Effect of Anhydrous GdCl₃ Doping on the Structural, Optical and Electrical Properties of PVP Polymer Electrolyte Films

M. Arasakumari  
Anna University

K Subramanian (kathsubramanianannauniv@gmail.com)  
Anna University

Research Article

Keywords: Polymer electrolyte films, dc conductivity, dielectric constant, Optical absorption, Cyclic Voltammetry studies

DOI: https://doi.org/10.21203/rs.3.rs-589123/v1

License: This work is licensed under a Creative Commons Attribution 4.0 International License.
Read Full License
Effect of anhydrous GdCl$_3$ doping on the structural, optical and electrical properties of PVP polymer electrolyte films

M. Arasakumari, K. Subramanian*

Department of Chemistry, Anna University, Chennai-600 025, Tamil Nadu, India

*Corresponding author E-mail: kathsubramanianannauniv@gmail.com

Abstract

Polymer electrolyte films containing GdCl$_3$ salt and polyvinyl pyrrolidone polymer have been prepared by solution cast technique. X-ray diffraction patterns confirm the amorphous nature of all the films. UV-Visible optical absorption properties reveal the complex formation of polymer electrolyte with GdCl$_3$ dopant. The absorption coefficient, direct band gap energy and indirect band gap energy are decreased with increasing GdCl$_3$ dopant. Both dielectric and ac conductivity studies exhibit that the dielectric constant value at low frequency and ac conductivity at high frequency increases with increasing GdCl$_3$ dopant concentration in PVP polymer. The complex impedance plots showed a single semi-circular arc for all the concentrations of CdCl$_3$ doped in PVP. The ac conductivity and ionic conductivity are about $3.96 \times 10^{-3}$ S/cm and $3.12 \times 10^{-3}$ S/cm at room temperature for 15 mol% GdCl$_3$ doped PVP polymer electrolyte films. The cyclic-voltammetry plots revealed large specific capacities with increasing in GdCl$_3$ dopant concentration. The estimated ionic conductivity is five orders of magnitude larger than that of PVP doped with other metal salts reported earlier. The present study strongly recommends that the CdCl$_3$ is worthy candidate for enhancing ionic conductivity of PVP and other polymers.

Keywords Polymer electrolyte films; dc conductivity; dielectric constant; Optical absorption; Cyclic Voltammetry studies

1. Introduction

Electrolyte films containing metal ions and conducting polymers have been known for their potential applications in ultra-capacitor, sensors and fuel cells. Generally, polymer electrolytes would exhibit two phases such as crystalline and amorphous phases. When these two phases are appeared in polymer electrolyte, the mechanism of ionic conductivity on polymer electrolyte films cannot be easily understood. The enhancement of ionic conductivity strongly depends on the amorphous nature of polymer electrolytes. The simultaneous movement of ions and the interaction of cation with anion also decrease the ionic conductivity of materials. Many researchers have suggested that the addition of a suitable metal salt in polymer network would drastically improve the charge transport which
leads to enhance the ionic conductivity of polymer electrolyte films. Till now, different polymers such as polyvinyl alcohol, polyvinyl chloride, polypropylene glycol, polyvinyl pyrrolidone, polyethylene oxide and polyvinylidene fluoride have been utilized to develop polymer electrolytes with high ionic conductivity at room temperature [1-10].

Among the polymer, polyvinyl pyrrolidone (PVP) have been chosen for its attractive properties such as the amorphous polymer, excellent film-formation with various salts, presence of carbonyl group (C=O), etc. The faster ionic mobility can be obtained in this type of polymer. The PVP polymer is worthy candidate for making polymer electrolyte films with doping of different metal ions due to its good mechanical and thermal stability, easy soluble in water and improved ionic conductivity. The significant improvement in polymer electrolyte film can be achieved by adding alkali metal salts in polymer electrolytes. Similar reports have already been reported earlier [2-9]. Apart from alkali metal salt-based polymer electrolytes, other metal salts such as divalent and trivalent metal salts were also used as the dopants in different polymers and polymer blends with the intention of enhancing the ionic conductivity but till now PVP doped with anhydrous GdCl$_3$ have not been reported [10-14].

In this paper, the structural, optical and electrical properties of PVP doped with various concentrations of anhydrous GdCl$_3$ have been discussed in detail. The 5, 10 and 15 mol% anhydrous GdCl$_3$ doped PVP polymer electrolyte films have been prepared by simple solution casting method. Gd$^{3+}$ trivalent metal ion was chosen as the dopant for reporting the significant changes in the charge transport of PVP polymer. To best of our knowledge, this is first report on the effect of GdCl$_3$ dopant on the ionic conductivity of PVP polymer electrolyte films.

2. Experimental details

2.1. Preparation of GdCl$_3$ doped PVP polymer electrolyte films

Thick films of anhydrous GdCl$_3$ doped PVP polymer electrolyte films were prepared using solution cast technique. An aqueous solution of PVP dissolved in double distilled water was continuously stirred at 70°C until the homogeneous solution is obtained. It is named as PVP stock solution. The 5 mol% of GdCl$_3$ dissolved in doubly distilled water was constantly stirred at room temperature for preparing GdCl$_3$ aqueous solution and then this solution was mixed with the stock solution of PVP. Then the mixture solution of GdCl$_3$ and PVP was continuously stirred for 2 h at room temperature. The resultant solution was poured on a cleaned glass plate and then kept into hot air oven to dry the solution at 70°C for 1 hr. After drying, the thick film was peeled off from the plate and kept in vacuum desiccators. Similarly, 10 and 15 mol% GdCl$_3$ doped PVP polymer electrolyte films were prepared.
2.2. Characterization

X-ray diffraction (XRD) studies on the films were carried using a Rigaku Miniflex-II desktop x-ray diffractometer in the 2θ diffraction angle of 15-60° using CuKα radiation (λ=1.5406 Å). UV-Visible optical absorption studies of all the films were characterized by PerkinElmer LAMBDA 35 UV-VIS-NIR spectrometer in the wavelength range of 200-600 nm. The charge transport properties of the polymer electrolyte films were studied using N4L Phase Sensitive Millimeter interfaced with Impedance Analyzer with a cell with stainless steel electrodes over a frequency range of 100 Hz-1 MHz in the temperature range of 303-363 K. The cyclic voltammetric analysis of the samples have been studied using Autolab 30 potentiostat with a scan rate of 0.05 mV s⁻¹ by placing polymer electrolyte film between two aluminum blocking electrodes in voltage range from -2.0 to 2.0 V.

3. Results and discussions

3.1. XRD studies

Fig. 1 shows XRD plots of 5, 10 and 15 mol% GdCl₃ doped PVP polymer electrolyte films. In Fig. 1, pure PVP shows a peak in the diffraction angle of 2θ at 21°, representing the semi crystalline of PVP [15]. XRD patterns of GdCl₃ doped PVP polymer electrolyte films exhibited that the increase in the GdCl₃ dopant concentrations in the PVP leads to decrease in the intensity which results the decrease in crystallinity of GdCl₃ doped polymer electrolyte films. It is clearly well agreed with the report of Hodge et al [16]. Addition of GdCl₃ to PVP polymer improves the amorphous phase of GdCl₃ doped PVP films with increasing GdCl₃ dopant concentration. It can be seen from Fig. 1 that no sharp peak was found for 15 mol% GdCl₃ in the PVP, indicating complete dissociation of GdCl₃ metal salt into the polymer which confirms the dominant role of amorphous phase in the PVP- GdCl₃ salt complexes and results the more diffusion of ions from higher concentration to lower concentration of segments with high ionic conductivity [1-16].

3.2. Optical absorption studies

UV-Visible optical absorption plot of pure PVP, 5, 10 and 15 mol% GdCl₃ doped PVP polymer electrolyte films is illustrated in Fig. 2a. From the figure, it has been clearly observed that pure PVP polymer film does not show any absorption peak whereas GdCl₃ doped PVP polymer electrolyte film exhibit a broad absorption peak. An addition of Gd³⁺ ions in the PVP film causes the broad absorbance peak in the optical absorption spectra of GdCl₃ doped PVP film. The absorption coefficient (α) can be determined by the following relation:
\[ I = I_0 \exp(-\alpha x) \]  

(4)

Hence

\[
\alpha = \frac{2.303}{x} \log \left( \frac{I}{I_0} \right) = \frac{2.303}{xA}
\]  

(5)

where \( x \) is the film thickness, \( I \) is incident intensity, \( I_0 \) is transmitted radiation and \( A \) corresponds to \( \log(I/I_0) \). Fig. 2b shows a plot between the absorption coefficient and photon energy. The absorption coefficient (\( \alpha \)) can be estimated by the straight line fitting on linear portion of the curve to zero absorption and is 5.22, 4.96, 4.87 and 4.72 eV for pure PVP, 5, 10 and 15 mol% GdCl\(_3\) doped PVP films. Both direct band gap energy and indirect band gap energy can be calculated from the plot of \((\alpha \nu)^2\) vs \(\nu\) and \((\alpha \nu)^{1/2}\) vs \(\nu\) using the following equations [17, 18].

\[
\alpha\nu = \beta_1 (\nu - E_{gd})^{1/2}
\]  

(6)

\[
\alpha\nu = \beta_2 (\nu - E_{gi})^2
\]  

(7)

where \( \nu \) is the optical energy, \( E_{gd} \) is the direct band gap energy, \( E_{gi} \) are indirect band gap energy of material, \( \beta_1 \) is the constant for direct transition and \( \beta_2 \) is the constant for indirect transition [17-18]. The direct band gap energy estimated from the Fig. 2c by the fitting of straight line is about 6.14, 5.34, 5.14 and 5.04 eV whereas the indirect band gap energy estimated from Fig. 2d is about 5.06, 4.99, 4.91 and 4.85 eV for PVP, 5, 10 and 15 mol% GdCl\(_3\) doped PVP polymer electrolyte films. The value of \( \alpha \), \( E_{gd} \) and \( E_{gi} \) are decreased with increase in GdCl\(_3\) dopant concentrations. Similar results have been obtained for polymer blend of polyethylene oxide and poly vinyl pyrrolidone doped with NaF salt and PVP polymer electrolytes doped by vanadyl ion [9, 14]. After doping GdCl\(_3\), some defects might be formed in the PVP film and cause a decrement in absorption coefficient, direct band gap energy and indirect band gap energy. In other words, the optical gap energy decreased with the concentration of GdCl\(_3\) dopant would be a reason for the enhancement on the disorderliness of the films [9, 14].

3.3. Dielectric properties

Fig. 3 (a and b) shows the real (\( \varepsilon' \)) and imaginary (\( \varepsilon'' \)) parts of room temperature dielectric constant plots of the pure PVP and GdCl\(_3\) doped PVP films. The GdCl\(_3\) doped PVP films exhibited the highest dielectric constant with the comparison of pure PVP film. It confirms that addition of GdCl\(_3\) metal salt would increase the dielectric constant of PVP films. The dielectric constant increases with decrease in frequency. An increment in dielectric constant with decrease in frequency sides also attributes to the space charge polarization which arises from the
electrodes. Fig. 3 (c and d) shows the real (\(\varepsilon'\)) and imaginary (\(\varepsilon''\)) parts of dielectric constant of 15 mol% GdCl\(_3\) doped polymer electrolyte film at different temperatures. It can be seen from the figure, the dielectric constant at low frequency increases with the rise in temperature. When the temperature is increased, the dipoles formed in the polymer electrolyte films has gained a sufficient kinetic energy and are orientated themselves which causes the enhancement in the dielectric constant [3, 4]. The dielectric constant decreases with increasing frequency and remains constant at high frequency side. This behavior is due to the ability of the dipoles to rotate themselves in the direction of applied electric field between electrolyte and electrode at their respective electrodes whereas the rotation of dipoles is lagging behind the applied electric field and thereby dielectric constant decreases at high frequencies [6].

### 3.4. AC conductivity analysis

AC conductivity plots of pure PVP and GdCl\(_3\) doped PVP films are shown in Fig. 4. The ac conductivity increases with increasing of GdCl\(_3\) concentration. It confirms that the mobility of anions has been completely stopped and leads to increase in the conductivity of polymer-salt complexes by the addition of Gd\(^{3+}\) cations in PVP polymer electrolyte film. It is worthy to note that the ac conductivity of GdCl\(_3\) doped polymer electrolyte films is larger than those of obtained in pure PVP film. The highest value of conductivity is about \(3.96 \times 10^{-3}\) S/cm at room temperature for 15 mol% GdCl\(_3\) doped PVP film. The highest value of ac conductivity also attributes to the reduction in glass transition temperature which gradually reduces the crystallinity of the PVP polymer film with doping of GdCl\(_3\) as discussed in XRD studies [6, 8]. A frequency independent region at low frequencies was observed in ac conductivity plot and is associated to the dc conductivity while dispersion of dipoles at high frequencies was observed and is associated to the ac conductivity. The results obeyed the Jonscher power law which is given below:

\[
\sigma(\omega) = \sigma_0 + A\omega^n
\]

where \(\sigma_0\), \(A\) and \(n\) are known as the dc conductivity, pre-exponential factor and the fractional exponent between 0 and 1. The value of \(n\) can be obtained by fitting Jonscher power law using experimental data and is varying from 0.78 to 0.98. The obtained \(n\) value lies between 1 and 0.5 reported as the standard value of an ideal electrolyte [6, 8, 19]. Fig. 5 shows the ac conductivity of 15 mol% GdCl\(_3\) doped PVP polymer electrolyte films at different temperatures. As the temperature increases, the conductivity at high frequencies also increases which is due to the enhancement in the mobility of charge carriers [19].
3.5. Complex impedance studies

Fig. 6 shows the complex impedance plots of pure and GdCl$_3$ doped PVP polymer electrolyte films at room temperature. The plots show a depressed semicircular arc over wide range of frequency. The semicircular arc represents the bulk properties of grains (dc resistivity). The diameter of the semicircular arc decreases with increasing concentration of GdCl$_3$ dopant increases. An intercept of semicircular arc on $Z'$ axis in the complex impedance plot gives the bulk resistance ($R_b$). The value of $R_b$ also decreases with GdCl$_3$ doping. The ionic conductivity ($\sigma_{dc}$) of electrolyte films can be determined using the following equation [20], $\sigma_{dc} = \frac{d}{R_b A}$, where $d$ and $A$ are the thickness and area of the sample. The estimated ionic conductivity is $1.32 \times 10^{-3}$, $1.75 \times 10^{-3}$, $2.47 \times 10^{-3}$ and $3.12 \times 10^{-3}$ S/cm for pure PVP, 5, 10 and 15 mol% GdCl$_3$ doped PVP polymer electrolyte film. The conductivity of 15 mol% GdCl$_3$ doped PVP polymer electrolyte film exhibits the maximum ionic conductivity and is more orders of magnitude greater than that of different polymers and polymer blends doped with different metal salts [4-7, 11, 12, 14, 21-25]. The estimated $\sigma_{dc}$ value for higher concentration of GdCl$_3$ doped film is about five orders of magnitude larger than the value obtained for PVP films doped with Mg$^{2+}$ ion and VO$^{2+}$ ion reported by Sreekanth et al. They have obtained the $\sigma_{dc}$ value of $3.21 \times 10^{-8}$ S/cm and $5.39 \times 10^{-8}$ S/cm at room temperature [14, 26]. The enhancement in $\sigma_{dc}$ with increasing in GdCl$_3$ salt might be attributed to dissolution of GdCl$_3$ salt in PVP with strong amorphous nature and boost the number of mobile charge carriers. A high dispersion can be obtained due to the strong interaction of PVP with GdCl$_3$ salt, thus the conductivity increased. Fig. 7 shows the temperature dependent complex impedance plots of 15 mol% GdCl$_3$ doped PVP film. A depressed semicircle along with inclined spike can be observed in the Fig. 7. The depressed semicircle represents the non-Debye nature of the 15 mol% GdCl$_3$ doped PVP polymer electrolyte film whereas the inclined spike can be associated to electrode surface polarization [3]. The inclined spike also attributes to the formation of double layer capacitance at the electrode-electrolyte interface due to movement of ions from one site to another side [12]. The diameter of the semicircular arc decreases with increasing frequency and temperature. Then the semicircular arc is disappeared in plot which shows only a spike above 363 K. The disappearance of semicircle at high temperature indicates the movement of Gd$^{3+}$ ions to contribute the conduction [21, 22]. To find the activation energy, the experimental data was fitted by the following Arrhenius exponential law:

$$\sigma_{dc} = \sigma_0 \exp \left( \frac{-E_a}{kT} \right)$$  \hspace{1cm} (2)
where $\sigma_0$ is the pre-exponential factor, $E_a$ is the activation energy, $k$ is the Boltzmann constant and $T$ is the absolute temperature [6]. Fig. 8 shows a plot of $\log \sigma_dk$ vs $1000/T$ (K$^{-1}$). The activation energy estimated from the Fig. 8 by fitting the Arrhenius equation mentioned above to the experimental data is about 0.118 eV which is smaller than those previously reported for polymer electrolyte films containing polyvinyl alcohol and LiFePO$_4$ salt [20]. The minimum $E_a$ value is required for overcoming the potential barrier in the electrolyte films.

### 3.6. Electrical modulus formalism

Fig. 9a shows the real ($M'$) part of room temperature electric modulus for pure PVP and GdCl$_3$ doped PVP polymer electrolyte films. In the Fig. 9a, the $M'$ at low frequency is very small due to the fact that electrode polarization is removed [8]. It can be also seen from the figure that the $M'$ value is decreased with increasing of the GdCl$_3$ concentrations. Fig. 9b shows the imaginary ($M''$) part of electric modulus for all the films at room temperature. An asymmetric peak has been observed in the imaginary part of electric modulus plot. The asymmetric peak is shifted towards the region of high frequency, indicating a decrement in relaxation time and thereby enhances the conductivity. Fig. 10 shows the (a) $M'$ and (b) $M''$ plots for 15 mol% GdCl$_3$ doped PVP polymer electrolyte film at different temperatures. In the Fig. 10a, the value of electric modulus decreases with increase in temperature. The value of $M'$ at high frequency side reveals the higher dispersion which tends to $M_\alpha$ due to the presence of conductivity relaxation. At low frequency side, $M'$ becomes to zero due to the fact that the value of electrode polarization is negligible [6, 8]. Fig. 10b shows a peak in imaginary part of electric modulus plot. The peak was disappeared at 353 K and 363 K due to the limitation in frequency range. When the large amount of charge carriers is accumulated at the electrode-electrolyte interface, the $M''$ plot shows the smallest value at low frequency. Fig. 11 shows a plot of $\log f_{\text{max}}$ vs $1000/T$ for finding activation energy ($E_a$). The following Arhenius equation has been used to estimate the value of $E_a$

$$\omega_m = \omega_0 \exp \left( \frac{-E_a}{kT} \right) \quad (3)$$

where $\omega_0$, $k$ and $T$ are the pre-exponential factor, Boltzman constant and absolute temperature [27]. The activation energy calculated by the least square fitting to the experimental data is about 0.13 eV. Fig. 12 shows a plot of $M''/M''_{\text{max}}$ vs frequency for 15 mol% GdCl$_3$ doped PVP polymer electrolyte film at different temperatures. A peak can be observed for each $M''/M''_{\text{max}}$ values. With increasing of temperature, the observed peak is shifted to higher
frequency side which suggests thermally activated process and leads to travel the charge carriers by hopping from one localized state to the other.

3.7. Cyclic Voltammetry studies

Fig. 13 shows the cyclic voltammetry curves for pure PVP and GdCl$_3$ doped PVP polymer electrolyte films. The cathodic and anodic peaks were appeared in the cell for 5, 10 and 15 mol% GdCl$_3$ doped PVP polymer electrolyte films, indicating that the GdCl$_3$ dopant in the PVP polymer electrolyte films did not interact with aluminium electrodes. The large area of a curve can be observed in Fig. 13 and area of the curve increases with increases in the concentration of GdCl$_3$ dopant. It represents the presence of higher specific charge than those observed in PVP film. It should be noted that the film undergoes a relatively broad reversible redox process, which illustrates its electroactivity. The cyclic voltammograms clearly shows the cyclability and reversibility of all of the electrolyte films [28, 29].

4. Conclusion

Polymer electrolyte films containing different concentrations GdCl$_3$ doped PVP have been synthesized using solution cast technique. XRD patterns reveal the decrease in the degree of crystallinity of PVP with addition of GdCl$_3$ dopant. Optical absorption studies exhibits the decrease in absorption coefficient, optical absorption edge and optical band gaps (both direct and indirect), representing the disorder of the polymer electrolyte films. The dielectric spectra show an increase in the dielectric permittivity at low frequency with increasing GdCl$_3$ dopant. The ac conductivity of the samples are found to be increased at high frequency side with increasing of GdCl$_3$ dopant concentrations as well as the and obeys the Jonscher power law. The complex impedance plots clearly represent the enhancement in the conductivity, with the addition of GdCl$_3$ dopant in PVP polymer, which is attributed to the formation of charge transfer complexes. The PVP film doped with 15 mol% GdCl$_3$ metal salt exhibits the highest conductivity. There was a good agreement between the activation energy of the dc conductivity and the activation energy estimated from modulus plots which suggests formation of the enthalpy of carrier is negligible in the present system. Modulus spectra show the non-Debye nature for these electrolytes. The cyclic voltammetry of the samples revealed the high specific charge capacities with the comparison of other polymer electrolytes. The present results suggest the PVP films doped with GdCl$_3$ as the good candidates for electrochemical device applications.

Conflict of Interest

The authors declare that they have no conflict of interest.
References

[1]. H. Kunteppa, Aashis S. Roy, Anil R. Koppalkar, M. V. N. Ambika Prasad, Physica B 406, 3997 (2011).

[2]. C. S. Ramya, S. Selvasekarapandian, Ionics 20, 1681 (2014).

[3]. M. Ravi, Y. Pavani, K. Kiran Kumar, S. Bhavani, A. K. Sharma, V. V. R. Narasimha Rao, Mater. Chem. Phys. 130, 442 (2011).

[4]. K. Sundaramahalingam, D. Vanitha, N. Nallamuthu, A. Manikandan, M. Muthuvinayagam, Physica B 547, 55 (2018).

[5]. K. Jeyabanu, K. Sundaramahalingam, P. Devendran, A. Manikandan, N. Nallamuthu, Physica B 572, 129 (2019).

[6]. Pankaj Singh, P. N. Gupta, A. L. Saroj, Physica B 578, 411850 (2020).

[7]. K. Naveen Kumar, Misook Kang, K. Sivaiah, M. Ravi, Ionics 22, 815 (2016).

[8]. Satyendra Kumar, G. K. Prajapati, A. L. Saroj, P. N. Gupta, Physica B 554, 158 (2019).

[9]. K. Kiran Kumar, M. Ravi, Y. Pavani, S. Bhavani, A. K. Sharma, V. V. R. Narasimha Rao, Physica B 406, 1706 (2011).

[10]. G. K. Prajapati, P. N. Gupta, Physica B 406, 3108 (2011).

[11]. Vanitha Durakkkan, Asath Bahadur Sultan, Nallamuthu Nallaperumal, Athimoolam Shunmuganarayanan, Ionics 24, 139 (2018).

[12]. M. Seshu Kumar, M. C. Rao, Mater. Res. Express 5, 075301 (2018).

[13]. C. Venkata Subba Rao, M. Ravi, V. Raja, P. Balaji Bhargav, Ashok Kumar Sharma, V. V. R. Iran. Polym. J. 21, 531 (2012).

[14]. K. Sreekanath, T. Siddaiath, N. O. Gopal, Y. Madhava Kumar, Ch. Ramu, J Sci-Adv. Mater. Dev. 4, 230 (2019).

[15]. El Metwally M. Abdelrazek, Amr M. Abdelghany, Shalabya I. Badr, Mohamed A. Morsi, J. Mater. Res. Technol. 7, 419 (2018).

[16]. R. M. Hodge, C. H. Edward, G. P. Simon, Polymer 37, 1371 (1996).

[17]. P. W. Davis and T. S. Shilliday, Phys. Rev. 118, 1020 (1960).

[18]. G. K. M Thutupalli, S. G. Tomlin, J. Phys. D: Appl. Phys. 9, 1639 (1976).
[19]. R. Mangalam, M. Thamilselvan, S. Selvasekarapandian, S. Jayakumar, R. Manjula devi, Ionics 23, 2837 (2017).
[20]. V. M. Mohan, Weiliang Qiu, Jie Shen, Wen Chen, J. Polym. Res. 17, 143 (2010) 143.
[21]. V. Parameswaran, N. Nallamuthu, P. Devendran, E. R. Nagarajan, A. Manikandan, Physica B 515, 89 (2017).
[22]. Wangyu Li, Ying Pang, Jingyuan Liu, Guanghui Liu, Yonggang Wang, Yongyao Xia, RSC Adv. 7, 23494 (2017).
[23]. Xiu Shen, Ruiyang Li, Haoshen Ma, Longqing Peng, Boyang Huang, Peng Zhang, Jinbao Zhao, Solid State Ion. 354, 115412 (2020).
[24]. Bashir Abubakar Abdulkadir, John Ojur Dennis, Muhammad Fadhlullah Bin Abd. Shukur, Mohamed Mahmoud Elsayed Nasef, Fahad Usman, Polym-Plast. Tech. Mat. 59, 1679 (2020).
[25]. Mangalam Ramaswamy, Thamilselvan Malayandi, Selvasekarapandian Subramanian, Jayakumar Srinivasalu, Manjuladevi Rangaswamy, Ionics 23, 1771 (2017).
[26]. K. Sreekanth, T. Siddaiah, N. O. Gopal, N. Krishna Jyothi, K. Vijaya Kumar, Ch. Ramu, S. Afr. J. Chem. Eng. 36, 8 (2021)
[27]. A. K. Jonscher Dielectric relaxation in solids. (Chelsea Dielectric Press, London, 1983).
[28]. R. C. Agrawal, S. A. Hashmi, and G. P. Pandey, Ionics 13, 295 (2007).
[29]. R. D. Armstrong, T. Dickinson, and P. M. Willis, J. Electroanal. Chem. 53, 389 (1974).
Fig. 1. XRD patterns of all the polymer electrolyte films.
Fig. 2. (A) absorption spectra, (B) $\alpha$ vs $h\nu$ plots, (C) $(\alpha h\nu)^2$ vs $h\nu$ plots and (d) $(\alpha h\nu)^{1/2}$ vs $h\nu$ plots of PVP polymer electrolyte films doped with different concentrations of GdCl₃.
Fig. 3. Frequency dependence of (A) real ($\varepsilon'$) and (B) imaginary ($\varepsilon''$) parts of dielectric permittivity for the different concentrations of GdCl$_3$ doped PVP polymer electrolyte films at room temperature. Frequency dependence of (C) real ($\varepsilon'$) and (D) imaginary ($\varepsilon''$) parts of dielectric permittivity of 15 mol% GdCl$_3$ doped PVP polymer electrolyte film at different temperatures.
Fig. 4. Frequency dependent AC conductivity plot of 0, 5, 10 and 15 mol% GdCl$_3$ doped PVP polymer electrolyte films at room temperature.
Fig. 5. Frequency dependent AC conductivity plot of 15 mol% GdCl₃ doped PVP polymer electrolyte film at different temperatures.
Fig. 6. Complex impedance plots for pure and GdCl₃ doped PVP polymer electrolyte films at room temperature.
Fig. 7. Complex impedance plots of 15 mol% GdCl$_3$ doped PVP polymer electrolyte film at different temperatures.
Fig. 8. log $\sigma_{dc}$ vs 1000/T plot for 15 mol% GdCl$_3$ doped PVP polymer electrolyte film at different temperatures.
Fig. 9. Frequency dependence of (A) real ($M'$) and (B) imaginary ($M''$) parts of electric modulus of different mol% of GdCl₃ doped PVP polymer electrolyte films.
Fig. 10. Frequency dependence of (A) real ($M'$) and (B) imaginary ($M''$) parts of electric modulus of 15 mol% GdCl$_3$ doped PVP polymer electrolyte film at different temperatures.
Fig. 11. $\log f_{\text{max}}$ vs $1000/T$ plot for 15 mol% GdCl$_3$ doped PVP polymer electrolyte film at different temperatures.

\[ Y = -5.21x + 8.59 \]

$R^2 = 0.98$
Fig. 12. Scaling behavior of 15 mol% GdCl₃ doped PVP polymer electrolyte film at different temperatures.
Fig. 13. Cyclic-voltammetry plots of (a) 0, (b) 5, (c) 10 and (d) 15 mol% GdCl₃ doped PVP polymer electrolyte films.
Figure 1

XRD patterns of all the polymer electrolyte films.
Figure 2

See the Manuscript Files section for the complete figure caption
Figure 3

See the Manuscript Files section for the complete figure caption
Figure 4

Frequency dependent AC conductivity plot of 0, 5, 10 and 15 mol% GdCl3 doped PVP polymer electrolyte films at room temperature
Figure 5

Frequency dependent AC conductivity plot of 15 mol% GdCl3 doped PVP polymer electrolyte film at different temperatures.
Figure 6

Complex impedance plots for pure and GdCl3 doped PVP polymer electrolyte films at room temperature.
Complex impedance plots of 15 mol% GdCl3 doped PVP polymer electrolyte film at different temperatures

Figure 7
Figure 8

See the Manuscript Files section for the complete figure caption
Figure 9

See the Manuscript Files section for the complete figure caption
Figure 10

See the Manuscript Files section for the complete figure caption.
See the Manuscript Files section for the complete figure caption
Figure 12

Scaling behavior of 15 mol% GdCl3 doped PVP polymer electrolyte film at different temperatures.
Figure 13

Cyclic-voltammetry plots of (a) 0, (b) 5, (c) 10 and (d) 15 mol% GdCl3 doped PVP polymer electrolyte films