# TRANSPORT PROPERTIES OF PEO: $KClO_4$ SOLID STATE POLYMER ELECTROLYTES

V. Madhusudhana Reddy[1], N. Kundana[2], T. Sreekanth[3]
[1]Associate Professor, Department of Science and Humanities,
Malla Reddy College of Engineering and Technology, Dhullapally, Hyderabad, Telangana, India
BV Raju Institute of Technology, Narsapur, Medak Dist, T.S., India.
[3]AssociateProfessor, Department of Physics, JNTUH College of Engineering
Nachupally (Kondagattu), Jagtial District, Telangana, India

**Abstract**

**Poly (ethylene oxide) (PEO) and several compositions of (PEO+$KClO_4$) polymer electrolytes were prepared in the Wt% ratios (90:10), (80:20) and (70:30) by solution – casting technique. Ionic and electronic transport numbers ($t_{ion}$ and $t_{ele}$) were calculated using Wagner's polarization method. The transference number calculations indicated that the charge transport in these polymer electrolytes is predominantly due to ionic, electronic involvement existence negligible. The dc conductivity has been obtained in the temperature range 303-373K.The composition dependence conductivity plots indicated an increase of conductivity with intensification of the concentration of the salt in the polymer. The conductivity-temperature plots exhibited an augmentation in conductivity with increase of temperature in PEO and it was also observed for complexed PEO polymer electrolyte systems.**

**Index Terms: dc conductivity, poly (ethylene oxide), polymer electrolyte, transport numbers, wagner's polarization technique.**

## I. INTRODUCTION

The modernization of the polymer engineering of artificial materials has launched several innovative polymers; some of which play a significant role in the expansion of solid-state ionic devices. Particularly, the polyethylene oxide (PEO)-based polymer electrolytes are the most widely reported polymer electrolytes because of the special properties like low glass transition temperature, high salt salvation capability, good chemical and mechanical properties of PEO. The ether oxygen of PEO chains crosslink with cations of the ionic salts and facilitate ion conduction through the polymer matrix [1, 2]. The segmental motion of polymer chains in such polymer electrolytes is understood to help cations to jump from one site to the other. However, PEO is inherently a semi-crystalline polymer; therefore, as a host, it offers only little flexibility of chains in the crystalline regions. As a result, PEO-based polymer–salt complexes offer ionic conductivity [3]. When combined with a variety of alkali – metal salts, PEO forms crystalline complexes that display relatively high conductivity [4]. This feature makes it an attractive material as solid electrolyte in high energy density battery [5].

Most studies were carried out on complexes of PEO with a number of alkali salts such as NaX (X:TFSI, FSI) [6], (PEO) lithium difluoro (oxalato) borate (LiDFOB) [7], PEO-$LiClO_4$ [8, 9], PEO-AgI [10], PEO-$LiCF_3SO_3$ [11], PEO/$NaClO_4$[12], (PEO+$KBrO_3$) [13], NaSCN [14], $NaYF_4$ & $KYF_4$ [15] and (PEO+$KIO_3$+plasticizer) [16] are reported. Potassium-based polymer electrolytes have several advantages compare to lithium-based polymer electrolytes. Potassium is much more abundant and lower priced than lithium. The softness of this metal makes it easier to achieve effective contacts to other components in the battery. However, potassium is less moisture resistance than lithium [16].

From these facts, the authors in the present work

presented the results of their investigation on (PEO+$KClO_4$) based polymer electrolytes. Transference number measurements, composition dependent conductivity and temperature dependent conductivity were employed to determined (PEO+$KClO_4$) polymer electrolyte systems.

## II. EXPERIMENTAL

Poly (ethylene oxide) (PEO) (Aldrich, M.W. $4X10^5$) and various compositions of (PEO+$KClO_4$) polymer electrolytes were prepared in the Wt% ratios (90:10), (80:20) and (70:30) by solution – casting technique by using methanol (water-free) as solvent. The solutions were stirred for 15-20 hr, were cast using polypropylene dishes, and were vaporized gradually at room temperature. At last, the films were dried systematically at $10^{-3}$ Torr [13]. Transport numbers of ionic ($t_{ion}$) and electronic ($t_{ele}$) were evaluated using Wagner's polarization technique [13]. In this study, freshly prepared films of (PEO+$KClO_4$) were polarized in the order of Ag / polymer electrolyte / C under a dc bias (step potential of 1.5 V). Subsequently current was examined as a function of time on a Keithly electrometer [Model 614]. The dc conductivity was obtained by using the lab made conductivity setup in the temperature range 303-373K. The dc-conductivity was obtained as a function of composition dependence dc conductivity and dc conductivity versus temperature [6].

## III. RESULTS AND DISCUSSIONS

*(i). Transference Numbers*

Transport numbers of (PEO+$KClO_4$) polymer electrolyte [*various wt% compositions like (90:10), (80:20) and (70:30)*] were estimated by using the Wagner's polarization method [17]. Where, the dc current versus time plots were obtained by application of dc voltage across the Ag / (PEO+ $KClO_4$) / C configuration. After polarization of the cell with dc voltage of 1.5V, the current versus time plot has been achieved for various composition of (PEO+ $KClO_4$). Fig.1, shows current versus time plot of (PEO+ $KClO_4$) (70:30) polymer electrolytes system. The calculated ionic ($t_{ion}$) and electronic ($t_{ele}$) transport numbers for all composition of (PEO+$KClO_4$) electrolytes were tabulated in the Table-1. From the Table-1, it is observed that, the ionic transference number data is found for these polymer electrolytes in the range of 0.94 to 0.98. These results evidently suggested that the charge transport in these (PEO + $KClO_4$) polymer electrolytes is mainly due to ions and in significant influence from electrons being negligible.

Table-1. Transference number data of (PEO+$KClO_4$) polymer electrolyte system along with some other reported polymer electrolyte systems.

| Polymer Electrolyte | Transference Number | | References |
|---|---|---|---|
| | $t_{ion}$ | $t_{ele}$ | |
| PEO+$NH_4ClO_4$ | 0.93 | 0.07 | [18] |
| PEO+$NH_4I$ | 0.97 | 0.03 | [19] |
| PEO+$(NH_4)_2SO_4$ | 0.98 | 0.02 | [19] |
| PEO+$AgNO_3$ | 0.91 | 0.09 | [20] |
| PEO+ $NaPF_6$ | 0.98 | 0.02 | [21] |
| PEO+$KIO_3$ | 0.99 | 0.01 | [22] |
| PEO+$KNO_3$ | 0.93 | 0.07 | [23] |
| PEO+$KClO_4$ (90:10) | 0.94 | 0.06 | Present |
| PEO+$KClO_4$ (80:20) | 0.95 | 0.05 | |
| PEO+$KClO_4$ (70:30) | 0.98 | 0.02 | |

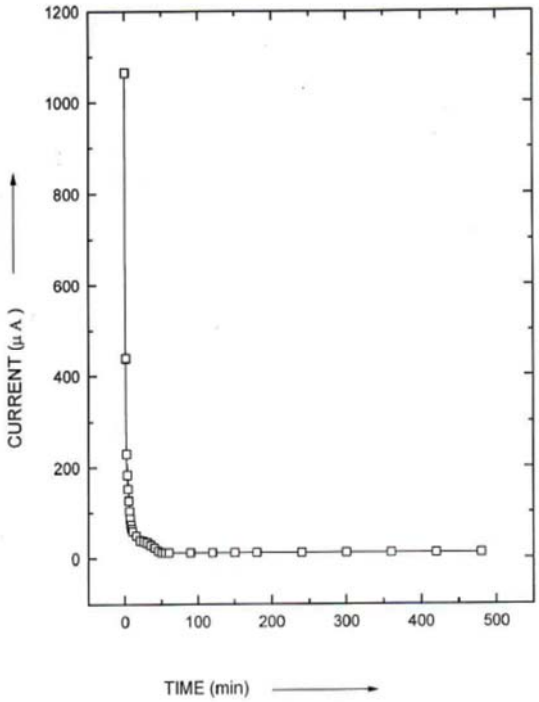


Fig.1. Polarization current versus time plot for the complexed [PEO+$KClO_4$] (70:30) film.

*(ii). Composition dependence of dc conductivity*

The electrical conductivity, "σ" was calculated as a function of composition of (PEO+$KClO_4$) polymer electrolyte at several temperatures. The composition dependence conductivity of (PEO+$KClO_4$) polymer electrolyte system is shown in Fig.2. The conductivity value of the (PEO+$KClO_4$) polymer electrolyte system for various compositions (wt.%) has been given in Table-2 for various temperatures. From the Table-2 and Fig.2, the following features were detected.

- The conductivity of pure PEO is about $8.35x10^{-10}$ $S.cm^{-1}$ at RT and its value augmented on complexing PEO with $KClO_4$ salt. The magnitude of variation was of the order of ~ $10^4$ times more in complexed films associated to that of PEO.
- Usually, the conductivity rises as the degree of crystallinity of the polymer declines and amorphous nature intensifies. In this present research work, (PEO+$KClO_4$) polymer electrolyte system conductivity increase continuous with increase of $KClO_4$ salt in PEO. It has been attributed to the reduction in the degree of crystallinity and growth in the degree of amorphous nature. These results were also confirmed from the X-ray diffraction investigations of these polymer electrolytes [24]. Similar remarks were finished in the conductivity-composition plots of a few PEO based systems [22, 25-26].

Table-2. dc electrical conductivity of PEO and (PEO+$KClO_4$) polymer electrolyte system at different temperatures

.

| **Polymer electrolyte ( Wt % )** | **Temperature in K** | | | |
|---|---|---|---|---|
| | *303K* | *323K* | *343K* | *373K* |
| | **Conductivity ( S. $cm^{-1}$ )** | | | |
| Pure PEO | $8.35x10^{-10}$ | $1.19xl0^{-9}$ | $1.12x10^{-8}$ | $9.94xl0^{-8}$ |
| PEO+ $KClO_4$ (90: 10) | $8.38xl0^{-6}$ | $1.02xl0^{-5}$ | $1.18xl0^{-5}$ | $1.08xl0^{-4}$ |
| PEO+ $KClO_4$ (80:20) | $3.57xl0^{-5}$ | $4.07xl0^{-5}$ | $5.27x10^{-5}$ | $1.28xl0^{-5}$ |
| PEO+ $KClO_4$ (70:30) | $1.07x10^{-4}$ | $1.76xl0^{-4}$ | $1.58xl0^{-4}$ | $2.86x10^{-4}$ |

*(iii). Conductivity versus Temperature Plots*

The temperature dependence of dc conductivity of (PEO+$KClO_4$) polymer electrolyte of various compositions was investigated in the temperature range 303-373K. The temperature dependence conductivity plots of PEO and various compositions of (PEO+$KClO_4$) polymer electrolyte system is shown in Fig.3. The temperature dependence of conductivity of polymer-salt complexes monitors several patterns as discussed by Ratner [27]. The following observations were found for (PEO+ $KClO_4$) polymer electrolyte system.

- In the temperature range of 303 to 373K, the conductivity was found to rise with growth of temperature in pure PEO and also in all the compositions of (PEO+$KClO_4$) polymer electrolyte.
- The conductivity-temperature plots follow the Arrhenius behaviour throughout, however with two regions with two activation energies above and below the melting point ($T_m$) of the polymer. In region I (i.e. below $T_m$) the conductivity of the PEO rises slowly with growth of temperature up to 70°C. At 70°C, there is an abrupt rise in conductivity. In the region-II (i.e., above $T_m$), the conductivity yet again increases with escalation of temperature. Similar behaviour was observed in all the compositions of $KClO_4$ complexed PEO polymer electrolytes. These results were also confirmed from differential scanning calorimetry (DSC) studies of (PEO+$KClO_4$) polymer electrolytes and were reported by V. Madhusudhana Reddy et al [24].
- The existence of two regions (region-l and II) in the conductivity-temperature plots and the abrupt growth in the conductivity at ~ 70°C which corresponds to the melting temperature ($T_m$) of the polymer PEO, there was an alteration from semi-crystalline phase to amorphous phase. Due to this phase change, the conductivity indicated a sudden rise at 70°C. Below $T_m$ (region-I), the growth of conductivity with temperature was understood as hopping mechanism between coordinating sites, local structural relaxations and segmental motions of polymer chain. However, where the amorphous region gradually increases, the polymer chain obtains faster internal modes in which bond rotations produce segmental

motion. This in turn favours the hopping inter-chain and intra-chain ion movements and the conductivity of the polymer electrolyte becomes considerable. The existence of two regions in the conductivity-temperature plots and the abrupt rise in conductivity at $T_m$ were investigated in a number of PEO based polymer electrolytes [5, 15, 18, 27- 29].

- The linear dissimilarity in σ versus 1/T plots below and above $T_m$ proposes an Arrhenius type thermally activated process. The conductivity (σ) can be expressed as

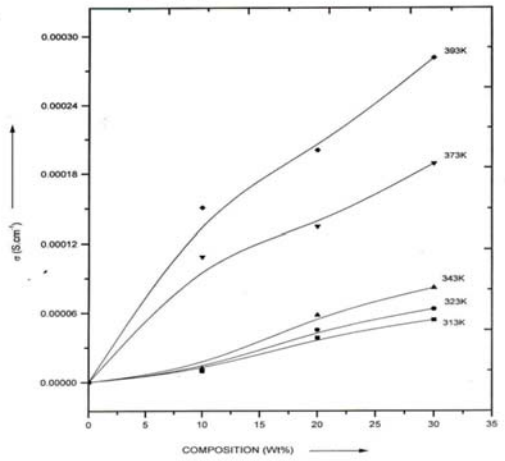


Fig.3. Composition dependence dc conductivity of (PEO+$KClO_4$) polymer electrolyte system at different temperatures.

$$\sigma = \sigma_o \, Exp \, (-E_a/kT)$$

Where $\sigma_o$ is pre-exponential factor, $E_a$ the activation energy and k is the Boltzmann constant. The obtained values of $\sigma_o$ and $E_a$ for (PEO+ $KClO_4$) complexes are shortened in Table-3.

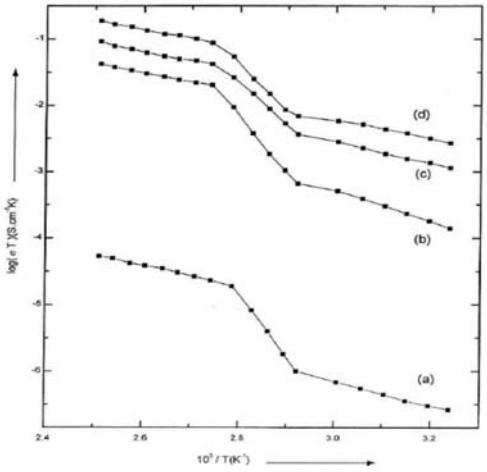


Fig.3. The temperature dependence of dc conductivity (a) Pure PEO, (b) [PEO+$KClO_4$] (90:10), (c) [PEO+$KClO_4$] (80:20), and (d) [PEO+$KClO_4$] (70:30).

Table -3. Activation energies and pre-exponential factors of (PEO+ $KClO_4$) polymer electrolyte system along with other reported polymer systems.

| Polymer electrolyte system | Semi crystalline before $T_m$ | | Amorphous after $T_m$ | | Reference |
|---|---|---|---|---|---|
| | $E_a$ (ev) | $\sigma_o$ ($S.cm^{-1}$) | $E_a$ (ev) | $\sigma_o$ ($S.cm^{-1}$) | |
| Pure PEO | 0.40 | $9.70x10^{-3}$ | 0.32 | $8.06x10^{-2}$ | [19] |
| PEO+NHI | 0.44 | $2.60x10^{2}$ | 0.17 | $1.26X10^{-1}$ | [19] |
| PEO+ $(NH_4)ClO_4$ | 0.49 | $4.54x10^{2}$ | 0.41 | $3.67x10^{2}$ | [29] |
| PEO+NaY $F_4$ (90:10) | 0.18 | $3.25x10^{-4}$ | 0.28 | $1.58x10^{-1}$ | [30] |
| PEO+NaY $F_4$ (80:20) | 0.24 | $6.19x10^{-3}$ | 0.38 | 3.46 | |
| PEO+KCl $O_4$ (90:10) | 0.09 | $7.17x10^{-5}$ | 0.16 | $3.53x10^{-4}$ | Present |
| PEO+ $KClO_4$ (80:20) | 0.12 | $6.15x10^{-4}$ | 0.27 | $2.20x10^{-2}$ | |
| PEO+ $KClO_4$ (70:30) | 0.15 | $3.83x10^{-3}$ | 0.13 | $2.37x10^{-3}$ | |

## IV. CONCLUSIONS

Poly (ethylene oxide) (PEO) and various compositions of (PEO+$KClO_4$) polymer electrolytes were prepared in the Wt% ratios by solution – casting technique. Wagner's polarization technique has been employed to determine the ionic and electronic transference numbers of (PEO+ $KClO_4$) polymer electrolytes system. The obtained transference number measurements showed that the charge transport in these polymer electrolytes is predominantly due to ionic, electronic contribution being negligible. The conductivity of pure PEO at room temperature is of the order of $\sim 10^{-10}$ $S.cm^{-1}$. The conductivity of complexed PEO films showed an increase of conductivity with increase of salt in PEO compared to pure PEO. The composition dependence conductivity plots showed a raise of conductivity with augment of the concentration of the salt in the polymer. This was explained as due to a change in the degree of crystallinity of the polymer due to the addition of the salts. The conductivity-temperature plots showed an increase in conductivity with increase of temperature in PEO and also in all complexed PEO polymer electrolyte systems. The conductivity-temperature plots follow the

Arrhenius behaviour throughout. The existence of two regions (region I and region II) in conductivity-temperature plots have been explained in terms of hopping mechanism between coordinating sites, local structural relaxations and segmental motions of the polymer chain. The activation energies ($E_a$) and pre-exponential factors ($\sigma_o$) were evaluated for all the polymer electrolyte systems.

## REFERENCES


[1]. J. R. Mac Callum and C. A. Vincent, "Polymer Electrolyte Review-I", Elsevier (Eds.), London, 1987.

[2]. F.M. Gray, "Solid Polymer Electrolytes", CVH, New York, 1991.

[3]. Kuldeep Mishra, Saurabh Singh Pundir and D. K. Rai, Effect of polysorbate plasticizer on the structural and ion conduction properties of PEO–NH4PF6 solid polymer electrolyte, Ionics Vol. 23, pp:105–112, 2017.

[4] C.R.A. Catlow, A.V. Chadwick, G.N. Greaves, L. Moroney, M.R. Worboys, An EXAFS study of the structure of rubidium polyethyleneoxide salt complexes, Solid State Ionics, Vol. 10, pp: 1107, 1983.

[5] M.B. Arman, J.M. Chabagn, M. Doclot, J., Fast Ion transport in solids, Vashishna, Mundey, Sheynoy, Eds.: North-Holland: New York, pp:131, 1979.

[6]. Andrea Boschin, Patrik Johansson, Characterization of NaX (X: TFSI, FSI) PEO based Solid Polymer Electrolytes for Sodium Batteries, ElectrochimicaActa, Vol. 175, pp:124-133, 2015.

[7]. Anji Reddy Polu, Hee-WooRhee, onic liquid doped PEO-based solid polymer electrolytes for lithium-ion polymer batteries, International Journal of Hydrogen Energy, Volume 42, Issue 10, pp: 7212-7219, 2017.

[8]. S. Das, A. Ghosh, Effect of plasticizers on ionic conductivity and dielectric relaxation of PEO-$LiClO_4$ polymer electrolyte, ElectrochimicaActa, Vol. 171, pp: 59-65, 2015.

[9]. J. Gurusiddappa, W. Madhuri, R. Padma Suvarna, K. PriyaDasan, Studies on the morphology and conductivity of PEO/$LiClO_4$, Materials Today: Proceedings, Vol. 3, Issue 6, pp:1451-1459, 2016.

[10]. B. Keshav Rao, Mohan L. Verma, First principle study of PEO-AgI polymer systems, Chemical Physics Letters, Vol. 679, pp: 176-180, 2017.

[11]. SasithornKlongkan, JantrawanPumchusak, Effects of Nano Alumina and Plasticizers on Morphology, Ionic Conductivity, Thermal and Mechanical Properties of PEO-LiCF3SO3 Solid Polymer Electrolyte, ElectrochimicaActa, Vol. 161, issue 10, pp: 171-176, 2015.

[12]. YatimLailunNi'mah, Ming-Yao Cheng, Ju Hsiang Cheng, John Rick, Bing-Joe Hwang, Solid state polymer nanocomposite electrolyte of $TiO_2$ / PEO / $NaClO_4$ for sodium ion batteries, Journal of Power Sources, Vol. 278, pp: 375-381, 2015.

[13]. T. Sreekanth, M. Jaipal Reddy, U.V. Subba Rao, Polymer electrolyte system based on (PEO +$KBrO_3$) its application as an electrochemical cell, Journal of Power Sources, Vol. 93 pp: 268-272, 2001.

[14] Y.L. Lee, B. Crist, Phase behavior and conductivity in poly (ethylene oxide)– sodium thiocyanate systems J. Appl. Phys.Vol. 60, pp: 2683, 1986.

[15] S.S. Rao, M.J. Reddy, E.L. Narsaiah, U.V.S. Rao, Development of electrochemical cell based on (PEO+NaYF4) and (PEO+KYF4) polymer, Mater. Sci. Eng. B, Vol.33, pp. 173, 1995.

[16]. T. Sreekanth, Characterization and Application of the (PEO+KIO3+Plasticizer) Solid State Polymer Electrolyte System, Journal of the Korean Physical Society, Vol. 62, Issue 8, pp: 1129-1133, 2013

[17]. J.B. Wagner and C. Wagner, Electrical Conductivity Measurements on Cuprous Halides, J. Chem. Phys. Vol. 26, pp: 1597, 1957.

[18]. S.A. Hashmi, Ajay Kumar, K.K. Maurya and S. Chandra, Proton conducting polymer electrolyte I: Polyethylene oxide + NH4ClO4, J. Phys. D. Appl. Phys. Vol. 23, pp: 1307, 1990.

[19]. K.K. Maurya, N. Srivastava, S.A. Hashmi and S. Chandra, Proton conducting polymer electrolyte: II poly ethylene oxide + $NH_4I$ system, J. Mat. Sci. Vol. 27, pp: 6357, 1992.

[20]. S. Chandra, S.A. Hashmi, M. Saleem and R.C. Agrawal, Investigations on poly

ethylene oxide based polymer electrolyte complexed with $AgNO_3$, Solid State Ionics,Vol. 67, Issues 1–2, pp: 1-7, 1993.

[21]. S.A. Hashmi and S. Chandra, Experimental investigations on a sodium-ion-conducting polymer electrolyte based on poly (ethylene oxide) complexed with $NaPF_6$, Material Science and Engineering: B, Vol. 34, Issue 1, pp: 18-26, 1995.

[22]. M. Jaipal Reddy, Peter P. Chu, T. Sreekanth, U.V. Subba Rao, PEO: $KIO_3$ polymer electrolyte system – its application to solid state electrochemical cell, Journal of Materials Science: materials in Electronics Vol. 12, pp: 153-156, 2001.

[23]. T. Sreekanth, M. Jaipal Reddy, S. Subramanyam, U.V. Subba Rao, Ion conducting polymer electrolyte films based on (PEO+$KNO_3$) system and its application as an electrochemical cell, Materials Science and Engineering B, Vol. 64, pp: 107–112, 1999.

[24]. Study of Characterization of (PEO+$KClO_4$) Polymer Electrolyte System, V. Madhusudhana Reddy, T. Sreekanth, International Journal of Research in Engineering and Technology, Vol. 03 Issue 02, pp: 263-267, 2014.

[25]. M. Jaipal Reddy, T. Sreekanth and U.V. Subba Rao, Conductivity and parametric studies of a (PEO+(glass) (15Na2O–15NaF–70B2O3)) cell, J. Power Sources Vol. 76, pp: 30, 1998.

[26]. M. Jaipal Reddy, T. Sreekanth and U.V. Subba Rao, Study of the plasticizer effect on a (PEO+$NaYF_4$) polymer electrolyte and its use in an electrochemical cell, Solid State Ionics, Vol. 126, pp: 55, 1999.

[27]. M.A. Ratner, In: Polymer Electrolyte Reviews-1, (eds.) J.R. Mac Callum and C.A. Vincent (Elsevier, London, New York) p.173, 1987.

[28]. C.A. Vincent, Progress in solid state chemistry, Prese City, Vol. 17, pp.145-147, 1987.

[29]. S Chandra, SA Hashmi, G Prasad, Studies on ammonium perchlorate doped polyethylene oxide polymer electrolyte, Solid State Ionics, Vol. 40/41, Part 2, pp: 651-654, 1990.

[30]. M. Jaipal Reddy, U.V. Subba Rao, Transport Studies of Poly (ethylene oxide) based polymer electrolyte complexed with sodium yttrium fluoride, J. Mater. Sci. Lett. Vol. 17, pp: 1613, 1998.