyte	Ionic conductivity (S cm^{-1})
GS-1 0.4 g GG: 1 wt%	3×10^{-3}
GS-2 0.4 g GG:0.75 wt%	7×10^{-3}
GS-3 0.4 g GG: 50 wt%	0.89×10^{-4}

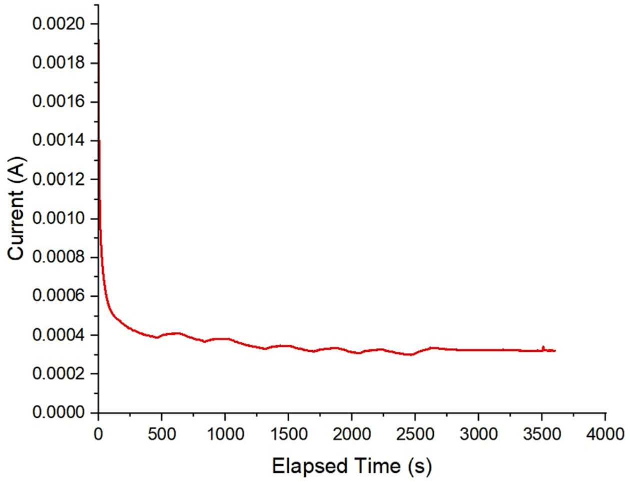

Figure 5. Polarization curve for 0.4 g GG–0.75 wt% NaI-based biopolymer electrolytes.

Based on the polarization curve, ions transference numbers were calculated using equation (2a)

$$t_{\mathrm{ion}} = I_s - I_o/I_o, \tag{2a}$$

$$t_{\mathrm{ele}} = I_s/I_o, \tag{2b}$$

where t_{ion} is the cation transport, t_{ele} is the electron transport, I_s the steady-state current, and I_o is the initial current

The highest conductivity value of 7×10^{-3} S cm^{-1} for the electrolyte of 0.4 g GG:0.75 wt% has a 0.80 ion transference number.

4. Conclusion

The GG–NaI-based electrolytes were prepared via the Solution casting technique. The complexation between GG and NaI has been revealed by FT-IR spectroscopy. From the TGA values, GG–NaI-based biopolymer electrolytes are stable up to 300 to 350°C. 3D optical profilometry measured that the electrolytes GS-1 and GS-2 are smoother than GS-3 electrolytes. The highest conductivity value of 7×10^{-3} S cm^{-1} for the electrolyte of 0.4 g GG: 0.75 wt% has a 0.80 ion transference number. Hence, prepared electrolyte is applicable for the fabrication of a coin cell, which will be validated for product development and commercialization.

Acknowledgements

We wish to acknowledge the University Grants Commission, New Delhi, India, for the financial support through

Savitribai Single Girl Child Fellowship, and the authorities of Avinashilingam Institute for Home Science and Higher Education for Women, Coimbatore, Tamil Nadu, India, for providing the necessary facilities to carry out the present research.

Funding

The funding was provided by University Grants Commission (UGCES-22-OB-TAM-F-SJSGC-1090).

References

[1] Khiar A S A and Arof A K 2010 *Ionics (Kiel)* **16** 123

[2] Iqbal D N, Shafiq S, Khan S M, Ibrahim S M, Abubshait S A, Nazir A *et al* 2020 *Int. J. Biol. Macromol.* **164** 499

[3] Ghauri Z H, Islam A, Qadir M A, Gull N, Haider B, Khan R U *et al* 2021 *Sci. Rep.* **11** 1

[4] Khan M U A, Iqbal I, Ansari M N M, Razak S I A, Raza, Sajjad A *et al* 2021 *Molecules* **26** 5937

[5] Gunasekaran A, Sorrentino A, Asiri A M and Anandan S 2020 *Sol. Energy* **208** 160

[6] Chiellini E and Solaro R 1996 *Adv. Mater.* **8** 305

[7] Premalatha M, Mathavan T, Selvasekarapandian S, Monisha S, Pandi D V and Selvalakshmi S 2016 *J. Non.-Cryst. Solids* **453** 131

[8] Singh P K, Bhattacharya B, Nagarale R K, Kim K and Rhee H 2010 *Synth. Metals* **160** 13

[9] Samsudin A S and Isa M I N 2012 *Bull. Mater. Sci.* **35** 1123

[10] Suvarnna K, Shanjitha S, Selvasekarapandian S and Kirubavathy S J 2023 *Bull. Mater. Sci.* **46** 112

[11] Sangeetha P, Selvakumari T M, Selvasekarapandian S and Mahalakshmi M 2023 *Polym. Bull.*. https://doi.org/10.1007/s00289-022-04669-2

[12] Chitra R, Sathya P, Selvasekarapandian S and Meyvel S 2019 *Mater. Res Express* **7** 15309

[13] Selvalakshmi S, Mathavan T, Selvasekarapandian S and Premalatha M 2017 *Ionics (Kiel)* **23** 2791

[14] Azarian M H and Wootthikanokkhan J 2020 *Ionics (Kiel)* **26** 5841

[15] Rajendran S and Saratha R 2021 *Mater. Today Proc.* **47** 819

[16] Tamilisai R, Palanisamy P N, Selvasekarapandian S and Maheshwari T 2021 *J. Mater. Sci. Mater. Electron* **32** 22270

[17] Hamsan M H, Shukur M F, Aziz S B, Yusof Y M and Kadir M F Z 2020 *Bull. Mater. Sci.*. https://doi.org/10.1007/s12034-019-2008-9

[18] Maithilee K, Sathya P, Selvasekarapandian S, Chitra R and Meyvel S 2023 *Bull. Mater. Sci.* **46** 114

[19] Abirami M, Saratha R and Shilpa R 2020 *Bull. Mater. Sci.* **43** 1

[20] Jenova I, Venkatesh K, Karthikeyan S, Madeswaran S and Joice Sheeba D 2023 *Mater. Today Proc.* **2214** 7853

[21] Vengadesh R C M and Selvasekarapandian K S 2022 *Polym. Bull.* **79** 3555

[22] Shilpa R and Saratha R 2020 *AIP Conf. Proc.* **2270** 100006

[23] Venkatesh K, Jenova I, Karthikeyan S, Madeswaran S, Arivanandhan M, Joice Sheeba D *et al* 2022 *Polym. Bull.* **202** 23

[24] Mudgil D, Barak S and Khatkar B S 2012 *Int. J. Biol. Macromol.* **50** 1035

[25] Dodi G, Hritcu D and Popa M I 2011 *Cell. Chem. Technol.* **45** 3

[26] Rawat P and Saro A L 2023 *Mater. Sci. Eng. B* **288** 16215

[27] Eswaragomathy S, Selvanayagam S, Selvasekarapandian S, MunirajVignesh N, AafrinHazaana S and MeeraNaachiyar R 2023 *Ionics (Kiel)* **29** 2329

[28] Nandhinilakshmi M, Vanitha D, Nallamuthu N, AnandhaJothi M and Sundaramahalingam K 2023 *Polym. Bull.* **80** 3793

[29] Perumal P, Selvasekarapandian S, Abhilash K P, Sivaraj P, Hemalatha R and Selvin P C 2019 *Vacuum* **159** 277

[30] Manjuladevi R, Selvin P C, Selvasekarapandian S, Shilpa R and Moniha V 2018 *AIP Conf. Proc.* **1942** 140075

[31] Brza M, Aziz S B, Raza Saeed S, Hamsan M H, Majid S R, Abdulwahid R T *et al* 2020 *Membranes (Basel)* **10** 1