Turkish Online Journal of Qualitative Inquiry (TOJQI)
Volume 11, Issue 4, October 2020: 1639-1650

Preparation and Electrical Characterisation of Tamarind Seed Polysaccharide (TSP) Biopolymer Electrolyte

Om Prakash Yadav* and Vinod Kumar Singh
Department of Physics,K.S Saket Post Graduate College, Ayodhya-224123, India
E-mail: dropyadav@gmail.com

Abstract: The natural, abundantly available, non-toxic, bio-compatible and bio-degradable biopolymers and polysaccharides had become more viable in the synthesis of polymer electrolytes lately. They became a prime interest forthe development of storage energy devices like Batteries, Fuel cells, sensors and supercapacitors due to their eco-friendliness and cost effectiveness over the other synthetic available solid polymer electrolytes. Tamarind seed polysaccharide a biopolymer extracted from tamarind seed has applications in food industry, cosmetics, pharmaceutical industry and dyeing industries due to its stabilising, thickening and gelling nature and is also an emulsifying agent. The biopolymer electrolytes were prepared by Tamarind Seed Polysaccharide (TSP) as a polymer matrixwith a range ofweight proportions of Sodium Citrate ($Na_3C_6H_5O_7$). Solvent casting technique was used to prepare the biopolymer membranes with distilled water as solvent. The obtained biopolymer electrolytes were investigated with Impedance Spectroscopy and Transference Number Measurements (TNM). The magnitude of ionic conductivity is found to be increased with increase in salt ratio and temperature. The dielectric parameters like complex dielectricand tangent loss were analysed from AC impedance spectroscopy with frequency range from 42 Hz to 1MHz. The AC impedance data analysis revealed that the biopolymer membrane of 1g TSP:0.3g $Na_3C_6H_5O_7$ has the highest ionic conductivity with $2.4 \times 10^{-4} Scm^{-1}$ at room temperature. The decrease in Activation Energy (E_a) with the increase in salt ratio confirmed the Arrhenius relation of the polymer membranes. From the transport number calculations, the transference number close to unity revealed that the conductivity is because of the ions as the predominant charge carriers.

Keywords:Biopolymer, solution casting technique, ionicconductivity, dielectric constant.

1. Introduction

The dire need of the hour is the production of energy storage appliances like fuel cells, batteries, super capacitors and handy electrochemical machines to overcome the existing energy crisis. The polymer electrolyte becomes the indispensable central part of the electrochemical devices. Polymer electrolyte had emerged as a promising alternative to overcome the issues like leakages, corrosion and short circuiting of liquid electrolytes with improved ionic conductivity at ambient temperatures, superior mechanical stability, long life cycle and developing better interfacial contacts with electrodes. Though wide range of research was carried out on synthetic polymer electrolytes but due to their adverse effects on environment, non-degradability, cost and toxicity paved way to a search of alternative biodegradable electrolyte for electrochemical devices. Biopolymer electrolytes (BPE) have fascinated the scientist and research group because of their promising characteristics like cost-effective, abundance in nature, biodegradability, eco-friendly and biocompatibility [1]. The major types of bio-polymers include polyesters, proteins and polysaccharides. The Polysaccharides consists of several units ofmonosaccharideschained with glycosidic bonds and aremajorly categorised as homo-polysaccharides that are made up of only single kind ofmono-saccharide and hetero-polysaccharides are made up of various monomeric elements[2].Seeds and roots from plant, cell wall of plant and bacteria, seaweed extractsetc. are the sources of polysaccharides. The polysaccharides like starch, cellulose, chitosan, carboxyl methyl cellulose pectin, agarose and carrageenenbased polymer electrolytes were already prepared and studied[3–10].

Tamarind Seed Polysaccharide (TSP) is a flavourless, neutral, natural and hydrophilic polysaccharide. It is white and light yellow in colour powder that flows freely and is soluble at about 80°C in hot water. Tamarind Seed Polysaccharide (TSP) is an excellent biopolymer among natural polymers with distinct characteristics like gelatinization and has capacity of food gums and easy film forming. TSP is used as stabiliser and emulsifier in food industries. It acts as a thickening agent excellently in textile industry because of its gelling capacity. It is also used in the manufacturing of bio-adhesive tablets. It is an anionic polysaccharide with lot of polar groups and its chemical structure is shown in figure 1. Very few authors have studied and reported TSP as the host polymer for the preparation of polymer electrolyte in the battery applications [11, 12].

The present study aims at developing a novel type ion-conducting bio-polymer films with TSP as a polymer matrixwith various compositions of Sodium Citrate ($Na_3C_6H_5O_7$) as a dopant. Not much consideration was given to the sodium salts based polymer electrolytes as per the best of information available. There are many advantages with the usage of sodium salts in the preparation of bio-polymer electrolytes in comparison to the lithium based bio-polymer electrolytes. Due to the sodium based polymer electrolytes softness, it is rather easy to preserve contact with the components of battery[13]. From the review of Vignarooban et al., [14], it is understood that there is momentum in the study and progress of sodium-ion batteries because of their abundance at a lesser cost in comparison with lithium (Li). Because of similarity in chemical composition of Na and Li, the electrolytes that are used for Li batteries are valid for Na-based batteries[15]. Furthermore, the rechargeable batteries based on Na are eco-friendly, non-toxic, and economic [16]. The Sodium Citrate doped TSP biopolymer electrolytes characteristics were studied by, Impedance Spectroscopy and Transport Number Measurements (TNM).

2. Material and method

2.1 Preparation of Biopolymer Membranes

In the present study tamarind seed polysaccharide (TSP) bought from Tokyo Chemical Industry, Japan and Sodium Citrate bought from Merck, Mumbai, India without further purification were utilised. The bio-polymer films were made with method of solution casting by dissolving 1g TSP in distilled water and vigorously stirring at 80^0Cwith the help of magnetic stirrer. To this 1g TSP stirred solution, the various concentrations of Sodium Citrate

($Na_3C_6H_5O_7$) [0.1, 0.2, 0.3, and 0.4 g] were added. A homogeneous viscous solution obtained after continuous stirring is poured on to the petri dishes and kept for evaporation of the solvent at 60^0C in hot air oven. After 24 hrs free standing thin films of 0.11 to 0.15 mm thickness were formed. The obtained films were subjected to furthercharacterization.

2.2 Characterisation

The biopolymer membranes obtained were subjected to characterisation techniques for further study. The spectra recorded in the range of wavenumber 4000 – 400 cm^{-1} with Perkin-Elmer Alpha-E spectrophotometer the FTIRspectroscopy to investigate the functional group of the membranes and the polymer and salt interaction. The ac conductivity and dielectric characteristics of the membranes were analysed with HIOKI 3532-50 LCR HITESTERin the 42 Hz to 1MHz frequency range and 303K to 373K temperature ranges. The bio-polymer membranes transference number with respect to ions (t_+) and electrons (t_-) were calculated with Wagner's polarization method.

3. Results and discussion

3.1. AC-impedance analysis

The material electrical characteristics are studied with AC-impedance spectroscopy. Usually, the cole-cole plots contains semi-circle at high frequency because of the parallel combination of bulk resistance R_b and capacitance C_b and an inclined spike at low frequency is due to the electrode/electrolyte interface. The resistor stands for the free movement of ions in the polymer matrix and the capacitor denotes the ions immobility due to the polarisation[17,18].

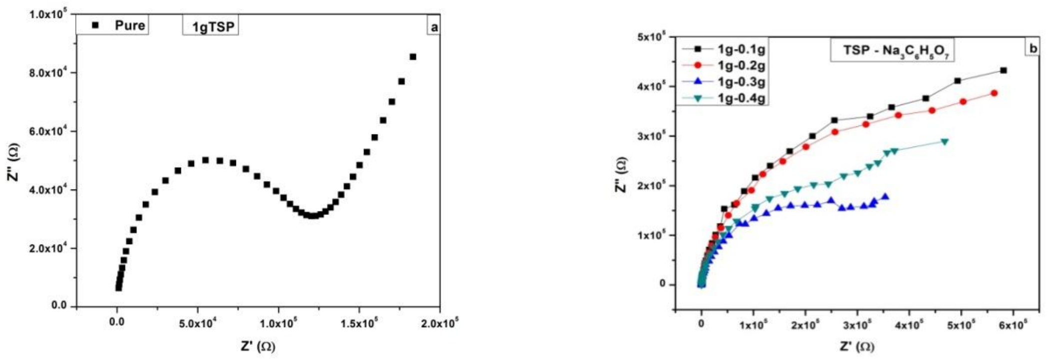

Figure2a) Cole-Cole plot for pure 1g TSP. b) Cole-Cole plot for 1g TSP with various proportions of Sodium Citrate ($Na_3C_6H_5O_7$)

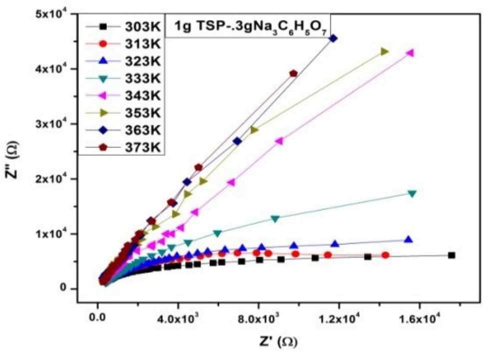

Figure 3: Cole-Cole plot for high conducting film (1gTSP:0.3g $Na_3C_6H_5O_7$) in the temperature range 303K-373K

The bulk resistance value R_b is taken from cole-cole plots depicted in figure 2 and the bio-polymer electrolyte film thickness was measured with screw gauge. The biopolymer electrolyte ionic conductivity(σ) was measured with the below formula.

$$\sigma = \frac{t}{R_b A}$$

Where t denotes the thickness of the film, R_b denotes the bulk resistance and the A is the area of the electrode.

Table 1:Values of ac and dc Conductivity of 1g TSP and various compositions of 1g TSP with $Na_3C_6H_5O_7$

Sl.no	Composition	Conductivity (σ_{ac} S/cm)	Conductivity (σ_{dc} S/cm)
1	Pure TSP	$3.17 x 10^{-8}$	$3.13 x 10^{-8}$
2	1 g TSP: 0.1g $Na_3C_6H_5O_7$	$1.3 x 10^{-4}$	$1.25 x 10^{-4}$
3	1 g TSP: 0.2g $Na_3C_6H_5O_7$	$1.5 x 10^{-4}$	$1.4 x 10^{-4}$
4	1 g TSP: 0.3g $Na_3C_6H_5O_7$	**$2.4 x 10^{-4}$**	**$2.3 x 10^{-4}$**
5	1 g TSP: 0.4g $Na_3C_6H_5O_7$	$1.7 x 10^{-4}$	$1.6 x 10^{-4}$

The conductivity of the pure TSP is found to be $3.17 x 10^{-8}$ Scm^{-1} and similar value is stated by premalatha et al.[11]. 1g TSP biopolymer electrolyte and TSP with different compositions of $Na_3C_6H_5O_7$ salt cole-cole plots are shown in figure 2.Two regions are clearly observed from the cole-cole plot of 1g TSP, there is a semicircle at higher frequencies and a spike at lower frequencies. Figure 3 illustrates the cole-cole plot of high conducting film of 1g TSP with 0.3g $Na_3C_6H_5O_7$ proportion, where as the temperature increases the inclined spikes tend to towards the y-axis.

The figure 4 a clearly points that ac conductivity increasesas the proportion of the $Na_3C_6H_5O_7$ increases upto 0.3g and later decreases for the composition of 0.4 g$Na_3C_6H_5O_7$. The figure 4 b depicts as the temperature increases for the high conducting film of 1g TSP with 0.3g $Na_3C_6H_5O_7$ composition bio-polymer electrolyte the conductivity increases.

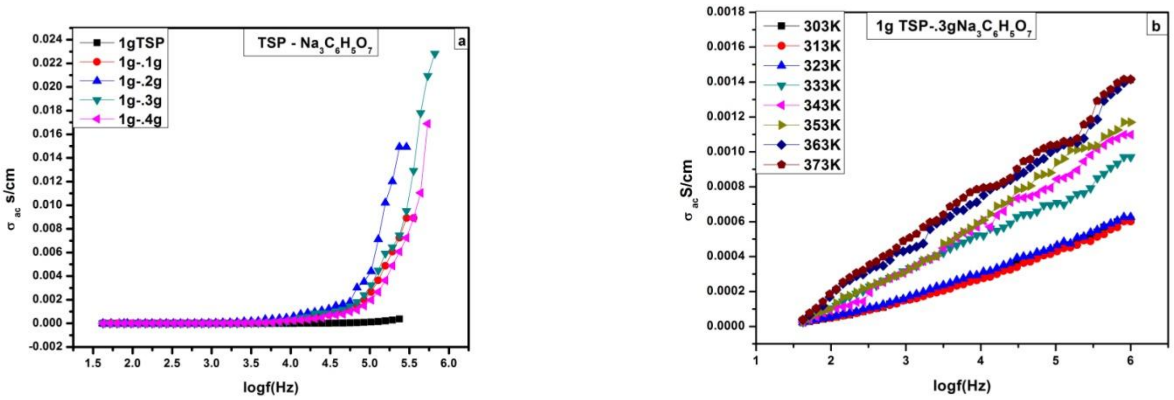

Figure 4: a) ac Conductivity plot for 1g TSP with various proportions of $Na_3C_6H_5O_7$ salt, b) conductivity plot for high conducting film (1gTSP:0.3g $Na_3C_6H_5O_7$) in the temperature range 303K-373K

Table 2: Conductivity values of the 1g TSP with various compositions of $Na_3C_6H_5O_7$in the temperature range 303K-373K

Sl.no	Composition	Conductivity σ_{ac} S/cm							
		303K	313K	323K	333K	343K	353 K	363 K	373 K
1	1gTSP:0.1g $Na_3C_6H_5O_7$	1.35x10^{-4}	1.48x10^{-4}	1.65x10^{-4}	1.78x10^{-4}	1.93x10^{-4}	2.20 x10^{-4}	2.47 x10^{-4}	2.97 x10^{-4}
2	1 gTSP: 0.2g $Na_3C_6H_5O_7$	1.52x10^{-4}	1.75 x10^{-4}	1.90 x10^{-4}	2.18 x10^{-4}	2.50 x10^{-4}	2.91 x10^{-4}	3.18 x10^{-4}	3.89 x10^{-4}
3	1 gTSP: 0.3g $Na_3C_6H_5O_7$	2.30 x10^{-4}	2.60 x10^{-4}	2.90 x10^{-4}	3.20 x10^{-4}	3.56 x10^{-4}	3.80 x10^{-4}	3.90 x10^{-4}	4.20 x10^{-4}
4	1 gTSP: 0.4g $Na_3C_6H_5O_7$	1.72 x10^{-4}	1.97 x10^{-4}	2.17 x10^{-4}	2.43 x10^{-4}	2.76 x10^{-4}	3.18 x10^{-4}	3.76 x10^{-4}	4.14 x10^{-4}

3.2 Analysis of Dielectric Spectra

The dielectric constant ε' measures the charge piled in an electrolyte film and the dielectric loss ε" gives energy loss when ions move under the rapid reverse polarity of electric field[19].The permittivity (ε*) or dielectric constant is specified by

$$\varepsilon^* = \varepsilon'(\omega) - i\varepsilon''(\omega)$$

where ε' &ε" are the real and imaginary part of dielectric permittivity that signify the energy storageand loss in each phase of the applied electric field[20].Figure 5a, b denotes the dielectric constant (ε′) and dielectric loss (ε″) variation with frequency for 1g TSP and 1g TSP with various compositions of $Na_3C_6H_5O_7$ bio-polymer electrolyte at room temperature. It is clear from figure 5a that the dielectric constant (ε’) value is high at low frequenciesand is constant at high frequencies. The high dielectric constant (ε’) value is because of the space charge created by heaping of ions, the charge carriers at the electrodes [21]. The value decrease of dielectric constant (ε’) at high frequencies is attributed to the incidenceof electric filed periodic reversal. From figure 5b, it is evident that the dielectric loss (ε″) is high at low frequencies because of the free charge carriers’ movement within the material [22].

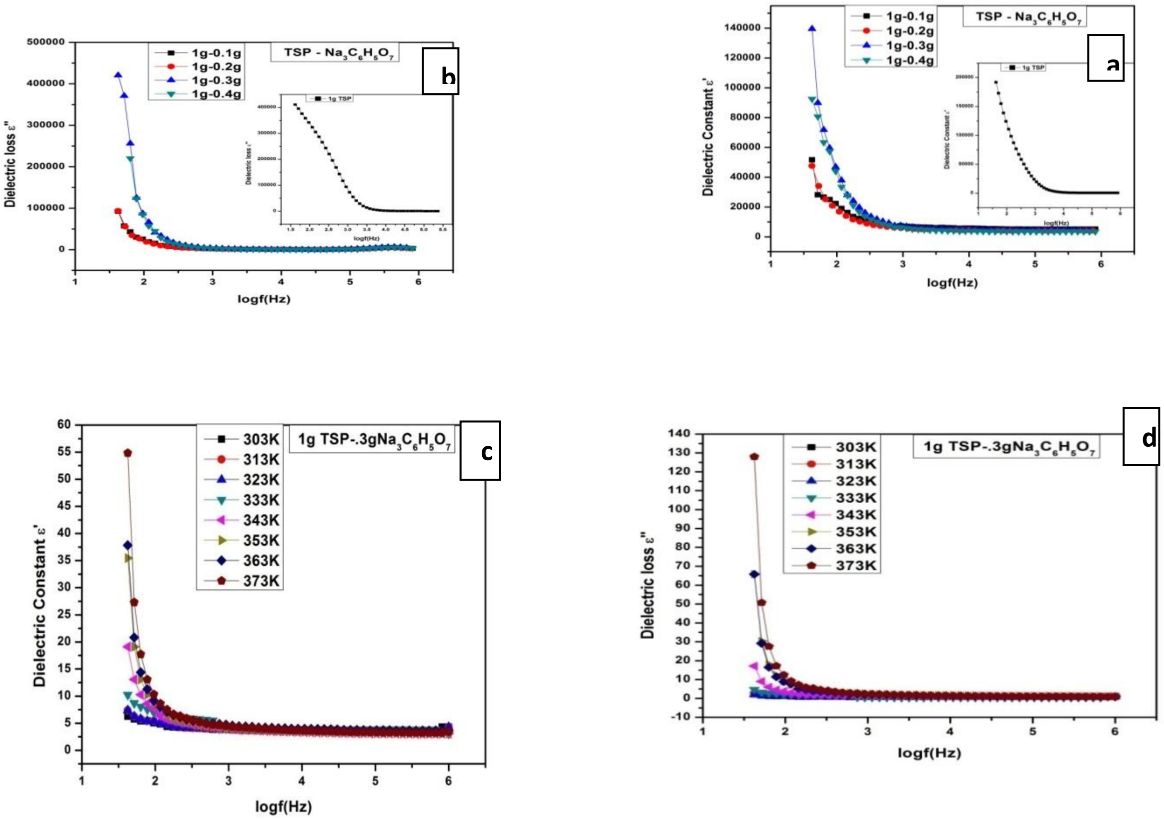

Figure 5a-b) The dielectric constant(ε′) and dielectric loss (ε″) as the function of frequency for 1g TSP with various compositions of $Na_3C_6H_5O_7$ salt, c-d) The dielectric constant(ε′) and loss(ε″) of high conducting film(1gTSP:0.3g $Na_3C_6H_5O_7$) at temperature range 303K – 373K.

The frequency dependent dielectric constant (ε′) and dielectric loss (ε″) for the high conducting film with proportion of (1gTSP:0.3g $Na_3C_6H_5O_7$) in temperature range shows the dielectric constant and loss increases as the temperature increases. The dielectric constant increase identifies with the charge increase within the bio-polymer electrolyte that leads to fractional enhancement of conductivity.

Figure 6 a-b) depicts the frequency dependent tangent loss (tanδ) at different compositions of 1g TSP with $Na_3C_6H_5O_7$ saltand tangent loss of the high conducting film at temperature range of 303K to 373K. It is evident from the below figures that the tangent loss decreases with increase in frequency. This attenuation of tangent loss with increase in frequency can be related to the interactions of phonon dipoles that tend to decrease the energy transfer to the dielectric medium characterising the amorphous behaviour of the polymers. The decrease in the tangent loss as the frequency increases indicates that the tangent loss depends on electronic polarisation only [23].

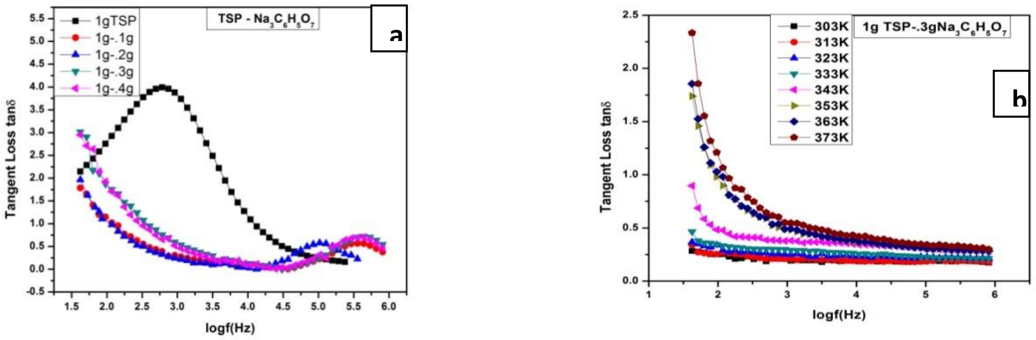

Figure 6: a)Tangent loss (tanδ) variation with frequency for 1g TSP with various compositions of $Na_3C_6H_5O_7$ salt, b) tangent loss (tanδ)variation with frequency of high conducting film (1gTSP:0.3g $Na_3C_6H_5O_7$) in the temperature range 303K -373K

3.3 Ionic Conductivity-Temperature

The biopolymer electrolyte conductivity increases as temperature increases as shown in table 2 because of the mobility and the volume increase as stated by Armand et al. [24]. The decrease in R_b value as temperature rises is because of the development of space around the volume of the atom and as well it overcomes the hydrostatic pressure forced by the adjacent atoms due to the vibrational energy of the polymer segment[25,26].

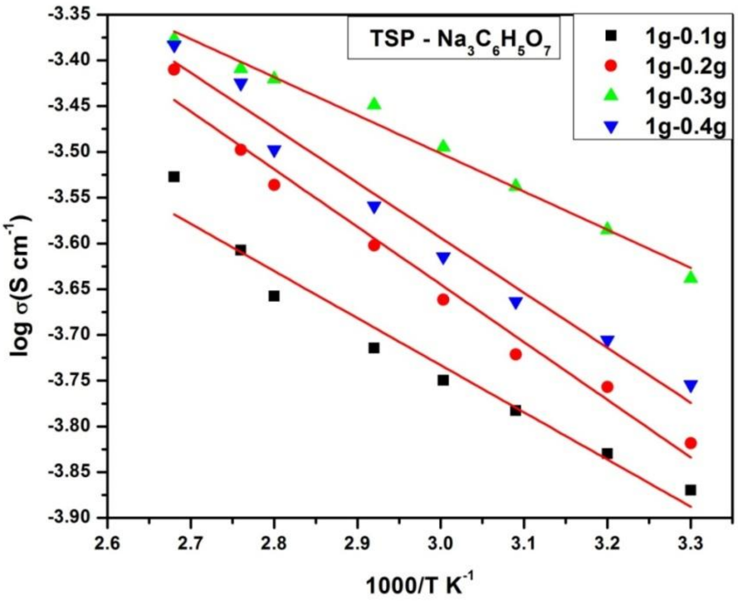

Figure 7:The temperature dependent ionic conductivity plot for 1g TSP with various proportions of $Na_3C_6H_5O_7$ salt bio-polymer electrolytes.

The 1000/T versus log σ plot for 1g TSP bio-polymer with various compositions of $Na_3C_6H_5O_7$ is depicted in figure 7. It is evident from the 1000/T versus log σ that temperature dependent biopolymer electrolyte obeys the below mentioned Arrhenius rule

$$\sigma = \sigma_0 \exp\left(-E_a/kT\right)$$

Where σ denotes the ionic conductivity, $\sigma_0$denotes the pre-exponential factor, $E_a$denotes the activation energy of the bio-polymer electrolyte, k denotes the Boltzmann constant, and T denotes the absolute temperature.

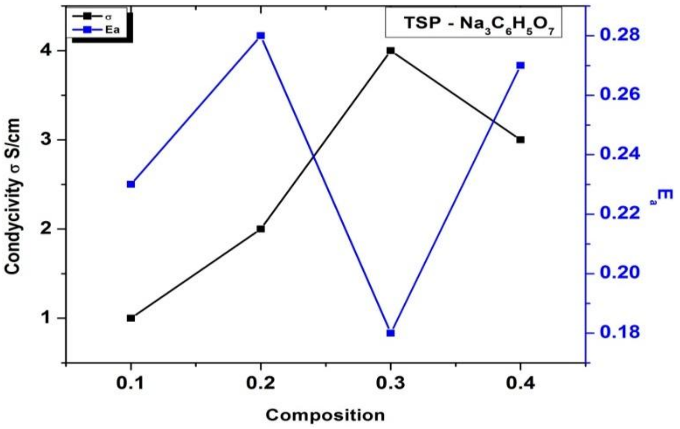

Figure 8: Variation of conductivity and activation energy with various compositions of 1g TSP with $Na_3C_6H_5O_7$ salt

From figure 8 it is apparent the activation energy decreases as the conductivity increases as the composition increases. The increase tend in conductivity is upto 1g TSP with 0.3g $Na_3C_6H_5O_7$ and decreases for the next higher concentration. The increase in conductivity is related to the ions mobility and decrease in conductivity beyond high conducting film concentration is due to the ion aggregation tending to the formation of ion clusters [27].

Table 3: The activation energy E_a and Regression result values for 1g TSP with various compositions of $Na_3C_6H_5O_7$ salt at room temperature

Sl.no	**Composition**	Activation Energy E_a	Regression Values
1	1 g TSP: 0.1g $Na_3C_6H_5O_7$	0.23	0.95
2	1 g TSP: 0.2g $Na_3C_6H_5O_7$	0.28	0.97
3	1 g TSP: 0.3g $Na_3C_6H_5O_7$	0.18	0.98
4	1 g TSP: 0.4g $Na_3C_6H_5O_7$	0.27	0.97

3.4 Transference Number Measurement(TNM)

The Transference Number Measurement is a dimensionless quantity that calculates the majority of charge carriers i.eions or electrons in the biopolymer electrolytethat are the reason for conductivity. It isrequired that the transport number (TN) to be approximately equal to unity (~ 1)which confirms the ionic conductivity of the biopolymer electrolyte. TheTNM is carriedout with the well knownWagner's dc polarization method.

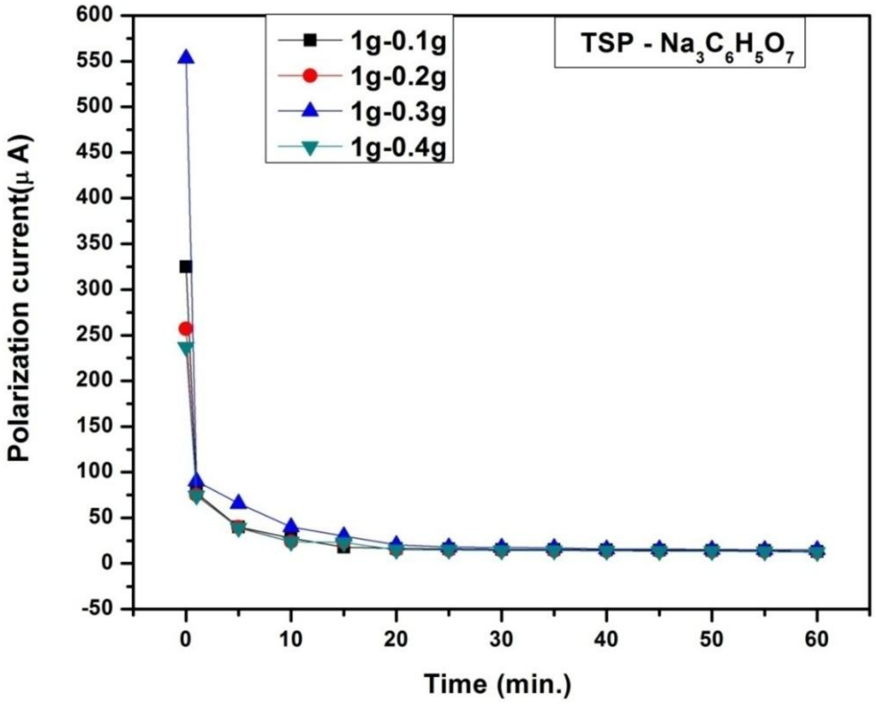

Figure 9: Variation of polarisation current with time for 1g TSP with various compositions of $Na_3C_6H_5O_7$ biopolymer electrolyte

The dc potential 1.5 V is applied across the biopolymer electrolyte placed between thestainless steel electrodes at room temperature. Figure9explains the plot of Polarization current as a function oftime for the1g TSP with various compositions of Sodium Citrate salt. The value of transferencenumber is measured with the below relation

$$t_+ = i_t - \frac{i_{ele}}{i_t}$$

$$t_- = (1 - t_+)$$

where, $i_t$is the sum current from ions and electrons and$i_{ele}$is the final current due to electrons. It is clearly understood that the initial sum current because of ions and electronsreduces with time because of the ionic species exhaustion in the biopolymer electrolyte and approaches a steady state [28]. The values of transference number are in the range of 0.94–0.97 for allthe compositions of bio-polymer electrolyte films. Thetransference number of ions (t_+) and transferencenumber of electrons (t_-) for the high conducting film is 0.97 and 0.03. This confirms the charge transportation of the biopolymer films are majorly because of the ions and the charge due to the electron contribution is insignificant.

3.5 Transport parameters

The anionic and cationic diffusion coefficients of the TSPpolymer matrix with different compositions of Sodium Citrate are measured with the below given equations [25] and their measured results are tabulated in Table 4.

n= Nρ(salt molar ratio/salt molecular weight)

$$D_+ + D_- = \frac{KT\sigma}{n(e)^2}$$

$$t_+ = \frac{D_+}{D_+ + D_-}$$

$D_+ = t_+ D$
$D_- = D - D_+$

Where N denotes the Avogadro number (6.023×10^{23} particles per mol), ρ is salt density, k is the Boltzman constant, T is the absolute temperature, t_+ionic transference number, D_+, $D_-$are the diffusion coefficients.

The cationic and anionic mobilities of all the preparedpolymer membranes have been calculated using the followingequations

$\mu = \mu_+ + \mu_- = \sigma/ne$

$t_+ = \mu_+/\mu_+ + \mu_-$
$t_- = 1 - t_+$
where t_- denotes electronic transference number, e is the charge of electron, μ_+, $\mu_-$are mobilities, n is the charge carriers number with respect to the salt concentration.

It is observed from the table 4 that the **μ_+**mobility is two orders greater than the**μ-** mobility that confirms the biopolymer electrolyte ionic nature.

Table 4: Values of transference number, mobility, diffusion coefficient of the 1g TSP with various compositions of $Na_3C_6H_5O_7$ at room temperature

Composition	**t_+**	**t_-**	**n (cm^3)**	**μ_+ (cm^2/VS)**	**μ- (cm^2/VS)**	**D_+ (cm^2/S)**	**D_- (cm^2/S)**
1g TSP	0.94	0.06	$2.94x10^{22}$	$6.298x10^{-11}$	$4.02x10^{-12}$	$1.65 x10^{-13}$	$1.1x10^{-14}$

1gTSP:0.1g $Na_3C_6H_5O_7$	0.96	0.04	$3.96x10^{20}$	$1.968x10^{-6}$	$8.3x10^{-8}$	$5.147x10^{-8}$	$2.15x10^{-9}$
1 g TSP: 0.2g $Na_3C_6H_5O_7$	0.95	0.05	$7.93x10^{20}$	$1.121\ x10^{-6}$	$5.9\ x10^{-8}$	$2.935x10^{-8}$	$1.54x10^{-9}$
1 g TSP: 0.3g $Na_3C_6H_5O_7$	0.97	0.03	$1.1x10^{21}$	$1.319x10^{-6}$	$4.1\ x10^{-8}$	$3.453x10^{-8}$	$1.07x10^{-9}$
1 g TSP: 0.4g $Na_3C_6H_5O_7$	0.95	0.05	$1.59x10^{21}$	$6.35\ x10^{-7}$	$3.3\ x10^{-8}$	$1.653x10^{-8}$	$8.7x10^{-10}$

Conclusion

TSP based biopolymer electrolyte with various compositions of sodium citrate ($Na_3C_6H_5O_7$) were prepared with solution casting method. AC impedance studies indicated the maximum ionic conductivity is **$2.4x10^{-4}$s/cm** for the film of composition 1g TSP with 0.3g $Na_3C_6H_5O_7$. The activation energy for the high conducting film is 0.18 ev calculated from Arrhenius plot. The charge carriers predominantly are ions and is confirmed with transference number value 0.97 obtained for the high conducting film.The results of mobility and diffusion coefficient confirm the abundant, biodegradable and non-toxic TSP-$Na_3C_6H_5O_7$ biopolymer electrolyte is very much suitable for electrochemical usage.

Reference

1. Avachat AM, Dash RR, Shrotriya SN (2011) Indian J Pharm Educ Res 45:86–99
2. Durai R, Rajalakshmi G, Joseph J, Kanchalochana SN, Hari V(2012) Int J Green Pharm 6:270
3. E. Raphael, C.O. Avellaneda, B. Manzolli, A. Pawlicka, (2010) Electrochim. Acta vol. 55 (4)1455–1459.
4. R. Leones, F. Sentanin, L.C. Rodrigues, I.M. Marrucho, J.M.S.S. Esperança, A. Pawlicka,M.M. Silva, (2012) Express Polym. Lett. vol. 6 (12) 1007–1016.
5. A.S. Ahmad Khiar, A.K. Arof, (2010) Ionics vol. 16 (2) 123–129.
6. L.V.S. Lopes, D.C. Dragunski, A. Pawlicka, J.P. Donoso, (2003) Electrochim. Acta vol. 48 (14–16) 2021–2027.
7. J.R. Andrade, E. Raphael, A. Pawlicka, (2009) Electrochim. Acta vol. 54 (26) 6479–6483.
8. A.S. Samsudin, H.M. Lai, M.I.N. Isa, (2014) Electrochim. Acta vol. 129 1–13.
9. A.S.A. Khiar, R. Puteh, A.K. Arof, (2006) Phys. B Condens. Matter vol. 373 (1) 23–27.
10. N.N. Mobarak, F.N. Jumaah, M.A. Ghani, M.P. Abdullah, A. Ahmad, (2015) Electrochim. Actavol. 175 224–231.
11. M. Premalatha, T. Mathavan, S. Selvasekarapandian, S. Monisha, D.VinothPandi, S. Selvalakshmi,(2016) Journal of Non-Crystalline Solids 453 131–140
12. L. Sampath Kumar & P. Christopher Selvin& S. Selvasekarapandian& R. Manjuladevi& S. Monisha& P. Perumal(2018) iconic, 05 april.

13. Reddy, C.V.S.; Jin, A.-P.; Zhu, Q.-Y.; Mai, L.-Q.; Chen, W. (2006) *Eur. Phys. J. E*, *19*, 471–476.

14. Vignarooban, K.; Kushagra, R.; Elango, A.; Badami, P.; Mellander, B.-E.; Xu, X.; Tucker, T.G.; Nam, C.; Kannan, A.M. (2016)*Int. J. Hydrogen Energy*, *41*, 2829–2846.
15. Li, Q.; Chen, J.; Fan, L.; Kong, X.; Lu, Y.(2016) *Green Energy Environ.* **2016**, *1*, 18–42.
16. Koduru, H.K.; Iliev, M.T.; Kondamareddy, K.K.; Karashanova, D.; Vlakhov, T.; Zhao, X.-Z.; Scaramuzza, N. (2016) *J. Phys. Conf. Ser.*, *764*, 012006.
17. Bhuvaneswari R, Karthikeyan S, Selvasekarapandian S et al (2014) Ionics 21:387–399
18. Macdonald JR (1992) Impedance Spectroscopy. Ann Biomed Eng 20:289–305

19. Woo H,Majid S, Arof A (2012) Mater Chem Phys 134:755–761
20. Dutta P, Biswas S, De SK (2002) Mater Res Bull 37:193–200
21. Armstrong RD, Dickinson T, Willis PM (1974) J ElectroanalChem 53:389–405
22. Kyritsis A, Pissis P, Grammatikakis J (1995) JPolymSci B PolymPhys 33:1737–1750
23. Shash, N. M. H. Khoder, F. Metawe, A. A. Negm (2013) J. Appl. Polym. Sci., 129: 2796–2805
24. Armand MB, Chabagno JM, Duclot MJ, Vashita P, Munday LN and Shoney G (1979) Elsevier, North-Holland, Amsterdam
25. Rajendran S, Sivakumar M, Subadevi R (2004) Mater Lett 58:641–649
26. N Krishna Jyothi, K K Venkata Ratnam, P Narayana Murthy, and K Vijaya Kumar, (2016) Bull. Mater. Sci., Vol. 39, No. 4, 1047–1055.
27. C.S. Ramya, S. Selvasekarapandian, T. Savitha, G. Hirankumar, (2007) Physica B 393 11.
28. Genova FKM, Selvasekarapandian S, Karthikeyan S, Vijaya N, Pradeepa R, Sivadevi S (2015) PolymSciSer A 57:851–862