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Electrical And Electrochemical Studies On Blend-Based Polymer Gel Electrolyte Containing Nano Filler (PVP: PVA): Benzoic Acid: Sio_2 System

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Abstract

The present work aims to develop a proton-conducting nanocomposite polymer gel electrolyte for electrochemical devices. With this perspective in mind, an attempt has been made to prepare and characterize the polyvinyl pyrrolidone (PVP): polyvinyl alcohol (PVA): benzoic acid (C_6H_5COOH): silicon dioxide (SiO_2**)** systems. The solution casting approach was utilized to generate the blend-based (PVP-PVA) polymer nanocomposite gel electrolyte films, while the sol-gel method was employed to prepare the nanofiller for the investigation. All the electrolyte films have been characterized by electrical and cyclic voltammetric (CV) measurements. The ionic conductivity of nanocomposite polymer gel electrolyte improves by one order at room temperature, with an optimum of 4.71×10^{-3} S/cm for 8 wt% SiO_2. The analysis of temperature-dependent conductivity shows that ion conduction is controlled by a combination of Arrhenius and Vogel-Tamman-Fulcher (VTF) behavior. The analysis of the VTF graph suggests that ionic and polymer segmental motions are strongly coupled. The studies indicate an increase in the dielectric constant as the frequency decreases. This behavior is indicative of the electrode polarization effect. All the results have been suitably explained.

Keywords: PVP, PVA, benzoic acid, polymer blend, SiO_2, VTF

1. Introduction

Over the past several decades, the escalation of environmental pollution and adverse climate shifts resulting from the utilization and consumption of oil, nuclear energy, and fossil fuels has reached a critical level, leading to significant challenges for human existence. Compared with conventional non-renewable energy sources, there has been an exclusive demand for renewable energy sources such as fuel cells, rechargeable batteries, supercapacitors, and dye-sensitized solar cells, which are non-toxic and safe for the environment. Now, the role of polymer electrolytes (PEs) in electrochemical devices cannot be ignored. In comparison with liquid electrolytes (LEs), polymer electrolytes have the most remarkable characteristics, including being free from leakage, thermal stability, high energy density, desired shape, and being lightweight. However, their applicability in different devices is restricted due to a lack of solvent retention ability over long periods and under diverse ambient temperatures. The earliest polymer electrolytes are solid polymer electrolytes (SPEs), exemplified by the poly (ethylene oxide) (PEO)-based electrolyte system, formed through the dissolution of salt in a polymer matrix with a high molecular weight [1-4]. However, SPEs face the inherent challenge of exhibiting low ionic conductivity at room temperature. The subsequent development involved the introduction of gel and composite polymer electrolytes, effectively mitigating the drawbacks associated with SPEs. In gel form, it integrates both the diffusive characteristics of liquids and the cohesive attributes of solids. The inadequate mechanical strength of gel polymer electrolytes (GPEs) may result in the impairment or leakage of entrapped liquid electrolytes, thereby impeding the widespread manufacturing of electrochemical devices. Composite polymer electrolytes (CPEs) have been studied to address the challenges presented by both poor ionic conductivities, a result of ion association, and low mechanical strength [5, 6]. The incorporation of diverse materials, including inorganic inert fillers with a high dielectric constant, into SPEs or GPEs demonstrates the potential to enhance ionic conductivity and strengthen mechanical properties. In recent times, researchers have tried to disperse non-interacting filler particles in pristine polymer electrolytes to overcome these limitations. Though several types of fillers like TiO_2, $BaTiO_3$, Al_2O_3, CNT, MWCNT, etc. have been tried in different polymer electrolytes to develop suitable nanocomposite polymer electrolytes, there is a famine of suitable proton-conducting polymer nanocomposite gel electrolytes [7]. In this investigation, blended polyvinyl pyrrolidone and polyvinyl alcohol (PVP-PVA) polymer electrolytes were prepared by incorporating benzoic acid as the doping salt. Polymer blends emerge as practical solutions, possessing distinctive properties that surpass those of individual polymers [8]. PVP-PVA was selected because of its attractive properties. PVP and PVA demonstrate characteristics such as non-toxicity, high chemical stability, elevated dielectric strength, biocompatibility, cost-effectiveness, and pronounced hydrophilicity. Within their structures, there are hydroxyl and carbonyl groups. These functional groups can serve as sites for hydrogen bonding, playing a crucial role in facilitating the formation of polymer electrolytes [9-12]. Both PVP and PVA exhibit solubility in dimethyl sulfoxide (DMSO) and can form high-degree complexes with a wide range of dopants. The formation of a polymer matrix involves blending PVP and PVA in a 70:30 ratio, with the introduction of ions facilitated by the addition of C_6H_5COOH. Nevertheless, the blended system presents certain drawbacks, including suboptimal dimensionality, ionic conductivity, and mechanical stability. Consequently, the incorporation of nanofillers, notably SiO_2, is employed to improve mechanical stability, electrochemical stability, and ionic conductivity.

2. Experimental details

The polymers used in this study, poly (vinyl pyrrolidone) (PVP) with a molecular weight of 360,000 and poly (vinyl alcohol) (PVA) with a molecular weight ranging from 124,000 to 186,000, have been procured from Sigma Aldrich. Benzoic acid (C_6H_5COOH, AR grade), chosen as a salt, played a crucial role in the subsequent steps. For the preparation of the PVP-PVA polymer blend, a precise ratio of 70:30 was dissolved separately in 10 ml of dimethyl sulfoxide (DMSO) at room temperature. The individual solutions were then meticulously mixed and stirred for 2 hours to attain a homogenous blending solution. To create the PVP: PVA: C_6H_5COOH electrolytes, a 0.6M solution of benzoic acid (C_6H_5COOH) was added with continuous stirring to the blended polymer solution. To augment the conductivity of the resulting blend, varying percentages of SiO_2 nanofiller were introduced. The solution was continuously stirred with a magnetic stirrer at room temperature until complete dissolution was achieved. The prepared solutions were poured into distinct, clean, and dry glass Petri dishes. The samples were then evaporated slowly at room temperature, forming dry and free-standing blended nanocomposite polymer electrolyte films. The synthesized blended polymer nanocomposite gel electrolytes, denoted as [(PVP: PVA): C_6H_5COOH: SiO_2], undergo comprehensive characterization using various experimental probes. This thorough analysis was conducted to measure their suitability and performance for potential applications in electrochemical devices.

3. Results and discussion

3.1 Wagner's Polarization

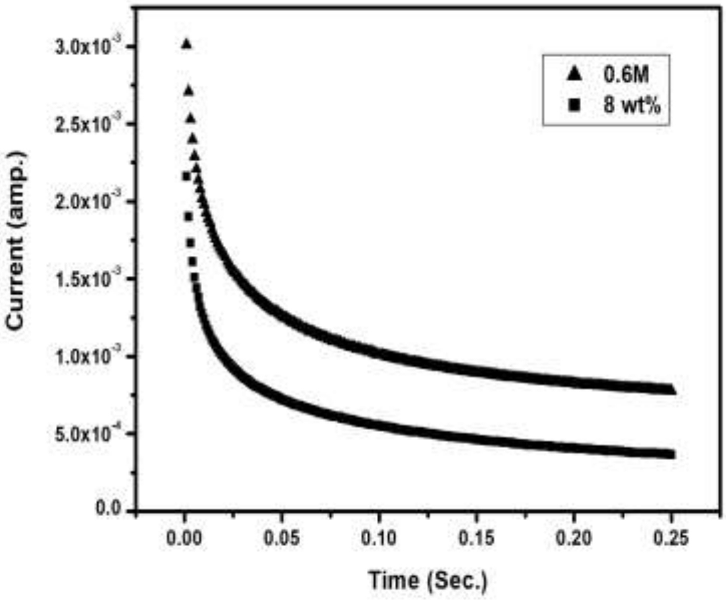


Figure 1. I-t Polarization curve of DMSO casted (▲) PVP: PVA: C_6H_5COOH (0.6 M) (■) PVP: PVA: C_6H_5COOH (0.6M): SiO_2 (8 wt%)

Ion conduction contributes greatly to the conductivity of the polymer electrolyte, whereas electron conduction is largely unimportant. The ionic conductivity of electrolytes is important to examine when considering the application of these devices, as they are thought to be the core of electrochemical devices. By using Wagner's polarization technique, the transference numbers for the films were measured by constructing a system of PVP:PVA:C_6H_5COOH with different concentrations of SiO_2 and polarizing it at 303K at a constant dc potential to assess the contribution of ions and electrons to the entire conductivity of the polymer electrolyte films. The equation used were

$$t_{ion} = \frac{I_{initial} - I_{final}}{I_{initial}} = \frac{I_{total} - I_{electronic}}{I_{total}} = \frac{I_{ionic}}{I_{total}} \qquad (1)$$

Where $I_{initital}$ is the initial current and I_{final} is the final current [13]. The ionic transference number (t_{ion}) was 0.78 for the blend-based polymer electrolyte at a 0.6M concentration of C_6H_5COOH. It increased to 0.83 upon the addition of 8 wt% of SiO_2 nanofiller, indicating the dominance of ionic charge transport over electronic transport in the blend-based nanocomposite polymer electrolytes. The results are presented in Figure 1.

3.2. Electrochemical Stability

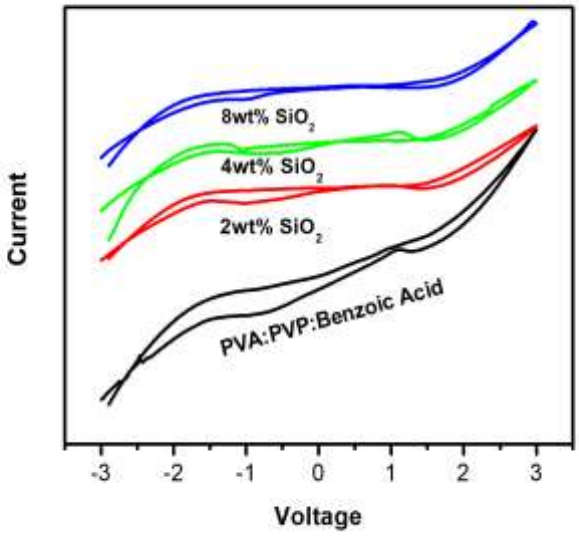


Figure 2. Cyclic voltammetry of PVP: PVA: Benzoic Acid: SiO$_2$ for different concentrations of SiO$_2$.

The electrochemical characterization of the SiO$_2$-soaked PVP: PVA: benzoic acid electrolyte system has been conducted through cyclic voltammetry, as depicted in Figure 2, where the Y-axis is expressed as current. The electrochemical stability window of the pristine polymer electrolyte system was not good. Therefore, incorporating SiO$_2$ nanofiller into the blend-based polymer electrolyte system led to an increase in the transport of the redox couple within a matrix with reduced viscosity created by the nanofiller. Another consequence of incorporating the nanofiller is the narrowing of faradic currents during the oxidation and reduction cycles within the stable region. The optimum electrochemical stability window is obtained from -1.52V to +1.54V for a concentration of 8 wt% of SiO$_2$ nanofiller.

3.3. Electrical Conductivity

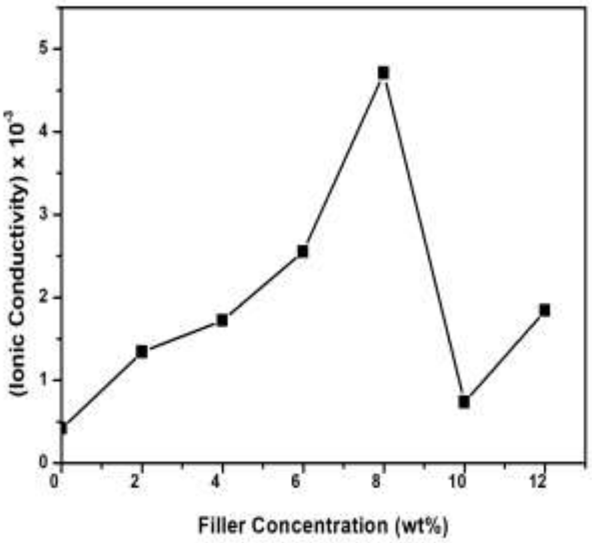


Figure 3. Variation of ionic conductivity of blend-based polymer electrolyte PVP-PVA-C_6H_5COOH as a function of different weight percent of SiO_2 nanofiller concentration.

In Figure 3, the graph illustrates the variations in ionic conductivity within the PVP-PVA-C_6H_5COOH-SiO_2 polymer nanocomposite blend-based system. It is noted that the polymer nanocomposite blend electrolytes, with a free-standing film, exhibit a maximum conductivity of about 4.71×10^{-3} S/cm for 8 wt% SiO_2 nanofiller at ambient temperature. These materials prove to be highly suitable for various device applications. The maximum conductivity after 6 wt% of SiO_2 nanofiller, as can be seen in the table, is due to the re-dissociation of ion aggregates and the increase in the amorphous nature of the blended system. This implies that higher amorphicity promotes the ion transport of H^+ ions within the polymer. However, beyond 8 wt%, aggregation of these nanoparticles takes place, leading to a decrease in conductivity.

Table. Ionic conductivity of SiO_2 doped blend-based polymer electrolyte films at room temperature.

Composition	Conductivity (Scm^{-1})
70PVP: 30PVA: 0.6M C_6H_5COOH: 0wt%SiO_2	4.17E-04
70PVP: 30PVA: 0.6M C_6H_5COOH: 2wt%SiO_2	1.34E-03
70PVP: 30PVA: 0.6M C_6H_5COOH: 4wt%SiO_2	1.72E-03
70PVP: 30PVA: 0.6M C_6H_5COOH: 6wt%SiO_2	2.55E-03
70PVP: 30PVA: 0.6M C_6H_5COOH: 8wt%SiO_2	4.71E-03
70PVP: 30PVA: 0.6M C_6H_5COOH: 10wt%SiO_2	7.33E-04

3.4. Dielectric and Electric Modulus Analysis

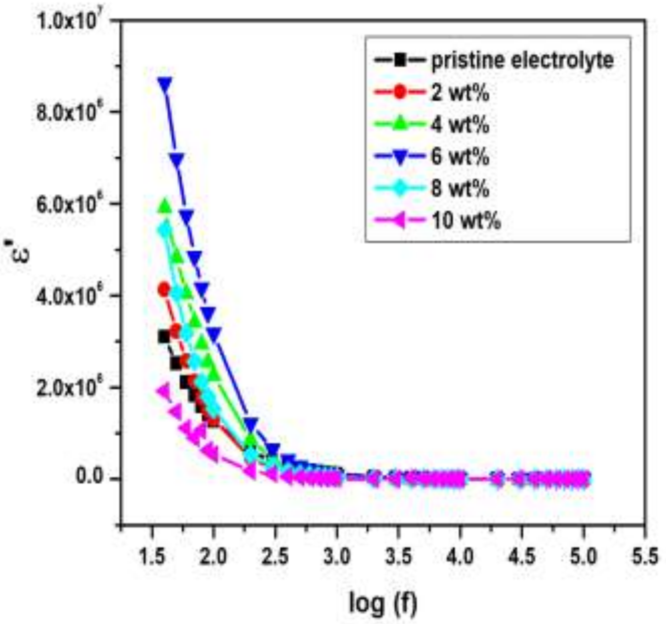


Figure 4. Variation of dielectric constant as a function of frequency for (0-10) wt% of SiO_2 nanofiller.

The variation of the dielectric constant *(Ɛ')* concerning frequency for pristine electrolytes and different concentrations of SiO_2 at room temperature is shown in Figure 4. It is revealed that the dielectric constant *(Ɛ')* in the low-frequency region is high for the 6 wt% composition of PVP-PVA-C_6H_5COOH-SiO_2 and gradually decreases up to 10 wt% of composition. The decrease in the dielectric constant *(Ɛ')* and its stabilization at a constant value from 8 wt% to 10 wt% composition is due to the rapid periodic reversal of the electric field, potentially explaining the lack of alignment of ions in the direction of the electric field [14-16]. The increase in the dielectric constant *(Ɛ')* for the 2 wt%, 4 wt%, and 6 wt% compositions is due to the accumulation of space charge polarization at the electrode-electrolyte interface [17,18]. The decrease in the dielectric constant for 8 wt% and 10 wt% may be associated with the large dissimilarity in the dielectric constant of the blended polymer (PVP-PVA) and nanofiller (SiO_2), which leads to inhomogeneity in the blended polymer matrix.

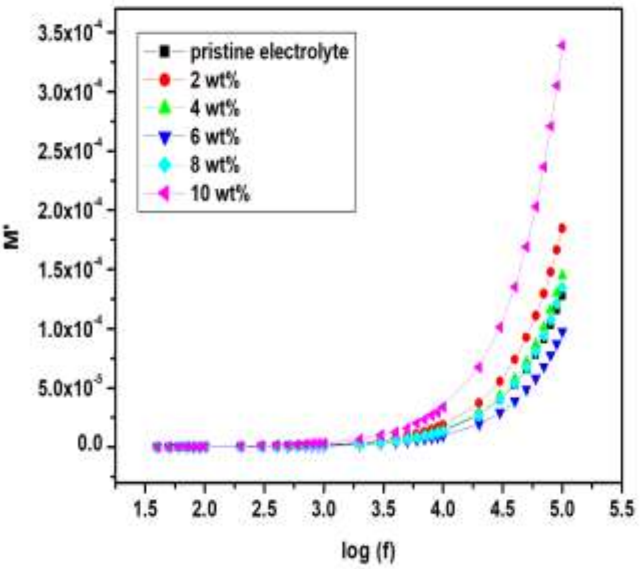


Figure 5. Modulus M′ spectra for different compositions of PVP: PVA: C_6H_5COOH: SiO_2 at ambient temperature.

The frequency-dependent electric modulus spectra show a long tail in the low-frequency region, indicating the electrode polarization phenomenon. Subsequently, the modulus gradually increases with frequency, reaching its maximum value for 10 wt% of SiO_2 nanofiller, corresponding to increased conductivity through a higher mobile ion concentration. The electric modulus of PVP: PVA: C_6H_5COOH: SiO_2 is determined by the following equation [16].

$$M' = \frac{\varepsilon'}{\varepsilon'^2 + \varepsilon''^2} \tag{2}$$

3.5. Tangent Loss Spectra Analysis

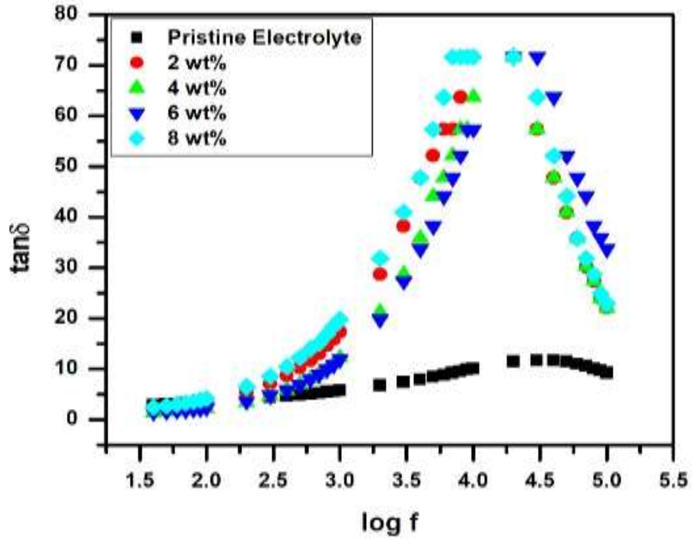


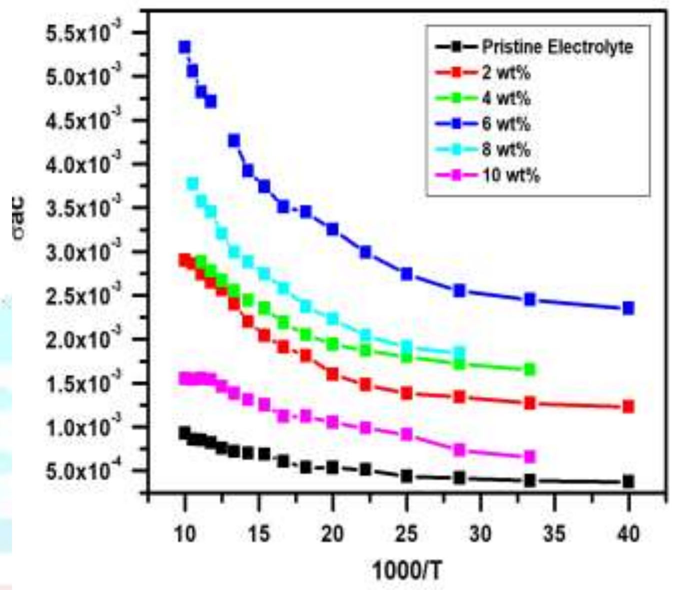
Figure 6. Tan δ vs. log frequency for different compositions of 70 PVP: 30 PVA: (0-10wt%) SiO_2 complexed with a 0.6M benzoic acid system at room temperature.

Figure 6 shows *tanδ* as a function of frequency at room temperature for the polymer blend composite [PVP (70 wt%), PVA (30 wt%)], [C_6H_5COOH (0.6 M)], and [SiO_2 (0-10 wt%)] system. From Figure 6, it is clearly shown that the addition of SiO_2 concentration in the blended system shifts the peak of the pristine electrolyte system toward lower frequencies. This behavior suggests that, in the low frequencies where tan δ increases, the presence of filler in the blended system signifies the persistence of the ohmic component of the current. The ohmic component of current exhibits a more pronounced increase compared to its capacitive counterpart. Conversely, at higher frequencies, where *tanδ* decreases, the ohmic component of the current demonstrates a nearly frequency-independent behavior [19-22].

3.6. Temperature Dependence Conductivity

Figure 7 depicts the variation in ionic conductivity of the blend-based composite system with the inverse of temperature. The conductivity spectra of the blended composite system exhibit a linear and curved formation, resulting from a combination of both Arrhenius and VTF behaviors.

Figure 7. σ versus 1000/T spectra for the blend-based system containing (0-10) wt% of SiO_2 filler.



The Arrhenius-like behavior illustrates an increase in conductivity with respect to the rise in temperature. The values of Arrhenius's behavior are calculated using the following equation [23,24].

$$\sigma = \sigma_0 \exp\left(\frac{E_a}{k_B T}\right) \qquad (3)$$

where σ_0 is the proportionality constant, E_a is the activation energy, k_B is the Boltzmann constant and T is the absolute temperature. The activation energy for proton ion transport is calculated from the slope of the spectra. From the figure, the VTF model exhibits non-linear behavior. The analysis of the VTF model reveals a strong interrelationship between ionic motion and polymer segmental relaxation. The non-linear Arrhenius spectra in this blend-based composite system obey the Vogel-Tamman-Fulcher (VTF) relation.

$$\sigma(T) = AT^{-1/2} \exp\left[-\frac{B}{k_B(T - T_0)}\right] \qquad (4)$$

The pre-exponential factor, denoted as A, pertains to the quantity of charged ions, while B represents the pseudo-activation energy linked to the motion of polymer segments, T_0 is the glass transition temperature, and k_B is the Boltzmann constant. As expected, an increase in temperature causes polymer expansion, thereby creating a larger free volume [7,25,26,]. The addition of 6 wt% SiO_2 concentration resulted in higher ionic conductivity at elevated temperatures, as these fillers created free volume, subsequently increasing segmental mobility and ion transport in the amorphous region. Further increases in filler concentration reduce the hopping mechanism rate from one coordination site to another.

3.7. A.C. Conductivity

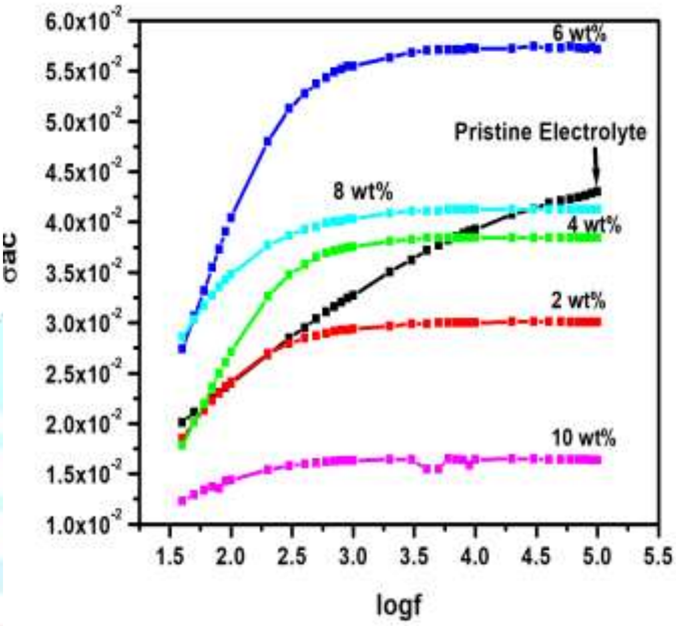


Figure 8. Variation of ionic conductivity for a polymer blend-based electrolyte system [PVP: PVA: C_6H_5COOH: SiO_2] at different frequencies.

The behavior of the A.C. conductivity of a nanocomposite blend-based polymer electrolyte for various concentrations of the filler as a function of frequency at room temperature is shown in Fig.8. From this figure, we can see that the conductivity rises as frequency increases in the low-frequency region, attributed to the electrode polarization effect [17]. Subsequently, a plateau region is observed at higher frequencies, where conductivity remains independent of frequency. This behavior obeys Jonscher's universal power law [27,28].

$$\sigma(\omega) = \sigma_{dc} + A\omega^{n} \tag{5}$$

where $\sigma(\omega)$ is the ac conductivity, σ_{dc} is the dc conductivity, A is the pre-exponential factor, and n is the fractional exponent between 0 and 1. In the higher frequency region, conductivity demonstrates saturation-like behavior, indicating the failure of ions to hop between different sites.

4. Conclusions

PVP- and PVA-based proton-conducting polymer nanocomposite blend electrolytes with different concentrations of SiO_2 nanofiller have been prepared using the solution-cast technique. An examination of the conductivity unveiled the highest ionic conductivity at ambient temperature, reaching 4.71×10^{-3} S/cm for the composition containing 70% PVP, 30% PVA, 0.6 M C_6H_5COOH, and 8 wt% SiO_2. Incorporating the SiO_2 nanofiller led to an augmented ionic conductivity in the blended electrolyte system compared to pristine electrolytes. This enhancement can be attributed to heightened ion mobility, improved correlation between salt molecules and chain segments, and an increased diffusion rate of charge carriers. However, higher SiO_2 content resulted in a reduction in segmental motion, leading to restricted ion transport. The study also encompassed an examination of the dielectric and a.c. conductivity of the samples. Cyclic voltammetry findings disclosed an electrochemical stability of up to ~1.54V for the PVP: PVA: Benzoic acid-added SiO_2 system. These electrolytes exhibit substantial potential for applications in solid-state batteries.

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