

Short communication

Influence of B_2O_3 doping on conductivity of $LiTiO_2$ electrode material

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Abstract

Fast ionic conductors $X LiTiO_2 - Y B_2O_3$ with $X:Y = 90:10$ and $80:20$ are prepared by the solid-state reaction method and subjected to ac conductivity measurements with silver electrodes in the frequency range 42 Hz to 5 MHz. The ac conductivity values are 6.47×10^{-5} and $2.2 \times 10^{-7} \Omega^{-1} \text{cm}^{-1}$, respectively. The ion hopping rate and charge carrier concentration are calculated by fitting the conductance spectra to the power law equation, using Almond and West formalisms. The charge carrier concentration is in the order of 10^{25} and is independent of temperature, which supports the strong electrolyte model. The conductivity relaxation time is calculated from the peak frequency of the modulus spectra. The effect of B_2O_3 substitution is discussed.

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1. Introduction

Lithium batteries are promising candidates for numerous energy-related applications which vary from microbatteries for portable electronics to power sources for electric vehicles [1]. To optimize battery performance, such as cycling ability, chemical and physical stability, and long life, various electrolyte compositions and electrode materials have been tested. Transition metal oxides are found to be promising electrode materials for lithium batteries [2]. In particular, manganese oxide (Mn_2O) and titanium dioxide (TiO_2) are promising materials because of their capability for accommodating Li ions. These materials have some disadvantages, however, such as loss of initial capacity during discharge [3]. Min et al. [4] have reported that the addition of glass formers, e.g. B_2O_3 and P_2O_5 , to $LiMn_2O_4$ compounds leads to increases in conductivity and structural stability. From a scientific point of view, such materials are interesting because the mechanisms that govern the ionic transport are often not well understood. Better insights into this problem are therefore needed to elucidate the role of the glass former in the conduction mechanisms. In this regard, the negative-electrode material lithium titanate, $LiTiO_2$, has been prepared and

doped with the glass former B_2O_3 . Since electrochemical impedance spectroscopy have proved indispensable to the study of ion dynamics in ion-conducting materials, it is used in the work reported here to examine Li ion dynamics in the materials.

2. Experimental

The $LiTiO_2$ material was prepared by the solid-state reaction method. The raw materials Li_2CO_3 (>99% purity), TiO_2 (99% purity) were ground into a fine powder by means of a mortar and pestle. The resultant powder was melted in a porcelain crucible at 900 °C. The appropriate amount of B_2O_3 for the two molar ratios 90 $LiTiO_2$ -10 B_2O_3 and 80 $LiTiO_2$ -20 B_2O_3 was added to the melted sample, which was then cooled and ground. The resultant powder was melted once again in the porcelain crucible at 1000 °C, and then quenched in ice bath. The quenched samples were crushed into fine powders and sprayed in a die. A pressure of around 4000 kg cm^{-2} was applied to form pellets with a thickness of 0.1 cm and a diameter of 1 cm. The samples were annealed at 500 °C for 24 h in an open air atmosphere. Electrical measurements were performed on annealed samples by means of a computer controlled HIOKI model 3532 LCZ Meter (frequency range 42 Hz to 5 MHz) in the temperature range 30–150 °C with silver as an electrode.

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3. Results and discussion

3.1. Conductance spectra analysis

The conductivity of all the samples obeys the Arrhenius law, i.e. it varies linearly with temperature. The conductivity data are listed in Table 1. The ac conductivity of 90 LiTiO₂–10 B₂O₃ and 80 LiTiO₂–20 B₂O₃ is 6.47×10^{-5} and 2.2×10^{-7} , respectively. The conductivity spectra of ionic conductors have been found to exhibit universal power-law behaviour [5], i.e.

$$\sigma' = \sigma_{dc} \left[1 + \left(\frac{f}{f_p} \right)^\alpha \right] \quad (1)$$

where σ' is the real part of the complex conductivity, σ_{dc} the dc conductivity, f_p the cross-over frequency, f the measured frequency and α the exponent of the power law ($0 < \alpha > 1$) [6–8]. Almond and West [9] have suggested that ac conductivity data such as the cross-over frequency and the power law exponent reveal important information on the ion dynamics, mobility and the Coulombic interaction between mobile ions, respectively. Conductivity spectra for all the samples at various temperatures are presented in Fig. 1. At low frequencies, a plateau characterizes the dc conductivity, and is followed by an increase in conductivity according to Eq. (1). The transition regime from dc to ac conductivity shifts to higher frequencies with increasing temperature.

Ionic hopping rates (ω_p) have been calculated from the conductivity spectra for all the samples at different temperatures using the formula proposed by Almond and West [9]. The charge-carrier concentration (c') has been calculated from the Almond and West definition for the dc conductivity of the ion-conducting material [10] which is given by:

$$\sigma_{dc} = \left(\frac{Ne^2 a^2}{kT} \right) \gamma c(1-c)\omega_p \quad (2)$$

and

$$c(1-c)N = c' \quad (3)$$

where γ is the correlation factor which is 1/6 for isotropic materials [11], e the electronic charge, k the Boltzman constant, T the absolute temperature, a the hopping distance (taken as 3 Å), and N is equivalent lattice site per unit volume. The charge carrier concentration calculated from Eq. (3) is found to be constant over the temperature range

studied. This implies that all the lithium ions which are responsible for the conductivity are in a mobile state, a suggestion that supports the strong electrolyte theory. The lower conductivity observed for 80 LiTiO₂–20 B₂O₃ is due to the low mobile ion concentration ($\sim 10^{23}$) compared with that ($\sim 10^{25}$) observed for both LiTiO₂ and 90 LiTiO₂–10 B₂O₃.

According to the jump relaxation model [12], which takes account of the coulomb interaction between mobile ions, parameter α in Eq. (1) relates to ratio:

$$\alpha = \left(\frac{\text{backhop rate}}{\text{site relaxation rate}} \right) \quad (4)$$

The backhop is the backward motion of a hopping ion to its initial site, which is caused by the coulomb repulsive interaction between mobile ions. The site relaxation is the shift of a site potential minimum to the position of the hopping ion, which is caused by a rearrangement of neighbouring ions.

The conductivity spectra of all the samples were fitted with Eq. (1) and the parameter α was extracted. The decrease in α with B₂O₃ substitution has been observed and it may be due to the formation of free sites for Li ion migration, which in turn reduces the backhop rate and hence decreases α .

3.2. Modulus spectra analysis

Generally two formalisms, namely, the conductivity formalism and the electric modulus formalism, have been adopted to study the frequency and temperature dependence of the conductivity [13]. In the modulus formalism, an electric modulus M^* is defined in terms of the reciprocal of the complex relative permittivity ϵ^* , i.e.

$$M^* = \frac{1}{\epsilon^*} = M' + iM'' \quad (5)$$

The frequency dependence of M'' at various temperatures for all the samples is shown in Fig. 2. The broad nature of the peaks can be interpreted as being the consequence of distributions of relaxation time. The maximum of the modulus spectra M'' shifts towards higher frequencies with increase in temperature. The angular frequency ω_{max} which corresponds to M''_{max} gives the relaxation times, τ_c , from the condition $\omega_{max}\tau_c = 1$ [14]. The relaxation energy E_m is estimated [15,16] using the following equation:

$$\omega_{max} = \omega_0 \exp\left(\frac{-E_m}{kT}\right) \quad (6)$$

Table 1
Transport parameters of LiTiO₂–B₂O₃

Sample	ac Conductivity ($\Omega^{-1} \text{ cm}^{-1}$)	E (eV)		α	β	t (s)
		E_m	E_d			
LiTiO ₂	4.7×10^{-6}	0.24	0.22	0.63	0.56	5.2×10^{-7}
90 LiTiO ₂ –10 B ₂ O ₃	6.47×10^{-5}	0.26	0.23	0.58	0.54	3.2×10^{-7}
80 LiTiO ₂ –20 B ₂ O ₃	2.2×10^{-7}	0.31	0.29	0.46	0.63	8.4×10^{-7}

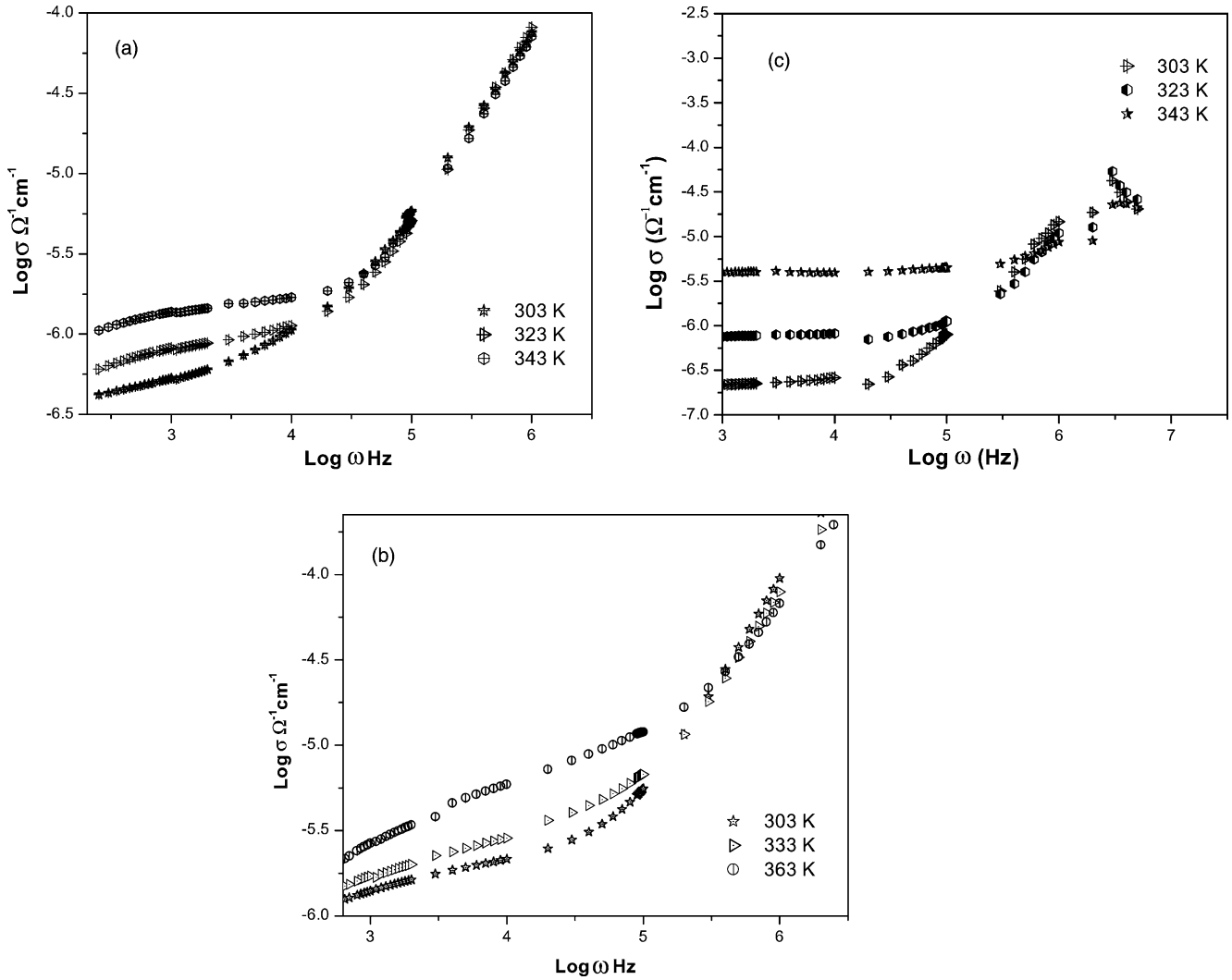


Fig. 1. Conductance spectra for (a) LiTiO_2 , (b) $90 \text{ LiTiO}_2\text{-}10 \text{ B}_2\text{O}_3$, (c) $80 \text{ LiTiO}_2\text{-}20 \text{ B}_2\text{O}_3$.

where ω_0 is angular frequency at infinite temperature and E_m the ionic relaxation energy. Values of the relaxation energy (E_m) and relaxation time (τ_c) for all the samples are given in Table 1. The values found for the present materials are typical of fast ionic conductors [17]. The value of E_m for the undoped sample is low compared with those of doped samples and this indicates that the structural disorder is due to B_2O_3 substitution.

The non-exponential conductivity relaxation can be described by a Kohlrausch Williams Watt (KWW) function $\phi(t)$, which represents the distribution of relaxation time in ion-conducting materials [18]. The electric modulus can be represented by:

$$M^* = M_\infty \left[1 - \int_0^\infty dt \exp(-i\omega t) \frac{d\phi}{dt} \right] \quad (7)$$

and

$$\phi = \phi_0 \exp \left[- \left(\frac{t}{\tau_0} \right)^\beta \right] \quad (8)$$

where τ_0 is the conductivity relaxation time and β the Kohlrausch exponent. The smaller the value of β , the greater is the deviation with respect to Debye-type relaxation. The β parameter is most often taken to be the result of correlated motions between ions. This means that the jump of a mobile ion in a material cannot be treated as an isolated event. Rather, it results in a time-dependent motion of other charge carriers in the surroundings. The value of the β parameter becomes smaller as the co-operation between charge carriers becomes more extended. For very small concentrations of charge carriers, the conductivity is essentially characterized by independent jumps, and the coupling between charge carriers is more extended when the concentration of mobile ions increases. In both glasses and crystalline ionic conductors, the coupling of charge carriers is reflected by a value of β close to 0.5 [19].

The β parameter corresponding to the studied samples was established for each composition as a function of temperature using modulus formalism. Using the modulus formalism, i.e. M'' spectrum, the corresponding full-width

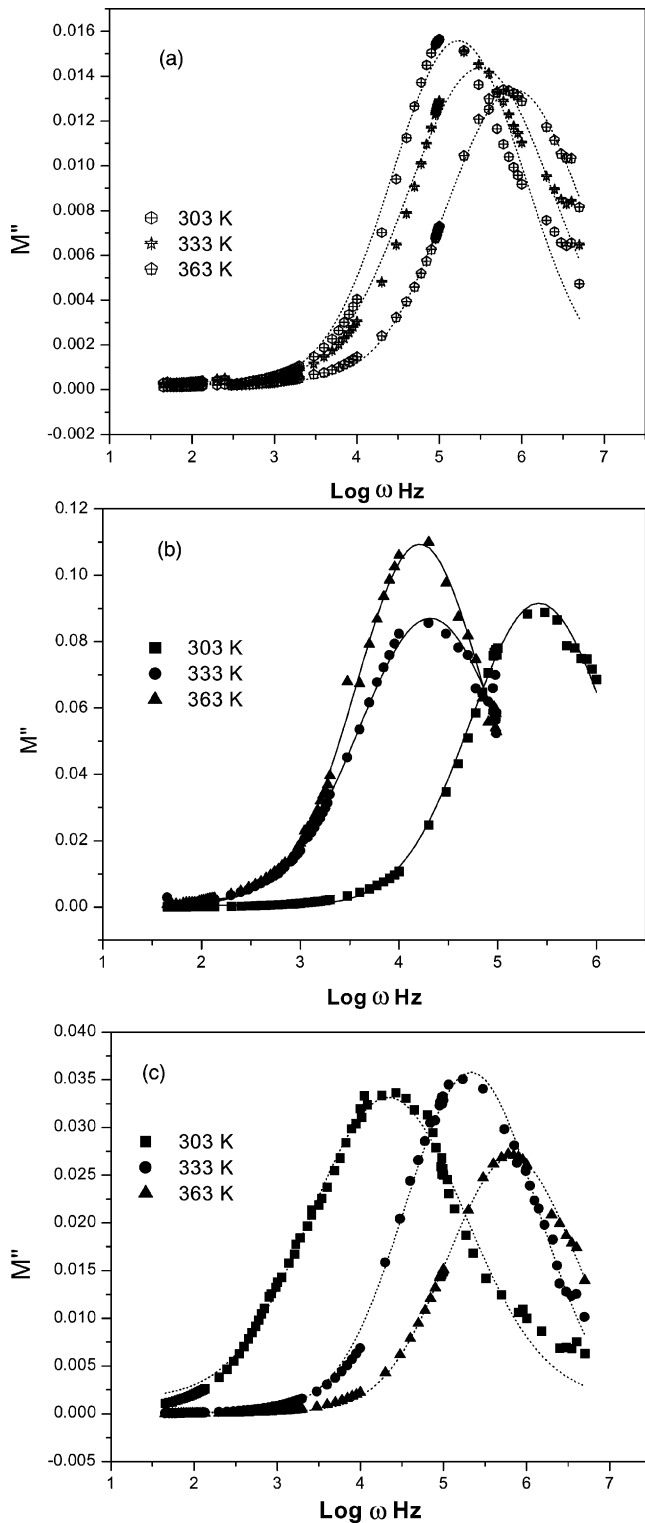


Fig. 2. Modulus spectra for samples (a) LiTiO_2 , (b) 90 LiTiO_2 –10 B_2O_3 , (c) 80 LiTiO_2 –20 B_2O_3 .

half height (FWHH) is wider than the breadth of the Debye peak (1.14 decades) and thus results in a value of $\beta = 1.14/\text{FWHH}$. The modulus peaks are fitted by using the software PEAKFIT and the FWHH values are extracted and

the corresponding β values calculated using the relation $\beta = 1.14/\text{FWHH}$. The β parameters for all the samples are listed in Table 1. The high value of the β parameter for the 80 LiTiO_2 –20 B_2O_3 sample indicates a decrease in charge-carrier concentration [20].

3.3. Dielectric spectra analysis

Analysis of the dielectric permittivity dependence on frequency and temperature is usually based on Debye Kramers–Kronig and Maxwell–Wagner relationships [21] of dielectric relaxation. The complex electric capacitance C^* in ion-conducting materials depends on the frequency, ω , according to the fractional power law [22], i.e.

$$C^* \propto (i\omega)^{n-1} \quad (9)$$

The exponent n varies with the conduction mechanism so that it can be used for monitoring the mode of conduction. A low dielectric loss conduction shows values of n which approach unity; it drops to zero for high dielectric loss conduction in high capacitance dielectrics. As for the impedance, the complex permittivity ϵ^* also is a combination of dielectric constants ϵ' and loss ϵ'' , which follow the same power law. The dielectric features ϵ' and ϵ'' show the same logarithmic dependence on ω with $n = 0.74$ at 343 K, which indicates high dielectric loss conduction [22], i.e.

$$\log \epsilon = \log A - (1 - n)\log \omega \quad (10)$$

Plots of ϵ'' versus $\log f$ for the 90% LiTiO_2 –10% B_2O_3 system at different temperatures are presented in Fig. 3. All the samples show the same trend and the observed variation in ϵ'' with frequency can be attributed to the formation of a space charge region at the electrode/electrolyte interface. The low frequency region is attributed to the

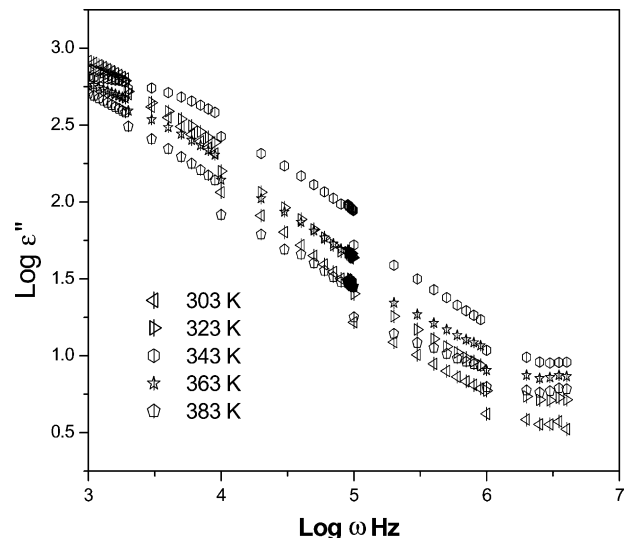


Fig. 3. $\text{Log } \epsilon''$ vs. $\text{log } \omega$ plots for 90 LiTiO_2 –10 B_2O_3 .

contribution of charge accumulation at the interface [23]. At high frequencies, due to high periodic reversal of the field at the interface, the contribution of charge carriers towards the dielectric constant decreases with increasing the frequency. Hence, ϵ'' decreases with increasing frequency. The values of ϵ'' reveal a linear fall in n with temperature (Fig. 3). This feature is useful for estimating the relaxation energy E_d by means of the following equation:

$$1 - n = \left(\frac{6k}{E_d} \right) T \quad (11)$$

The values of E_d for all the samples are given in Table 1. It is seen that the dielectric relaxation energy is equal to the relaxation energy (E_m) which is estimated by modulus relaxation, within experimental error. This suggests that the charge carriers that are responsible for both conductivity and relaxation processes are the same.

4. Conclusions

LiTiO₂–B₂O₃ material has been prepared by a solid-state reaction method at two molar ratios 90:10 and 80:20. The substitution of 10 mol% of B₂O₃ in the LiTiO₂ system increases the conductivity and this may be due to the formation of non-bridging oxygen which facilitates the conduction of lithium ions. By contrast, addition of 20 mol% of B₂O₃ gives a lower conductivity because of the low concentration of lithium ions.

References

- [1] M. Wakihara, O. Yamamoto (Eds.), *Lithium Ion Batteries*, VCH, Kodansha, Tokyo, 1998.
- [2] G. Pistoia (Ed.), *Lithium Batteries, New Materials, Development and Perspectives*, Elsevier, New York, 1994.
- [3] F. Lubin, A. Leceref, M. Broussely, J. Labat, *J. Power Sources* 34 (1991) 161.
- [4] J. Min, L. Chen, J. Wang, R. Xue, W. Cui, *Phys. Stat. Sol. (a)* 146 (1994) 771.
- [5] A.K. Jonscher, *Nature* 67 (1977) 673.
- [6] D.P. Almond, G.K. Duncan, A.R. West, *Solid State Ion.* 8 (1983) 159.
- [7] D.P. Almond, A.R. West, R.J. Grant, *Solid State Commun.* 44 (1982) 1277.
- [8] D.P. Almond, C.C. Hunter, A.R. West, *J. Mater. Sci.* 19 (1984) 159.
- [9] D.P. Almond, A.R. West, *Solid State Ion.* 9–10 (1983) 277.
- [10] D.P. Almond, A.R. West, *Solid State Ion.* 23 (1987) 27.
- [11] E.F. Haireidinor, N.F. Uvarov, H.K. Patel, S.W. Martin, *Phys. Rev. B* 50 (1994) 13259.
- [12] K. Funke, *Solid State Ion.* 94 (1997) 27.
- [13] B. Rolling, *Solid State Ion.* 105 (1998) 185.
- [14] P.B. Macedo, C.T. Moynihan, R. Bose, *Phys. Chem. Glasses* 13 (1972) 171.
- [15] M.B. Sayed, *J. Phys. Chem. Solids* 53 (1992) 1041.
- [16] M.B. Sayed, *Zeolites* 16 (1996) 157.
- [17] A. Pawlowski, Pawlacyk, B. Hilczer, *Solid State Ion.* 44 (1990) 17.
- [18] G. Williams, D.C. Watts, *Trans. Faraday Soc.* 66 (1970) 80.
- [19] C.T. Moynihan, L.B. Boesch, N.L. Laberge, *Phys. Chem. Glasses* 14 (1973) 122.
- [20] H.K. Patel, S.W. Martin, *Phys. Rev. B* 45 (1992) 10292.
- [21] V.V. Daniel in: *Dielectric Relaxation*, Academic Press, London, 1967, pp. 73 and 203.
- [22] A.K. Jonscher, J.M. Reau, *J. Mater. Sci.* 13 (1987) 568.
- [23] F.S. Howell, R.A. Bose, P.B. Macedo, C.T. Moynihan, *J. Phys. Chem.* 78 (1974) 639.