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Journal of Materials Research and Technology
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Original Article

Role of nano-capacitor on dielectric constant enhancement in PEO:NH₄SCN:xCeO₂ polymer nano-composites: Electrical and electrochemical properties



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ARTICLE INFO

Article history:

Received 18 February 2020

Accepted 8 June 2020

Available online 1 July 2020

Keywords:

PEO nano-composite

CeO₂ nanoparticle

Impedance study

Ionic conductivity

Electrochemical properties

EDLC

ABSTRACT

Solution casting technique has been successfully employed to prepare nano-composite films. Various weight ratios of cerium oxide (CeO₂) nanoparticle were added to a PEO:NH₄SCN:xCeO₂ polymer matrix to enhance the ionic conductivity at ambient temperature. The electrical and electrochemical properties of the composite electrolyte systems have been investigated using impedance, dielectric properties (ϵ^* , $\tan\delta$, and M^*), transfer number measurement (TNM), linear sweep voltammetry (LSV), and cyclic voltammetry (CV) techniques. The highest ionic conductivity of $\sim 8.57 \times 10^{-4}$ S/cm is obtained for the system incorporated with 3 wt.% of CeO₂ filler. This study presented a new approach and the complex permittivity confirmed that the real part value of dielectric constant (ϵ') for all samples has found to be much higher than the imaginary part (ϵ'') value. The appearance of the peaks at a characteristic frequency in the loss tangent indicates the existence of relaxation. Low dielectric modulus is observed for 3 wt.% of CeO₂ incorporated. The TNM measurements confirmed the ionic conductivity of NCSPEs and ion transport t_{ion} of films have been found to be 0.84, 0.96 and 0.92 for 1 wt.%, 3 wt.%, and 5 wt.% of CeO₂, respectively. The system

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<https://doi.org/10.1016/j.jmrt.2020.06.022>

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incorporated with 3 wt.% of CeO₂ has discovered to be electrochemically stable up to 1.4 V. From the CV analysis it is noticeable that the energy storage mechanism of the EDLC is a combination of double-layer capacitance and pseudo capacitance. A value of 88.9 F/g is achieved at 20 mV/s.

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1. Introduction

Polymer electrolytes have been extensively studied by the worldwide researchers in the recent years, due to their importance in theoretical studies and their potential application in different fields such as polymer science, electrochemistry, organic and inorganic chemistry. The electrical and optical properties of polymer based electrolytes and nano-composites are crucial to be investigated [1]. Wide range electrochemical stability, leakage-free nature, light weight, solvent free characteristics, easy preparation techniques, safety and durability are the most significant advantages of solid polymer electrolytes (SPEs) [2,3]. The (SPEs) with good mechanical stability and flexibility can provide a better contact between electrode and electrolyte for electrochemical device applications [4]. However, poor electrical conductivity of solid polymer electrolytes at room temperature restricts their practical performances [5]. The occurrence of the ionic transport of solid polymer electrolytes can be observed only in the amorphous polymer regions [6]. Polyethylene oxide (PEO) is one of the host polymers in the preparation of solid polymer electrolyte for the metal ion conducting batteries, because it has high electrochemical stability with ion dissociation ability and nontoxicity. However, PEO has helical structure with semi-crystalline polymer so it can exist in both crystalline and amorphous phase, as well as low melting point (60 °C) [7–9]. Unfortunately, PEO-based polymer electrolyte has low conductivity at temperature <70 °C due to phase crystallinity. Nonetheless, good conductivity value is supposed to be at least 10⁻⁴ S/cm and this can be achieved only at temperature range between 80 and 100 °C. Thus, this issue limits its practical applications [10–13]. In the literature different approaches were proposed to enhance the conductivity of PEO-based polymer electrolyte. One of the approaches is to use inorganic salts particularly alkali metal salts like lithium, sodium and potassium salts. PEO possesses good solvating ability because ether oxygen atom has lone pair electrons and cations are strongly coordinated with the polymer [14–16]. Different inorganic salts such as LiCF₃SO₃, LiClO₄, LiPF₆ and NaIO₄ are reported by Ahn et al. [17] and Koduru et al. [7]. Additionally, the literature documented that the conductivity issue of SPE for energy device applications can be solved using inorganic salts specially alkali metal salts [18–21]. A number of studies reported that the ionic conductivity increased with higher salt concentration [22]. Another popular method includes the addition of nano inorganic fillers to improve the ionic conductivity for instance TiO₂, Al₂O₃, SiO₂, ZrO₂ and Ag NPs [17,23,24]. Cerium oxide (CeO₂) as a highly relevant nanoparticle has attracted a great attention due to its exceptional chemical and physical characteristics that can be applied in various fields like

fuel cell, catalyst, ultraviolet absorber, medicine, electrodes for sensors, etc. It can act as a membrane stability enhancer in the fuel cell application, even when present in a small amount, it has the ability to extend the durability of fuel cell membranes [25–28]. Consequently, in the CeO₂ structure, several oxygen vacancies exist that becoming high mobility of oxygen. Additionally, cerium oxide can switch between Ce³⁺ and Ce⁴⁺ oxidation states, relying on whether it is available in the case of reducing or oxidizing [29]. Dey et al. were reported the effect of CeO₂ nanoparticle in the PEO:NH₄ClO₄ salt complex. It was demonstrated that the CeO₂ has a great impact on ionic conductivity of the PEO based SPE systems [30].

Dielectric relaxation and ion conduction mechanism in solids are among the most intensively studied topics in condensed matter physics. Particularly, the study of dielectric relaxation in solid polymer electrolytes is a powerful approach which extracts information about the characteristics of cation–polymer interactions. Additionally, the dielectric constant plays a fundamental role to show the dissolving ability of polymer material for a salt [31,32]. In our previous works we observed a high value of dielectric loss parameter (ϵ'') compared to dielectric constant (ϵ') parameter [31–36].

From physics viewpoint, high dielectric constant value compared to dielectric loss parameter is crucial; especially for advanced materials which have wide range applications in modern technology e.g. battery and electrical double layer capacitor (EDLC). Nano-materials may constitute nano-capacitor through the electrolyte system. The contribution of many nano-capacitors to the ion dissociation and producing space charge polarization may enhance the dielectric constant which in turn improves the charge storage capacity. The main challenge in the field of polymer electrolyte is to prepare a system with high charge storage property and low dielectric loss value. Electrical double layer capacitor (EDLC) is considered as one of the main category of electrochemical capacitors in addition to hybrid and pseudo capacitor. EDLC can be used in carbon-based electrodes and various choices of electrolyte material. These capacitors can be a good alternative to other kinds of charge storage especially rechargeable batteries. In a non-Faradaic charge storage mechanism, the accumulation of charges takes place on the surface of carbon electrodes forming double-layer capacitor [37,38]. EDLC has good endurance, high thermal stability, good power density, low cost, high safety and excellent cyclability [3]. As the EDLC is connected to the power supply one electrode turns to a negatively charged electrode which attracts cations and repulses anions while a reverse action takes place at the positive electrode [39]. In the present study, the influence of cerium oxide (CeO₂) nanoparticles on the electrochemical properties of PEO:NH₄SCN based nano-composite polymer electrolyte will be investigated using various techniques.

Table 1 – The composition of the prepared PEO:NH₄SCN:CeO₂ systems.

Sample code	(PEO)(1) (g)	NH ₄ SCN (wt.%)	CeO ₂ (wt.%)
PEOCE1	1	40	1
PEOCE2	1	40	3
PEOCE3	1	40	5

2. Experimental details

2.1. Materials and preparation of polymer electrolyte

Poly (ethylene oxide) PEO with molecular weight of 5,000,000 g mol⁻¹ from Alfa Aesar, ammonium thiocyanate (NH₄SCN 99% purity) from Merck, cerium dioxide (CeO₂) nanoparticle (size ≤20 nm, purity 99.9%) from Sigma Aldrich, acetonitrile (ACN 99.9% purity) from Alpha Chemika have been used as raw materials for the preparation of nano-composite solid polymer electrolyte. All the chemicals were used with no further purification. For this purpose, 1 g of PEO was dissolved in 40 ml of ACN solution. Subsequently, a constant weight ratio (40 wt.%) of NH₄SCN was added to the solution. The solution was stirred continuously with the magnetic stirrer at room temperature until complete dissolution was achieved. Finally, various weight ratios of CeO₂ were added to the polymer salt mixture and stirred until a clear solution was obtained. CeO₂ content in the prepared samples was varied from 1 to 5 wt.%. The samples were coded as PEOCE1, PEOCE2, and PEOCE3 incorporated with PEO:40% NH₄SCN incorporated with 1 wt.%, 3 wt.% and 5 wt.% of CeO₂ nanoparticle, respectively. The solutions were then spilled into different clean and dry glass Petri dishes, covered with filter paper to avoid any impurities. Finally, samples were allowed to evaporate slowly at room temperature, in order to obtain dry and a free-standing PEO nano-composite solid polymer electrolyte films. Table 1 shows the composition of the prepared samples.

2.2. EIS spectroscopy

Electrical impedance spectroscopy of the prepared films was performed in the frequency range between 50 Hz and 1 MHz using LCR meter (HIOKI 3531 Z Hi-tester, Japan). For this measurements, a pair of stainless steel electrode was used as blocking electrode to keep thin films of nanocomposite solid polymer electrolyte (diameter=2 cm). The Nyquist plot for complex impedance (Z*), real (Z') and imaginary (Z'') parts were examined. Thus, the bulk resistance (R_b) was measured through the Nyquist plot with the real axis.

2.3. LSV and TNM measurement

Linear sweep voltammetry (LSV) was conducted to evaluate the electrical stability of the nano-composite solid polymer electrolyte (NCSPE) by measuring the decomposition voltage of the best conducting sample at room temperature. Digi-IVY DY2300 potentiostat at the 5 mV s⁻¹ sweep rate was utilized. The sweeping potential was from 0 to 2.5 V. At room

temperature, direct current DC polarization technique was used to analyze the transference number measurement as a function of time. V&A instrument DP3003 was used and the cell was polarized at 0.20 V. The transference number of ions (t_{ion}) was measured for each sample of NCSPEs films. The cell arrangement of both LSV and TNM was the same which was stainless steel (SS)| highest conducting electrolyte| SS.

2.4. Cyclic voltammetry (CV) measurements of EDLC

Digi-IVY DY2300 potentiostat was employed to study the cyclic voltammetry (CV). A voltage range from 0 to 0.9 V was used to analyze CV for the EDLC with the maximum conductive nano-composite solid polymer electrolyte film at room temperature. Planetary ball miller (XQM-0.4) was used for the process of dry mixing. The mixture of powders which consisted of 3.25 g of activated carbon and 0.25 g of carbon black was mixed at a rotational speed of 500 r/min for 15 min. Polyvinylidene fluoride (PVdF) was dissolved in 15 ml of N-methyl pyrrolidone (NMP). The powder was poured and stirred in the dissolved solution of NMP-PVdF. A thick black solution was obtained which was coated on an aluminum foil using a doctor blade. The foil was dried at 60 °C in an oven. The dried electrodes were cut into a circle with area of 2.01 cm². The highest conducting electrolyte was placed between two carbon electrodes in a CR2032 coin cell. This coin cell EDLC was placed in a Teflon holder for further testing.

3. Results and discussion

3.1. Impedance and DC conductivity study

For better understanding the electrical properties of the electrolyte material and ion mobility at the electrode/electrolyte interfaces, the electrochemical impedance spectroscopy (EIS) technique is vital [40]. This technique is performed by applying an alternate electric signal to the SPE over a broad range of frequencies at ambient temperature, from which the electrochemical system can be studied and the ionic conductivity can be determined. Two stainless steel discs were used as blocking electrode, to sandwich the solid polymer electrolyte films [41]. The movement of ions and concentration of charge carriers are affected by polymer electrolyte film conductivity [42]. Fig 1 shows the impedance plots of PEO:NH₄SCN:CeO₂ at room temperature by varying the content of CeO₂. Normally, the complex impedance plot consists of a high frequency semi-circle region, which is due to the bulk effect of the electrolyte (bulk combination with bulk resistance) and a low frequency spike due to the effect of blocking electrodes [38,41]. Bulk resistance is presented by semicircle at high frequency while spike at low frequency is due to charge double-layer. The interception between a semicircle and spike can be considered as the bulk resistance (R_b) [43]. From the Nyquist plots, it can be revealed that as the ratio of nanocomposite fillers increased from 1 wt% to 3 wt%, the diameter of the semicircle shrunk, which illustrated that the R_b has been reduced. 5% CeO₂ increase the R_b again due to the immobile polymer chains or blocking effect. This would lower the charge carriers

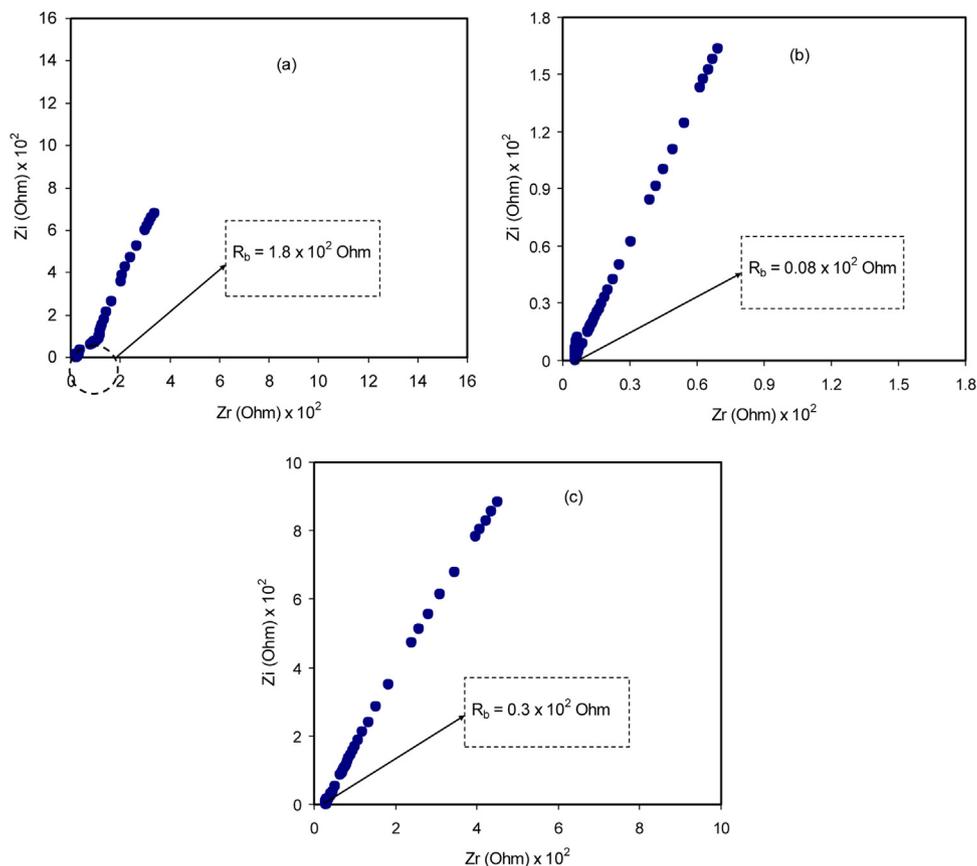


Fig. 1 – The impedance plot for solid polymer electrolytes based on PEO:NH₄SCN (a) 1% CeO₂, (b) 3% CeO₂, (c) 5% CeO₂.

Table 2 – The conductivity value of PEO:NH₄SCN:CeO₂ systems.

Sample designation	DC conductivity (S/cm)
PEOCE1	3.81×10^{-5}
PEOCE2	8.57×10^{-4}
PEOCE3	2.28×10^{-4}

and cause a reduction in the conductivity of the systems. The reduction of the semicircle indicated that the amorphous nature of the polymer system enhanced [44,45]. On the other hand, the disappearance of the semicircle signified the non-Debye behavior of polymer electrolytes [46]. DC conductivity (σ_{dc}) for each system is calculated using the following equation and presented in Table 2:

$$\sigma_{dc} = \left(\frac{1}{R_b} \right) \times \left(\frac{t}{A} \right) \quad (1)$$

where t is the thickness of the sample and A is the area of the electrode. The influence of CeO₂ nanoparticles on the ionic conductivity of PEO:40%NH₄SCN systems were investigated by utilize varying content of CeO₂. The maximum ionic conductivity is 8.57×10^{-4} S/cm for PEO:40%NH₄SCN:3%CeO₂ nano-composite solid polymer electrolyte system. The ionic conductivity increased as the nanocomposite ratio increased by up to 3%. Further increase in the CeO₂ nanoparticle content above 3% resulted in lower conductivity because of the

overcrowding the ions in the polymer network [47]. This conductivity is much greater than the recorded value of (7×10^{-7} S/cm) in the literature for PEO:NH₄SCN electrolyte [48]. It is well reported that both ionic associations, and PEO crystallinity can be greatly impacted by the hydrogen bonds of PEO and NH₄SCN which in turn effect on the overall conductivity of the prepared SPE [49]. The use of nanoparticle as a conductivity enhancer was proven. Various nanofillers have been added to the PEO based polymer electrolyte systems such as SiO₂, TiO₂ with the highest ionic conductivities at room temperature of 8×10^{-6} S/cm, and 3×10^{-5} S/cm, respectively which reported by Scrosati et al. [24] and for the PEO:LiClO₄:Al₂O₃ was 4×10^{-5} S/cm examined by Ahn et al. [17]. Qi et al. [50] reported that the PEO-LiClO₄-CeO₂ NSPEs with the maximum conductivity of 1.71×10^{-5} S/cm. Hence, the current study of PEO:NH₄SCN:CeO₂, has a higher ionic conductivity than PEO-LiClO₄-CeO₂ system.

3.2. Dielectric properties

3.2.1. Study of dielectric constant and dielectric loss

Dielectric constant analysis is an essential method to identify phase transitions, and ionic transport mechanism in polymer composites. Through this analysis one can extract information regarding the dielectric relaxation behavior and relate it to their ionic conductivity upon frequency. Dielectric properties of the polymer composite systems are illustrated based

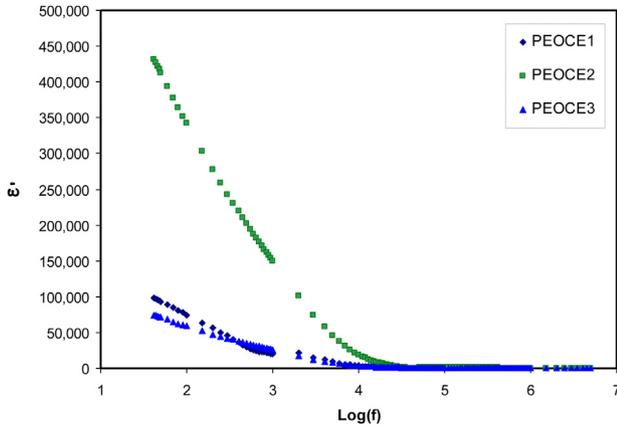


Fig. 2 – Variation of the real part of dielectric constant as a function of frequency for (PEOCE1–PEOCE3) electrolyte samples at room temperature.

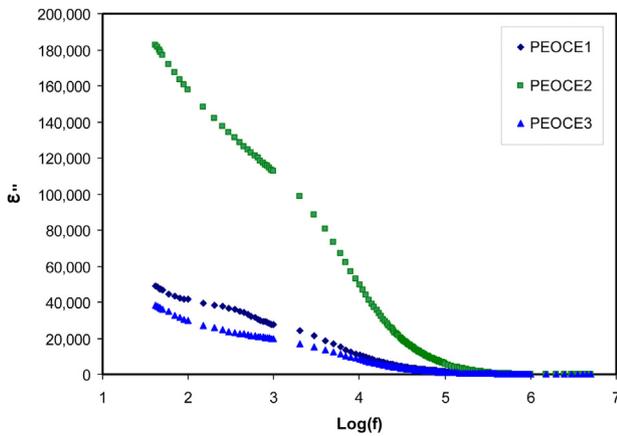


Fig. 3 – Variation of the imaginary part of dielectric constant as a function of frequency for (PEOCE1–PEOCE3) electrolyte samples at room temperature.

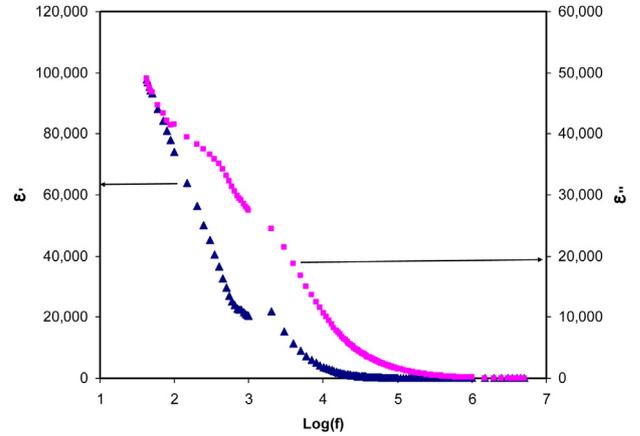


Fig. 4 – Variation of the complex permittivity as a function of frequency for PEOCE1 electrolyte sample at room temperature.

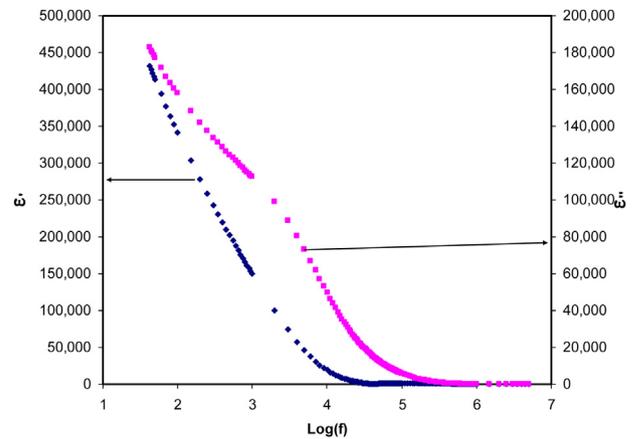


Fig. 5 – Variation of the complex permittivity as a function of frequency for PEOCE2 electrolyte sample at room temperature.

on the plots of the real (ϵ') and imaginary part (ϵ'') of complex permittivity which can be calculated from the formulas below:

$$\epsilon' = \frac{Z''}{\omega C_0(Z'^2 + Z''^2)} \quad (2)$$

$$\epsilon'' = \frac{Z'}{\omega C_0(Z'^2 + Z''^2)} \quad (3)$$

where ω is the angular frequency, C_0 is the vacuum capacitance, Z'' is the imaginary part of impedance and Z' is the real part of impedance [51]. Figs. 2 and 3 demonstrate the ϵ' and ϵ'' as a function of frequency at room temperature for PEOCE1, PEOCE2, and PEOCE3 samples. It can be seen that at the low frequency the dielectric constant reach the maximum value because of the high concentration of charged species. While, large electric dispersion at the higher frequency region can be observed. Sharp rise in the dielectric constant at the low-frequency region for PEOCE2 sample indicates the higher ionic conductor, which reflects the influence of ion species polarization and ionic mobility conductors [52].

The value of dielectric constant reaches to zero at the higher frequency region, due to the reduction in electronic polarization [53]. One can note that, as the frequency increased, the dielectric constant gradually dropped and approached constant value at the very high frequency region. However, due to the dipoles alignment to the direction of the field in a low-frequency region the dielectric constant is increased [54]. From the figures, both ϵ' and ϵ'' are increased with addition of larger weight percent ratio of CeO_2 nanoparticle up to 3 wt.% of PEO systems. Nevertheless, further increase in the CeO_2 content to 5 wt.% caused a dramatic drop in the dielectric constant, resulted from the blocking effect at the electrode/electrolyte interface.

Figs. 4–6 provide information on the complex permittivity as a function of frequency at room temperature for PEOCE1, PEOCE2, and PEOCE3, respectively. It is obvious that the value of the ϵ' for all PEO: NH_4SCN : CeO_2 nanocomposite polymer electrolytes much higher than the ϵ'' value. Among the samples, the maximum value of the dielectric constant for the PEOCE2 sample has been recorded while the minimum value obtained from the PEOCE3 sample. As mentioned in introduc-

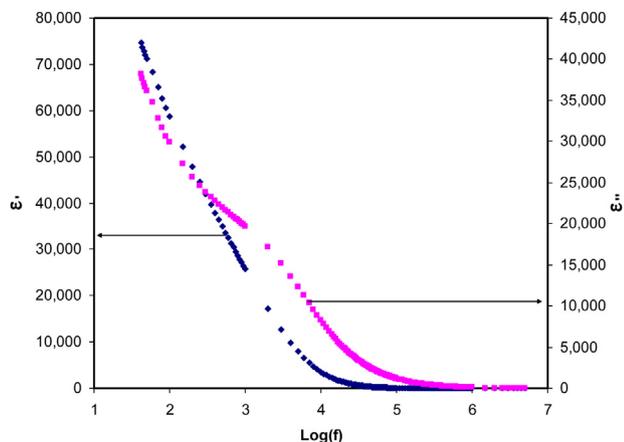


Fig. 6 – Variation of the complex permittivity as a function of frequency for PEOCE3 electrolyte sample at room temperature.

tion section we observed a high value for ϵ'' in comparison to ϵ' parameter in our previous works for polymer based electrolytes and nanocomposites [31–36]. It is well established that the high dielectric constant value compared to dielectric loss parameter is suitable for electrochemical device application. The possible explanation for the high value of ϵ' in comparison to ϵ'' is the development of many nano-capacitors inside the PEO nano-composite electrolyte. The nano-capacitors promote ion dissociation and creating space charge polarization which may improve the dielectric constant which. The main challenge in the field of polymer electrolyte is to prepare a system with high charge storage property (high dielectric constant) and low dielectric loss value. From Figs. 4–6, it is obvious that the value of ϵ' is nearly double that of ϵ'' . The high value of ϵ' refers to high value of capacitance ($\epsilon' = C/C_0$) and thus high charge storage property ($C = Q/V$).

3.2.2. Tangent loss ($\tan\delta$) relaxation peak study

Study of dielectric relaxation phenomena is considered as a vital method to explore the molecular interaction in the solid polymer-based electrolytes [55]. The segmental motion of the polymer backbone within the polymer matrix plays an important role in ions transference that can be perceivable with the relaxation process [56]. Accordingly, to observe the relaxation behavior in the PEOCE electrolyte films, the tangent loss ($\tan\delta$) was analyzed. The loss tangent ($\tan\delta$) can be defined as a ratio of dielectric loss per dielectric constant and it is a measure of electrical energy lost ratio to the stored energy in a periodic field [57,58]. The variation of loss tangent ($\tan\delta$) versus frequency measured at room temperature for the PEO:NH₄SCN electrolyte systems incorporated with the various amount of CeO₂ nanoparticle is presented in Fig. 7. Its noticeable that the loss tangent rise with increasing frequency, and reached the highest value at specific frequencies, owing to the rapid increase of the active components (i.e., ohmic) of current than the reactive components (i.e., capacitive). Further increase in frequency leads to a drop in the ($\tan\delta$), which is due to the reactive components proportionally rise with the frequency, and the active components of current are independent of frequency practically [59–61]. It can be argued that the appear-

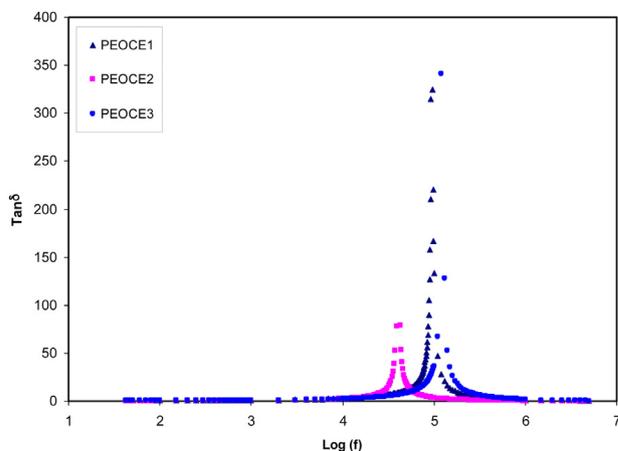


Fig. 7 – Variation of the tangent loss ($\tan\delta$) as a function of frequency for the PEOCE electrolyte samples at room temperature.

ance of the peaks at a characteristic frequency indicates the existence of dipoles relaxation in the whole samples [62,63]. It is well documented that the increase of segmental motion of polymeric chain reduces the relaxation time which in turn facilitates the transport process. This is mathematically formulated in $\tau = 1/2\pi f_{\max}$, where τ is the relaxation time for the ionic charge carrier. In other words, as long as the ion fluence increase, the relaxation time is diminished which reflected the rise in ionic conductivity because of the increment in the segmental motion of the system. These perceptions purpose that there is an increment in the amorphous region in the PEOCE2 based NCSPE [56].

3.2.3. Electric modulus study

Dielectric modulus is one of the most powerful mechanisms to further understand the conductivity relaxation phenomenon which detects the bulk dielectric nature and cover up the influence of electrode polarization effect. In particular, the modulus spectroscopy plot can be used to separate the components which have the same resistance but different in capacitance, recognize polarization of electrode, relaxation time, bulk properties, as well as electrical conductivity. Complex modulus (M^*) can be classified as imaginary and real parts. The dielectric modulus of PEO:NH₄SCN:CeO₂ polymer electrolytes were calculated from the impedance data (i.e., Z' and Z'') by utilizing the following equations [64–66]:

$$M' = \frac{\epsilon'}{(\epsilon'^2 + \epsilon''^2)} = \omega C_0 Z'' \quad (4)$$

$$M'' = \frac{\epsilon''}{(\epsilon'^2 + \epsilon''^2)} = \omega C_0 Z' \quad (5)$$

Figs. 8 and 9 show the variation of real part (M') and imaginary part (M'') of electrical modulus at ambient temperature respectively, for CeO₂ ratio-dependent PEO:NH₄SCN composite polymer electrolyte as a function of frequency. Long-tail observed at the low-frequency region of both (M' , M'') for all CeO₂ based nanocomposite polymer electrolyte. This is a good evidence for the electrode polarization influence com-

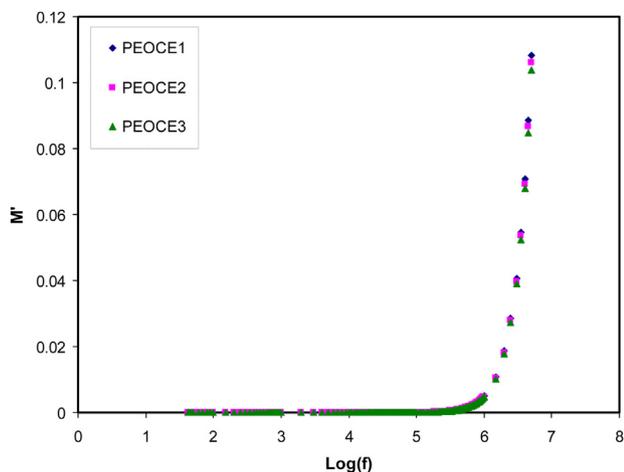


Fig. 8 – Variation of real modulus (M_r) for (PEOCE1, PEOCE2 and PEOCE3) composite electrolyte systems at room temperature as a function of frequency.

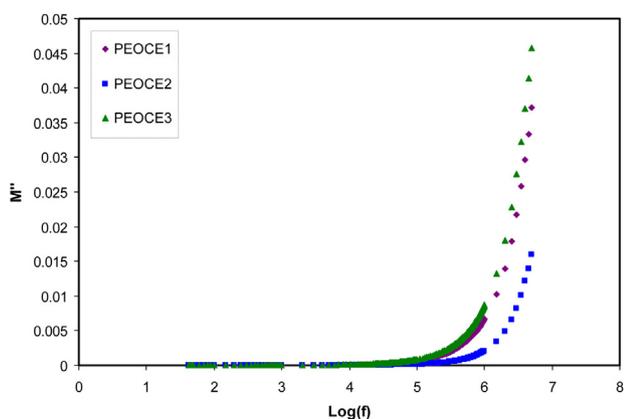


Fig. 9 – Variation of imaginary modulus (M_i) for (PEOCE1, PEOCE2 and PEOCE3) composite electrolyte systems at room temperature as a function of frequency.

pete eliminated with the large capacitance effect [67,68]. The value of complex modulus (M' , M'') increased as the frequency rises, and reached maximum at the higher frequency regions. This is related to the lack of returning force governing the movement of ions [66]. From the modulus plots, the relaxation time can be noticed at a high-frequency end and designated that the polymer composite electrolyte films are ionic conductors [69]. Nonetheless, the absences of relaxation maybe due to the limited frequency range of the instrument [54]. Between the CeO_2 weight percent ratios the imaginary modulus spectrum demonstrated that the film PEOCE2 has low-intensity modulus which means that it has a higher ionic conductivity.

3.3. TNM study

Transference number measurement has been done using the DC polarization method, to determine the contribution of ion species in the solid composite polymer electrolyte systems. Both ions and electrons species take part in the total of ionic transport [70,71]. Two essential parameters are used to comprehend the conductivity of materials which are t_{ion} and

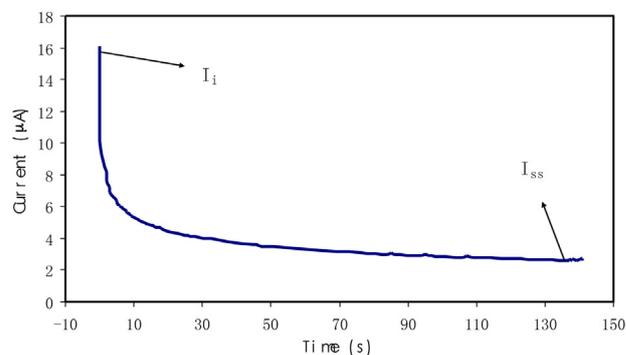


Fig. 10 – Polarization current for PEOCE1 system as a function of time.

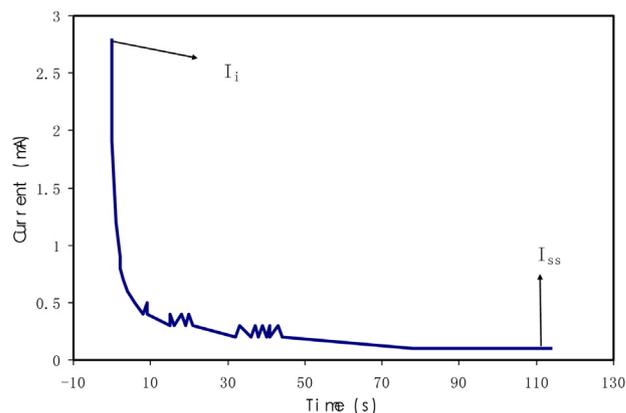


Fig. 11 – Polarization current for PEOCE2 system as a function of time.

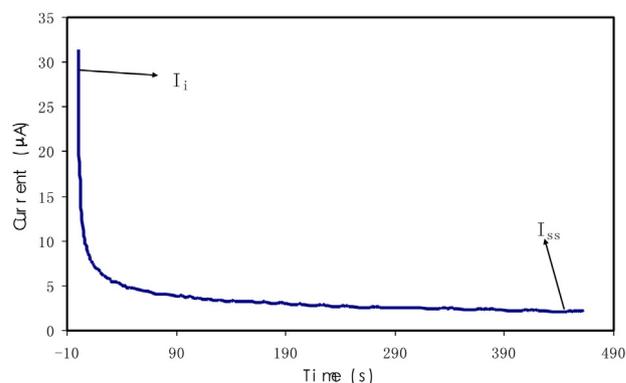


Fig. 12 – Polarization current for PEOCE3 system as a function of time.

electron transference number (t_e). Non-blocking electrode is an electrode where both ion and electron can pass through while for blocking electrode, only electrons can pass through the electrodes. t_e should be smaller than the ion t_{ion} for polymer composite electrolyte since films are ionic conductor, and signifying the dominance of ions to the overall conductivity [72,73]. Figs. 10–12 represent the plots of polarization current against time for the PEOCE1, PEOCE2 and PEOCE3 films, respectively. It was observed that the initial current value drop rapidly with time for all PEO: NH_4SCN : CeO_2 systems. This might be due to the reduction of ions in the NCSPEs. At the

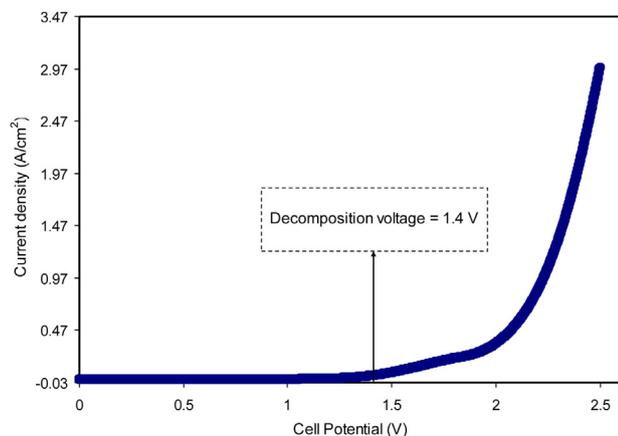


Fig. 13 – linear sweep voltammetry for PEOCE2 sample with highest conductivity.

steady-state phase, since only electron can migrate along the electrolyte interface, the cells become polarized [74]. The value of t_{ion} can be determined using the following equations:

$$t_{ion} = 1 - t_e \quad \text{or} \quad t_{ion} = I_i - I_{ss}/I_i \quad (6)$$

where I_i and I_{ss} are the initial current and steady-state current, respectively. The value of initial and steady-state current are extracted from the TNM plot. The calculated t_{ion} values are 0.84, 0.96 and 0.92 for PEOCE1, PEOCE2, and PEOCE3, respectively. Among the NCSPEs, PEOCE2 (3 wt.% CeO₂) has the highest t_{ion} and it is near to the ideal value of unity. These results approve that ions is the most vital conducting species in the electrolyte [70,72–74]. Other studies reported that good electrolytes possess $t_{ion} > 0.90$ [75,76].

3.4. LSV study

Linear sweep voltammetry analysis is utilized to determine the electrochemical stability of the maximum conducting PEO:NH₄SCN:xCeO₂ system. High electrochemical stability of an electrolyte is very crucial for any electrochemical device applications [39,74]. Fig. 13 illustrates the LSV plot for PEOCE2 film sample at room temperature. No obvious increment in current value from 0 to 1.4 V. As the potential is >1.4 V, current value increase sharply as the potential increased. The lowest requirement has been found to be ~1 V in ammonium salt-based energy storage technologies [77]. Hence, PEOCE2 can be used as an electrodes separator in EDLC application. The decomposition voltage of PEO-PMMA-LiClO₄ with 3 wt% of various nanoparticle films has been investigated by Dhatarwal [78] where the value of decomposition voltage for SiO₂, Al₂O₃, ZnO, and SnO₂ is ~3 V, which is higher than the present work value. The authors also stated that the electrochemical performance of the electrolyte can be affected by dielectric constant, particle size and structure. In this case, the author used polymer blend of PEO-PMMA instead of a single PEO in this work. Polymer blend possesses more functional groups and higher dielectric properties than a single polymer. These characteristics enhance the number of charge carriers in the

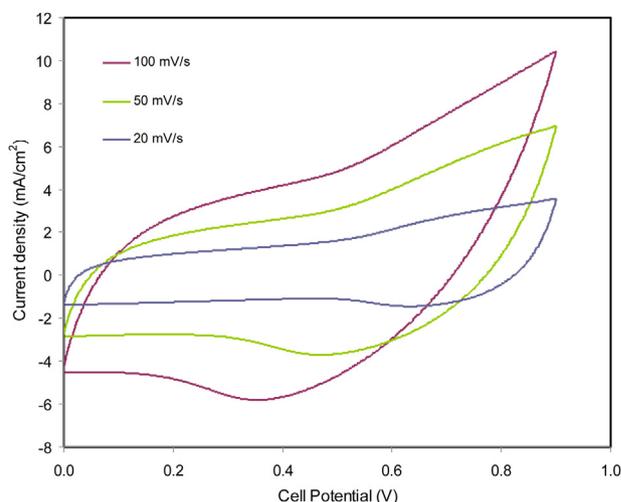


Fig. 14 – CV of the EDLC fabrication for PEOCE2 sample in the potential range 0–0.9 V at the scan rate 20, 50 and 100 mV s⁻¹ at room temperature.

electrolyte which resulting in improvement of conductivity as well as decomposition potential.

3.5. CV study

The charge transfers and charge storage behavior at the electrode/electrolyte interface can be analyzed using CV analysis [79–81]. Fig. 14 shows the CV plot of the EDLC at various scan rates (100, 50, 20 mV s⁻¹) with potential range up to 0.9 V. In order to determine the specific capacitance (C_{spe}) of the fabricated EDLC is using the following equation [82]:

$$C_{spe} = \int_{V_i}^{V_f} \frac{I(V)dV}{2mv(V_f - V_i)} \quad (7)$$

where $I(V)dV$ is the area of the CV which is obtained using the Origin 9.0 software through the integration function. The chosen V_i and V_f in the present work are 0 V and 0.9 V, respectively. v is the scan rate and m is the weight of active material. The values of C_{spe} for fabricated EDLC are 46.8, 67.2 and 86.9 F/g for 100, 50 and 20 mV/s, respectively. This result is comparable to our previous work using NH₄SCN-based EDLC where the C_{spe} from CV is 66.3 F/g [39]. An EDLC by Sudhakar et al. [83] with xanthan gum: LiClO₄:glycerol system achieved 74 F/g at 5 mV/s. Liew et al. [84] reported that 52.78 F/g is achieved for EDLC with activated carbon electrode and PVA:NH₄CH₃COO:BmImI electrolyte. It is also noticeable that the value of C_{spe} is higher at low scan rate compared to high scan rate. At low scan rate, efficient ionic conduction can be achieved where ions can form proper charge-double layer at the surface of the electrolyte which resulting in the increment of capacitance [85,86]. It can be observed that each CV plot possesses a small bump or peak. This signifies that the energy storage mechanism of the EDLC in this work is combination of double layer capacitance and pseudocapacitance. The existence of small bump in the CV plots could be to presence of

Table 3 – The capacitance value of PEOCE2 sample at the scan rate of 20, 50 and 100 mV/s.

Scan rate (mV/s)	Capacitance (F/g)
100	46.8
50	67.2
20	86.9

CeO₂ in the electrolyte. The redox reaction can be expressed using the following equation:



CeO₂ is known as reversible redox material with pseudocapacitive behavior [87].

Pseudocapacitance is produced by an electron charge-transfer between electrode and electrolyte coming from an adsorbed ion and de-solvated. No chemical reaction occurs among adsorbed ion and atoms of the electrode. Pseudocapacitance and double-layer capacitance both contribute inseparably to the total capacitance value [88] (Table 3).

4. Conclusion

In the current study, the influence of cerium oxide CeO₂ nanoparticle on the PEO:40%NH₄SCN solid polymer electrolyte (SPE) systems have been investigated. Electrical and dielectric properties of NCSPE films have been evaluated through impedance, dielectric and modulus spectroscopy. Various techniques such as TNM, LSV, and CV have been characterized. The highest ionic conductivity at room temperature has been achieved with 3 wt.% CeO₂ where the conductivity increased from 3.81×10^{-5} S/cm to 8.57×10^{-4} S/cm. A reduction in conductivity value can be observed if CeO₂ content exceeded 3 wt.%. From dielectric analysis, dielectric constant (ϵ') for all samples has found to be much higher than the dielectric loss (ϵ'') value. The LSV showed that the PEO:40%NH₄SCN:3%CeO₂ possessed electrochemical stability up to 1.4 V. Ions has identified as the primary charge carriers in the electrolyte and gave bigger contribution to the total conductivity compared to electron. t_{ion} of the sample with 3 wt.% CeO₂ has discovered to be 0.96. The outcomes from CV analysis revealed that the presence of CeO₂ in the electrolyte introduce a small pseudocapacitive behavior. Both double-layer capacitance and pseudocapacitance contribute to the total capacitance in the EDLC. A maximum specific capacitance of 86.8 F/g has been achieved at 20 mV/s.

Conflicts of interest

The authors declare no conflicts of interest.

Acknowledgements

The authors gratefully acknowledge the financial support for this study from Ministry of Higher Education and Scientific Research-Kurdish National Research Council (KNRC), Kurdistan Regional Government/Iraq. The financial support from the

University of Sulaimani and Komar University of Science and Technology are greatly appreciated.

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