

# Effect of salt concentration on Plasticized PMMA based polymer electrolyte system for battery applications

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**Abstract :** Solid polymer electrolyte films of plasticized poly (methyl-methacrylate) (PMMA) with NaClO<sub>4</sub> have been prepared by solution cast technique. The features of complexation of the electrolytes were studied by X-ray diffraction (XRD). DC conductivity of the films was measured in the temperature range 303-393 K. In the temperature range studied, three regions with different activation energies were observed. Transference number data showed that the charge transport in this system is predominantly due to ions only. Batteries of configuration Na/(PMMA+DMF+NaClO<sub>4</sub>)/(I<sub>2</sub>+C+electrolyte) were fabricated and the discharge characteristics of these cells were studied under a constant load of 100KΩ.

**Keywords -** Polymer electrolyte film, DC conductivity, activation energy, transference number, discharge characteristics.

## I. INTRODUCTION

Polymer electrolytes have been found to have a great deal of advantages in replacing conventional liquid electrolytes. These advantages includes high specific energy, high energy density, leak proof, high ionic conductivity, wide electrochemical stability windows, light, solvent free condition and easy processability [1]. The interest in the study of polymer electrolyte system is due to the potential application of these materials in a great variety of electrochemical devices such as high energy density batteries, fuel cells, sensors, and electrochromic devices [2-6].

PMMA is an amorphous polymer and it is a colorless, transparent, plastic with an excellent life period and good mechanical properties. Extensive research has been carried out on Lithium salts complexed polymer electrolytes. However, only a few attempts have been made on electrolytes based sodium ion complexed films. Use of sodium in the poly electrolytes has several advantages over their lithium counter parts. Sodium is available in abundance at a cheaper cost than lithium. It is feasible to obtain solid electrolytes of sufficiently high conductivity because sodium does not form any alloy with the electrode materials, such as aluminum and nickel. Furthermore, the softness of these materials makes it easier to achieve and maintain contact with other components in the battery. Investigations have also been made [7-9] on sodium ion-conducting polymer electrolyte based on PEO, polypropylene oxide (PPO), and polybismethoxy ethoxy phosphazene (MEEP) complexed with NaI, NaClO<sub>4</sub>, NaSCN, and NACF<sub>3</sub>SO<sub>3</sub>.

In the present paper, we report the effect of sodium salt concentration on conductivity, transference number and discharge profile of plasticized PMMA based polymer electrolyte system.

## II. EXPERIMENTAL

### 2.1 Polymer electrolyte films preparation

In the present study films of plastisized PMMA (a plasticizer, Dimethyl formamide (DMF) (2ml) was added to the PMMA) and NaClO<sub>4</sub> complexed films were prepared in the weight ratio (95:05), (90:10), (85:15) and (80:20) by solution cast technique using tetrahydrofuran as solvent. The solutions were thoroughly stirred for 10-12 hours to get a homogeneous solution. The stirred solution was cast onto polypropylene dishes and allowed to evaporate slowly at room temperature. After one or two days solid polymer layers formed as thin films with nearly 150 μm thickness at the bottom of dishes. These films were dried in a vacuum (10<sup>-3</sup> torr) to eliminate the residual traces of water, then carefully separated from the dishes and stored in evacuated desiccators.

### 2.2 Characterization techniques

X-ray diffraction (XRD) studies were performed using SEIFERT X- ray diffractometer. The DC conductivity of pure PMMA+DMF and NaClO<sub>4</sub> doped polymer electrolytes was studied as a function of temperature ranging from 303 K to 393 K, and the activation energies were evaluated. The total ionic transference number (t<sub>ion</sub>) was evaluated by means of Wagner's polarization technique [10]. In this technique, freshly prepared polymer electrolyte films were polarized in the configuration Na/polymer electrolyte/C under a dc bias (step potential of 1.5 V). The resulting current was monitored as a function of time. After polarizing the electrolyte, the transference number t<sub>ion</sub> was calculated from the initial current I<sub>i</sub> and the final residual current I<sub>f</sub>, i.e.,

$$t_{ion} = (I_i - I_f) / I_i$$

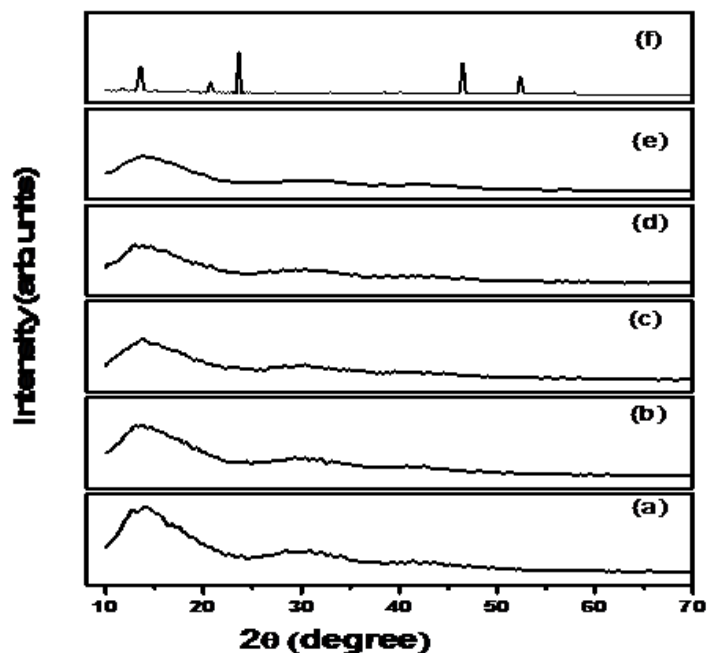
$$t_{ele} = 1 - t_{ion}$$

Using PMMA+DMF+NaClO<sub>4</sub> polymer electrolytes, electrochemical cells with configuration Na/PMMA+DMF+NaClO<sub>4</sub>/(I<sub>2</sub>+C+electrolyte) were fabricated. The discharge characteristics of the cells were studied under a constant load 100 kΩ. The initial current in the battery when constant load of 100 kΩ was connected to the battery was taken as short-circuit current.

### III. RESULTS AND DISCUSSION

#### 3.1 XRD Studies

In order to investigate the influence of sodium salt on plastisized PMMA structure, XRD studies were performed. Figure 1 (a–f) shows the XRD patterns of plastisized PMMA complexed with NaClO<sub>4</sub> salt. Comparison of the XRD patterns of complexed PMMA+DMF films with those of pure PMMA+DMF reveals the following differences. Peaks observed for 2θ values around 14° are less intense in complexed PMMA+DMF films compared to those in pure PMMA+DMF film. This indicates that the addition of NaClO<sub>4</sub> salt causes a decrease in the degree of crystallinity of the PMMA+DMF complex. The crystalline peaks for 2θ values at 14, 23, 46 and 52° corresponding to NaClO<sub>4</sub> (Fig. 1f) are absent in complexed PMMA+DMF. This indicates the absence of any excess (uncomplexed) salt in the complexed plasticized polymer electrolyte films. Therefore, it may be confirmed that complexation has taken place in the amorphous phase. This amorphous nature resulted in greater ionic diffusivity with high ionic conductivity, as amorphous polymers have flexible back bone [11].



**Fig 1: XRD plots of (a) PMMA+DMF (b) PMMA+DMF+NaClO<sub>4</sub> (95:05) (c) PMMA+DMF+NaClO<sub>4</sub> (90:10) (d) PMMA+DMF+NaClO<sub>4</sub> (85:15) (e) PMMA+DMF+NaClO<sub>4</sub> (80:20) and (f) NaClO<sub>4</sub> salt**

#### 3.2 DC Conductivity

The variation of room temperature (303 K) dc conductivity ( $\sigma$ ) as a function of composition of NaClO<sub>4</sub> in PMMA+DMF for different weight percent ratios of NaClO<sub>4</sub> is shown in Fig 2. The conductivity of pure PMMA+DMF was  $4.47 \times 10^{-9} \text{ Scm}^{-1}$  at room temperature and its value increased approximately ten times on complexing it with 5 wt% NaClO<sub>4</sub>. As the dopant concentration was progressively increased upto 20 wt% of NaClO<sub>4</sub>, there was a gradual but slow increase in the conductivity. But when the dopant concentration was increased beyond 20 wt%, the conductivity started decreasing. The increase in conductivity at lower dopant concentrations of NaClO<sub>4</sub> may be attributed to the increase of charge carriers and decrease in the crystallinity of the polymer electrolyte [12].

Figure. 3 shows that conductivity vs temperature plots, which follow an Arrhenius nature throughout, with three different activation energies in three regions (region I, II and region III). In region-I, the conductivity of pure PMMA increased slowly with increase in temperature up to 60 °C. Around a particular temperature range (60–90 °C), there was a sudden increase in the variation of  $\sigma$  leading to region-III. This may be due to a transition from a semicrystalline phase to an amorphous phase. According to Druger et al. [13, 14], in polymer electrolytes, the change of conductivity with temperature is due to segmental motion, which results in an increase in the free volume of the system. This increase in free volume would also facilitate the motion of ionic charge [15]. The linear variation of  $\sigma$  vs  $1000/T$  plots can be expressed by the relation,

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

where  $\sigma_0$  is the proportionality constant,  $E_a$ , the activation energy, and  $k$ , the Boltzmann constant.

The activation energies, for all the three regions, were calculated from the slopes of  $\log \sigma$  vs  $1000/T$  plots and the values are shown in Table 1. The activation energy is a combination of energy of charge carrier creation (defect formation) and the energy of ion migration that can be evaluated by linear fitting of the Arrhenius plots [16]. Therefore, it can be suggested that the activation energy is the energy required to provide a conductive condition for the migration of ions. From the table it was found the activation energies decreased with increasing salt concentration. This may be due to the fact that the addition of small amounts of dopant forms charge transfer complexes in the host lattice and increases the conductivity by providing additional charges in the lattice resulting in a decrease of activation energy.

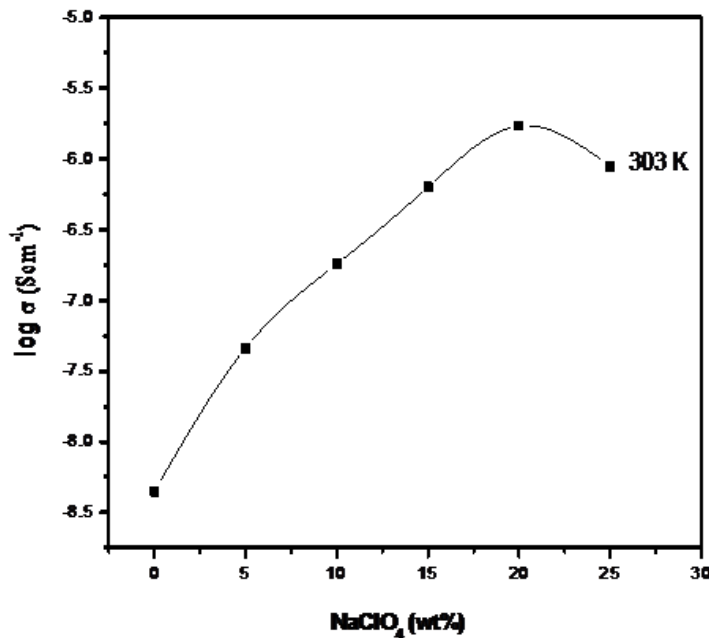


Fig 2: Composition vs conductivity plots of PMMA+DMF+NaClO<sub>4</sub> polymer electrolyte system at room temperature

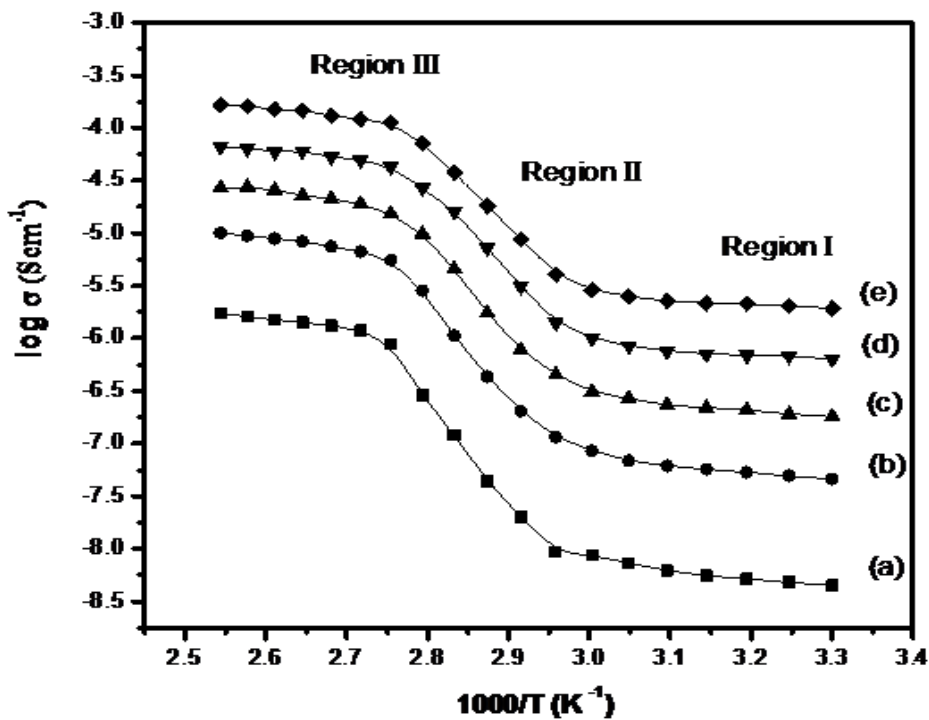


Fig 3: log  $\sigma$  vs  $1000/T$  plots of (a) PMMA +DMF (b) PMMA+DMF+NaClO<sub>4</sub> (95:05) (c) PMMA+DMF+NaClO<sub>4</sub> (90:10) (d) PMMA+DMF+NaClO<sub>4</sub> (85:15) (e) PMMA+DMF+NaClO<sub>4</sub> (80:20)

Table 1: Activation energies and transference numbers of Plasticized PMMA based polymer electrolyte system

Polymer electrolyte system (wt%)	Activation energy (eV)			Transference numbers	
	Region I	Region II	Region III	$t_{ion}$	$t_{ele}$
PMMA+DMF	0.27	1.86	0.20	----	----
PMMA+DMF+NaClO <sub>4</sub> (95:05)	0.24	1.75	0.18	0.93	0.07
PMMA+DMF+NaClO <sub>4</sub> (90:10)	0.20	1.63	0.16	0.95	0.05
PMMA+DMF+NaClO <sub>4</sub> (85:15)	0.17	1.50	0.14	0.96	0.04
PMMA+DMF+NaClO <sub>4</sub> (80:20)	0.14	1.42	0.12	0.98	0.02

### 3.3 Transference numbers

Electronic and ionic transference number measurements play an important role in explaining the conductivity of polymer electrolyte films. Transference numbers of (PMMA+DMF+NaClO<sub>4</sub>) electrolyte system were evaluated using Wagner's polarization technique. In this method, the DC current is monitored as a function of time on application of a fixed DC voltage of 1.5 V across the cell in the configuration Na/(polymer electrolyte)/C. After polarization, the current versus time plot was drawn (Fig. 4). The transference numbers were calculated from the polarization, current vs time plot. The resulting data are given in Table 1. For all the compositions of the (PMMA+DMF+NaClO<sub>4</sub>) electrolyte system, the values of ionic transference numbers are in the range 0.93– 0.98. This suggests that the charge transport in these electrolytes is predominantly ionic with a negligible contribution from electrons [17].

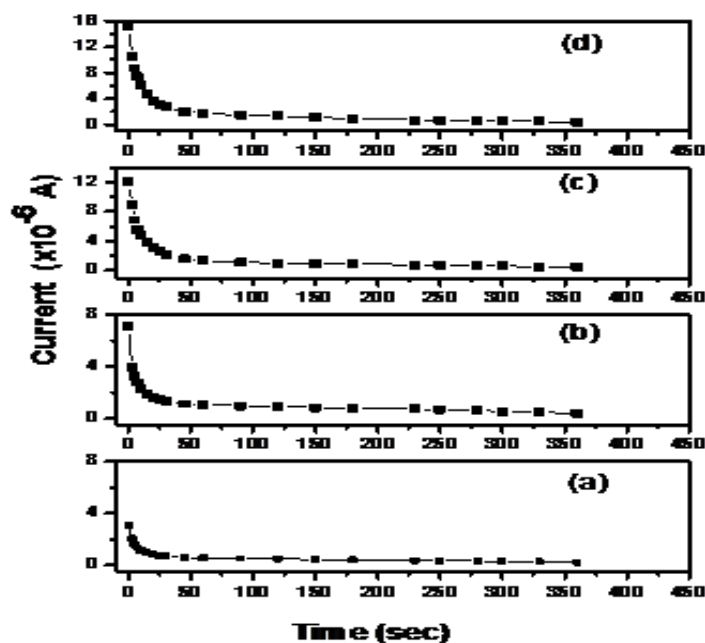


Fig 4: Current vs time plots of (a) PMMA+DMF+NaClO<sub>4</sub> (95:05) (b) PMMA+DMF+NaClO<sub>4</sub> (90:10) (c) PMMA+DMF+NaClO<sub>4</sub> (85:15) (d) PMMA+DMF+NaClO<sub>4</sub> (80:20)

### 3.4 Discharge profile

Using (PMMA+DMF+NaClO<sub>4</sub>) polymer electrolyte films, solid state electrochemical cells were fabricated in the configuration Na (anode)/ (PMMA+DMF+NaClO<sub>4</sub>) / (I<sub>2</sub>+C+electrolyte)(cathode) for various compositions of (PMMA+DMF+NaClO<sub>4</sub>) with ratios (95:05), (90:10), (85:15) and (80:20). Their discharge profiles were recorded for a constant load of 100 kΩ at room temperature. Fig.5 shows the discharge profiles of these polymer batteries. The open circuit voltage (OCV) and short circuit current (SCC) of these cells were measured. The initial sharp decrease in the voltage and current for all the cells may be because of the polarization and/or formation of a thin layer of sodium salt at the electrode – electrolyte interface [18].

Various other cell parameters such as current density, discharge time for plateau region, power density, energy density etc were evaluated for various compositions of the electrolyte system and are given in the Table 2. along with OCV and SCC.

It was observed that all parameters showed an increase with increasing percentage of NaClO<sub>4</sub> in the PMMA+DMF polymer electrolyte. The maximum values were obtained for the electrolyte with the composition (PMMA+DMF+NaClO<sub>4</sub>) (80:20). This may be due to the high ionic conductivity and higher degree of amorphosity of this system when compared to other systems.

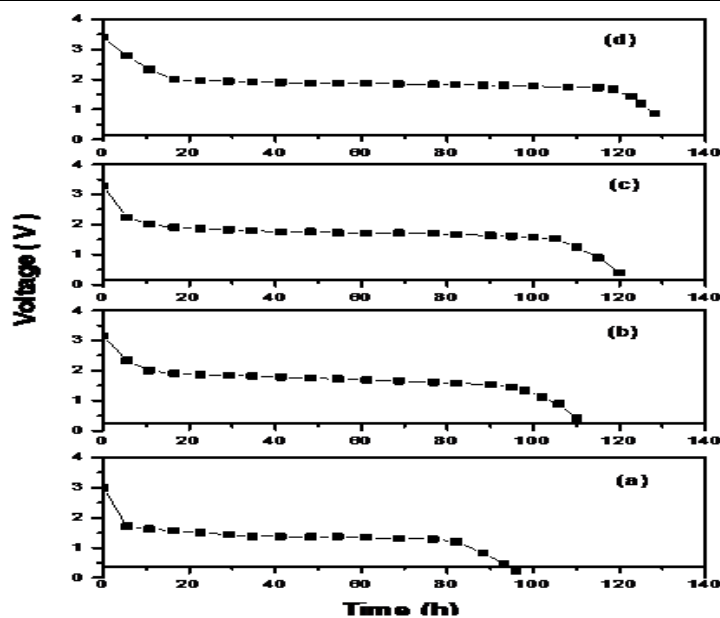


Fig 5: Voltage vs time plots of (a) PMMA+DMF+NaClO<sub>4</sub> (95:05) (b) PMMA+DMF+NaClO<sub>4</sub> (90:10) (c) PMMA+DMF+NaClO<sub>4</sub> (85:15) (d) PMMA+DMF+NaClO<sub>4</sub> (80:20)

Table 2: Discharge characteristics of solid electrochemical cells of the polymer electrolyte system in the configuration Na/PMMA+DMF+NaClO<sub>4</sub>/I<sub>2</sub>+C+electrolyte

Cell parameters	Na/PMMA+DMF+NaClO <sub>4</sub> /I <sub>2</sub> +C+electrolyte (95:05)	Na/PMMA+DMF+NaClO <sub>4</sub> /I <sub>2</sub> +C+electrolyte (90:10)	Na/PMMA+DMF+NaClO <sub>4</sub> /I <sub>2</sub> +C+electrolyte (85:15)	Na/PMMA+DMF+NaClO <sub>4</sub> /I <sub>2</sub> +C+electrolyte (80:20)
Open circuit voltage (V)	2.99	3.15	3.28	3.40
Short circuit current (mA)	1.19	1.27	1.33	1.37
Effective area of the cell (cm <sup>2</sup> )	1.33	1.33	1.33	1.33
Cell weight (gm)	1.40	1.40	1.41	1.42
Discharge time for plateau region (h)	82	97	110	122
Power density (W/kg)	2.55	2.86	3.11	3.28
Energy density (Wh/kg)	209	277	342	400
Current density (mA/cm <sup>2</sup> )	0.899	0.958	1.006	1.031
Load (kΩ)	100	100	100	100

#### IV. CONCLUSIONS

In summary, it could be concluded that the structure, conductivity and discharge properties of plasticized PMMA polymer electrolyte films can be influenced by complexing it with NaClO<sub>4</sub> salt. The XRD study reveals the amorphous nature of the polymer electrolytes. These studies indicate that the dc conductivity of pure PMMA+DMF and (PMMA+DMF+NaClO<sub>4</sub>) films increased with increasing temperature and dopant concentration. Transference number data showed that the conductivity is mainly due to ions rather than electrons. Parameters were evaluated for (plasticized PMMA+ NaClO<sub>4</sub>) polymer electrolyte cells. These cells exhibit better performance, which indicates that these cells are suitable for fabricating solid-state batteries.

## REFERENCES

- [1] J.Y. Kim, S.H. Kim, "Ionic conduction behavior of network polymer electrolytes based on phosphate and polyether copolymers" *Solid State Ionics*, 124 (1999) 91.
- [2] J. Gao, J. Liu, W. Liu, B. Li, Y. Xin, Y. Yin, Z. Zou, "Proton Exchange Membrane Fuel Cell Working at Elevated Temperature with Ionic Liquid as Electrolyte" *Int. J. Electrochem. Sci.*, 6 (2011) 6115.
- [3] Jinisha B, Manoj M M, Anil Kumar K M, Pradeep "Development of a novel type of solid polymer electrolyte for solid state lithium battery applications based on lithium enriched poly (ethylene oxide) (PEO)/poly (vinyl pyrrolidone) (PVP) blend polymer" *Electrochimica Acta*, 235 (2017) 210
- [4] J.Ramesh babu, K.Rravindranath, K. Vijaya kumar,, "Preparation and Characterization of Nano-Dy<sub>2</sub>O<sub>3</sub>-Doped PVA + Na<sub>3</sub>C<sub>6</sub>H<sub>5</sub>O<sub>7</sub> Polymer Electrolyte Films for Battery Applications" *Advances in Materials Science and Engineering*, volume (2018) 1-9.
- [5] T. R. Heera, and L. Cindrella, "Synthesis and Characterization of NiS/MnS Core-Shell Embedded Conducting Polyaniline Composite for Photovoltaic Application" *International journal of Polymeric materials* 59 (2010) 607.
- [6] U. Sasikala, P. Naveen kumar, VVRN Rao and A. K. Sharma, "Structural, electrical and parametric studies of a PEO based polymer electrolyte for battery applications" *International journal of engineering science & advanced technology* 2 (2012) 722.
- [7] D. Fautex, M. D. Lupien, C. D. Robitaille, "Phase Diagram, Conductivity, And Transference Number Of PEO - NaI Electrolytes Electrochemical Science And Technology - Technical Papers" *J Electrochem Soc* 134(11) (1987) 2761.
- [8] S. G. Greenbaum, Y. S. Pak, M. C. Wintersgill, J. J. Fontanella, J. W. Schultz, "NMR, DSC, DMA and High Pressure Electrical Conductivity Studies In PPO Complexed With Sodium Perchlorate Solid - State Science And Technology - Technical Papers" *J Electrochem Soc* 135 (1988) 235.
- [9] S. G. Greenbaum, K. J. Ademic, Y. S. Pak, M. C. Wintersgill, J. J. Fontanella "NMR, DSC and electrical conductivity studies of MEEP complexed with NaCF<sub>3</sub>SO<sub>3</sub>", *Solid State Ionics* 28-30( 1988) 1042.
- [10] J. B. Wagner, C. Wagner, "Electrical Conductivity Measurements on Cuprous Halides", *J Chem Phys*, 26(1957) 597-1601.
- [11] A. A. Mohamad, N. S. Mohamad, M. Z. A. Yahya, R. Othman, S. Ramesh, Y. Alias and A. K. Aroof, "Ionic conductivity studies of poly(vinyl alcohol) alkaline solid polymer electrolyte and its use in nickel-zinc cells", *Solid State Ionics*, 156(2003) 171.
- [12] Ch. V. Subba Reddy, A.K. Sharma and V.V.R.N.Rao, "Electrical and optical properties of polyblend electrolyte", *Polymer*, 47(2006) 1318.
- [13] S. D. Druger, A. Nitzam, M. A. Ratner, "Dynamic bond percolation theory: A microscopic model for diffusion in dynamically disordered systems. I. Definition and one-dimensional case", *J Chem Phys* 79 (1983) 3133.
- [14] S. D. Druger, M. A. Ratner, Nitzam, "Generalized hopping model for frequency-dependent transport in a dynamically disordered medium, with applications to polymer solid electrolytes" *A Phys Rev B* 31, 1985, pp. 3939-3947.
- [15] T. Miyamoto, K. Shibayama, "Free-volume model for ionic conductivity in polymers" *J App Phys* 44(1973) 5372(5).
- [16] M. J. Reddy, T. Sreekanth, and U.V.S. Rao, *Solid State Ionics* 126(1999) 1401.
- [17] V. M. Mohan, V. Raja, P. Balaji Bhargav, A. K. Sharma, V. V. R. N. Rao, "Structural, electrical and optical properties of pure and NaLaF<sub>4</sub> doped PEO polymer electrolyte films" *Jr.Polym. Res*, 14(2007) 283.
- [18] A.A. Mohammad, N.S. Mohammad, M.Z.A. Yahya, S.Ramesh ans A.K.Aroof, *Solid State Ionics*, 156 (2003) 171.