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Ion Conductivity Enhancement in Ba-Nano Ferrite Dispersed [PVA: (NH4CH2COO)2] Gel Polymer Electrolytes

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Abstract **- The present study attempted to as synthesis a nanosized Ba-ferrite drugged PVA-based nano composite gel polymer electrolyte (NCGPEs) for electro-chemical device applications. To synthesis NCGPE films, nanosized Ba- ferrite were chemically synthesized and distributed in a matrix electrolyte of PVA: (NH4CH2COO)2. The XRD results for the synthesized filler particle show the development of nano ferrite, with hexaferrite as the predominant phase. Further XRD experiments on NCPGE demonstrate that the amorphous character improves as the concentration of nano fillers in composite electrolytes increases. OM and SEM examinations of NCPEs reveal a diverse distribution of fillers. Cyclic voltammetry indicates an optimal electrochemical window of ±2V with acceptable recyclability. Ionic conductivity of electrolyte measured using impedance spectroscopy approach indicates improvement in electrical conductivity following dispersal of nano. Conductivity behavior shows a change in conductivity by an order of magnitude upon ferrite dispersal.**

Keywords **– Arrhenius character, Ba- ferrite, ionic charge transport, NCGPE, and VTF.**

1. Introduction

Since the first report on ionic substances recognized as solid polymer (SPE) in (1973) [1,2], this sub domain of solid electrolytes has drawn the attention of researchers with diverse scientific backgrounds. Polymer electrolytes are classified into several categories, with new techniques and technological uses emerging. The properties, benefits, and applications of three types of polymer electrolytes: gel polymer electrolytes, solid polymer electrolytes, and composite polymer electrolytes. Following that, we will analyze the characteristics and performance of several polymer hosts, drawing on some relevant and current research. Figure 1 categorizes PEs into three distinct categories depending on their condition and configuration.

The attempts to solve the disadvantages and limits of solid polymer electrolytes resulted in the development of a new sort of material, composite polymer electrolytes (CPEs). Researchers demonstrate many ways for preparing and designing CPEs (figure2). They include polymer mixing, cross-linking polymer matrices, combranched copolymers, binary salt systems, the insertion of additives such as plasticizers, the doping of nanomaterials, impregnation with ionic liquid, and reinforcing with inorganic filler. The performance of composite polymer electrolytes (CPE) is governed by aspects such as the structure and interaction of atoms/ions/nanoparticles within the system, the mobility and quantity of ion conducting species, and the dielectric characteristics.

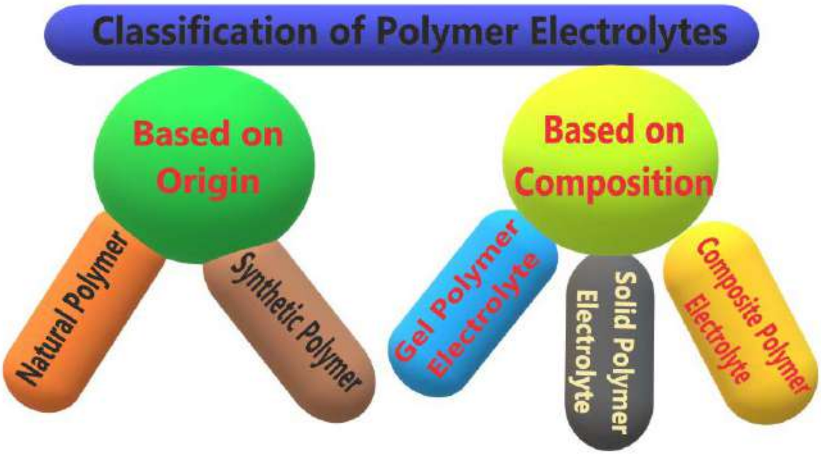

Fig. 1 Classification of polymer electrolytes

Composite polymer electrolytes can be made in many methods, however all processes can be classified into two basic classes. (i) the inorganic component is produced and subsequently combined with a polymer electrolyte; or (ii) the inorganic component is created in situ inside a polymer electrolyte.

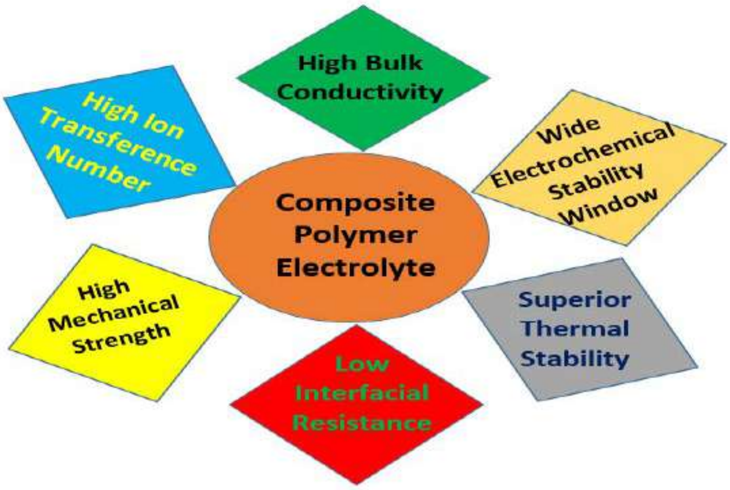

Fig. 2 Composite Polymer electrolyte

Among other polymer electrolytes, PVA is extensively studied polymers, which possesses good dielectric properties and wide temperature application window (T_m to T_g range) besides its solvent swollen ability which make it a potential host for development of polymer gel electrolytes. In spite of industrial importance and wide applications of PVA, the ions conduction mechanism remains unresolved. Through their experimental studies, a number of researchers have demonstrated that anion/cation mobility takes place in the amorphous phase and that a complex process involving PVA segmental motion facilitates its diffusion [3]. Salts with large anions should have low lattice energy for salt dissociation because larger anions have more charge delocalisation [4-5]. Furthermore, it is anticipated that a big anion may disrupt crystallisation processes, which will likely exacerbate the amorphous phase. It is anticipated that each of these elements will greatly increase the ionic conductivity of systems. Incorporating nanometric-sized inorganic/organic fillers into matrix electrolytes reduces the system's crystallinity and encourages ion migration through thin interface layers, which may be a non-reluctant route. Thus, ion transport tends to improve [6]. Alternatively, polymer gel electrolytes have been looked upon as favorable electrolyte material as they possess conductivities approaching to that of liquid electrolyte [7]. However liquid exudation when retained for long period which eventually leads to loss of ionic conductivity. In recent years blend based and filler dispersed gel electrolyte have been reported to overcome to this difficulty of polymer gel electrolytes [8]. Recently Al_2O_3 and CNT doped PVA-NH_4SCN gel electrolytes have been reported by Agrawal et al [8,9] with noteworthy enhancement in ionic conductivity and better mechanical and electrochemical integrity. In these systems liquid can be retained in gel matrix for long periods. Ferroelectric, ferrites, and bi-functional oxides are recent additions to the ceramic filler family that have shown effective in the creation of nanocomposite polymer electrolytes [10]. Addition of such filler particles have opened new application areas such as drug delivery systems, magneto electric applications etc. Additions of ferrite fillers to PVA matrix are likely to enhance the polar characteristics of PVA making it electrically more conductive. Upon doping PVA based pristine electrolytes with ferrites, it may reside at various sites. It may go substitution on polymer chain at the amorphous or crystalline boundaries and preferentially into amorphous region of polymer. Furthermore, it has been asserted earlier that addition of ferrite creates additional hopping sites for the charge carriers and hence increases ion concentration and so increase the conductivity [11,12]. In view of the above, innovation has been done to use nano sized Ba-ferrite ceramics materials as filler in development of PVA-$(NH_4CH_2COO)_2$ electrolyte based NCPEs followed by its characterization.

2. Experimental Details

2.1 Synthesis of Ba-ferrite nanopowders

Fig. 3 Flow Chart for Synthesis of Ba-ferrite nanopowders

A high-purity ferric nitrate [Iron (II) nitrate monohydrate $Fe(NO_3)_3.9H_2O \geq 98.0\%$], Barium nitrate $Ba(NO_3)_2 \geq 99.0\%$ and citric acid $C_6H_8O_7.H_2O$ were used as raw materials to prepare a precursor solution (Figure3). The nitrates were liquified in double distilled water mixture keeping the pH of solution fixed around (6-7) range. The resulting solution was magnetically stirred for long duration at 80^{0}C to transform into gel form. This gel was dried at 150^{0}C for 22 hours. After thermal treatment at 450^{0}C [for 2hours] of the gel, it was grinded to obtain fine powder of Ba-ferrite, for synthesis of NCPE.

2.2 Synthesis of NCPGE

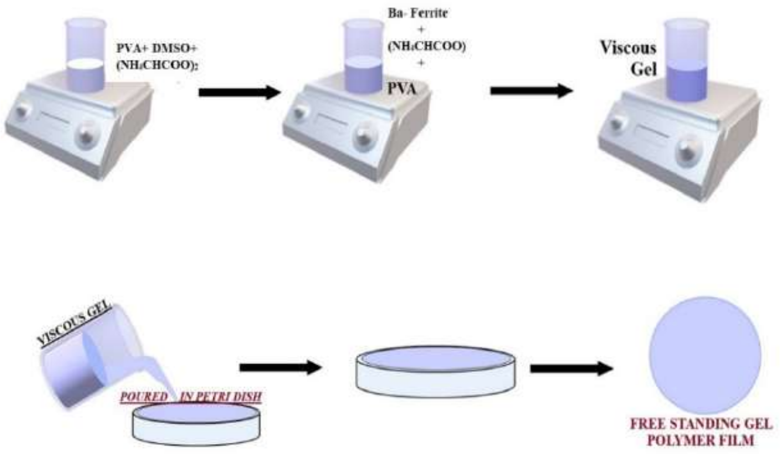

Fig. 4. Synthesis of composite electrolyte with solution cast technique

As received Polyvinyl alcohol (PVA) (M.$_W$. =85,000-140, 000, 98.99%, Acros organic) and salt $(NH_4CH_2COO)_2$ (Aldrich AR Grade) were used for the synthesis of composite electrolyte with solution cast technique (Figure 4). Pristine polymer electrolyte solution was prepared in common co-solvent DMSO. Subsequently, sol-gel derived Ba-ferrite powder was dispersed stochiometrically in PVA-$(NH_4CH_2COO)_2$ solution (in DMSO at 60^{0}C) and continuously stirred for 10-12 hours. The gelatinous polymeric solution was finally cast in polypropylene dish. The so formed solution cast films where finally dried at 30^{0}C in B.O.D. incubator for controlled evaporation followed by vacuum drying to obtain the solvent free standing films.

2.3. Characterization

XRD measurement of nano filler powder was carried out on make model (Rikagu Mini Flex-II). X-ray diffraction (XRD) in the 2Θ range 15^0 to 80^0 with Cu-Kα target (λ=1.5406Å). The particulate morphology of ferrite powder was characterized using Scanning Electron Microscope (Carl Ziess make SEM Model Supra TM 40VP) and Optical Microscope. C-V and I-t measurements were executed for CH-electrochemical workstation (CH instruments model CH608) to determine electrochemical window and nature of charge transport. Electrical conductivity measurement was performed on Hioki make LCR meter in the frequency range 40Hz-100 KHz between 293K and 363K.

3.Results and Discussion

3.1 XRD Studies

Structural characterization of the barium ferrite powder was performed through XRD studies for phase identification and estimation of particle size before using it for synthesis and characterisation of nanocomposite polymer electrolytes. Figure **5** shows the XRD pattern of sol-gel derived ferrite powder. The pattern depicts many crystalline peaks elucidating crystalline morphology. Comparison of this XRD data with JSPDS data reveals the presence of mixture of Barium hexa ferrite ($BaFe_{12}O_{19}$) phase ($2\Theta = 30.3^0$, 35.6^0 37^0,57^0, and 63^0) and Barium mono ferrite ($BaFe_2O_4$) phase ($2\Theta = 27.6^0$, 43.4^0, 46.8^0 and 49.2^0). Appearance of a shoulder peak around 33.3^0 can be co-related to formation of $BaCO_3$ in traces. Similarly minor peaks around 30^0, 53.7^0 and 63.3^0 were detected which reveals the presence of α-Fe_2O_3 as impurity in ferrite powder. Presence of $BaCO_3$ and α-Fe_2O_3 is possibly due to calcination of gel powder at lower temperature [13]. Though XRD pattern indicates presence of $BaFe_{12}O_{19}$, $BaFe_2O_4$, α-Fe_2O_3 and $BaCO_3$ in the powder the major component comprises of hexa ferrite.

Crystallite size of as synthesized particles was estimated for the most intense peak of hexaferrite ($2\Theta = 35.6^0$) and mono ferrite ($2\Theta = 43.4^0$) using well known Debye Scherrer relation [14].

$$d = \frac{0.9\lambda}{\beta cos\theta} \quad (i)$$

where, β is full width at half maxima in radian, Θ the Bragg's angle and λ the wavelength of incident X-ray beams. Average particle size comes out to be 15.36 nm which ascertains nanometric size of ferrite fillers.

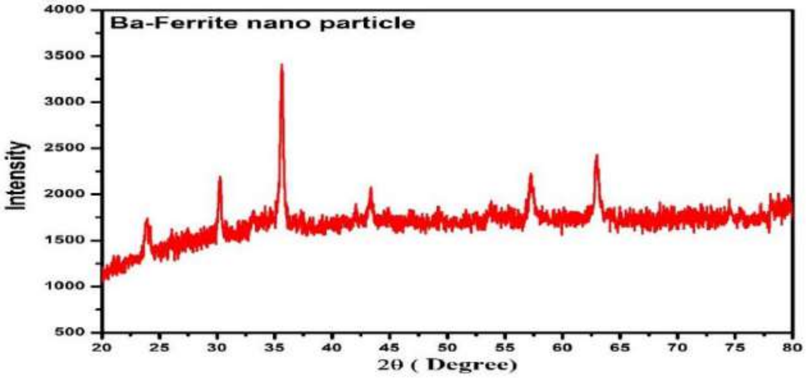

Fig. 5. XRD pattern of sol-gel derived ferrite nano powder.

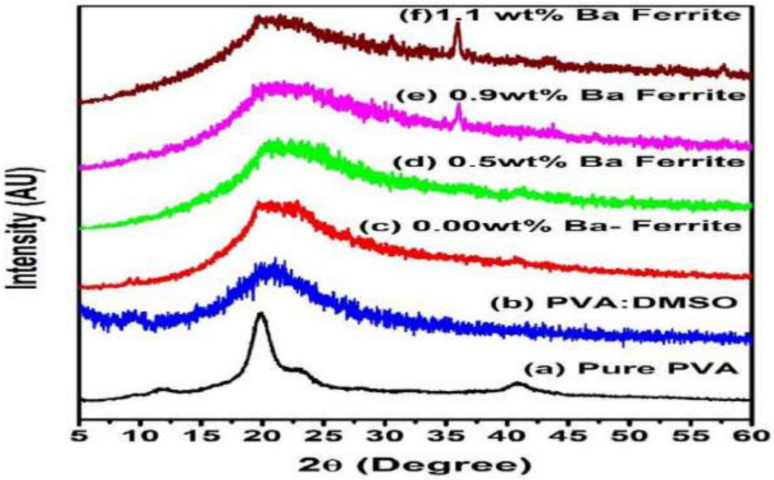

Fig. 6. XRD pattern of (a) Pure PVA, (b) PVA: DMSO and NCPGE in 0.8M NH4(CH2COO)2 with Ba-ferrite conc.(c)0.0wt%, (d)0.5 wt%, (e) 0.9wt% and(f) 1.1wt%.

The XRD pattern of polymer gel electrolytes of DMSO: NH_4 $(CH_2COO)_2$: PVA without and with Ba- ferrite nano a filler along with ferrite is shown in figure **(6)**.

All the XRD pattern illustrates enhance in broadness of prominent peak of polymer gel electrolyte post-addition of nano filler. A relatively sharp characteristic peak at **2θ**=19.6^0 and shoulder around **2θ**=9^0 have been observed in an earlier work on DMSO casted PVA gel films. [7]Awadhiya &Agrawal . Upon dispersal of 0.5wt% Ba- ferrite nano filler, the peak widens and shifts towards greater **2θ** extent due to intercalation of ferrite in gel matrix. Interestingly the small shoulder peaks at 2θ=36.1 and 43.7 appear the pattern b.These small peaks may possibly be due to shifting of 35.94^0 and 43.3^0 peaks of Ba hexaferrite after interaction with salt and polymer. No other peak corresponding to that of Ba ferrite [figure1] could be tracked in XRD pattern to suggest strong interaction of filler particle with matrix electrolyte. As the concentration of filler is raised to 0.9wt% the intensity and broadness of peaks with total disappearance of 36.1 and 43.74 peak (diffractogram b) occurs indicating complete absorption of Ba-ferrite particles. At a concentration of 1.1wt %, the characteristics reflections of ferrite nano filler start reappearing due to segregation. XRD showed that Ba-ferrite nano filler are dispersed allover the polymer matrix with highest uptake of 0.9wt%.XRD studies show Ba-ferrite-polymer- salt interaction with amorphous behavior.

3.2 Optical and SEM Studies

Figure **7** depicts the optical micrographs of as synthesized nano ferrite powder dispersed in KBr, pristine electrolyte and NCPE dispersed with different filler concentration. In optical image (figure 7**a**) oriented rod shaped like structure of pure Ba-ferrite is visible with heterogeneous dispersion in KBr pellet. Average size of these rod shaped particles has been found to be 150 - 200 nm. SEM image of barium ferrite powder was also recorded to understand the morphological feature of sol-gel derived ferrite particles (figure 7 **e** and **f**). SEM image of the product calcined at 450^{0}C for 3h in air shows hexagonal plate shape with non-homogeneous distribution of particles. Further, the particles are also agglomerated in different sizes and shapes. Similar features have been reported by Topal et al [15] and Sozeri et al [16]. Careful examination of SEM images also depicts few round shaped particles indicating the presence of mono ferrites as well. These observations are in conformity with XRD results (figure**5**). Polymer host PVA is known to possess micro porous structure. After doping of salt the pore size is seen to decrease with trapping of liquid electrolyte within the pores and its interaction with PVA. Thus pristine electrolyte system assumes amorphous morphology as also displayed here (figure 7**b**). Optical image of [PVA: $(NH_4CH_2COO)_2$]: x wt% Ba-ferrite (where, x=0.7 and 0.9 wt %) are given in figure7(**c-d**). At low concentrations of filler they are seen as heterogeneous dispersion. Addition of filler in PVA matrix electrolyte appears to disturb the original structure of the polymer as concentration of filler enhances. Comparison of view graphs 7(**c-d**) on one hand reflects increase in homogeneity of dispersed particles and on the other hand due to disturbance of original structure it acquires spinodal decomposition type phase separation as reported for PEO:NH_4SCN:Al-Zn ferrite system [17].

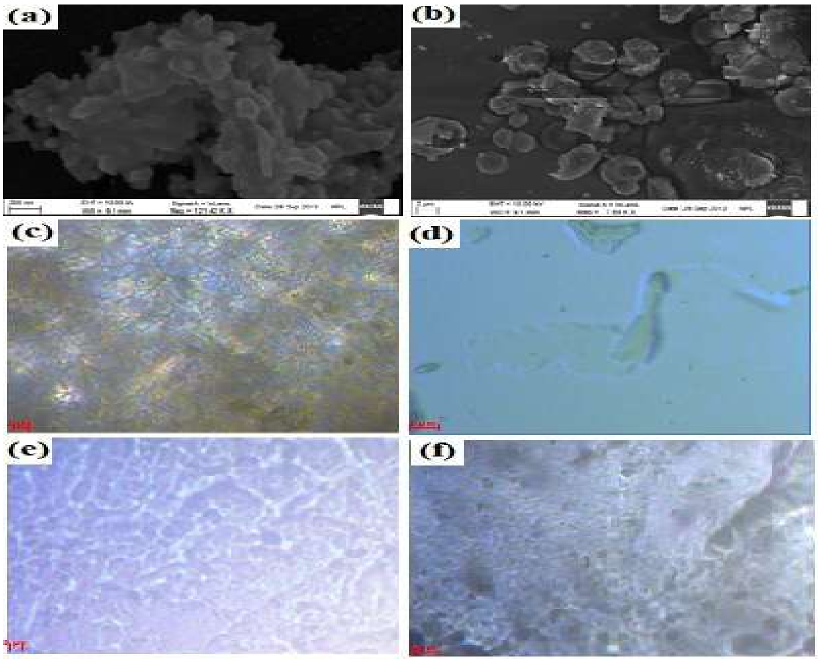

Fig. 7. (a&b) SEM of Ba- Ferrrite,(c) optical micrographs of(Ba-Ferrite) and (d-f) Ba- doped Nanocomposite Polymer electrolyte.

3.3 CV Studies

Figure 8 shows the cyclic voltametry for pristine and nano barium ferrite filled composite electrolytes. Small cathodic and anodic peaks were observed around ±1.3V in all composite electrolytes when the experiments were performed for repeated cycles. A small oxidation peak appear at 0.5V which correspond to NH4$^+$/H$^+$ ion there by indicating protonic conduction in composite electrolytes[9,18].

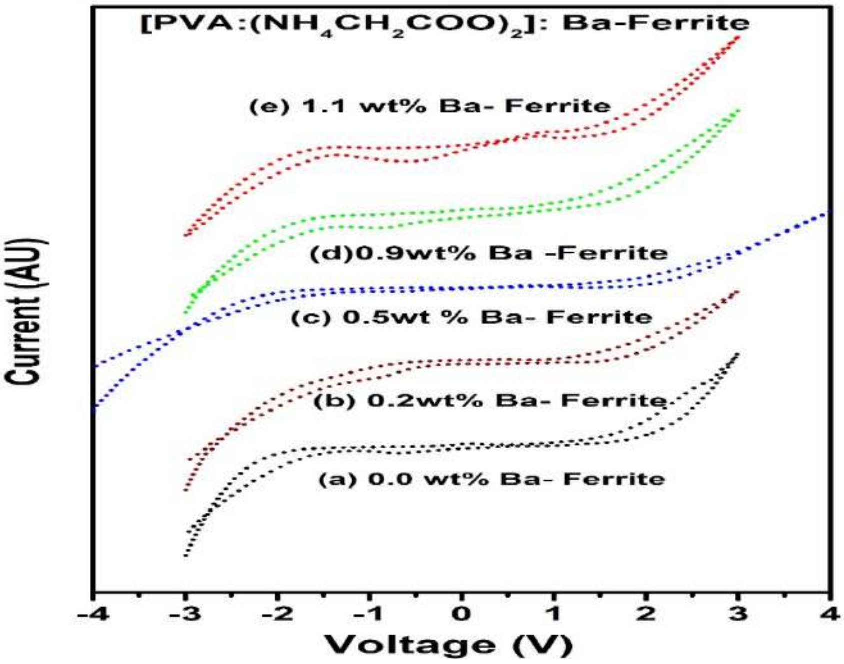

Fig. 8. The cyclic voltametry for pristine and nano barium ferrite filled composite electrolytes.

On addition of barium ferrite nanofiller in polymer gel electrolyte, the electrochemical stability is seen to augment (±2V) till 0.5wt% filler content. Subsequent addition of Ba-ferite gradually decreases electrochemical stability till 0.9 wt% ferrite concentration before increasing again at 1.1wt% filler where electrochemical window is -1.4V to +1.4V.

Large value of electrochemical window (±2V) suggests its utility in ionic devices particularly in solid state batteries. Reversibility feature of electrolyte system were studied for 10 cycles (figure 9). As the samples show considerable shift in electrochemical window after 10 cycles though overall drop in electrochemical efficiency is small.

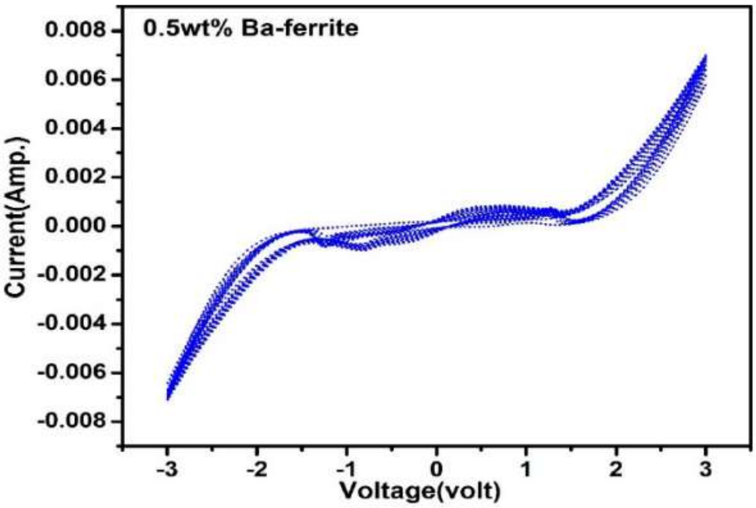

Fig. 9. The cyclic voltametry for repeated (10 cycle) nano barium ferrite filled composite polymer electrolytes

3.4 Ion Transport Studies

In view of the earlier reports on PVA-(NH4CH2COO)2 electrolyte system, the likely mobile species in [PVA-(NH4CH2COO) 2]: x% Ba ferrite (where x = 0.5, 0.7 and 0.9 wt %) polymer composite electrolyte system are too expected to be protonic. The variation of current with time on the application of small dc potential (V=0.5volt) is shown in figure 10. Total ionic transference number (tion) was calculated using the relation,

$$t_{ion} = \frac{i_{initial} - i_{final}}{i_{initial}} \quad (iii)$$

Optimum value of t_{ion} was found to be around 0.98 for composite electrolyte system containing 0.5wt% Ba-ferrite filler. Such a high value of total ionic transference number ascertains ionic nature of charge transport in electrolyte.

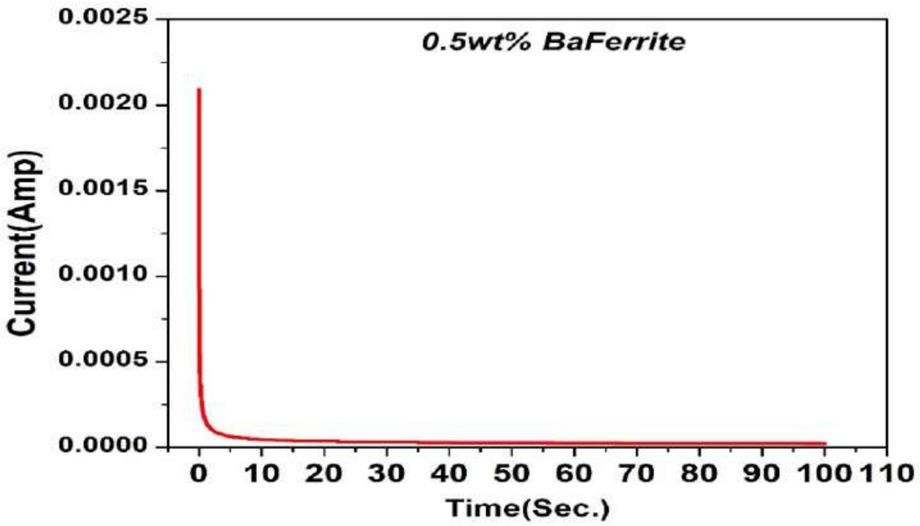

Fig. 10. Wagner's polarization plot of nanocomposite polymer electrolyte at 0.5wt% Ba-Ferrite

3.5 Conductivity Behavior

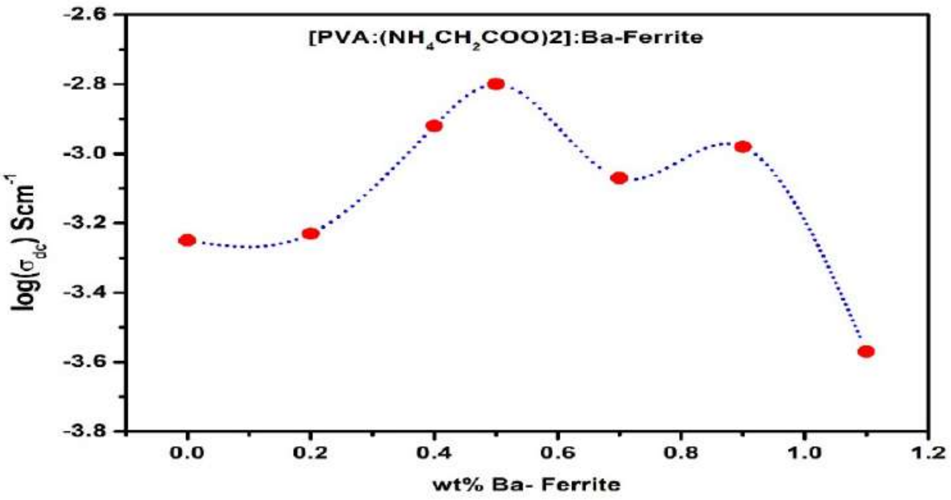

Fig. 11. Bulk conductivity as a function of filler concentration for Ba-ferrite dispersed NCPGE

Figure 11 depicts behavior of bulk conductivity for Ba-ferrite dispersed NCPGE conductivity is seen to augment upon addition of filler upto around 0.5wt% Ba-ferrite before decreasing till 0.7wt% ferrite content. On further addition ferrite in the electrolyte system conductivity again increases marginally and finally a sharp fall is noticed. Such a behavior is typical of composite polymer electrolyte [7, 10, 19].

Also, upon addition of filler particles enhancement in amorphous behavior has been noticed during optical imaging. Hence both these factors coupled together cause significant increase in ionic conductivity in correspondence with the relation:

$$\sigma = ne\mu \qquad (ii)$$

When the concentration of filler increases beyond 0.5wt%, ion association effect described by breathing chain model [20] comes into play forcing the presence of non-conducting ion pairs. Thus, conductivity dips down due to loss in concentration of free ion for migration. When filler concentration increases beyond 0.7wt% again, conductivity rises by a small amount owing to dominance of system morphology over decreasing trend of n the number of carrier concentration responsible for ionic conduction. As a consequence, conductivity increases. Finally, agglomeration of filler takes place at high concentration which creates tortuous pass-ways for ion transport and so significant fall in conductivity take place.

Figure 12 display temperature dependent behaviour of NCPE alongwith that of pristine electrolyte system. In the absence of filler, the conductivity behaviour can be best explained by combination of VTF and Arrhenius behaviour described by following relations:

$$\sigma = \sigma_o \exp\left(-\frac{E_a}{KT}\right) \qquad (iii)$$

$$\sigma = \sigma_o T^{-1/2} \exp\left(-\frac{E_a}{T - T_0}\right) \qquad (iv)$$

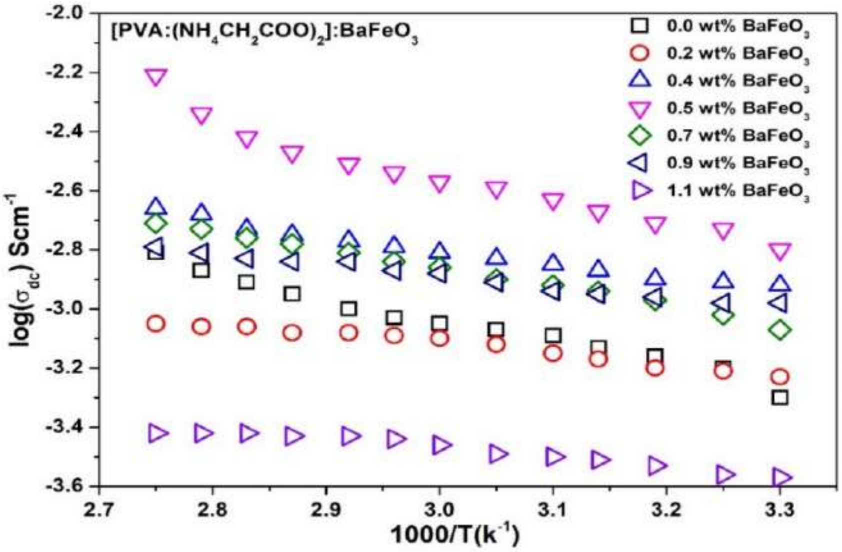

Fig. 12. Display temperature dependent behaviour of NCPE

As the amorphous region increases with addition of filler, the polymer chain acquires faster internal motion and bond rotation causing enhancement in segmental motion. It is interesting to note that upon addition of filler to form NCPGE variation in conductivity is restricted to within an order of magnitude. At high filler concentrations VTF character transcends into Arrhenius behavior so that overall behavior can be best described by relation (iv).

4. Conclusion

Formation of nanometric Ba-ferrite has been ascertained from XRD & SEM studies. Crystalline peaks of Ba-ferrite correspond to formation of mono and hexa phase Ba ferrite. Particle size calculated using Scherrer's formula was to be found 15.25 nm. SEM image depicts the presence of mono and hexa ferrite. Optical investigation reveals spinodial decomposition structure. Amorphous morphology is reflected in the optical images of composite electrolytes. Best electrochemical stability of electrolyte system has been achieved (-2 V to +2 V) for 0.5wt% Ba-ferrite filler doped system. Electrolyte films show ionic charge transport. Conductivity behavior shows a change in conductivity by an order of magnitude upon ferrite dispersal. Combination of VTF & Arrhenius character is revealed in temperature dependant conductivity studies.

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