Synthesis and characterization of multifunctional ZnBr₂/PVA polymer dielectrics

Jagadish Naik*, R. F. Bhajantri^{†,‡}, Sunil G. Rathod*,
T. Sheela* and V. Ravindrachary*

**Department of Physics, Mangalore University
Mangalagangothri - 574 199, Karnataka, India*

*†Department of Physics, Karnatak University
Pavate Nagar, Dharwad - 580 003, Karnataka, India*

‡rfbhajantri@gmail.com

Received 24 May 2016; Revised 2 October 2016; Accepted 8 October 2016; Published 9 November 2016

Different weight percentage of ZnBr₂ doped poly(vinyl alcohol) (PVA) free standing composite films were prepared using solution casting method. These films were characterized for analyzing structural, dielectric, electrochemical properties. This paper mainly focused to understand the contribution of physical phenomenon on conductivity in terms of dielectric parameters. FTIR spectrum confirms the interaction between ZnBr₂ and PVA. Pseudo-capacitive behavior observed from cyclic voltammograms. Dielectric properties of the composites follow non-Debye type behavior. The conducting phenomenon occurs due to hopping of ions between coordination sites present in the composite and the segmental relaxation of polymer chain.

Keywords: Poly(vinyl alcohol); polymer electrolytes; cyclic voltametry; dielectrics; zinc bromide.

1. Introduction

Dielectric spectroscopy in materials is based on determining the frequency-dependent complex permittivity.¹ This provides the information on dielectric permittivity, electrical conductivity, and molecular dynamics of wide range of material compositions. The dielectric parameters related to relaxation processes plays fundamental role in understanding phenomenon involved in ion conducting polymers. For example, the ability of the polymer matrix to dissolve salt will be measured in terms of dielectric constant. Frequency-dependent conductivity and relaxation processes are very much sensitive to the motion of charged species and dipoles present in the polymer matrix, that means the dielectric parameters are strongly dependent on the nature of additive and temperature.² It is also used for studying the charge distribution, visco-elastic state, physical structure and thermal motion of the polar groups, which gives the information about the dielectric behavior of a polymer. Higher dielectric constant is easier to achieve by introducing additives in materials, but it also enhances energy dissipation (dielectric loss). It is difficult to prepare a material having high dielectric constant, high break down strength with low dielectric loss.¹ Designing dielectric material to achieve desired dielectric properties requires careful consideration of net polarity of the combined structures. If combination involves polar polymer and highly polarizable elements like aromatic ring structures, bromide, iodide may yield better dielectric properties.^{2,3}

Fast growing micro and nano electronic devices require materials with high dielectric strength, high dielectric permittivity, low dielectric loss and high tunability in the wide frequency range. Traditionally, the dielectric materials were made from inorganic materials like mica, silica, etc. Nowadays, polymers have been attracted as a dielectrics because of their ability to achieve giant dielectric constant, stable capacitance, low dielectric loss, high dielectric break down strength, long life time and high insulation characteristics, which are essential properties for super capacitor, electrical cable insulation, organic emitting diodes, photovoltaic cells, nonvolatile memories, electronic packaging and components. The power sources like batteries, fuel cells depend on size, chemistry, voltage, specific energy, specific power, self-life, etc. The advantages like low cost, flexibility, high ionic conductivity and portability made researchers to look at polymer composites for battery applications. The combination of flexible devices generates extensive opportunities for the multifunctional units of common hard electronics. Many investigations have been reported on polymer electrolytes using Li⁺, Na⁺, K⁺ monovalent ions in batteries. Due to low operating voltage, these polymer batteries have shown low energy density. Therefore, researchers are looking towards potential higher energy multivalent metal ions like Zn²⁺, Mg²⁺, Al³⁺, etc.^{4,5}

The basic and applied scientific research related to poly(vinyl alcohol) (PVA)-based composites have been reported

for various applications ranging from insulators to solid-state conducting devices. PVA is a most attractive polymer, because it possesses hydrophilic in nature, high density of reactive functional groups, inexpensive and abundantly available. Flexibility in PVA polymer chains arises due to either intra or inter molecular associations and dependent on temperature, contributes largely to the relaxation processes aided by segmental motions and group rotation in chains. Its properties like high dielectric strength, good charge storage capacity, high mechanical strength and additive-dependent property, makes PVA as the potential polymer, applied as a dielectric.⁶

Zinc related compounds are getting more attention, because of their great energy storage capacity, inherent electrochemical reversibility, high ionic conductivity at low-temperature, high solubility of zinc salts and the availability of rugged, compact, nontoxic and long-lived positive electrodes competitive cost, abundant in nature, safety in oxygen and humid atmosphere. Ionic radii of Li^+ (68 pm) and Zn^{2+} (74 pm) are comparable. Hence, in place of lithium ions, Zn^{2+} ion may be used.^{5,7} Zinc bromine flow batteries are known for high efficiency and low cost energy storage devices, but low operating current density is the drawback. Its theoretically high energy density (432 Wh/Kg^{-1}) attracted many researchers to consider zinc bromine as a battery element. Formation of $\text{Br}^{2-}/\text{Br}^{3-}$ elements, Zn^{2+} interactions with Br^{2-} leads to higher storage and chemical energy conversion to make Zinc Bromine as potential element for battery application. $\text{Zn}-\text{Br}_2$ battery has disadvantages also like self-discharging phenomena associated with high solubility of Br_2 in aqueous electrolytes and Zinc dendrite formation. To overcome with these difficulties, bromine extraction by organic solvent, using charcoal, introducing bromine complex formation reaction was used but these approaches depressed Br^{2-} activity. The highest performance of ZnBr_2 in flow battery, made us to think about ZnBr_2 in the form of solid polymer electrolyte.^{5,8}

There are few attempts reported regarding ZnBr_2 and PVA-based electrolytes separately. E Sheha *et al.* reported the dielectric and frequency-dependent conductivity behavior of sulfuric acid doped sodium bromide/PVA composite for the application of magnesium-based batteries.⁹ Bhargav *et al.* prepared NaBr doped PVA, resulted in enhancement of conductivity with respect to concentration as well as temperature.¹⁰ Temperature- and concentration-dependent variation in dielectric parameters were reported by Hema *et al.* for ammonium bromide/PVA composites. Cantu *et al.* studied ZnBr_2 catalyzed chemical effects in poly (acrylonitrile-co-butadiene).¹¹ Peng *et al.* achieved capacity up to 19 mAhmL^{-1} and an energy efficiency of 69% for TiO_2 filled ZnBr_2 /Nafion-based dye sensitized solar cells.¹² Hagan *et al.* prepared ZnBr_2 /PEO to understand the structural and conductivity in polymer electrolytes.¹³

Recently, Mengoli *et al.* reported about the addition of bromine related compounds in polymer electrolytes and

stated that the $\text{Br}^-/\text{Br}^{3-}$ couple could be cycled within the polymer, but the stability of polymer composite is insufficient for battery application.¹⁴ Only some parameters related to dielectric behavior were extensively studied for many insulating materials. Understanding the dielectric nature of these materials including PVA was partial. The studies on the effect of different additives in polymer composites have been reported for understanding the variation in fundamental properties.¹⁴

We aimed to prepare the ZnBr_2 doped PVA composites looking at successful story of ZnBr_2 as flow battery and PVA as dielectric matrix for many electrolytic composites. Incorporation of ZnBr_2 may increase the conductivity to the PVA matrix as well as variation in dielectric behavior. Therefore, we report the study of dielectric behavior in ZnBr_2 doped PVA composite and its various applications. To the best of our knowledge, there is no work reported on the dielectric, structural and electrochemical properties of ZnBr_2 /PVA polymer composite. PVA is a biocompatible, nontoxic and synthetic polymer, having good transparency and fast charge transfer at electrode–nanocomposite interface.

2. Experimental Details

2.1. Materials and preparation of polymer composites

The polymer PVA with molecular weight 125,000 was procured from Himedia laboratories Pvt. Ltd India. The ZnBr_2 of molecular weight $229.19 \text{ gm mole}^{-1}$ procured from Loba Chemie Pvt. Ltd. India. The ZnBr_2 /PVA composites were prepared by solution casting method using an aqueous solvent. A predetermined weight % (wt.%) of PVA dissolved in double distilled water and stirred it for 48 h at 40°C for complete dissolution. The calculated weight of ZnBr_2 was also dissolved in distilled water separately to prepare 5 to 25 wt.% composites. Then both these solutions were mixed and stirred at room temperature continuously until the solution becomes viscous. The resulting solution was poured on to a cleaned Petri glass plates kept in a hot air oven and dried under air atmosphere at ambient temperature. After complete drying, the films were peeled off and kept in vacuum desiccators for further study.¹⁵ We got the composite films of thickness about $70 \mu\text{m}$.

2.2. Characterization methods

The infrared spectra were recorded using a Shimadzu FTIR-8700 spectrophotometer in the wave number range of $400\text{--}4000 \text{ cm}^{-1}$ with resolution of 4 cm^{-1} . The electrochemical performance of the composite films has been evaluated using CH electrochemical analyzer by sandwiching the films between Zinc pasted steel electrode and platinum electrodes with the scan rate of 0.01 mV/s and 0.05 mV/s . The dielectric measurements in the frequency range from 4 Hz to 5 MHz have been performed at room temperature and at different

temperatures using HIOKI-IM3570 high precession impedance analyzer interfaced to a computer by sandwiching the film samples between two steel electrodes of 1.3 cm diameter.¹⁶ Before measurement, the samples were again dried to reduce the solvent residual effect and the instrument were calibrated with open circuit and closed circuit using standard methods to reduce errors. The capacitance and dielectric loss factors were measured and repeated four to five times for repeatability in the values.

3. Results and Discussion

3.1. FT-IR analysis

The interaction between metal halide salt and polymer matrix has been studied using FTIR plots in transmittance mode as shown in Fig. 1. The changes induced due to addition of ZnBr_2 in vibrational modes of PVA were analyzed. Presence of PVA shows strong IR bands in the higher wave number region. The most characteristic feature of the broad band of PVA is observed at 3358 cm^{-1} . Upon addition of ZnBr_2 , this band shifted to 3421 cm^{-1} with loosing broadness. This band is assigned to O–H stretching present in inter and intra molecular hydrogen bonds of the composite. The IR band at 2941 cm^{-1} is occurred due to stretching of C–H from alkyl group and this band was shifted to 2914 cm^{-1} . The band at 1736 cm^{-1} got shifted towards 1785 cm^{-1} is assigned to C=O stretching. The band at 1436 cm^{-1} has shifted towards

1460 cm^{-1} attributed to the C–H₂ bending. The other bands at 1377 cm^{-1} and 1267 cm^{-1} were assigned to C–H₂ wagging and C–H rocking. The band at 1096 cm^{-1} is assigned for C–O stretching, O–H band and C–H deformation of Pure PVA, 947 cm^{-1} is for trans C–H wagging and C–H out of plane bending. The band for skeletal C–O stretching is observed at 850 cm^{-1} and the intensity of this band is decreased with respect to ZnBr_2 concentration. The band at 671 cm^{-1} is attributed to O–H twisting and another broad band peaking at 617 cm^{-1} is observed and assigned to cis C–H wagging. Broadness of this peak also reduced as ZnBr_2 content increased. The intensity of the bromide band at 2363 cm^{-1} is increased with increase in ZnBr_2 wt.%. These variations in FTIR spectrum clearly confirm the interaction between ZnBr_2 and PVA matrix and formation of ZnBr_2 /PVA composite.^{15,17}

3.2. Dielectric studies

The relaxation response of the polymer composite (dielectric medium) to an external electric field of microwave frequencies is expressed in terms of dielectric permittivity (ϵ^*) as follows:

$$\epsilon^* = \epsilon' + i\epsilon''.$$

It contains real part (ϵ' -dielectric constant) and imaginary part (ϵ'' -dielectric loss) and were calculated using the standard formula given below.

$$\epsilon' = \frac{Cd}{\epsilon_0 A} \quad \text{and} \quad \epsilon'' = \epsilon' \tan \delta,$$

where C is capacitance, d is thickness of the sample, A is the area of the electrode and ϵ_0 is the permittivity of the free space ($8.85 \times 10^{-12}\text{ SI}$).^{16,18,19} Dielectric constant arises in polymers due to polarization of dipoles by the application of electric field. Dielectric constant illustrates the contribution of doping in enhancing the number of charge carriers in the polymer composite. Our prepared composites containing ion channels are selectively permeable to different ions. In the composite, the positively charged and negatively charged ions were separated over a polymer matrix randomly or may be attached to the polymer chains with weak interactions. When potential is applied across the electrolyte, these ions start moving towards corresponding electrodes and make a barrier of ions. This barrier produces dielectric constant.

Figure 2(a) represents frequency-dependent dielectric constant for different wt.% of ZnBr_2 doping in PVA. A typical well-known behavior observed at lower frequency region is an increase in dielectric constant as ZnBr_2 concentration increased in PVA. The increase in dielectric constant at lower frequency is due to polarization effect, contributed by the charge carriers, accumulated near the electrode. The decrease in dielectric constant with increase in frequency is due to inability of dipoles present in the polymer composite to orient themselves in the direction of the applied electric field. The inertia of the dipole opposes to rotate along with oscillating

Fig. 1. FTIR spectra of ZnBr_2 /PVA polymer composite.

Fig. 2. Dielectric constant versus frequency (a) at room temperature for different concentrations of ZnBr₂ doped PVA and (b) 20 wt.% ZnBr₂ doped PVA composites at different temperatures.

electric field. The polarization decreases due to accumulation of charge carriers and hence, the dielectric constant decreases. The temperature-dependent dielectric constant is shown in Fig. 2(b). The dielectric constant increases with increase in temperature due to enhancement in the contribution of ionic mobility and polarization effect.²⁰ It shows that the charge carriers are thermally activated. With rising temperature the higher charge carrier density and orientation are facilitated. The dielectric constant shows maximum for 20 wt.% ZnBr₂ doped PVA composite.

3.3. Dielectric loss studies

Dielectric loss is another important parameter to determine the energy density of the polymer under varying electric fields. Dielectric loss originates due to conduction losses, dipole losses and vibrational losses. The frequency dependence of the dielectric loss for the ZnBr₂ doped PVA composites are presented in Fig. 3(a). The dielectric loss of the 20 wt.% ZnBr₂ doped PVA reaches about 560 compared to 38 for 5 wt.% ZnBr₂ doped PVA film. The larger value of dielectric loss at low frequency is due to the presence of

Fig. 3. Dielectric loss versus frequency (a) at room temperature for different concentrations of ZnBr₂ doped PVA and (b) 20 wt.% ZnBr₂ doped PVA composites at different temperatures.

moving charges in polymer matrix. High dielectric loss observed at lower frequency region may be due to the presence of high energy barrier for a switching dipole direction and strong polarization hysteresis, and also due to the loss in electric conductivity, caused by the incorporation of the $\text{Zn}^{+2}\text{Br}^{-2}$. The dielectric loss decreased with increase in frequency, due to immobility and reversibility of dipoles, and better segmental stability, build in the polymer network. Figure 3(b) depicts the frequency dependence of dielectric loss at different temperatures. The dielectric loss also increases with increase in temperature. The increase in temperature may results in increase in the viscosity, which enhances the friction of the rotating dipoles and degree of dipole orientation. During migration, the charge carriers may be trapped in the dielectrics which produce distortions like lattice defects, impurity centers, voids, strains. These defects distort the field and enhance the dielectric loss.^{18,19} Both dielectric loss and dielectric constant increases at lower frequency range confirms that the prepared composites follow non-Debye effect, due to the presence of electrode polarization and space charge effect.²¹ Compared to pure PVA, the ZnBr_2 doped PVA composites shown an increment in the dielectric properties. This increment is attributed to the interaction between ZnBr_2 and PVA matrix. This interaction also enhances the conducting pathways in the polymer matrix which helps in mobility of ions.

3.4. Electric modulus studies

The complex electric modulus is one among the other inter-related parameters like impedance, admittance and permittivity which contributes to total conductivity of the material. The electric modulus provides information about the conductivity and conductivity related relaxation in polymers. It

expresses the relaxation of the electric field, when electric displacement remains constant in the material. The electrical modulus (M^*) is the reciprocal of complex permittivity (ϵ^*).

$$M^* = \frac{1}{\epsilon^*} = M' + iM'',$$

where M' and M'' are the real and imaginary parts of the electrical modulus. M' and M'' can be expressed in terms of complex dielectric parameters with following equations.¹⁸

$$M' = \frac{\epsilon'}{\epsilon'^2 + \epsilon''^2} \quad \text{and} \quad M'' = \frac{\epsilon''}{\epsilon'^2 + \epsilon''^2}.$$

Figure 4(a) represents the variation of dielectric modulus M' as a function of frequency at room temperature for different wt.% of ZnBr_2 doped PVA composites. At lower frequencies the value of M' is not equal to zero and also with increase in ZnBr_2 wt.% the M' decreases at lower frequencies, indicates that the contribution of electrode polarization has considerable effect on the conductivity phenomenon. It is clearly seen that the real part of the dielectric modulus M' increases and reach constant value with increase in frequency.

The plateau regions present in the lower frequency and higher frequency regions were the confirmation of presence of electrode polarization effect contributing towards dielectric and electric properties of the polymer composites. The almost constant values for M' at higher frequencies is because of the presence of less effective interfacial polarization. When the frequency is high, the large dipoles formed at interfaces do not follow the electric field. Figure 4(b) represents the variation of dielectric modulus M' as a function of frequency at different temperatures for 20 wt.% of ZnBr_2 doped PVA composite. The decrease in M' values with increase in temperature is due to increased motion of large parts of

Fig. 4. Real part of electric modulus versus frequency (a) at room temperature for different concentrations of ZnBr_2 doped PVA and (b) 20 wt.% ZnBr_2 doped PVA composites at different temperatures.

Fig. 5. Imaginary part of electric modulus versus frequency (a) at room temperature for different concentrations of ZnBr₂ doped PVA and (b) 20 wt.% ZnBr₂ doped PVA composites at different temperatures.

molecular chains in the polymer. As an increase in temperature, the orientation of large dipoles becomes easier. Therefore M' decreased, consequently ε' increased. The temperature becomes ineffective at higher frequencies, because the inability of the dipoles orient themselves at higher frequencies.^{18,19}

Imaginary part of the dielectric modulus versus frequency plot as shown in Fig. 5(a) is an evident for relaxation process. As increase in ZnBr₂ wt.% the M'' decreased at lower frequency. This is because, as increase in wt.% the capacitance increased, due to large number of charge carriers accumulated at electrode–electrolyte interface (electrode polarization effect). At higher frequencies, a broad range peak is observed and this peak represents the conductivity relaxation for the relaxation time distribution of free charge carriers. The broad nature predicts a non-Debye type behavior. As increase in ZnBr₂ the intensity of the relaxation peak decreased due to large amount of free charge carrier concentration and motions within the polymer matrix. Figure 5(b) shows the temperature-dependent behavior of M'' with respect to frequency for 20 wt.% doped polymer composite. The value of M'' decreased with increase in temperature.^{19,22}

Reorientation of dipoles in the polymer composite leading to a phenomenon called dielectric relaxation and the presence of dielectric relaxation process will show a peak in ε'' spectrum. But the long range conduction process and dielectric relaxation process is different. In a polymer electrolyte, each ion was surrounded by electrical potential. During movement of ions from one site to another site, the electrical potential will disturb and form a perturbed potential. This perturbed potential will disturb motion of any other ion comes in its field. This kind of cooperative motion of ions leads to a conduction process with distribution of relaxation time. The

observed nonexponential decay in the spectrum represents both the phenomenon. To distinguish these two processes, the comparison between M^* and ε^* plots are required. No peaks were observed in the dielectric spectra (ε''). The modulus spectra (M'') show a peak at higher frequency region. This is evident for conduction process, which involves both ionic motion and polymer segmental motion. In this polymer composite the conducting phenomenon occurs due to charge migration of ions between coordination sites present in the polymer composite as well as the segmental relaxation of polymer chain.¹⁹

3.5. Ionic conductivity studies

When a potential is applied across the electrode, the polymer matrix becomes freely permeable to ions. This leads to rapid movement of ions followed by the reversal of the polarity at the electrode. Rearrangement of ions towards the electrode results in conducting phenomenon. The ionic conductivity depends on many parameters like number of charge carriers, charge migration between the coordinate sites of the polymer host, the polymeric chain segmental motions and the morphological structure of the polymer. The frequency-dependent conductivity were calculated using formula

$$\sigma_{ac} = 2\pi f \varepsilon_0 \varepsilon' \tan \delta,$$

where f is the frequency, ε_0 is the permittivity of the free space, ε' is the dielectric constant, $\tan \delta$ is loss factor.¹⁶ The frequency-dependent conductivity spectra of PVA-based electrolyte with various ZnBr₂ concentrations at room temperature are shown in Fig. 6(a). The polymer PVA acts as a medium for ionic movement. The increase in AC conductivity with respect to frequency is the result of ionic motion

Fig. 6. AC conductivity versus frequency (a) at room temperature for different concentrations of ZnBr_2 doped PVA and (b) 20 wt.% ZnBr_2 doped PVA composites at different temperatures.

facilitated by the conducting pathways formed due to doping of ZnBr_2 . The figure shows dispersion in low frequency region and plateau at higher frequency region. Dispersion region observed at lower frequency due to space charge polarization at the blocking electrode. It is the signature of presence of electrode polarization phenomenon. Higher frequency plateau region occurred because of hopping of mobile ions and also confirms the formation of conductive pathways that facilitate ionic motion and hence high ionic conductivity is achieved. Inability of the dipoles to perform consecutive hops in particular time period leads to the formation of plateau region in disordered solids. Looking at conductivity plots and dielectric constant plots one can tell that the ion motion and polymer chain segmental motions were coupled.²³ Enhancement in the dielectric loss with increase in ZnBr_2 wt.% can be correlated to conductivity. PVA exhibits intense dielectric α -transition due to the presence of rotation of polar bonds of the side groups. Addition of salt changes chemical composition of the monomer due to the formation of hydrogen bonds with OH groups in the complexation process. In turn the polymer becomes flexible with increase in conductivity.

The conductivity increased with increase in temperature as observed in Fig. 6(b). This kind of behavior is the evidence for conductivity and it is the thermally activated process. At high frequency region, the AC conductivity is governed by Jonscher power law equation

$$\sigma_{ac} \propto \omega^s,$$

where s is frequency exponent and ω is angular frequency. The total conductivity can be expressed as

$$\sigma_{ac} = \sigma_{dc} + A\omega^s,$$

where σ_{dc} is DC conductivity and A is pre-exponential factor.²² The frequency exponent s can be calculated by slope in

the high frequency region of log conductivity versus log frequency graph and tabulated in Table 1. According to Jonscher, if $s \approx 1$, then phenomenon is related to DC conductivity, if $0 < s < 0.7$, then the phenomenon is related to correlated barrier hopping (CBH) mechanism, if $0.7 \leq s < 1$, then the transport phenomenon is related to quantum mechanical tunneling (QMT) modal. In CBH modal, the thermally activated charge carriers hop between two localized sites over the potential barrier separating them. In QMT modal the charge carrier motion is provided by phonon assisted QMT between localized states near the Fermi level. In our case the calculated values for s is decreased with increase in temperature and its value is well in between 0 and 0.7 ($0 < s \leq 1$). These results confirm the existence of CBH mechanism. The s value nearly equals to 0.7 tells that the contribution of QMT may not be neglected completely, but the contribution will be very less. From these s values, we calculated the maximum barrier height (W_m) given by standard formula

$$W_m = \frac{6K_B T}{1 - S},$$

where K_B is Boltzmann constant and T is temperature, and tabulated in Table 1. The maximum barrier height increased

Table 1. Temperature-dependent AC conductivity parameters.

Temperature (K)	$s \pm 0.0015$	W_m (eV)	λ_{wm} (nm)	$-\log A \pm 0.01$
303	0.74878	6.237011	198.925	12.42
313	0.64707	4.586103	270.535	11.65
323	0.69157	5.415443	229.104	12.04
333	0.67628	5.319401	233.241	12.55
343	0.57836	4.206689	294.935	7.96
353	0.60835	4.660835	220.026	8.05

Fig. 7. Cyclic voltammograms of ZnBr_2 doped PVA composites at room temperature for scan rate of (a) 0.01 Vs^{-1} and (b) 0.05 Vs^{-1} .

with increase in temperature. Wavelengths corresponding to W_m were calculated using the formula

$$\lambda_{W_m} = \frac{hc}{W_m}.$$

The energy corresponding to the wavelengths is in the ultraviolet range. The charge carriers reside in the potential well formed due to Coulombic repulsive force between charge carriers (ions). Many ions present in the system, therefore potentials superpose with each other and yields single ion potential. When the ions get enough energy, then the ions will hop from one site to another. During hopping, it may back hop to initial site or it may move continuously in the forward direction by creating new absolute potential with increase in the back hop barrier height. Therefore, W_m gives the energy required for hopping. The values of $\log(A)$ tabulated in Table 1 are obtained from the intercept of the plot of $\log$ conductivity versus $\log$ frequency in the high frequency region, where the $\log(A)$ represents the DC conductivity at zero frequency. As increase in temperature, the calculated DC conductivity decreases, and the electrons were scattered more frequently by lattice vibrations or phonons in the polymer composite, which enhances the resistivity of the polymer composite leading to decrease in DC conductivity. Overall ac conductivity follows universal dynamic response, which is widely observed in disordered materials like conducting polymers, ionically conducting glasses, doped crystal systems. It will affect the charge transport behavior in charge carriers.^{19,24}

3.6. Cyclic voltametry studies

The electrochemical stability of PVA/ ZnBr_2 electrolyte was analyzed using two electrode system over the range $\pm 1.5 \text{ V}$ at scan rates of 0.01 Vs^{-1} and 0.05 Vs^{-1} shown in Fig. 7(a).

The PVA/ ZnBr_2 solid polymer electrolytes were sandwiched between zinc pasted steel electrode and platinum coated glass plate to carry out experiment. We carried this experiment to understand whether these electrolytes showing capacitive behavior or not? These results will announce the applicability of these electrolytes towards power storage and electrochromic devices. The increase in area under the voltammograms with respect to ZnBr_2 wt.% was observed. It reveals that the energy capacity depends on ZnBr_2 concentration in the electrolyte. The presence of ZnBr_2 in composite increases the conductivity of the system. Hence, areal broadening in the voltammograms were observed. Without any distortion in the rectangular window of the voltammograms, these composites exhibit the typical capacitive behavior of the electrolyte with good reversibility and chemical stability. There is no visible peak from a faradic current over a scanned range. This is the indication of charge and discharge occurring reversibly at the electrode-electrolyte interface. The area under the CV curve also increased with increase in scan rate.²⁵

4. Conclusion

In this work, the flexible, light weight and efficient ZnBr_2 /PVA electrolytes were prepared. In the FTIR spectrum, the shifted peak position, decreased broadness in OH band was observed. The presence of Cis C-H wagging also reduced as increase in ZnBr_2 concentration. The intensity of bromide peak increased with respect to ZnBr_2 wt.%. The variation in the FTIR spectrum confirms the interaction between the ZnBr_2 and PVA matrix. The dielectric constant and dielectric loss increased with increase in wt.% of ZnBr_2 at lower frequency and decreased exponentially with increase in frequency. It shows that the composite follows a non-Debye type behavior. Imaginary and real part of the electric modulus spectrum shows an opposite nature, compared to dielectric

constant and dielectric loss. This confirms the conductivity arises due to charge migration of ions and polymer chain segmental motion. The AC conductivity spectrum shows dispersion in lower frequency region and plateau at higher frequency region. The calculated value for frequency exponent is decreased as increase in frequency, obeying CBH modal. The conductivity occurs due to hopping process. But the value for s is nearer to 0.7 at lower temperatures. This indicates that the tunneling phenomenon also contributes to conductivity at lower temperatures. All the dielectric parameters varied with respect to temperature and the prepared materials were thermally active. From the cyclic voltammograms, we conclude that the prepared electrolytes were pseudo-capacitive in nature. For the industrial use, the prepared samples required modification in conducting properties, although the prepared samples shown good compatibility, good conducting properties. Addition of nano fillers requires an enhancement in mechanical properties.

Acknowledgments

The authors are thankful to Science and Engineering Research Board (SERB), Department of Science and Technology (DST), Government of India for the research projects (SR/FTP/PS-011/2010) and (SB/EMEQ-089/2013). The authors are thankful to USIC Mangalore University for providing FTIR measurements. The authors are also thankful to USIC Karnatak University, Dharwad for providing CV measurement facility.

References

- X. Hao, A review on the dielectric materials for high Energy storage application, *J. Adv. Dielect.* **3**(1), 1330001 (2013).
- A. Erste, L. Fulanovic, L. Coga, M. Lin, Y. Thakur, Q. M. Zhang and V. Bobnar, Stable dielectric response of low-loss aromatic polythiourea thin films on Pt/SiO₂ substrate, *J. Adv. Dielect.* **6**(1), 1650003 (2016).
- Y. Zhang, T. Christen, X. Meng, J. Chen and J. Rocks, Research progress on space charge characteristics in polymeric insulation, *J. Adv. Dielect.* **6**(1), 1630001 (2016).
- L. Zhang, L. Chen, X. Zhou and Z. Liu, Morphology- dependent electrochemical performance of zinc hexacyanoferrate cathode for zinc-ion battery, *Sci. Rep.* **5**, 18263 (2015).
- A. G. Einset, W. S. Schlindwein, R. J. Latham, R. G. Linford and R. Pynenburg, Investigation of ZnBr₂:PEO Polymer Electrolyte Characteristics, *J. Electrochem. Soc.* **138**(6) 1569 (1991).
- E. A. V. Etten, E. S. Ximenes, L. T. Tarasconi, I. T. S. Garcia, M. M. C. Forte and H. Boudinov, Insulating characteristics of polyvinyl alcohol for integrated electronics, *Thin Solid Films* **568**, 111 (2014).
- A. R. Polu, R. Kumar and G. M. Joshi, Effect of zinc salt on transport, structural, and thermal properties of PEG-based polymer electrolytes for battery application, *Ionics* **20**, 675 (2014).
- M. Mastragostino and S. Valcher, Polymer salt as a bromine complexing agent in a ZnBr₂ modal battery, *Electrochem. Acta* **28** (4), 501 (1983).
- E. Sheha and M. K. El-Mansy, A high voltage magnesium battery based on H₂SO₄-doped (PVA)_{0.7}(NaBr)_{0.3} solid polymer electrolyte, *J. Power Sources* **185**, 1509 (2008).
- P. Balaji Bhargav, V. M. Mohan, A. K. Sharma and V. V. R. N. Rao, Characterization of poly (vinyl alcohol)/sodium bromide polymer electrolytes for electrochemical cell applications, *J. Appl. Polym. Sci.* **108**, 510 (2008).
- Y. V. Cantu, R. Hauge, L. Norman and W. E. Billups, ZnBr₂ – catalyzed chemical effects in poly (acrylonitrile-co- butadiene), *J. Appl. Polym. Sci.* **89**, 1250 (2003).
- M. Peng, K. Yan, H. Hu, D. Shen, W. Song and D. Zou, Efficient fiber shaped zinc bromide batteries and dye sensitized solar cells for flexible power sources, *J. Mater. Chem. C* **3**, 2157 (2015).
- W. P. Hagan, R. J. Latham, R. G. Linford and S. L. Vickers, Zinc polymer electrolytes in battery systems, *Solid State Ionics* **70/71**, 666 (1994).
- G. Mengoli, M. M. Musian, D. Pletcher and S. Valcher, Studies of Zn/ZnX₂, polyaniline batteries. I. X=Cl and Br, *J. Appl. Electrochem.* **17**, 515 (1987).
- R. F. Bhajantri, V. Ravindrachary, A. Harisha, V. Crasta, S. P. Nayak and B. Poojary, Microstructural studies on BaCl₂ doped poly(vinyl alcohol), *Polymer* **47**, 3591 (2006).
- R. F. Bhajantri, V. Ravindrachary, A. Harisha, C. Ranganathaiah and G. N. Kumaraswamy, Effect of barium chloride doping on PVA microstructure: Positron annihilation study, *Appl. Phys. A* **87**, 797 (2007).
- E. M. Abdelrazek, I. S. Elashmawi, A. El-khodary and A. Yassin, Structural, optical, thermal and electrical studies on PVA/PVP blends filled with lithium bromide, *Curr. Appl. Phys.* **10**, 607 (2010).
- H. Y. Guan, Z. B. Guo, J. J. Ding and F. Lian, Ionic conductivity and dielectric behavior of novel Poly (vinyl formal) - based single-ion-conductor polymer electrolytes, *J. Appl. Polym. Sci.* **133**, 43510 (2016).
- M. Hema, S. Selvasekerapandian, A. Sakunthala, D. Arunkumar and H. Nithya, Structural, vibrational and electrical characterization of PVA-NH 4 Br polymer electrolyte system, *Physica B* **403**, 2740 (2008).
- S. Karthikeyan, S. Sikkanthar, S. Selvasekarapandian, D. Arunkumar, H. Nithya and J. Kawamura, Structural, electrical and electrochemical properties of polyacrylonitrile- ammonium hexafluorophosphate polymer electrolyte system, *J. Polym. Res.* **23**, 51 (2016).
- J. S. Karthika, B. Vishalakshi and J. Naik, Gellan gum-graft-Polyaniline, An electrical conducting biopolymer, *Int. J. Biol. Macromol.* **82**, 61 (2016).
- J. Tahalyani, K. K. Rahangdale, R. Aepuru, B. Kandasubramanian and S. Datar, Dielectric investigation of conducting fibrous non-woven porous mat fabricated by one-step facile electro spinning process, *RSC Adv.* **6**, 36588 (2016).
- B. Chatterjee, N. Kulshrestha and P. N. Gupta, Nano composite solid polymer electrolytes based on biodegradable polymers starch and poly vinyl alcohol, *Measurement* **82**, 490 (2016).
- D. K. Pradhan, R. N. P. Choudhary and B. K. Samantaray, Studies of dielectric relaxation and AC conductivity behavior of plasticized polymer nanocomposite electrolytes, *Int. J. Electrochem. Sci.* **3**, 597 (2008).
- C. W. Liew, S. Ramesh and A. K. Arof, Investigation of ionic liquid-doped ion conducting polymer electrolytes for carbon-based electric double layer capacitors (EDLCs), *Mater. Des.* **92**, 829 (2016).