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Study of Electrical and Electrochemical Behaviour on Hot-press Synthesized Nano-Composite Polymer Electrolyte (NCPE) Membranes: [(70PEO: 30 KNO_3) + x SiO_2]

R. C. Agrawal[*], *Y. K. Mahipal*

Solid State Ionics Research Laboratory, School of Studies in Physics & Astrophysics, Pt. Ravishankar Shukla University, Raipur – 492010, Chhattisgarh, INDIA
[*]E-mail: rakesh_c_agrawal@yahoo.co.in

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Poly (ethylene oxide) (PEO) based Nano-Composite Polymer Electrolyte (NCPE) membranes: (70PEO: 30KNO_3) + x SiO_2, where x = 0, 1, 2, 3, 5, 8, 10, 12 wt. (%), have been casted by hot-press/ solution free technique. Solid Polymer Electrolyte (SPE) composition: (70PEO: 30 KNO_3) (wt. %), reported earlier as highest conducting film with room temperature conductivity (σ_{rt}) ~ 3.98 x 10^{-7} Scm^{-1}, has been used as the I^{st} – phase host matrix and SiO_2 filler particles of nano-dimension (~ 8 nm) as II^{nd} – phase dispersoid. The fractional dispersal of SiO_2 filler (viz. x = 5 wt. %) in I^{st} – phase SPE host resulted into nearly three fold increase in the room temperature conductivity. This NCPE film: (70PEO: 30 KNO_3) + 5 SiO_2 has been referred to as Optimum Conducting Composition (OCC) NCPE film. Scanning Electron Microscopy (SEM), X-Ray Diffraction (XRD), Differential Scanning Calorimetry (DSC) and Fourier Transform Infrared (FTIR) techniques have been used to study the morphological, structural, thermal and spectroscopic responses respectively of NCPE OCC film material. The ion transport behaviour has been characterized in terms of basic ionic parameters viz. conductivity (σ), mobility (μ), mobile ion concentration (n) and ionic transport number (t_{ion}). The frequency dependent dielectric response has also been studied in the temperature range 303-353 K. The newly synthesized NCPE OCC membrane has been sandwiched between K -metal anode and different cathodes to fabricate all-solid-state battery having following cell configurations:

Cell # 1 : K (anode) // NCPE film// C+I_2+ Electrolyte (cathode)
Cell # 2 : K (anode) // NCPE film// MnO_2+C + Electrolyte (cathode)

Open Circuit Voltage (OCV) values ~ 2.18 & ~ 2.08, have been obtained for Cells # 1 & # 2 respectively. The cell performance has been studied at room temperature by recording cell potential discharge profiles with time under different load conditions. Some important cell parameters have been evaluated in the plateau region of the discharge profiles.

Keywords: Nano-Composite Polymer Electrolyte (NCPE), hot-press technique, ionic conductivity, ionic transport number etc.

1. INTRODUCTION

Ion conducting electroactive polymers or polymer electrolytes in thin flexible forms show great technological potentials to fabricate all-solid-state mini/micro electrochemical power sources viz. batteries, fuel cells, supercapacitors etc. [1-20]. Pure polymeric materials are known for their poor electrical conductivity. They are often referred to as insulators. However, polymers can be made electroactive i.e. electron, ion and/or mix conducting by complexing / dissolving electronic and / or ionic salts. The first ion conducting solid polymer was reported in 1973 [1] and subsequently, the first solid polymer electrolyte (SPE) based film battery was practically demonstrated in 1979 [2]. Since then, wide variety of SPE film materials, involving different mobile ionic species viz. H^+, Ag^+, Li^+, Na^+, K^+, Mg^{2+}, etc., have been investigated [3-20]. In the synthesis of majority of SPE films, reported in the past, high molecular weight polar polymer viz. poly (ethylene oxide) PEO has been used commonly / extensively as polymeric host matrix. This is due to the fact that PEO possesses relatively higher electrochemical stability as well as an exceptional ability to dissolve wide variety of salts as compare to other polymers [2, 20]. The polar and flexible main chain dissociates the salt and hence, carrier ions are generated. These ions can migrate through the amorphous region of the polymer via interchain / intrachain segmental motion. The degree of amorphousity of the polymer predominantly controls the ion conduction phenomenon in the polymer salt complexes. Larger is the amorphous region in the polymeric host, higher would be the ionic conductivity. However, PEO based SPEs often exhibit low ionic conductivity ($< 10^{-4}$ Scm^{-1}) at room temperature, hence, not much useful for practical device applications. Nevertheless, the room temperature conductivity of SPEs can be significantly increased by fractional dispersal of low dimension (µm or nm) particles of an insulating / inert filler materials such as Al_2O_3, SiO_2, TiO_2 etc. [9-20] . Such systems are known as composite polymer electrolytes in which the enhancement in the conductivity is predominantly due to the increase of amorphous region in PEO as a consequence of the dispersal of the filler particles. When nano-size filler particles are dispersed, they are referred to as Nano-Composite Polymer Electrolytes (NCPEs). Akin to 2- phase inorganic composite electrolytes [21], NCPEs are also 2 – phase organic composite electrolytes in which SPE acts as I^{st} – phase host matrix and nano-particles of filler material as II^{nd} – phase dispersoid [20]. The dispersal of nano particles also brings substantial improvements in several other materials properties of NCPE films viz. mechanical stability, intimate electrode / electrolyte contacts as well as enhanced interfacial reactivity during battery applications [20]. SPE and / or NCPE films are usually casted by the traditional solution cast method. However, an alternate procedure, popularly referred to as hot-press (extrusion) technique, has been developed for casting SPE/NCPE films [9 - 20]. This technique is recently getting wider acceptability due to the fact that it has several merits. It is relatively, not only quicker and inexpensive but a completely dry / solution free film casting procedure as compare to the traditional method.

The paper reports hot-press casting of NCPE membranes: [70PEO: 30 KNO_3] + x SiO_2. SPE film composition: [70PEO: 30 KNO_3], identified earlier having highest ionic conductivity at room temperature [22], has been used as I^{st} – phase host matrix and nano-particles (~ 8 nm) of SiO_2 as II^{nd} – phase dispersoid. SiO_2-dependent conductivity measurements on different films revealed the highest conducting film which has been referred to as Optimum Conducting Composition (OCC) NCPE film.

The characterization of morphological, structural, spectroscopic and thermal properties has been done using SEM, XRD, FTIR and DSC techniques respectively. The ion transport property has been studied in terms of basic ionic parameters viz. conductivity (σ), mobility (μ), mobile ion concentration (n) and ionic transference number (t_{ion}). These parameters have been determined experimentally using ac/dc techniques. Sandwiching NCPE OCC film between K-metal anode and two different cathodes (viz. C+I_2; C + MnO_2), all solid state batteries have been fabricated and the discharge performances have been tested under varying current drain states.

2. EXPERIMENTAL

For hot-press casting of NCPE films: [70PEO: 30 KNO_3] + x SiO_2, where x = 0, 1, 2, 3, 5, 8, 10, 12 wt. (%), AR grade chemicals: poly (ethylene oxide) (PEO) (Mw ~ $6x10^5$, Aldrich, USA), KNO_3 (purity > 99.9%, Reidel, India), SiO_2 (> 99.99%, size ~ 8 nm, Aldrich, USA) have been used, as supplied. The details on hot-press film casting procedure have been discussed in our earlier papers [13-19].

Conductivity (σ) - measurements have been carried out at a fixed ac frequency (viz 5 KHz) as well as by varying the frequency in the range 1 Hz to 100 KHz for Impedance Spectroscopy (IS) using an LCR meter [HIOKI 3522-50, Japan]. 'Log σ - x' variation at room temperature revealed NCPE OCC film, as mentioned. Ionic mobility (μ) and ionic transference number (t_{ion}) in NCPE OCC film material, placed between two Stainless Steel (SS) blocking electrodes, have been measured by a dc polarization Transient Ionic Current (TIC) technique [23-25]. An x-y-t recorder (Graphtec WX – 2300) was employed for recording 'current – time' plots. Since, in polymer electrolytes both cations and anions are mobile, the value of ionic transference number obtained by TIC technique would be a sum total of both cationic and anionic transport. In order to separate out the cationic (K^+) transport number in the present system, a combined ac/dc technique, suggested by Evans et al [26], has been used and for this NCPE film was placed between two K-metal electrodes. The dielectric response in the NCPE OCC film material as a function of frequency has been studied at different temperatures using the LCR meter mentioned.

Surface morphology of NCPE OCC film was obtained with the help of Scanning Electron Microscope (JEOL - JSI microscope). The materials characterization on NCPE OCC as well as pure PEO films was done by X - ray diffraction (XRD) analysis using CuKα radiation (Expert-pro, MRD, Panalytical). FTIR spectra were recorded by Spectrophotometer (IR Affinity – 1, Shimadzu, Japan). The thermal response was studied by Differential Scanning Calorimetry (DSC, NITSCH-200 PC) in the static nitrogen atmosphere at a heating rate of 10^0C/min. in the temperature range -60 to 100 ^{0}C.

The newly synthesized NCPE OCC film was sandwiched between anode and cathode in the following cell configurations:

Cell # 1 : K (anode) // NCPE film// C+I_2 + Electrolyte (cathode)

Cell # 2 : K (anode) // NCPE film// C+MnO_2 + Electrolyte (cathode)

The cell performances were tested at room temperature by discharging the batteries through different load resistances. A high impedance digital Voltmeter [ESCORTS – 97] was employed for the cell potential measurements.

3. RESULTS & DISCUSSION

3.1. Electrical property studies

As mentioned, the ion transport property characterization on hot-press casted SPE membranes: (PEO: KNO_3) of different salt concentrations has been reported earlier [22].

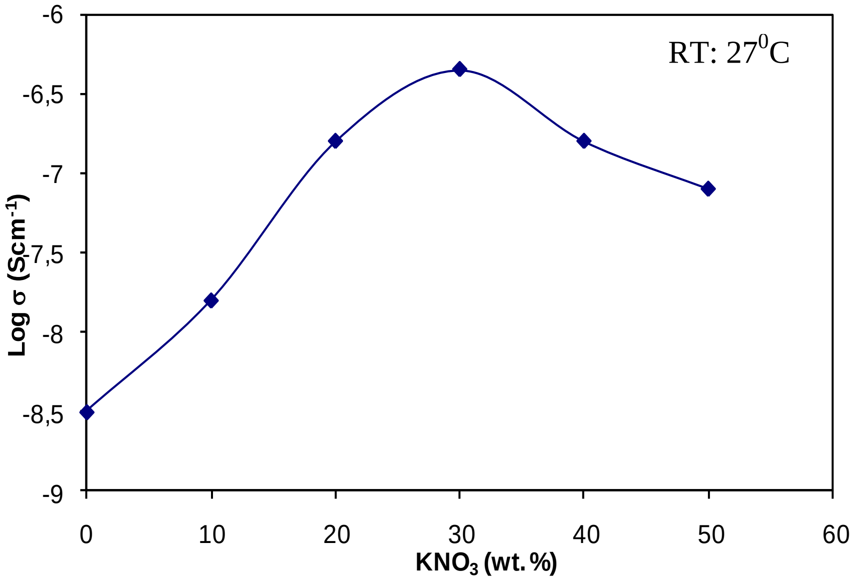

Figure 1. Salt concentration dependent conductivity variation for SPE films: (PEO: KNO_3) [22]

The variation of room temperature conductivity of these SPE films as a function of salt ratio has been reproduced here in fig. 1. It can be noted that σ increased rapidly as the salt concentration increased by 30 wt. (%), however, σ - decreased on further addition of salt by 40-50 wt. (%). SPE films beyond 50 wt. (%) appeared brittle and less stable. SPE film: (70PEO: 30 KNO_3) exhibited highest conductivity (σ) ~ $3.98 \times 10^{-7}\ \Omega^{-1}cm^{-1}$ at room temperature (27^{0}C) and has been selected as Ist – phase host matrix for the preparation of NCPE films, as mentioned. The initial increase in σ was attributed to the dissociation of KNO_3, resulting thereby into generation of carrier ions. The complexation of salt in PEO also increases of amorphous region in polymer which, in turn, give rise to increased ionic mobility and hence, the ionic conductivity. The decrease in σ (beyond 30 wt. %) due to the association / aggregation of ions which has resulted into decrease in the number of mobile ions. Using SPE composition: (70PEO: 30 KNO_3) as Ist – phase, Nano-Composite Polymer Electrolyte (NCPE) membranes: [70PEO: 30 KNO_3] + x SiO_2, have been hot-press casted by dispersing fractional amounts (x in wt. %) of SiO_2 nano-particles as IInd – phase, as mentioned. SiO_2 – concentration dependent conductivity, measured at room temperature on different NCPE films, has been plotted in fig. 2.

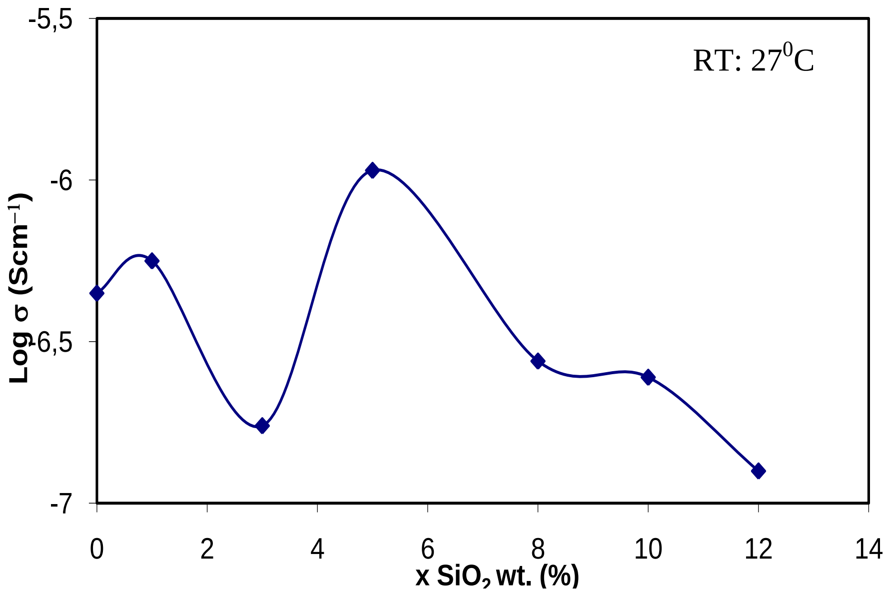

Figure 2. 'Log σ - x' plot for NCPE films: (70PEO: 30KNO_3) + x SiO_2

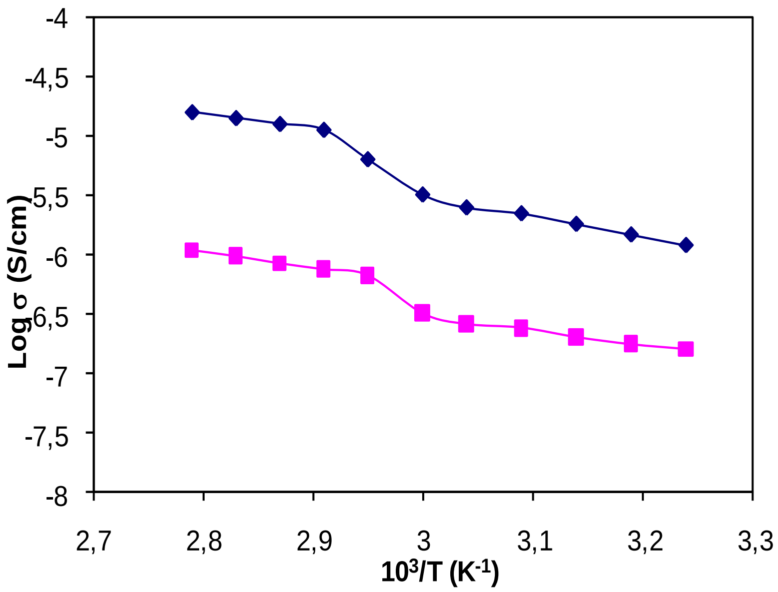

Figure 3. 'Log σ –1/T' plots for hot-press casted films: SPE host: (70 PEO: 30 KNO_3) (■) [22], NCPE: (70 PEO: 30 KNO_3) + 5 SiO_2 (♦).

One can clearly notice the appearance of two σ - maxima at x = 1 & 5 wt. (%) in 'log σ - x' plot. However, since the conductivity value of NCPE film for x = 5 wt. (%) was relatively higher, this NCPE film: (70PEO: 30 KNO_3) + 5 SiO_2, with room temperature conductivity (σ) ~ 1.07 x 10^{-6} S/cm, has been referred to as OCC. An enhancement of more than 3-fold in the room temperature conductivity of SPE host has been achieved by dispersing SiO_2 nano-particles. Moreover, this film appeared relatively more stable / flexible mechanically. The existence of two conductivity maxima has been observed in the majority of NCPE films reported in the past and has been explained on the basis of two percolation model, suggested by Laxmi & Chandra [27]. It has been proposed that two kinds of transport mechanism operative in these systems. Accordingly, the first σ - maxima is possibly due to the dissociation of ion aggregates and / or undissociated salt which resulted into the generation of free ion carriers as a consequence of addition of nano-sized SiO_2 particles. The second σ - maxima as well as the conductivity variation around this ratio is related to the well-known 2-phase composite effect and can be explained on the basis of space-charge and /or percolation model [21, 28, 29].

Fig. 3 shows 'log σ - 1/T' plots for NCPE OCC film and the filler free I^{st} – phase SPE host [22]. The conductivity of both SPE/NCPE films initially increased linearly with temperature followed by a slight upward change in the slope ~ 65-70^{0}C then increased linearly again. The upward jump in σ is due to the well-known semi-crystalline amorphous phase transition of polymer PEO which usually occurs at the melting temperature (T_m) ~ 65^{0}C. 'Log σ - 1/T' plot below T_m clearly exhibits the Arrhenius behaviour, hence, can be expressed by equation:

$$\sigma = \sigma_0 \exp(-E_a/kT) \qquad (1)$$

where σ_0 is the pre-exponential factor and E_a is the activation energy which can be computed by least square linear fitting of the data and we obtained E_a values: 0.34 and 0.31 eV for SPE film and NCPE OCC films respectively.

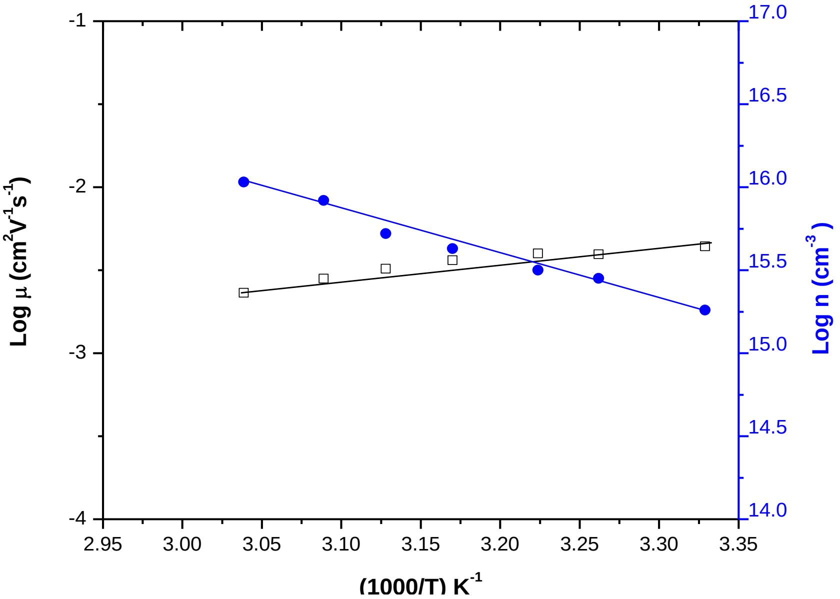

Figure 4. 'Log μ - 1/T' [□] and 'log n -1/T' [●] plots for NCPE OCC film: (70PEO: 30 KNO_3) + $5SiO_2$.

Other basic ionic parameters viz. Ionic mobility (μ), mobile ion concentration (n) and total ionic transference number in NCPE OCC films have also been determined as mentioned. μ has been measured at different temperatures below T_m using TIC technique; subsequently, n has been evaluated with the help of basic equation n = σ/ μ.q. Table 1 lists the room temperature values of these ionic parameters as well as the value of ionic transference number (t_{ion}), as discussed below.

Table 1. Room temperature (27^0C) values of some basic ionic parameters viz. ionic conductivity (σ), ionic mobility (μ), mobile ion concentration (n), ionic transference number (t_{ion}).

Film	σ (Scm^{-1})	μ ($cm^2V^{-1}s^{-1}$)	n (cm^{-3})	t_{ion}	Ref.
Pure PEO	3.16×10^{-9}	-	-	-	[22]
SPE film: (70PEO: 30 KNO_3)	3.98×10^{-7}	5.24×10^{-3}	1.81×10^{15}	0.98	[22]
NCPE OCC Film: (70PEO: 30 KNO_3) + 5 SiO_2 wt. (%)	1.07×10^{-6}	3.63×10^{-3}	2.31×10^{15}	0.98	Present Study

Fig. 4 shows 'log μ - 1/T' and 'log n – 1/T' plots for NCPE OCC film. It can be seen that μ remained almost unaltered while n increased with increasing temperature. This is indicative of the fact that as the temperature increased more carrier ions are generated in the system. Besides evaluating μ the total ionic (cationic and anionic) transport number (t_{ion}) can also be determined from 'current – time' TIC plot. Fig. 5 shows a typical TIC plot for NCPE OCC film. The total current approached close to zero in about 2 hrs indicating that the mobile ions in the cell SS //NCPE OCC// SS, subjected to an external dc potential, have been completely polarised at the respective electrode / electrolyte interfaces.

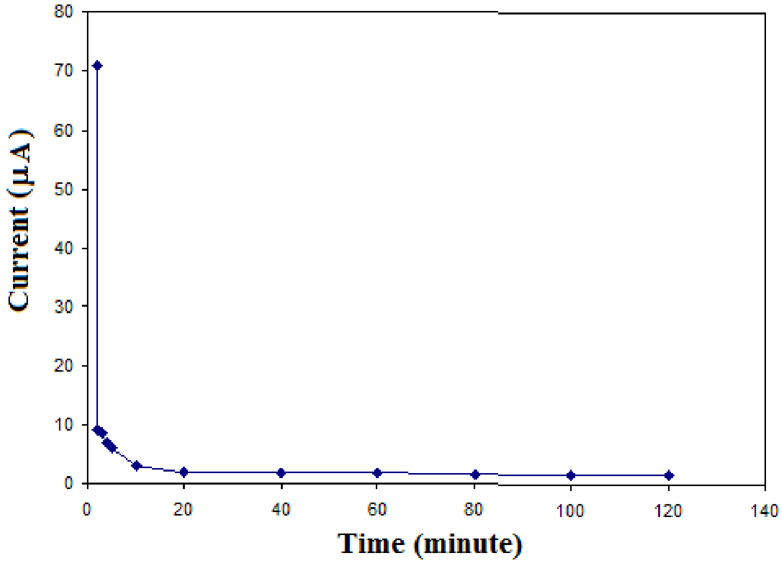

Figure 5. Variation of polarizing current as a function of time in a typical cell: SS//NCPE film// SS

From the initial and final current values we obtained t_{ion} ~ 0.98. This is further indicative of the fact that NCPE OCC film material is predominantly an ion conducting medium. However, the cationic transport number is a key parameter as regards to the performance of the electrolyte in a battery is concerned. In order to evaluate K^+ - ion transport in the present NCPE system, a combined ac/dc technique suggested by Evans et. al. [26] has been used, as mentioned. NCPE OCC film, placed between two K-metal electrodes, was subjected to an external fixed dc potential (ΔV) = 0.5 V for 5 hrs. The cell resistance of the film sample was measured before and after polarization using IS technique. Fig. 6 shows the complex impedance (Z′-Z″) plots for the cell before and after polarization. From the two semi-circles (depressed with centers below the real axis), the cell resistances $R_b \equiv R_0$ and $R_s \equiv R_b + R_i$, before and after polarization respectively, have been obtained.

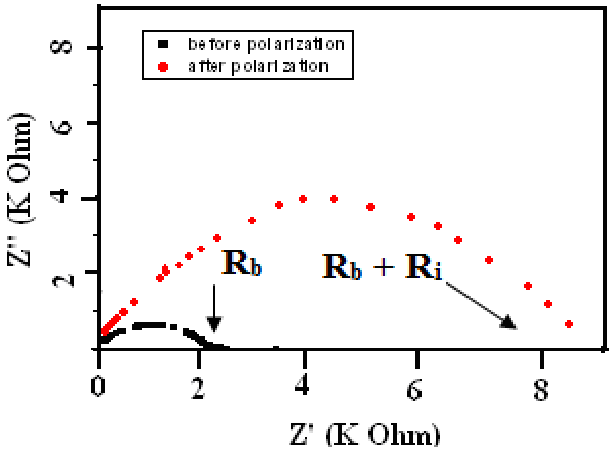

Figure 6. Complex impedance (Z′-Z″) plots before and after cell polarization

The variation of the cell current during polarization, as show in fig. 7, gave values of initial (I_0) and final (I_s) currents. Hence, the cationic (K^+) transference number (t_+) has been evaluated with the help of following equation:

$$t_+ = \frac{I_s (\Delta V - R_0 I_0)}{I_0 (\Delta V - R_s I_s)} \qquad (2)$$

Substituting the data in the equation we obtained t_+ ~ 0.36 for the present NCPE OCC film: (70PEO: 30 KNO_3) + 5 SiO_2. The cationic transference number has usually been reported to have such a low value in the polymer electrolyte materials [20]. Study of frequency dependent dielectric responses provides insight informations regarding the relaxation behaviour and percolation effect. The complex dielectric constant of NCPE OCC film material has been measured at varying frequency in the frequency range 10 mHz to 100 kHz. The complex dielectric constant (ε^*) is expressed in terms of real (ε') and imaginary (ε'') parts by following equation:

$$\varepsilon^* = \varepsilon' + \varepsilon'' = 1/\, j\omega C_0 Z^* \qquad (3)$$

where ω is the angular frequency (≡ 2πν), C_0 is the parallel plate (empty) capacitance and Z^* is the complex impedance. In general, the real part of dielectric constant is a direct measure of energy stored from the applied ac field. The imaginary part, also known as dielectric loss, is the energy loss due to the transportation of charge carriers as well as their polarization effect. The values of complex dielectric constant (ε^*) for NCPE OCC film measured at different frequencies in the range 10 mHz to 100 KHz and temperatures (303 - 353 ^{0}K) are plotted in fig. 8.

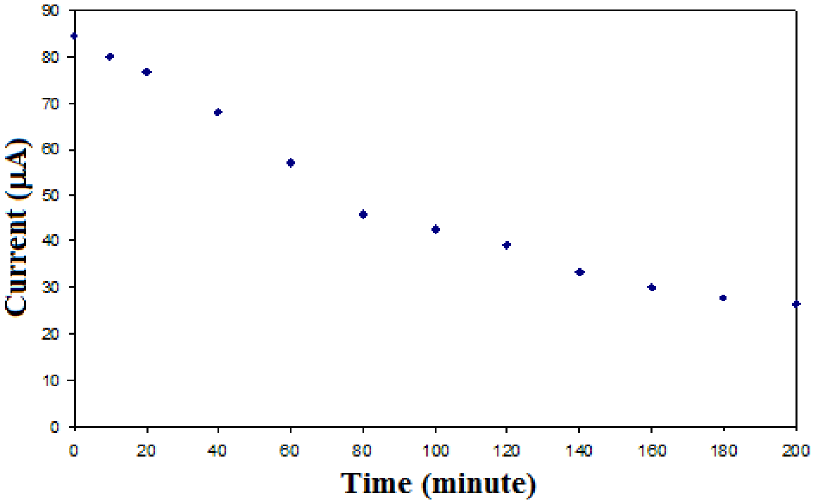

Figure 7. Polarization current versus time plot for the cell: K// NCPE film// K

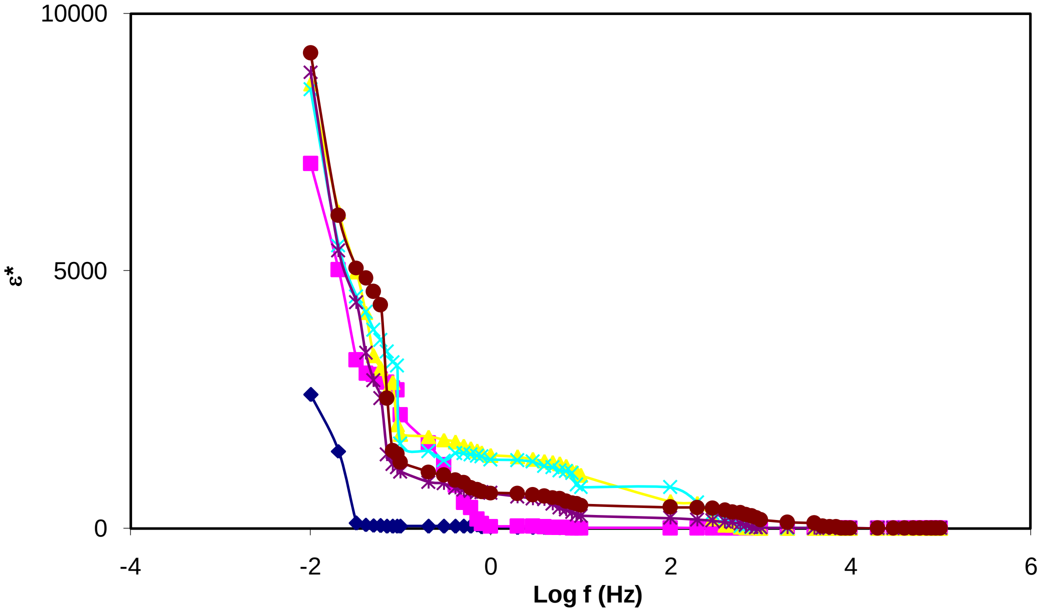

Figure 8. The frequency response of complex dielectric constant (ε^*) for NCPE film at different temperatures: (♦) 303, (■) 313, (Δ) 323, (+) 333, (○) 343, (-) 353 ^{0}K.

The sharp rise in ε^* in the low frequency region at all temperatures can be attributed to the build-up of space charge layer near electrode / electrolyte interface which has partially blocked the charge transport. In the high frequency region, ε^*decreased and finally, attained saturation. This is suggestive of effective participation of PEO dipoles in the dielectric polarization.

3.2. Materials property studies

Fig. 9 (a, b) shows SEM micrographs for hot-pressed films of SPE: (70PEO; 30 KNO_3) and NCPE OCC: (70PEO: 30 KNO_3) + 5 SiO_2.

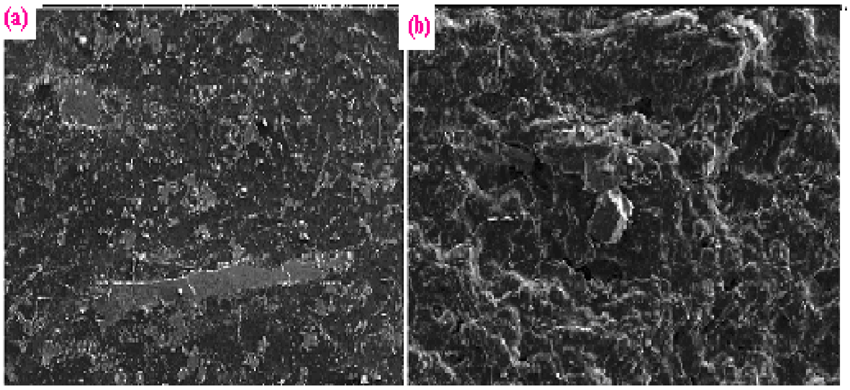

Figure 9. SEM surface morphology of films: (a) SPE host: (70PEO:30KNO_3), (b) NCPE: (70PEO: 30KNO_3) + 5 % SiO_2.

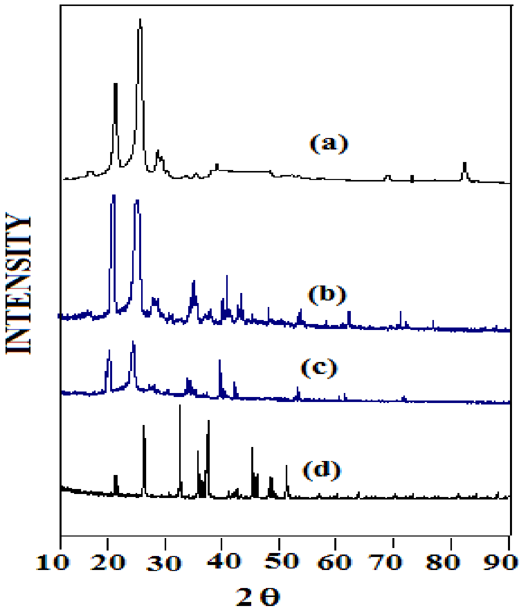

Figure 10. XRD pattern for (a) Pure PEO, (b) SPE host: (70PEO: 30KNO_3), (c) NCPE: (70PEO: 30 KNO_3) + 5SiO_2, (d) KNO_3.

The surface morphological pictures clearly indicated the uniform distribution of salt as well as SiO_2 particles in the respective films. Fig. 10 (a-d) illustrates the XRD patterns for films of pure PEO, SPE (I^{st} – phase host) and NCPE OCC as well as polycrystalline powder of KNO_3. Comparison of these patterns clearly confirmed the complexation of salt in the polymeric host, as many of the peaks related to the salt appeared along with PEO peaks, although slightly displaced with decreased intensity. The positions of two main peaks of PEO remained almost intact even after complexation of salt in PEO in SPE and dispersal of SiO_2 (in NCPE). However, the intensity of PEO main peaks has been decreased substantially specially in NCPE film. This is indicative of decrease in degree of crystallinity and / or increase of amorphousity in PEO.

FTIR spectroscopic responses for films of pure PEO, SPE (I^{st} – phase) and NCPE OCC are shown simultaneously in fig. 11 (a-c) for direct comparison.

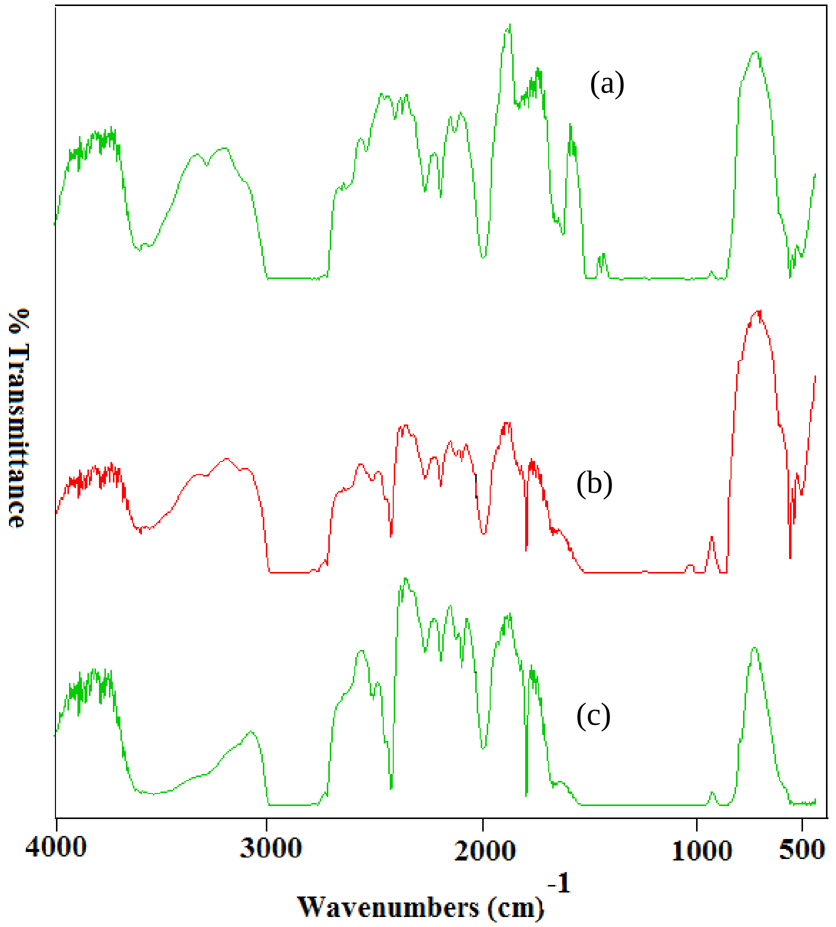

Figure 11. FTIR spectrographs for (a) Pure PEO, (b) SPE host: ($70PEO:30KNO_3$), (c) NCPE: ($70PEO: 30KNO_3$) + 5 % SiO_2.

The main spectral features of pure PEO viz. broad absorption bands corresponding to symmetric / anti-symmetric stretching modes (C-H) of CH_2 group around 2950-2800 cm^{-1}; broad vibrational bands corresponding to symmetric / anti-symmetric C-O-C stretching modes around 1100-1000 cm^{-1}; gauche (OC-CO) conformation in between 950-800 cm^{-1} etc. are all present in the spectra of SPE & NCPE OCC films. However, slight variations in the shapes occurred which is indicative of the complexation of salt in the polymer. No substantial changes could be noticed due to the presence of SiO_2 filler particles which may probably be due to its dispersal in the fractional amount.

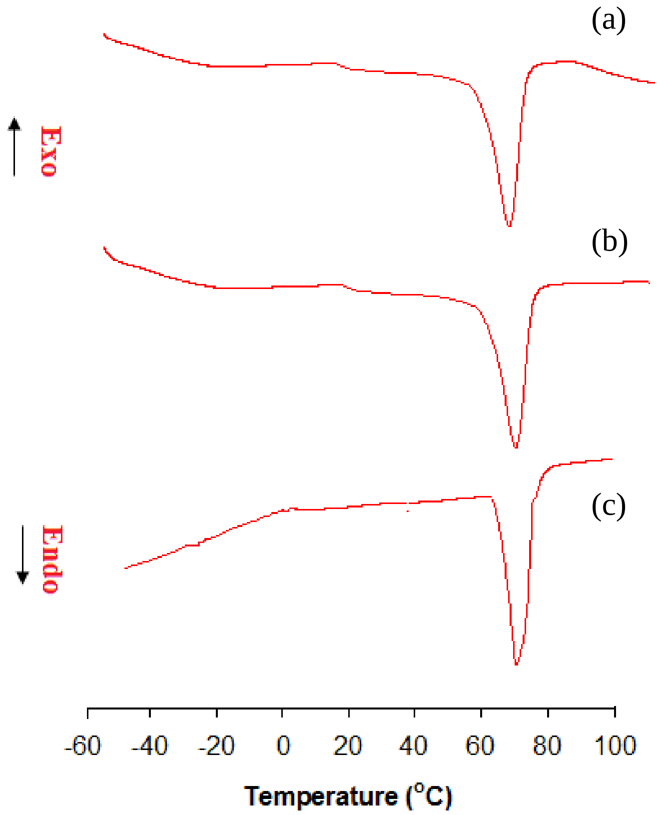

Figure 12. DSC thermograms for: (a) pure PEO, (b) SPE host: ($70PEO{:}30KNO_3$), (c) ($70PEO{:}30KNO_3$) + 5 % SiO_2

Fig. 12 (a-c) shows DSC thermograms for film materials of pure PEO, SPE (I^{st} – phase host) and NCPE OCC. The dominant endothermic peak ~ 65 - 70^0C, belonging to the semi-crystalline – amorphous phase transition temperature (T_m) of PEO, is clearly visible in all the DSC curves. However, slight shifts in the peak position could be noticed which may be due to complexation of salt KNO_3 in PEO.

3.3. Electrochemical property studies:

As mentioned, using NCPE OCC film, all-solid-state batteries have been fabricated as Cell # 1 and # 2 and discharged through two load resistances 1 MΩ and 100 KΩ at room temperature. The Open Circuit Voltage (OCV) values: ~ 2.18 and 2.08 V have been obtained for Cells # 1 and #2 respectively. Figures 13 and 14 shows the cell potential discharge profiles for Cells # 1 & # 2 respectively. The cell potential of both the batteries decayed to nearly half of their OCV value in 25-30 hrs. However, the rate of decay has been fairly low during discharging through 1 MΩ load. The final decay afterward is due to the build – up of polarization and increase in the internal resistance of the cell. Some important cell parameters have been calculated in the plateau regions of both the discharge profiles and listed in Table 2. It is obvious that these all-solid-state batteries performed satisfactorily especially during low current drain states.

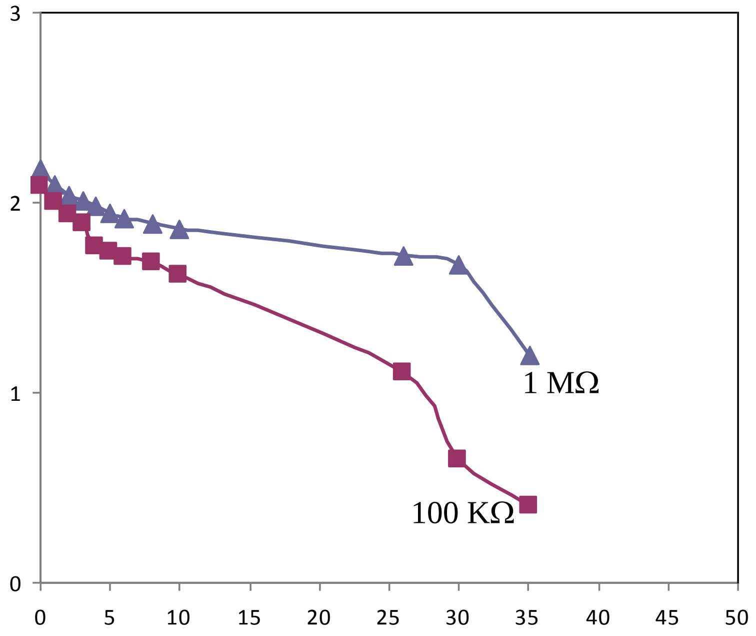

Figure 13. Cell potential discharge profile as a function of time for Cell # 1: (▲) 1 MΩ, (■) 100 K Ω.

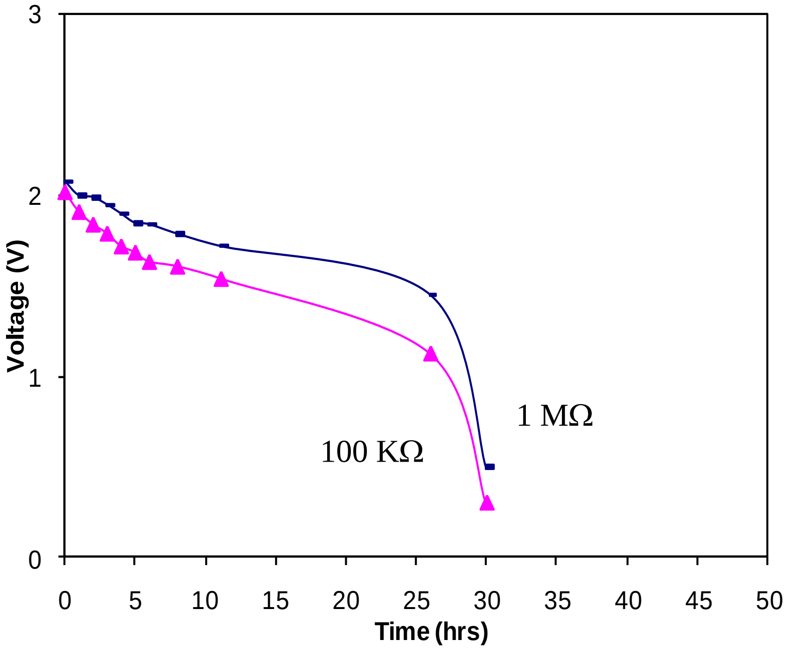

Figure 14. Cell potential discharge profile as a function of time Cell # 2: (▲) 100 KΩ, (-) 1 M Ω.

Table 2. Some important battery parameters calculated in the plateau regions of cell – potential discharge profiles of Cells # 1 & #2 at room temperature.

	Load	**Open Circuit Voltage (V)**	**Current Density (µA/cm^2)**	**Discharge capacity (µA.h)**	**Power Density (mW/gm)**	**Energy Density (mW/cc)**
# 1	1 MΩ	2.18	0.97	39.6	3.34	15.92
	100 KΩ	2.08	0.76	26	2.34	9.97
# 2	1 MΩ	2.08	0.79	27	2.54	10.36
	100 K Ω	2.02	0.74	22.22	2.29	8.28

4. CONCLUSION

A new NCPE film: (70PEO: 30 KNO_3) + 5 SiO_2 has been synthesized by hot-press / completely – dry technique. The hot-press technique is a least expensive/solvent free/dry procedure of SPE/NCPE film casting and can be preferred over the traditional solution cast method. Fractional dispersal of nano-SiO_2 in to SPE host: (70PEO: 30 KNO_3) enhanced the room conductivity by more than 3 – fold. The complexation of the salt in the polymer has been confirmed by SEM, XRD, DSC, FTIR studies.

The total ionic transport number measurement indicated that the film material is predominantly an ion conducting medium with both cations and anions movements. However, the cations (K^+) transport number measured separately using combined ac/dc technique has been found to be $t_+ = 0.36$.

The cell potential discharge performance, studied under varying load conditions, indicated that they can be used quite satisfactorily especially under low current drain states.

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References

1. D. E. Fenton, J. M. Parker, P. V. Wrigth, *Polymer* 14 (1973) 589.
2. M. P. Armand, J. M. Chabagno, M. Diadat, 'Fast Ion Transport in Solids' (Eds.) Vashistha P., Mundy J. M. and Sheny G. K. (North Holland 1979) p. 135.
3. M. B. Armand, *Ann. Rev. Mater. Sci.* 16 (1986) 245.
4. M. A. Ratner, D. F. Shriver, *Chem. Rev.* 88 (1988)109.

5. J. R. Mac Callum, C. A. Vincent, (Eds.) Polymer Electrolyte Reviews, Vol. 1, 2 (Elsevier Applied Science Publisher, London 1987 & 1989).
6. K. Murata, *Electrochimica Acta*, 40 (1995) 2177.
7. P. G. Bruce, (Ed.) *Solid State Chemistry*, (Cambridge University Press, Cambridge 1995).
8. F. M. Gray, *Polymer Electrolytes* (Royal Society of Chemistry Monographs, Cambridge 1997).
9. F. Capuano, F. Croce, B. Scrosati, *J. Electrochem. Soc.* 138 (1991) 1918;
10. F. Croce, G. B. Appetecchi, L. Persi, B. Scrosati, *Nature* 394 (1998) 456;
11. G. B. Appetecchi, F. Croce, L. Persi, F. Ronci, B. Scrosati, *Electrochem. Acta* 45 (2000) 1481;
12. G. B. Appetecchi, J. Hassoun, B. Scrosati, F. Croce, F. Cassel, M. Salomon, *J. Power Sources* 124 (2003) 246;
13. R. C. Agrawal, Angesh Chandra, *J. Physics D: Appl. Phys*. 40 (2007) 7024;
14. G. P. Pandey, S. A. Hashmi, R. C. Agrawal, *Solid Sttae Ionics* 179 (2008) 543;
15. R. C. Agrawal, A. Bhatt, Y. K. Mahipal, *New J. Phys*. 10 (2008) 043023;
16. G. P. Pandey, S. A. Hashmi, R. C. Agrawal, *J. Phys. D: Appl. Phys*. 41 (2008) 055409;
17. A. Chandra, R. C. Agrawal, Y. K. Mahipal, *J. Phys. D: Appl. Phys*. 42 (2009) 135107;
18. G. P. Pandey, R. C. Agrawal, S. A. Hashmi, *J. Phys. D: Appl. Phys*. 43 (2010) 25550;
19. R. C. Agrawal, Y. K. Mahipal, Rehana Ashrafi, *Solid State Ionics* (2010) (in press).
20. R. C. Agrawal, G. P. Pandey , "Solid Polymer Electrolyte: Materials designing and all-solid-sttae battery applications: an overview" (Topical Review), *J. Phys. D: Appl. Phys*. 41 (2008) 223001.
21. R. C. Agrawal, R. K. Gupta, Superionic Solids: Composite Electrolyte Phase – An Overview, *J. Mater. Sci.* 34 (1999) 1131.
22. R. C. Agrawal, Y. K. Mahipal, Angesh Chandra, Alok Bhatt, in: S. Chandra (Series Eds.). "Electroactive Polymers: Materials & Devices" Vol. III (Mac Millan Publishers, New Delhi, 2009), p. 231.
23. J. B. Wagner, C. Wagner, *J. Chem. Phys*. 26 (1957) 1597.
24. M. Watanabe, K. Sanui, N. Ogata, T. Kobayashi, Z. Ontaki, *J. Appl. Phys*. 57 (1985) 123.
25. S. Chandra, S. K. Tolpadi, S. A. Hashmi, *Solid State Ionics* 28-30 (1988) 651.
26. J. Evans, C. A. Vincent, P. G. Bruce, *Polymer* 28 (1987) 2324.
27. N. Lakshmi, S. Chandra, Phys. *Stat. Solidi* (a) 186 (2001) 395.
28. A. Bunde, W. Dieterich, H. E. Roman, *Phys. Rev. Lett*. 55 (1985) 5.
29. J. Maier, Solid State Ionics 70-71 (1994) 43; J. Maier, *Prog. Solid State Chem*. 23 (1995) 171.