

Conductivity and parametric studies of a (PEO + (glass)(15Na₂O–15NaF–70B₂O₃)) cell

M. Jaipal Reddy, T. Sreekanth, U.V. Subba Rao *

Department of Physics, Osmania University, Hyderabad, 500 007, India

Received 30 April 1998; accepted 8 June 1998

Abstract

Ion conducting polymer electrolyte films based on poly(ethylene oxide) (PEO) complexed with a glass (15Na₂O–15NaF–70B₂O₃) are prepared by a solution—cast technique. The complexation of the glass with PEO is confirmed by X-ray diffraction analysis. DC conductivity in the temperature range 303–373 K and transference number measurements are performed in order to investigate the charge transport in the polymer electrolyte system. The conductivity of the (PEO + glass) electrolyte is about 10⁴ times larger than that of pure PEO at room temperature. The transference number data show that the charge transport in this polymer electrolyte system is predominantly due to ions. Using these polymer electrolytes, solid-state electrochemical cells are fabricated. Various parameters associated with these cells are evaluated and compared with those of other reported cells. © 1998 Elsevier Science S.A. All rights reserved.

Keywords: Conductivity; Ion; X-ray diffraction

1. Introduction

Polymer electrolytes are an important class of materials because of their application in high-energy batteries, fuel cells, gas sensors, display devices, etc. [1–4]. These polymers are preferred over crystalline materials because of their wide range of composition, good interfacial contact between the electrode–electrolyte, and ease of preparation in different forms. Polyethylene oxide (PEO), in particular, is an exceptional polymer which can dissolve high concentrations of a wide variety of salts to form polymeric electrolytes [5]. There have been reports of the complexes of PEO with a number of alkali salts, viz., LiBF₄, LiPF₆ and Li(C₆H₅) [6], LiSCN [7], LiSO₃CF₃ and LiClO₄ [8], NaSCN [9], NaPF₆ [10], NaYF₄ and KYF₄ [11]. Investigations have also been made [12–14] of sodium ion-conducting polymer electrolytes based on PEO, poly(propylene oxide) (PPO), and poly bismethoxy ethoxy ethoxy phosphazene (MEEP) complexed with NaI, NaClO₄, NaSCN, NaCF₃SO₃. Some Ag⁺-ion conducting polymer complexes with PEO have also been examined [15–17]. Reports have

appeared on PEO-based electrolytes using divalent cationic salts as dopants [18–21]. The effect of addition of β-Al₂O₃ has been studied in PEO + LiClO₄ [22] and PEO + NaSCN [23] systems. Chandra et al. [24] evaluated a composite polymer electrolyte (PEO + NH₄I + Al₂O₃) which showed improved film stability.

In the work presented here, solid-state electrochemical cells based on (PEO + glass (15Na₂O–15NaF–70B₂O₃)) electrolyte films are fabricated. The main aim in choosing this electrolyte system is to improve the ionic nature of the polymer by introducing an amorphous glass material. Several experimental techniques such as X-ray diffraction (XRD), composition dependent conductivity, temperature dependent conductivity in the temperature range 303 to 373 K and transference number measurements are employed to characterize these polymer electrolyte films.

2. Experimental

Film (thickness: 100 to 150 μm) of pure PEO (Aldrich, MW ≈ 6 × 10⁵) and various compositions of complexed films of PEO with a fine powder of glass (15Na₂O–15NaF–70B₂O₃) were prepared in the wt.% ratios (90:10),

* Corresponding author. Tel.: +91-842-868-951; Fax: +91-842-869-020

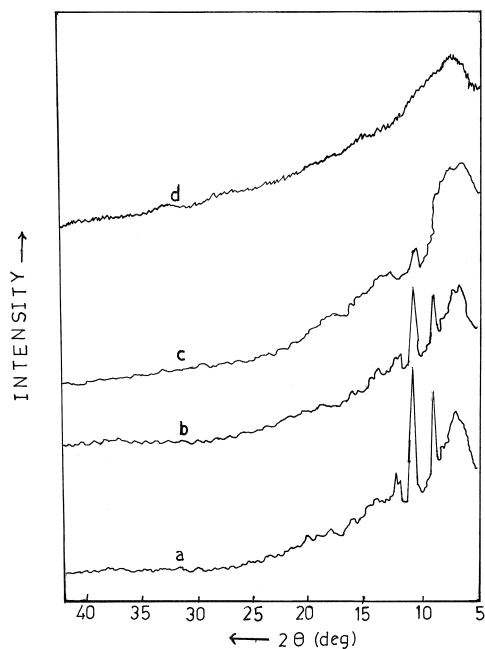


Fig. 1. X-ray diffraction patterns of: (a) PEO; (b) (PEO+glass) (80:20); (c) (PEO+glass) (60:40); (d) glass.

(80:20), (70:30) and (60:40) by a solution-cast technique using methanol (water free) as solvent. The solutions were stirred for 10–12 h and then cast on to polypropylene dishes and evaporated slowly at room temperature. The final products were vacuum dried thoroughly at 10^{-3} Torr. The XRD spectra of all the films were obtained by means of a SEIFERT X-ray diffractometer in the range $2\theta = 5$ to 60° .

The d.c. conductivity was measured using an in-house instrument [11], in the temperature range 300 to 373 K. The ionic and electronic transport numbers (t_{ion} , t_{ele}) were evaluated by means of the Wagner's polarization technique [25]. In this technique, a freshly prepared film of (PEO + glass) was polarized with a configuration of Na/(PEO + glass)/C under a d.c. bias (step potential of 1.5 V). The resulting current was monitored as a function of time with a Keithly electrometer [Model 614].

Solid-state electrochemical cells were fabricated with a configuration of Na/polymer electrolyte/(I₂ + C +

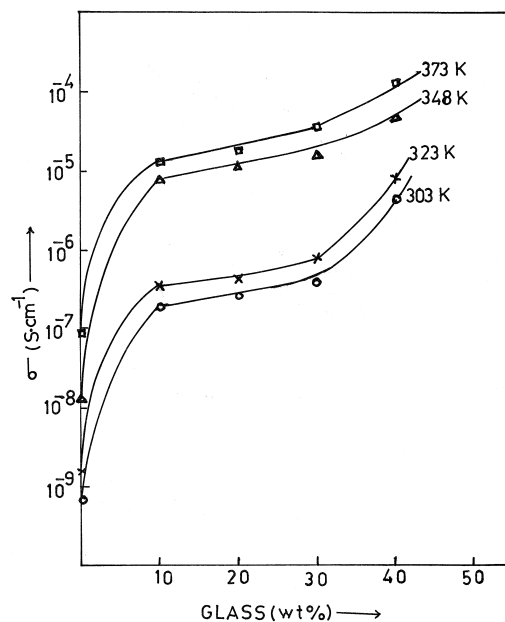


Fig. 2. Composition vs. conductivity plots of (PEO+glass) polymer electrolyte system at different temperatures.

electrolyte). Details of the fabrication of the electrochemical cell are given elsewhere [26]. The discharge characteristics of the cells were monitored under a constant load of 100 k Ω .

3. Results and discussion

The complexation of PEO with various salts has been studied using XRD and vibrational spectroscopic analysis [11,27–32]. The XRD patterns of pure PEO, PEO + glass (15Na₂O–15NaF–70B₂O₃) and glass (15Na₂O–15NaF–70B₂O₃) are given in Fig. 1. A comparison of the spectra of complexed PEO films with that of pure PEO and glass reveals the following differences.

(i) The diffraction peaks between $2\theta = 5^\circ$ and 15° have less intensity for complexed PEO than for pure PEO. This indicates that the addition of glass causes a decrease in the degree of crystallinity of the polymer.

Table 1

Conductivity data of PEO and (PEO + glass (15Na₂O–15NaF–70B₂O₃)) at different temperatures

Polymer electrolyte (wt.%)	Conductivity (S cm ⁻¹)			
	303 K	323 K	348 K	373 K
PEO	8.35×10^{-10}	1.91×10^{-9}	1.12×10^{-8}	9.94×10^{-8}
(PEO + glass) (90:10)	3.32×10^{-7}	5.28×10^{-7}	9.95×10^{-6}	1.99×10^{-5}
(PEO + glass) (80:20)	3.86×10^{-7}	5.62×10^{-7}	1.05×10^{-5}	2.10×10^{-5}
(PEO + glass) (70:30)	5.18×10^{-7}	8.92×10^{-7}	1.73×10^{-5}	5.89×10^{-5}
(PEO + glass) (60:40)	6.85×10^{-6}	9.43×10^{-6}	7.18×10^{-5}	1.46×10^{-4}

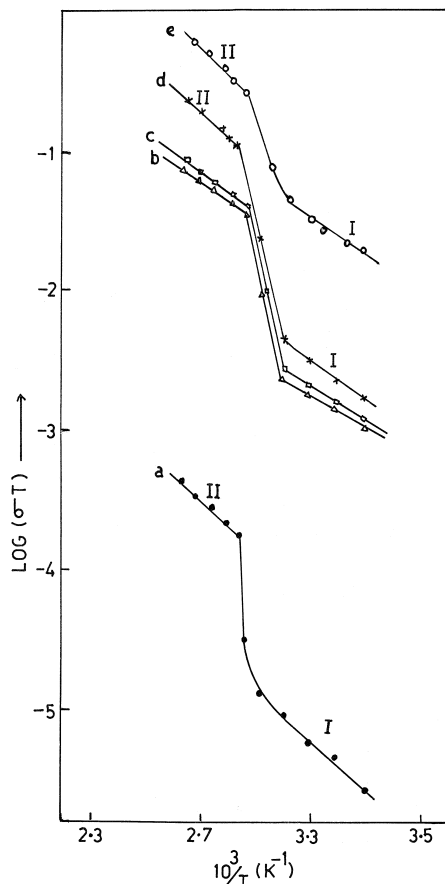


Fig. 3. Temperature dependent conductivity of: (a) Pure PEO; (b) (PEO + glass) (90:10); (c) (PEO + glass) (80:20); (d) (PEO + glass) (70:30); (e) (PEO + glass) (60:40).

(ii) Peaks corresponding to the polymer PEO are also present in the complexed PEO films. This shows the simultaneous presence of both crystalline complexed and uncomplexed PEO.

(iii) The peaks exhibit a decrease in intensity with broadening at higher concentrations of glass in the polymer. This indicates a decrease in the crystalline phase and a dominant presence of the amorphous phase.

Table 2

Activation energies (E_a) and pre-exponential factors $(\sigma T)_0$ of (PEO + glass) polymer electrolyte system

Polymer electrolyte (wt.%)	Region I		Region II	
	E_a (eV)	$(\sigma T)_0$ ($S\text{ cm}^{-1}\text{ K}$)	E_a (eV)	$(\sigma T)_0$ ($S\text{ cm}^{-1}\text{ K}$)
PEO	0.32	3.45×10^{-4}	0.35	9.7×10^{-2}
(PEO + glass) (90:10)	0.21	1.87×10^{-3}	0.28	1.95×10^{-1}
(PEO + glass) (80:20)	0.24	6.28×10^{-3}	0.29	2.86×10^{-1}
(PEO + glass) (70:30)	0.28	4.25×10^{-2}	0.34	4.12
(PEO + glass) (60:40)	0.29	8.42×10^{-1}	0.39	5.67×10^1

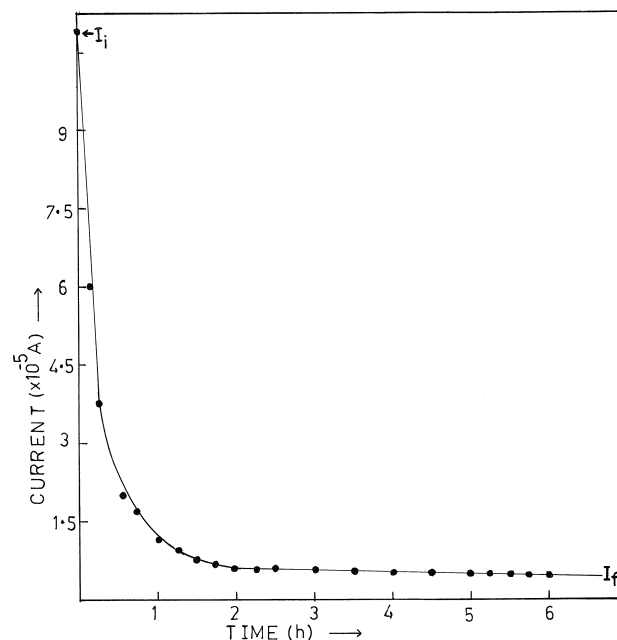


Fig. 4. Current vs. time plot of (PEO + glass) (60:40) polymer electrolyte system.

Thus, the XRD data for these films clearly confirm the formation of a complex between the glass and the PEO polymer.

The variation of d.c. conductivity, σ , as a function of the glass composition in PEO at various temperatures is given in Fig. 2 and Table 1. The following conclusions can be drawn.

The conductivity of pure PEO is $\sim 10^{-10}\text{ S cm}^{-1}$ at room temperature and its value increases sharply to $\sim 10^{-7}\text{ S cm}^{-1}$ on forming a complex with 10 wt.% glass. The increase in conductivity becomes slower on further addition of glass, i.e., the value is $\sim 10^{-6}\text{ S cm}^{-1}$ in 60:40 PEO:glass.

In general, it is believed that the conductivity increases as the degree of crystallinity decreases or, in other words, the flexibility of the polymeric back bone increases. The continuous increase in conductivity in the present study of the (PEO + glass) system with increasing glass concentration is attributed to the decrease in the degree of crystallinity as observed by XRD analysis.

The variation of conductivity as a function of temperature for pure PEO and for different compositions of PEO

Table 3

Transference numbers of (PEO + glass) polymer electrolyte system

Polymer electrolyte (wt.%)	Transference numbers	
	t_{ion}	t_{ele}
(PEO + glass) (90:10)	0.92	0.08
(PEO + glass) (80:20)	0.93	0.07
(PEO + glass) (70:30)	0.93	0.07
(PEO + glass) (60:40)	0.95	0.05

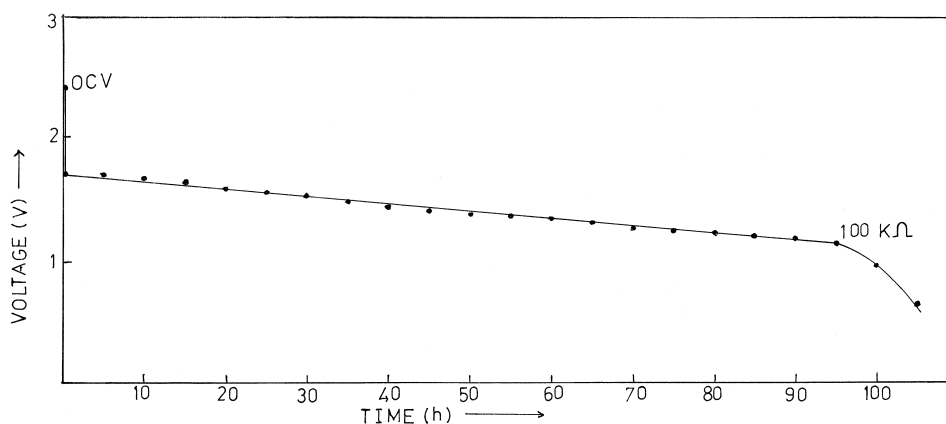


Fig. 5. Discharge characteristics of solid-state electrochemical cell in the configuration Na/(PEO + glass) (60:40)/(I₂ + C + electrolyte).

+ glass) polymer electrolyte over the temperature range 303 to 373 K is shown in Fig. 3. The following features are observed.

(i) The conductivity increases with temperature in pure PEO and also in all the compositions of the (PEO + glass) polymer electrolyte system.

(ii) The conductivity vs. temperature ($\sigma T - 10^3/T$) plots follow Arrhenius behaviour throughout, but with two regions with activation energies below (region I) and above (region II) the melting point (T_m) of the polymer. In region I the conductivity increases slowly with temperature up to 66°C; there is then a sudden increase in conductivity. In the region II (i.e., above T_m), the conductivity again increases with temperature. Similar behaviour has been observed in all compositions of the (PEO + glass) polymer electrolyte system.

Thus, at the melting point ($T_m = 66^\circ\text{C}$) of the polymer, there is a change from a semicrystalline to an amorphous phase. Because of this phase change, the conductivity displays a sudden increase. Below T_m (region I), the increase of conductivity with temperature is interpreted as a hopping mechanism between coordinating sites, local structural relaxations and segmental motions of the polymer. As the amorphous region progressively increases (region II), however, the polymer chain acquires faster

internal modes in which bond rotations produce segmental motion. This, in turn, favours the hopping inter-chain and intra-chain ion movements and, accordingly, the conductivity of the polymer electrolyte becomes high. The existence of two regions in the conductivity–temperature plots has been observed for a number of PEO based polymer electrolytes [11,29,31–33].

The linear variation of the $\sigma T - 10^3/T$ plots below and above T_m suggests an Arrhenius-type, thermally activated process. The conductivity can be expressed as:

$$(\sigma T) = (\sigma T)_0 \exp(-E_a/kT) \quad (1)$$

where: $(\sigma T)_0$ is a pre-exponential factor; E_a is the activation energy; k is the Boltzmann constant. The calculated activation energies (E_a) and pre-exponential factors $(\sigma T)_0$ for pure PEO and the (PEO + glass) polymer electrolyte system are listed in Table 2.

The transference numbers corresponding to ionic (t_{ion}) and electronic (t_{ele}) transport have been evaluated in (PEO + glass) electrolyte system using Wagner's polarization method. In this technique, the d.c. current is monitored as a function of time on application of fixed d.c. voltage (1.5 V) across a Na/(PEO + glass)/C cell. The plot for a (PEO + glass) of (60:40) composition is given in Fig. 4. The transference numbers (t_{ion} and t_{ele}) are calculated

Table 4
Cell parameters

Cell parameters	PEO + glass (90:10)	PEO + glass (80:20)	PEO + glass (70:30)	PEO + glass (60:40)
Effective area of the electrolyte, cm ²	1.34	1.34	1.34	1.34
Cell weight, g	0.595	0.521	0.565	0.545
Open-circuit voltage (OCV), V	2.12	2.12	2.32	2.45
Short-circuit current (SCC), μA	100	112	425	815
Discharge time for plateau region, h	50	51	85	98
Power density, mW kg ⁻¹	48.57	55.47	54.20	64.20
Energy density, mW h kg ⁻¹	2428.5	2828.97	4607	6291.6

Table 5
Comparison of present cell parameters with earlier reported data

Solid-state electrochemical cell configuration	Open-circuit voltage, OCV (V)	Short-circuit current, SCC (μA)	Discharge time for plateau region (h)	Reference
Ag/(PEO + AgNO ₃)/I ₂ + C + electrolyte	0.61	4.4	48	[17]
Na/(PEO + NaYF ₄)/I ₂ + C + electrolyte	2.45	560	96	[11]
K/(PEO + KYF ₄)/I ₂ + C + electrolyte	2.40	240	51	[11]
Na-Hg/(PEO + NaPF ₆)/V ₂ O ₅ + C + electrolyte	2.26	–	–	[10]
Na/(PEO + glass)/I ₂ + C + electrolyte	2.45	815	98	Present

from the polarization current vs. time plot using the equations:

$$t_{\text{ion}} = (I_1 - I_f)/I_1 \quad (2)$$

$$t_{\text{ele}} = I_f/I_1 \quad (3)$$

where I_1 is the initial current and I_f is the final residual current. The resulting data are given in Table 3. For all the compositions of the (PEO + glass) electrolyte system, the values of the ionic transference numbers t_{ion} are in the range 0.92 to 0.95. This suggests that the charge transport in these polymer electrolyte films is predominantly due to ions; only a negligible contribution comes from the electrons.

Using (PEO + glass) polymer electrolyte films, solid-state electrochemical cells have been fabricated with the configuration Na(anode)/(PEO + glass)/(I₂ + C + electrolyte) (cathode). Sodium metal was used as the negative-material, and a mix of iodine (I₂), graphite (C) and electrolyte in the ratio 5:5:1 as the positive.

The discharge characteristics of the cell Na/(PEO + glass) (60:40)/(I₂ + C + electrolyte) at ambient temperature for a constant load of 100 kΩ are presented in Fig. 5. The initial sharp decrease in voltage of these cells may be due to polarization and/or formation of a thin layer of sodium salt at the electrode/electrolyte interface. The open-circuit voltage (OCV) and short-circuit current (SCC) and other cell parameters for these cells are given in Table 4. Values for the parameters of a number cells reported earlier along with data for the present polymer electrolyte cells are given in Table 5.

It is clear that the parameters of cells with the (PEO + glass) electrolyte films are comparable with those reported earlier for various other cells. This suggests a possible application of these cells as solid-state batteries.

4. Conclusions

The conductivity of (PEO + (glass)(15Na₂O–15NaF–70B₂O₃)) electrolyte is about 10⁴ times larger than that of pure PEO. This increase in conductivity is attributed to an increase in the amorphous content of the polymer due to the addition of glass.

Data for ionic transport numbers in these polymeric electrolyte films indicate that the charge transport is predominantly due to ions.

The parameters of these cells are found to be comparable with those reported earlier for various other cells. This suggests a possible application of these cells as solid-state batteries.

Acknowledgements

The authors thank Professor K.S.N. Murthy, Head, Department of Physics, Osmania University, Hyderabad, for

his encouragement. One of the authors, MJR thanks CSIR, New Delhi for the award of a Fellowship.

References

- [1] M.B. Armand, *Ann. Rev. Mater. Sci.* 16 (1986) 245.
- [2] M.A. Ratner, D.F. Shriver, *Chem. Rev.* 88 (1988) 109.
- [3] J.R. Owen, *Superionic Solids and Solid Electrolytes—Recent Trends*, in: A.L. Lasker, S. Chandra (Eds.), Academic Press, New York (1989), p. 111.
- [4] J.R. MacCallum, C.A. Vincent (Eds.), *Polymer Electrolyte Reviews*, Elsevier, London (1987).
- [5] M.B. Armand, *Polymer Electrolyte Reviews*, in: J.R. MacCallum, C.A. Vincent (Eds.), Elsevier, London (1987), p. 1.
- [6] E.A. Reitman, M.L. Kaplan, R.J. Cava, *Solid State Ionics* 17 (1985) 67.
- [7] P.R. Sorensen, T. Jacobson, *Electrochim. Acta* 27 (1982) 1675.
- [8] D. Fauteux, C. Robitaille, *J. Electrochem. Soc.* 133 (1986) 307.
- [9] Y.L. Lee, B. Crist, *J. Appl. Phys.* 60 (1986) 2683.
- [10] S.A. Hashmi, A. Chandra, S. Chandra, *Solid State Ionics: Materials and Applications*, in: B.V.R. Chowdari et al. (Eds.), World Scientific, Singapore (1992), p. 567.
- [11] S. Sreepathi Rao, M. Jaipal Reddy, E. Laxmi Narsaiah, U.V. Subba Rao, *Mater. Sci. Eng. B* 33 (1995) 173.
- [12] D. Fauteux, M.D. Lupien, C.D. Robitaille, *J. Electrochem. Soc.* 134 (1987) 2761.
- [13] S.G. Greenbaum, Y.S. Pak, M.C. Wintersgill, J.J. Fontanella, J.W. Schultz, *J. Electrochem. Soc.* 135 (1988) 235.
- [14] S.G. Greenbaum, K.J. Ademic, Y.S. Pak, M.C. Wintersgill, J.J. Fontanella, *Solid State Ionics* 28–30 (1988) 1042.
- [15] T.M.A. Abrantes, L.J. Alcacer, C.A.C. Sequeira, *Solid State Ionics* 18/19 (1986) 315.
- [16] S. Chandra, S.A. Hashmi, M. Saleem, R.C. Agrawal, *Solid State Ionics* 66 (1993) .
- [17] S. Sreepathi Rao, K.V.S. Rao, Md. Shareefuddin, U.V. Subba Rao, S. Chandra, *Solid State Ionics* 67 (1994) 331.
- [18] R. Huq, G.C. Farrington, *J. Electrochem. Soc.* 135 (1988) 524.
- [19] R. Huq, G.C. Farrington, *Solid State Ionics* 28–30 (1988) 990.
- [20] A.G. Einest, W.S. Schlindwein, R.J. Latham, R.G. Linford, R. Pynenburg, *J. Electrochem. Soc.* 138 (1991) 159.
- [21] A. Patrik, M. Glasse, R. Latham, J.I. Yamiki, *Solid State Ionics* 40/41 (1990) 483.
- [22] J.E. Weston, B.C.H. Steele, *Solid State Ionics* 7 (1982) 75.
- [23] H. Yuankang, C. Zhusheng, Z. Zhiyi, *Materials for Solid State Ionics*, in: B.V.R. Chowdari, S. Radhakrishna (Eds.), World Scientific, Singapore (1986), p. 333.
- [24] Amita Chandra, P.C. Srivastva, S. Chandra, *Solid State Ionics, Materials and Applications*, in: B.V.R. Chowdari et al. (Eds.), World Scientific, Singapore, 1992, p. 397.
- [25] J.B. Wagner, C. Wagner, *J. Chem. Phys.* 26 (1957) 1597.
- [26] M. Jaipal Reddy, D. Srinivas Reddy, S. Sreepathi Rao, U.V. Subba Rao, *Materials Letters* 23 (1995) 129.
- [27] B.L. Papke, M.A. Ratner, D.F. Shriver, *J. Phys. Chem. Solids* 42 (1981) 493.
- [28] B.L. Papke, M.A. Ratner, D.F. Shriver, *J. Electrochem. Soc.* 129 (1982) 1434.
- [29] K.K. Maurya, N. Srivastava, S.A. Hashmi, S. Chandra, *J. Mater. Sci.* 27 (1992) 6357.
- [30] H. Yang, R. Huq, G.C. Farrington, *Solid State Ionics* 40/41 (1990) 663.
- [31] K.K. Maurya, S.A. Hashmi, S. Chandra, *J. Phys. Soc. Jpn.* 61 (1992) 1709.
- [32] S.A. Hashmi, A. Kumar, K.K. Maurya, S. Chandra, *J. Phys. D. Appl. Phys.* 23 (1990) 1307.
- [33] S.S. Sekhon, H. Kumar, *Bulletin of Electrochemistry* 12 (1996) 750.