Ionic Conductivity Studies of Biodegradable Polymer Electrolyte for Mg Ion Batteries

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Solid biopolymer electrolyte was prepared from potato starch (PS) blended with polyvinyl pyrrolidone (PVP) polymer and magnesium sulphate ($MgSO_4$) using solution casting technique. XRD revealed the amorphous structure and FTIR studies shows complexation of the salt with polymer with different weight ratios for PS:PVP:$MgSO_4$. Ionic conductivity was calculated using AC impedance studies and the sample with the concentration of PS:PVP:$MgSO_4$ (35:35:30 wt.%) is having the highest ionic conductivity 4.2142×10^{-4} S/cm at 273 K. For this sample, electrochemical studies like linear sweep voltammetry have given the stable voltage and the stable redox potential obtained from cyclic voltammetric studies. Dielectric studies have proven the charge holding capacity thus shows stability in conducting the ions. Thus, these results strengthen the solid biopolymer electrolyte to use as electrolyte in the Mg^{2+} ion-based batteries.

Keywords: Solid biopolymer electrolyte, Potato starch, Poly vinyl pyrrolidone, Optical studies, Magnesium ion battery.

INTRODUCTION

An increase in the population leads to large energy demand in their necessities. Electrical energy plays a characteristic role in their major requirements in their regular life, which is produced from different types of sources like solar energy, wind energy, *etc*. And there is a need to store that electrical energy so that can use in different aspects [1]. Batteries are one of the best energy storage devices for people needs. The electrolyte acts as a key to a battery which attracts attention many researchers. In 21st century, solid polymer electrolytes (SPEs) are widely used in batteries as they are safe, flexible to use and contains the high energy density which possess longer time stability and stimulates good conductivity [2]. Although majority of the electrolytes are preparing from organic solvent system or else lithium ion-based electrolytes. But, now-a-days everyone is looking at the affordable, renewable and ecofriendly with good conductivity electrolytes [3].

For these requirements, a biopolymer comprising root starch (potato starch) contains a particle size about 30 to 40 μm and has high molecular weight gives more strengthen and more viscous in nature [4], ready to dissolve in natural solvent H_2O.

Such type of biopolymers can avoid the solvents which are non-renewable and toxic in nature (*e.g.* DMS, NMMO) [5], moreover presence of C=O in potato starch [6] effectively makes the active hydrogen bonding, which results in the formation of an amorphous solid biopolymers. These are the main criteria to prepare high performance electrolytes.

Coming to the charge carriers, the ions produced from the salt ($MgSO_4$) are generally added to the polymer, since such salts contain some special characteristics like ready to dissolve in solvent like water and won't react with atmospheric gases like O_2 and moreover it is an ecofriendly [7]. In this article, we proceeded to prepare the electrolyte with good conductivity using a polymer PVP blended with potato starch, as several studies proven that PVP is having less toxicity and moreover, it will dissolve in water at room temperature so that it will reach the highest amorphous nature, which will be helpful to blend with the potato starch [8]. In this work, PVP is blended with a potato starch like a host polymer and these solid biopolymer electrolytes may have applications in a wide range. Since, solid polymer electrolytes do not contain any leakage problem (major disadvantage of liquid electrolytes) and solvent free. Biopolymer electrolytes have good mechanical stability,

flexibility with good energy density, which are the major requirements for the batteries [9].

EXPERIMENTAL

Potato starch with mesh size 90% was purchased from S.D. Fine Chem Limited, India. Magnesium sulphate 98.5% extra pure from Loba Chemie Pvt. Ltd, India. Polyvinyl pyrrolidone (PVP) (*m.w.* 36,000) purchased from Sigma-Aldrich Chemicals, India. Weighed the samples PVP:PS:MgSO₄ with a ratio of (50:50:00, 40:40:20, 35:35:30, 30:30:40 wt.%). Later, films were synthesized using solution casting technique. For pure film PS:PVP:MgSO₄ (50:50:00 wt.%) preparation, 85% of solvent (distilled water) was heated at 80 ºC about 1 h, after that added the potato starch solution (0.5 g starch dissolved in 15% of solvent) slowly by stirring followed by PVP (0.5 g) with continuous the stirring process until the formation of homogeneous solution of starch and polymer PVP took place. To this pure sample, added MgSO₄ salt (0.2 g, 0.35 g, 0.3 g) and continued the process of stirring up to 48 h. After that transfer the reaction mixtures into Petri dishes and leave them to dry after that keeps them into vacuum oven for 24 h at 50 ºC and 48 h at 40 ºC. Finally, the films get dried completely, ready for the characterization and desiccators can be used for further storage of prepared electrolytes.

Characterization: The XRD patterns were recorded on PAN analytical empyrean diffractometer using Cu$K\alpha$ (λ = 1.5405 Å), with an angle range between 2θ = 10º to 70º. FTIR transmittance spectral studies gives information about different functional groups formed by the complexation of the polymer and salt mixture which is done by using Perkin-Elmer Alpha-E spectrophotometer. The Optical UV-absorption studies were done by using JASCO V-670 spectrometer of wavelength within range 200-800 nm. The conductivity and dielectric analyses were performed with a frequency range from 42 Hz to 1 MHz on solid biopolymer electrolytes using 3532-50 HIOKI LCR HITESTER.

RESULTS AND DISCUSSION

XRD analysis: From XRD studies, the pure film shows the crystalline peaks (Fig. 1), because of hydrogen bonding (both inter and intra) of salt mixed polymer results in the narrow peaks [10,11] at an angle between 17-19º in 2θ angle. Similarly the semi-crystalline nature of the other films (PS:PVP:MgSO₄, 30:30:40, 35:35:30, 40:40:20 wt.%) were within the same range of 17-19º. The sample PS:PVP:MgSO₄ (35:35:30 wt.%) show the narrow peak due to its amorphous nature as there is a complexation between salt and polymer when compared with sample PS:PVP:MgSO₄ (30:30:40 wt.%) and PS:PVP:MgSO₄ (40:40:20 wt.%), which reflect the sharp peaks due to their semi-crystalline nature [12].

FTIR studies: The FTIR spectrum (Fig. 2) shows the presence of carbonyl group in PVP, which is basic in nature but in presence of a metal ion, is in acidic nature. The PVP contains carbonyl group interacts with Mg²⁺ ions and it disturb the crystalline in the complexes form which turns polymer electrolyte sample into amorphous form [13]. The pure form
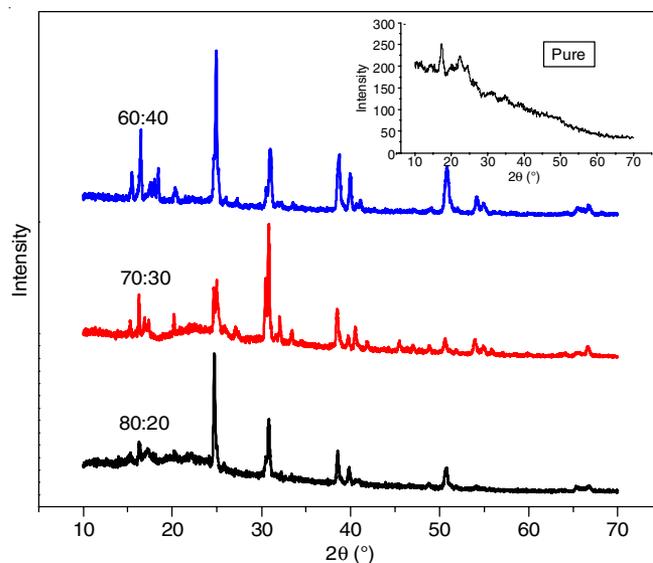

Fig. 1. XRD spectra of pure film PS:PVP:MgSO₄ (50:50:00 wt.%) and PS:PVP:MgSO₄ (40:40:20, 35:35:30, 30:30:40, wt.%)
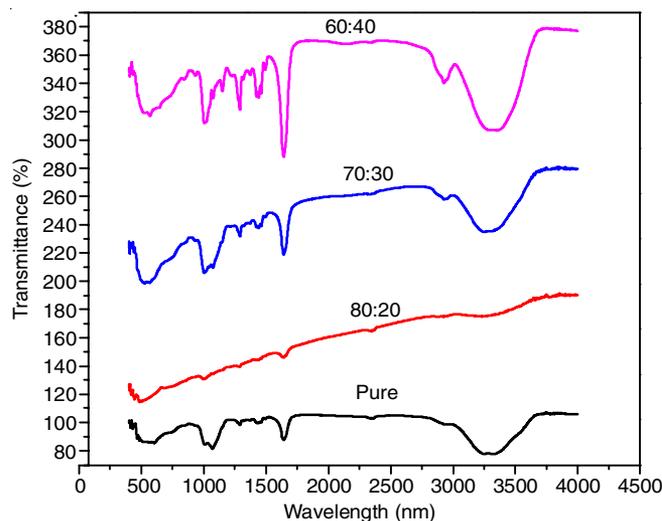

Fig. 2. FTIR spectra of pure PS:PVP:MgSO₄ (50:50:00 wt.%) and PS:PVP:MgSO₄ (40:40:20, 35:35:30, 30:30:40, wt.%)

of potato starch contains C-O absorption bands at 1120 cm⁻¹, O-H group can be observed at 3450 cm⁻¹. And the polyvinyl pyrrolidone (PVP) contains C-N group at bending frequency of 1260 cm⁻¹ and C=O group at 1655 cm⁻¹, O-H group at 3345 cm⁻¹ and also it contains C-H at 1446 cm⁻¹, CH₂ deformation modes in pyrrolidone, the salt MgSO₄ mixed with potato starch and PVP polymer blended system with 20 wt.%, 40 wt.%, 60 wt.% shows some variations in the spectrum with pure one. It is observed that a broad peak at bending frequency of 1136 cm⁻¹, which is responsible for SO₄²⁻ ion (Fig. 2). For pure film PS:PVP (50:50:00 wt.%) contains a broad band of O-H at stretching frequency of 3450 cm⁻¹ due to increasing in the MgSO₄ salt concentrations of PS:PVP:MgSO₄ (30:30:40, 35:35:30, 40:40:20 wt.%) as 3433 cm⁻¹, 3428 cm⁻¹ and 3331 cm⁻¹, respectively because of interactions between the salt ions-polymer ions. There is a narrow peak observed with a stretching frequency 1571 cm⁻¹ which is responsible for the C=O group

TABLE-1
FTIR DATA OF PURE SAMPLE PS:PVP:MgSO$_4$ (50:50:00 wt.%), PS:PVP:MgSO$_4$ (30:30:40, 40:40:20, 35:35:30 wt.%) SAMPLES

Assignments	Pure potato starch	PVP	Potato starch: PVP:MgSO$_4$ (50:50:00 wt.%) pure	Potato starch: PVP: MgSO$_4$ (30:30:40 wt.%)	Potato starch: PVP pure: MgSO$_4$ (40:40:20 wt.%)	Potato starch: PVP pure: MgSO$_4$ (35:35:30 wt.%)
O-H stretching	3450	3393	3450	3433	3321	3428
C-H stretching	2893	1446	1420	–	–	–
C=O stretching	–	1730	1571	1565	1554	1561
COO- Asymmetric stretching frequency	–	2980	–	–	–	–
CH$_2$ wagging	–	1260	1246	–	–	–
C-N stretching	–	–	–	1792	1780	1783
C-O in C-O-C of potato starch	1126	–	1110	–	–	–
C-O stretching frequency of potato starch	–	–	–	1295	–	–
SO$_4^{2-}$ bending frequency of MgSO$_4$	–	–	–	1135	1132	1126

in pure form PS:PVP:MgSO$_4$ (50:50:00 wt.%) which undergoes down field on addition of MgSO$_4$ in different concentrations like PS:PVP:MgSO$_4$ (30:30:40, 35:35:30, 40:40:20 wt.%) as stretching frequency 1565 cm^{-1}, 1561 cm^{-1} and 1554 cm^{-1}, respectively (Table-1). With this changes and shifting in the spectra of different concentrations, complexation has been taken place in different ratios of samples with MgSO$_4$ comparatively with the pure sample PS:PVP:MgSO$_4$ (50:50:00 wt.%).

UV-visible studies: The UV absorption studies of different concentration samples have been carried in between the range of 200-800 nm. UV studies gives the electronic excited states by UV light absorption also called energy bands, as it occurs due to absorption so it is an absorption edge [14]. The energy bands are of two types, conduction and valence bands. If the valence and conduction bands gets overlap each other gives the direct band gap where crystal momentum is zero, if the valence and conduction bands gets separated gives the indirect band gap where crystal momentum is non-zero [15]. It indicates that there is a flow of electrons in conduction band, which is restricted in the case of valence band. Based on absorption-edge we will calculate optical band gap that contains direct and indirect band gaps in the given samples. In Fig. 3, the pure film PS:PVP:MgSO$_4$ (50:50:00 wt.%) sample spectrum shows a peak at 218 nm for C=O ($\pi \rightarrow \pi^*$) group of PVP polymer and this peak shows more intensity for inorganic salt added samples on increasing the absorbance on Y-axis, due to more interactions between the salt MgSO$_4$ and polymer PVP [16]. Absorption edge or absorption coefficient α of samples with different concentrations can be calculated by using the formula [17]:

$$\alpha = 2.303\left(\frac{A}{L}\right)$$

where α is the absorption coefficient, A is the absorbance and L denotes the thickness of sample.

In Fig. 4, band gap of the film PS:PVP:MgSO$_4$ (35:35:30 wt.%) is having less band gap with 4.65 eV. Direct band gap $(\alpha h\nu)^2$ and indirect band gap can be measured by using the formulas [14]:

$$(\alpha h\nu)^2 = B(h\nu - E_{gd}) \text{ for direct allowed transitions}$$

$$(\alpha h\nu)^{1/2} = B(h\nu - E_{gi}) \text{ for indirect allowed transitions}$$
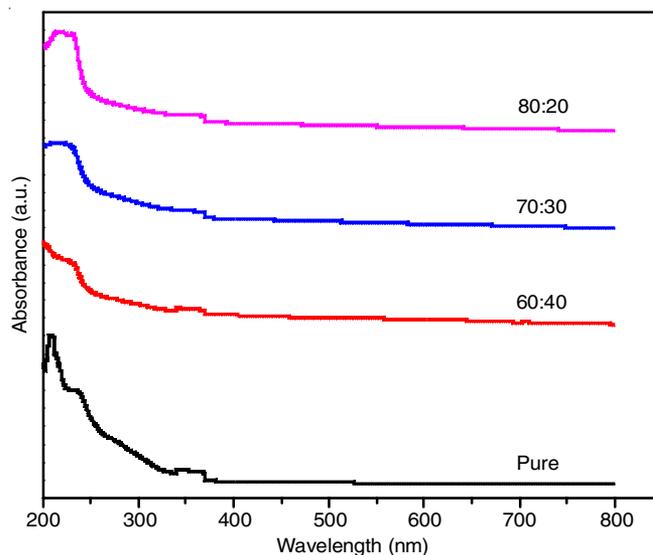

Fig. 3. Spectra of absorbance *vs.* wavelength of different sample pure PS:PVP:MgSO$_4$ (50:50:00 wt.%), PS:PVP:MgSO$_4$ (30:30:40, 35:35:30, 40:40:20 wt.%)
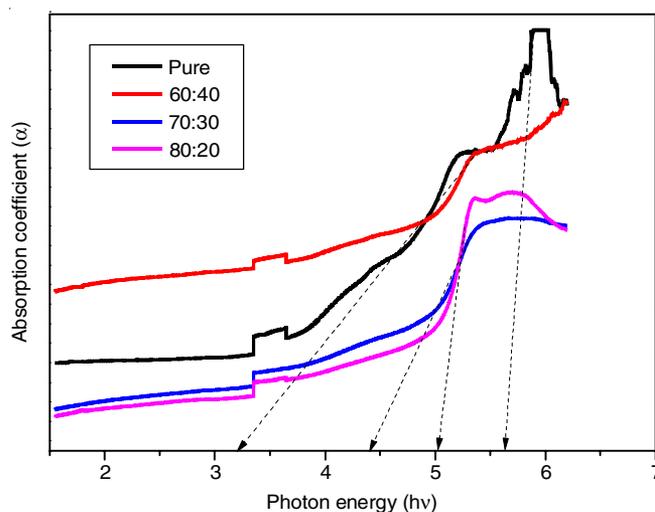

Fig. 4. Spectra of α *vs.* hν of different ratios samples pure PS:PVP: MgSO$_4$ (50:50:00 wt.%), PS:PVP:MgSO$_4$(30:30:40, 35:35:30, 40:40:20 wt.%)

where α is the absorption coefficient, hν denotes the photon energy and E$_g$ denotes the optical band gap.

In Fig. 5, direct band gap for PS:PVP:MgSO$_4$ (35:35:30 wt.%) is having less direct band gap as 4.7. From Fig. 6, indirect band gap of sample pure PS:PVP:MgSO$_4$ (35:35:30 wt.%) as 3.54 eV. Among all these concentrations PS:PVP: MgSO$_4$ (35:35:30 wt.%) is showing less indirect band gap due to more interactions between the salt and polymer in it. From this UV absorption analysis, one can say that PS:PVP:MgSO$_4$ (35:35:30 wt.%) solid biopolymer electrolyte will allow more transitions between valence band and conduction bands which will enhances the conductivity properties (Table-2).
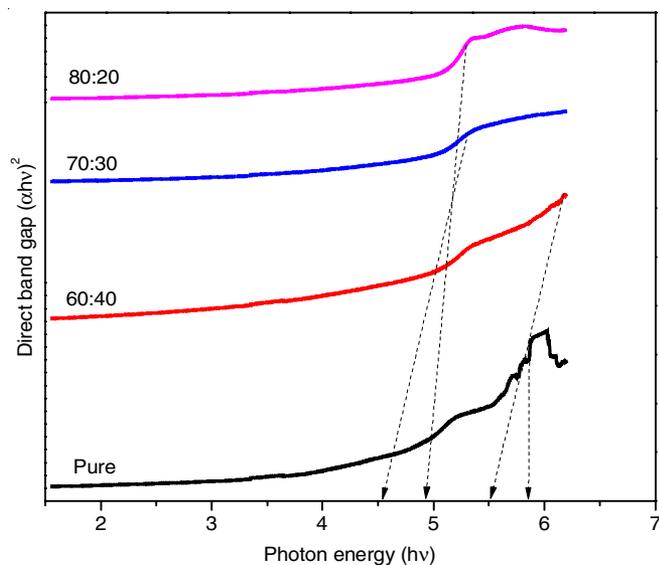

Fig. 5. Spectra αhν *vs.* hν of different ratios of sample pure PS:PVP:MgSO$_4$ (50:50:00 wt.%), 60:40PS:PVP:MgSO$_4$(30:30:40, 35:35:30, 40:40:20 wt.%)
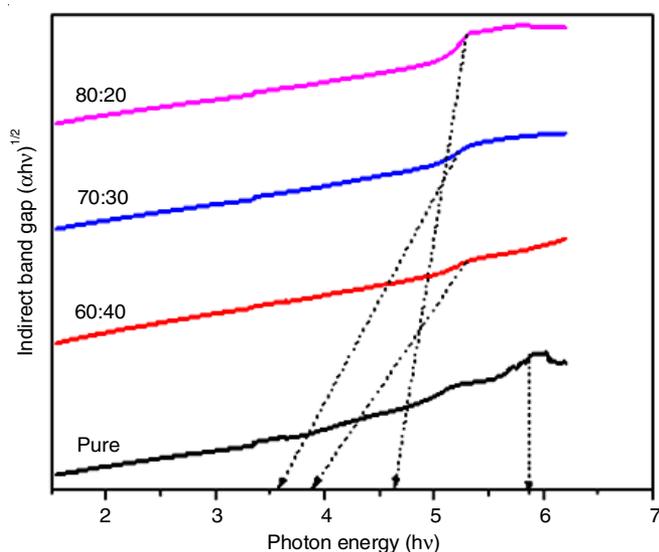

Fig. 6. Spectra (αhν)^2 *vs.* hν of different ratios of samples pure PS:PVP: MgSO$_4$ (50:50:00 wt.%)60:40 PS:PVP:MgSO$_4$(30:30:40, 35:35:30, 40:40:20 wt.%)

AC conductivity studies: The AC conductivity studies have been performed by using 3532-50 HIOKI LCR HITESTER at the frequency ranges between 42 Hz to 1 MHz. As we know that the size, concentration and charge of the charge carriers

TABLE-2
BAND GAP VALUES FOR SOLID
BIOPOLYMER ELECTROLYTES

Polymer electrolyte	Absorption edge (eV)	Direct band gap (eV)	Indirect band gap (eV)
50:50:00 (PS+PVP:MgSO$_4$)	5.7	5.85	5.84
30:30:40 (PS+PVP: MgSO$_4$)	5.6	5.57	3.82
35:35:30 (PS+PVP:MgSO$_4$)	4.65	4.7	3.54
40:40:20 (PS+PVP:MgSO$_4$)	4.95	4.93	4.62

will decide the conductivity [18] with the help of bulk resistance r, we can measure the conductivity from the formula: σ = t/a × r [19], where, 't' is the thickness of our sample (cm), 'a' is the contact area (cm^2) of sample and 'r' is the bulk resistance. Polymer acts as back bone for the conduction of ions in solid biopolymer electrolytes. To act as charge carrier, Mg^{2+}cation follow inter and intra hopping mechanism that depends up on capability of dissociation of salt and flexibility of back bone polymer (Fig. 7), the highest conductivity that is 4.2142 × 10^{-4} S/cm will be observed for concentration PS:PVP:MgSO$_4$ (35:35:30 wt.%) (Table-3), but the sample PS:PVP:MgSO$_4$ (30:30:40 wt.%) with more salt concentration shows less conductivity 7.577 × 10^{-5} S/cm (Table-3) comparatively with 35:35:30 and 40:40:20, which is due to immobile ions aggregation [20]. From Fig. 7, it is assured that this solid biopolymer electrolyte can conduct ions through it.
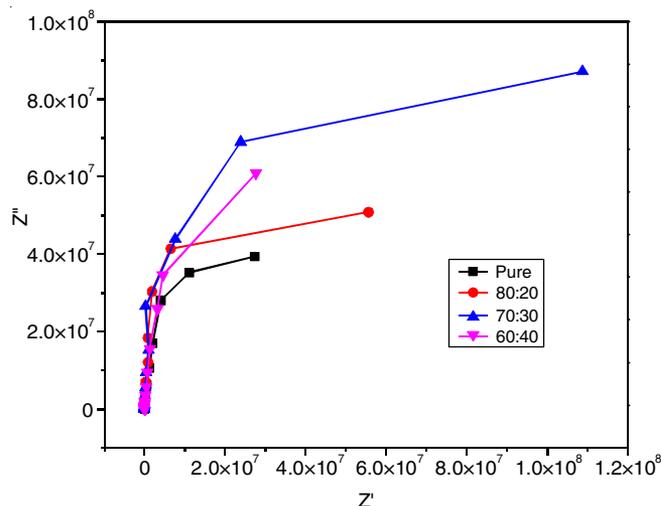

Fig. 7. Ionic conductivity of pure PS:PVP:MgSO$_4$ (50:50:00 wt.%) PS:PVP: MgSO$_4$ (40:40:20, 35:35:30, 30:30:40 wt.%)

TABLE-3
CONDUCTIVITY STUDIES OF DIFFERENT SAMPLES

Films	Conductivity at room temperature
PS:PVP:MgSO$_4$ (50:50:00 wt.%)	3.5720 × 10^{-9} S/cm
PVP:PS:MgSO$_4$ (40:40:20 wt.%)	3.5720 × 10^{-5} S/cm
PVP:PS:MgSO$_4$ (35:35:30 wt.%)	4.2142 × 10^{-4} S/cm
PVP:PS:MgSO$_4$ (30:30:40 wt.%)	7.5770 × 10^{-5} S/cm

Dielectric studies: To study the dielectric properties of high conducting solid biopolymer electrolyte PS:PVP:MgSO$_4$ (35:35:30 wt.%) electrolyte, a 3532-50 HIOKI LCR HITESTER was used. In this, at an initial frequency the best conductivity sample shows the high dielectric constant which can be defined

as an amount of dipole moment alignment with in the given quantity [21]. At room temperature, on increase in the frequency on x-axis, dielectric constant (ε') will be decreasing (Fig. 8), this is because of decreasing in the polarization at electrode – electrolyte interface [22] and it can be calculated by using the following formula [21]:

$$\varepsilon' = \frac{c_p t}{\varepsilon_0 a}$$

where c_p is parallel capacitance, t thickness of the sample (μm), ε_0 is permittivity of free space.
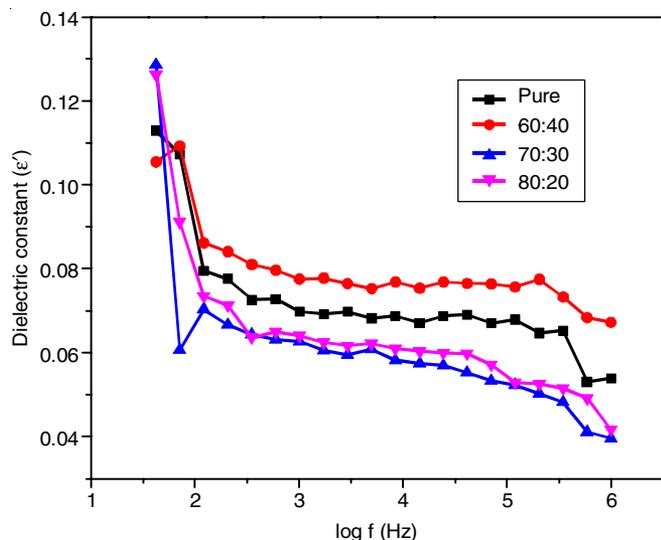

Fig. 8. Dielectric constant of the sample PS:PVP:MgSO$_4$(35:35:30 wt.%) electrolyte

In a same way, dielectric loss in Fig. 9 can be defined as energy loss by the ion in motion. At room temperature, there is a decrease in the dielectric loss (ε'') while increase in the log frequency on *x*-axis, this is because of decline in the magnitude of dispersion that will caused by the reduced proportion of the material in amorphous state [22] and it can be calculated by using the formula [21]:
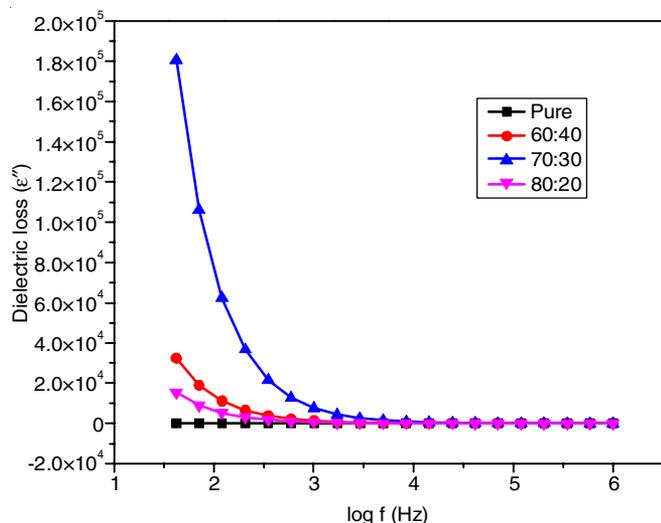

Fig. 9. Dielectric loss of highest conductivity sample PS:PVP:MgSO$_4$ (35:35:30 wt.%)

$$\varepsilon'' = \frac{\sigma}{\omega \varepsilon_0}$$

where σ means of ionic conductivity, $\omega = 2\pi f$ means angular frequency, ε_0 means permittivity of free space.

At room temperature, tangent loss in Fig. 10, which can be obtained by the ratio between the dielectric constant (ε') and dielectric loss (ε''), which will increase with respect to the increase in log frequency [21], it can be given as follows:

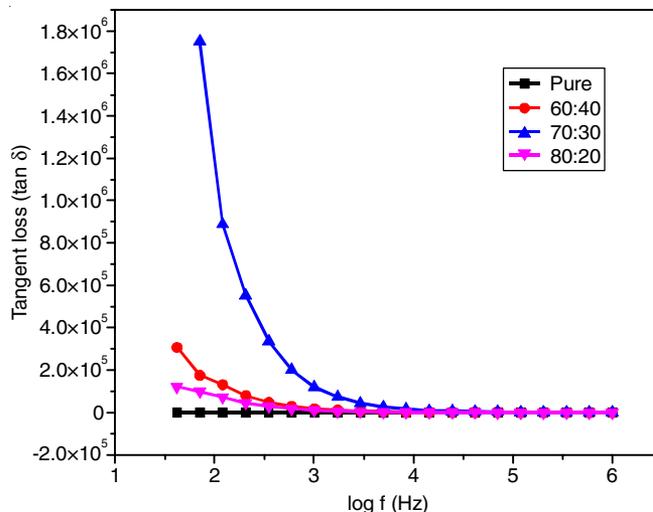$$\tan\delta = \frac{\varepsilon''}{\varepsilon'}$$

Fig. 10. Tangent loss of best conductivity sample PS:PVP:MgSO$_4$ (35:35:30 wt.%)

Linear sweep voltammetry: To study the electrochemical stability of highest conducting solid biopolymer electrolyte, we have performed the LSV studies as Ag/solid biopolymer electrolyte/Ag (35:35:30 wt.%) by using PARSTAT PMC 2000A. A rapid increase in the current at 0.48 V within the potential range of -0.4 V to 1.4 V were observed (Fig. 11), where the voltage break-down occurs, which shows the solid polymer electrolyte's electrochemically stable value that helps to estimate the lifetime performances of batteries [23]. From this potential value, one can say that before 0.48 V there is no countable current flow [24]. And also LSV studies have proven that the prepared solid biopolymer electrolyte shows the potential stability up to 0.48 V. The obtained potential value of polymer electrolyte is adequate to the electrochemical application with promising current flow from 0.48 V for magnesium ion-based batteries.

Cyclic voltammetry studies: The CV analysis of highest conducting polymer electrolyte (35:35:30 wt.%) with conductivity 4.2142 $\times$ 10^{-4} S/cm was done at scan rate of 50 Mv/s by using PARSTAT PMC 2000A with a fabricated cell of Ag/SPE/Ag. In CV analysis, the cyclic voltammogram varies with scan rates as if the scan rate is more the graph will be in rectangular due to rapid migration of ions will be there at large scan rates. The magnesium ion conduction in solid biopolymer electrolytes is shown in Fig. 12 with the potential value ranges from 0.2 V to 1.0 V and the peaks of current have been observed
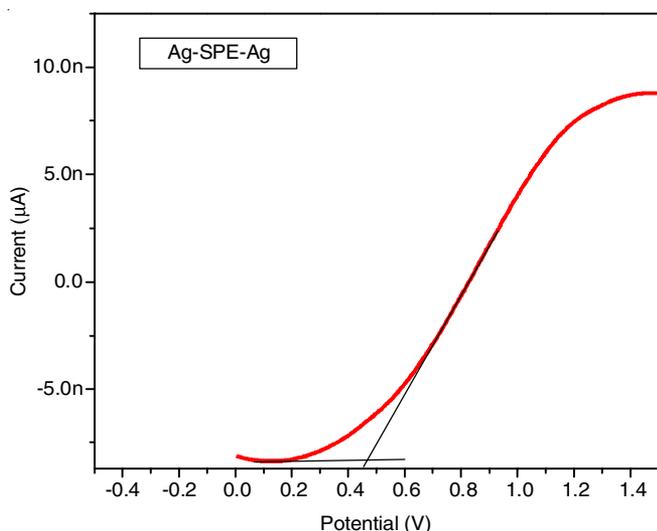
Fig. 11. Linear sweep voltammetry LSV of highest conducting sample (PS:PVP:MgSO$_4$) (35:35:30 wt.%)
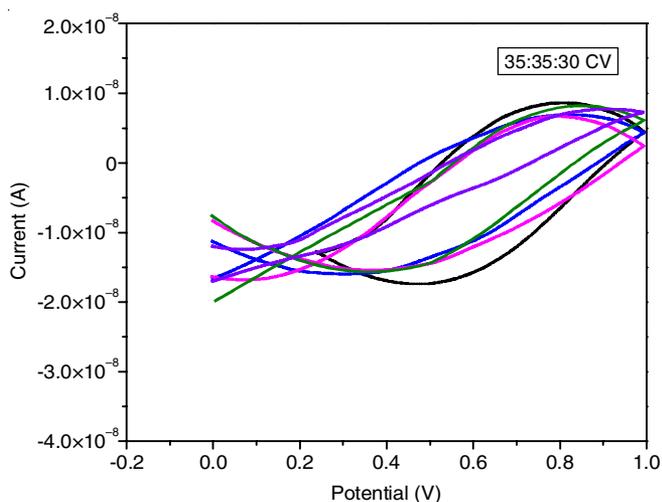

Fig. 12. Cyclic voltmeter studies of highest conducting sample PS:PVP: MgSO$_4$ (35:35:30 wt.%) electrolyte

characteristically from the the cyclic voltammogram, which gives that the deposition and resolution occurs at of conducting ions of Mg^{2+} at the interface of Ag/SPE [25]. The oxidation peak can be observed at 0.85 V, cathode peak can be observed at 0.45 V and the voltage of the solid polymer electrolyte is 1 V. Fig. 12 shows that the electrolyte is capable to have stable cycles of oxidation and reduction for the application purpose of charging-discharging batteries.

Conclusion

Solid state biopolymer electrolytes prepared from the potato starch (PS) blended with PVP (polyvinylpyrrolidone) polymer and inorganic salt MgSO$_4$ by solution casting technique. Characterization studies such as XRD, FTIR and UV-visible (200-800 nm) demonstrated that the electrolyte with the concentration of PS:PVP:MgSO$_4$ (35:35:30 wt.%) shows the good amorphous form by complexation with the salt. The conductivity studies performed at 42 Hz to 1MHz, showed that the electrolyte concentration of PS:PVP:MgSO$_4$(35:35:30

wt.%) has highest ionic conductivity 4.2142 × 10^{-4} S/cm at room temperature. From dielectric studies, charge holding capacity of PS:PVP:MgSO$_4$ (35:35:30 wt.%) has been calculated. The LSV and CV studies of highest conducting electrolyte PS:PVP:MgSO$_4$ (35:35:30 wt.%) showed the stability in the potential as stable redox potential. These results proved that this solid biopolymer electrolyte can be a potential candidate as electrolyte in the Mg^{2+} ion-based batteries.

CONFLICT OF INTEREST

The authors declare that there is no conflict of interests regarding the publication of this article.

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