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Modified transport properties of $LiNbO_3$ dispersed Li_2CO_3 composite system for electrochemical CO_2 sensor

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ABSTRACT

In the present investigation, $LiNbO_3$ dispersed Li_2CO_3 composite of varying volume fraction is prepared. Its validity of placement in ionic conductor is verified by determining ionic transference number by Wagner's dc polarization technique and bulk electrical conductivity is estimated with complex impedance spectroscopy. Two different conduction mechanisms are revealed by the complex impedance plots at low and high frequencies. Significant enhancement in the ionic conductivity has resulted due to enhancement in vacancies at the grain boundary interface facilitated by the localized polarization of carbonate grains due to the presence of ferroelectric phase. The effect on electrode kinetics is studied by characterizing an electrochemical CO_2 gas sensor with this composite as sensing electrode which showed significant reduction in response time and recovery time (<10 sec). The use of such composite systems will benefit the development of fast electrochemical devices. Copyright © 2014 VBRI press.

Keywords: Composite solid electrolyte; impedance spectroscopy; transport number, electrochemical gas sensor.

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Introduction

Electrochemical CO_2 gas sensors are advantageous for their high selectivity, direct electrical readout and scope for miniaturization. The major drawbacks associated with them are slow response/recovery time, lack of long term stability and high operating temperature. It uses a solid electrolyte sandwiched between test electrode (gaseous) and reference electrode (gaseous/solid). Being a major component, the solid electrolyte should possess high ionic conductivity and negligible electronic one at relatively low temperatures (<400^{o}C). Also sensing electrode should equilibrate fast with the test gas resulting into better sensing kinetics.

Different mechanism for enhancement of conductivity in solid electrolytes such as isovalent or aliovalent doping, use of binary electrolyte or dispersion of insulating phase (composite) has been investigated for different ionic conductors **[1, 2]**. A maximum increase of two orders of magnitude in ionic conductivity of solid ionic conductor has been obtained when dispersed with sub-micron size inert phase particles. The first composite of this type was LiI dispersed with Al_2O_3 **[3]**. Since then a large number of composite solid electrolytes have been investigated by dispersing different inert materials e.g. α,β,γ-Al_2O_3, SiO_2, α-Fe_2O_3, MgO, Fly-ash, ZrO_2 into pure solid ionic conductors viz. LiBr, LiCl, CuCl, AgI, HgI_2, CaF_2, AgCl, Li_2SO_4, Ag_2SO_4, Na_2CO_3, some glasses etc. From the study of complex of impedance spectroscopy, it has been reported that the enhanced defect concentration at the grain boundary interface of solid electrolyte is resulting into the significant rise in ionic conductivity **[4]**. In earlier investigation on dispersion of ferroelectrics in Li_2SO_4 and glass, a remarkable enhancement in ionic conductivity has been observed as the consequence of formation of highly diffused space charge layer across the interface of the host matrix and dispersoid **[5]**. Saito et al have studied the effect of particle size and dielectric constant of $PbZrTiO_3$ (PZT) and $BaTiO_3$ in $Na_4Zr_2Si_3O_{12}$ (NZS), and observed conductivity enhancement **[6, 7]**. The composite solid electrolytes are used for device fabrication for their added advantage of high ionic conductivity besides the usual properties such as isotropy in electrical and mechanical properties, ease of preparation in desired shape and size **[8, 9]**.

In the present investigation $LiNbO_3$ dispersed Li_2CO_3 composite of varying volume fractions are prepared and its ac and dc conductivities are investigated with complex impedance spectroscopy and Wagner's dc polarization techniques respectively. Significant enhancement in ionic conductivity at relatively low temperatures has been observed with negligible increment in electronic conductivity below 500^{o}C. The impedance spectroscopy data revealed enhancement in Li^+ ion vacancy concentration at the grain boundary interface. The effect on electrode kinetics is studied by characterizing an electrochemical CO_2 gas sensor with highest conducting composition as electrolyte and sensing electrode **[10].** The present electrolyte system enables the fast kinetics at sensing electrode and ion migration in the bulk of the electrolyte resulting in to improved CO_2 sensor characteristics.

Experimental

Preparation of lithium niobate

Lithium niobate is prepared using conventional solid state sintering method. The initial ingredients Li_2CO_3 and Nb_2O_5 of purity 99.99 (Sigma-Aldrich, USA) were dried over night at 200^{o}C and then weighed into appropriate mole ratio. After thoroughly mixing under acetone for an hour, the mixture was calcined at 800^{o}C for 6 hours and then crushed and pelletized (3 tonnes/cm^2). The pellets roughly of dimensions 12 mm diameter and 2-3 mm thickness were sintered in platinum crucible at 1100^{o}C for 24 hrs. The process of crushing, pelletizing and sintering the sample is repeated for three times. Formation of desired compound is confirmed by powder XRD data analysis.

Similar procedure is adopted for the preparation of open reference electrode material, $Li_2Ti_6O_{13}$, by taking initial ingredients Li_2CO_3 and TiO_2 (Aldrich, USA).

Preparation of composite electrolyte

Well dried initial ingredients, $LiNbO_3$ and Li_2CO_3, were crushed and sieved (particle size <40 micron) for uniform distribution of dispersoid into host. Five compositions of different weight fractions of $LiNbO_3$ (10 to 50%) in Li_2CO_3 were mixed thoroughly under acetone and then heated in quartz ampoules up to the melting point of lithium carbonate so as to form a good interface between the grains of two systems. The ingots were crushed and used for further investigations.

Ac conductivity measurement

Ac electrical conductivity measurements were performed on well sintered pellets of all the compositions of composite solid electrolyte. Ohmic contacts were formed by sputtering Au film on both the surfaces of the sample pellets (RF- DC Sputtering Unit, Hind Hi-Vac, India). Complex impedance data was recorded as a parametric function of frequency (5 Hz to 13 MHz) using LF impedance analyser (HP 4192A, USA) for different temperatures ranging from 325 to 447^{o}C.

DC conductivity measurement

Electronic conductivity was estimated from transport number measurement by using Wagner's dc polarization technique keeping both the electrodes of blocking type **[11]**. A dc voltage of 500 mV was applied to every sample pellet using voltage source of Keithley-617 Electrometer (USA) and the corresponding current was recorded as a parametric function of time at different fixed temperatures (200-550^{o}C).

Sensor characterization

Plate type CO_2 gas sensor with highest conducting composition as electrolyte and sensing electrode was fabricated with following cell configuration:

Air, Pt / $Li_2Ti_6O_{13}$ + TiO_2 / $5Li_2CO_3$: $5LiNbO_3$ / Pt, CO_2, Air (A)

The emf produced by the sensor cell for different partial pressures of CO_2 gas embedded in air was recorded with Keithley-617 Electrometer (USA). The sensors were tested for response/recovery time and stability.

Results and discussion

The complex impedance plots of various compositions belonging to Li_2CO_3 + $LiNbO_3$ composites at different temperatures are obtained as shown in **Fig. 1**.

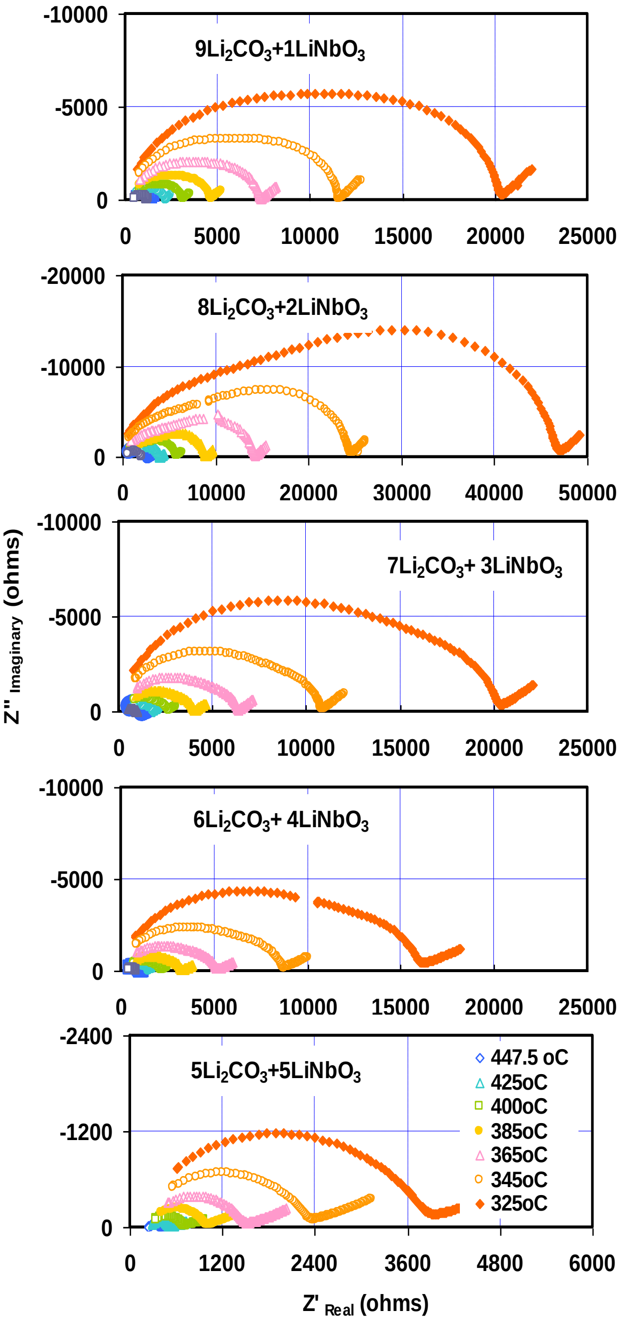

Fig. 1. Impedance plots for Li_2CO_3: $LiNbO_3$ compositions at various temperatures showing different mechanisms of conduction.

These figures clearly reveal the presence of two overlapping depressed semicircular arcs for all the five compositions in the frequency range (5 Hz to 13 MHz) suggesting two different conduction regimes within the composite material. The surface interaction at Li_2CO_3/ $LiNbO_3$-heterojunction is analogous to that of a moderately ion conductor/insulator interface giving rise to a space charge layer **[12]**. Probable surface reactions are:

$$Li_{Li} + V_A = Li_A^{\cdot} + V_{Li}' \qquad (I)$$

$$Li_A + V_i = Li_i^{\cdot} + V_A' \qquad (II)$$

Where, A and Li indicate the interface and regular lithium carbonate lattice sites, respectively. The former (attractive interaction) reaction has a consequence that the Li ions would be sucked out of Li_2CO_3 volume and the vacancy concentration is enhanced near the interface. Whereas, the latter one (repulsive interaction) drives Li^+ into Li_2CO_3 interstitial sites, thereby enhancing the Li^+ ion concentration.

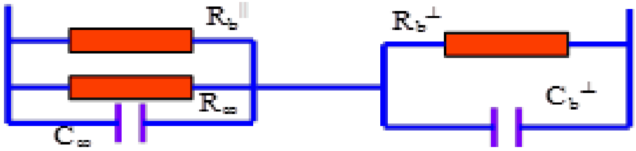

Fig. 2. Equivalent circuit which describes the impedance of heterogeneous composite and refers to the || and ⊥ effects of the interfacial contacts.

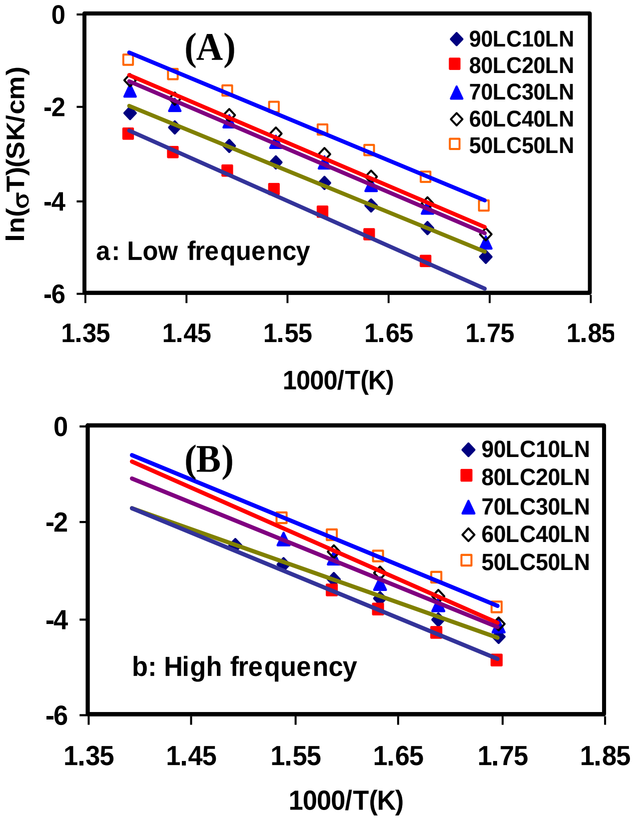

Fig. 3. Arrhenius plots for **(A)** low and **(B)** high frequency regions of Li_2CO_3:$LiNbO_3$ composite. (LC: Li_2CO_3 and LN: $LiNbO_3$).

In order to unfold the type of interaction taking place for a particular composite system, the two semicircular arcs at low and high frequencies in the complex impedance plots, are foreseen to be due to three separate conduction mechanisms. The high frequency relaxation is supposed to be due to conduction parallel to interfaces ($R_b^{\parallel}$) and bulk of the electrolyte grain (R_∞); whereas, low frequency conduction is due ion migration perpendicular to the interface ($R_b^{\perp}$) **[13].** With this the equivalent circuit for the composite system is proposed as shown in **Fig. 2**. Two different values of bulk resistance in low and high frequency region were measured by manually fitting semicircle on different complex impedance plots. The **Fig. 3 a & b** depicts Arrhenius plots for low and high frequency regions separately.

The mean value of activation energy obtained for ion migration through the bulk and parallel to the interface in above system is found to be 0.32 eV. It is found comparable to the activation enthalpy 0.25-0.35 eV observed in case of divalent doped system $xBaCO_3:(100-x)Li_2CO_3$, x:0-10. A comparison of activation energies for the composite as well as doped system is shown in **Fig. 4**.

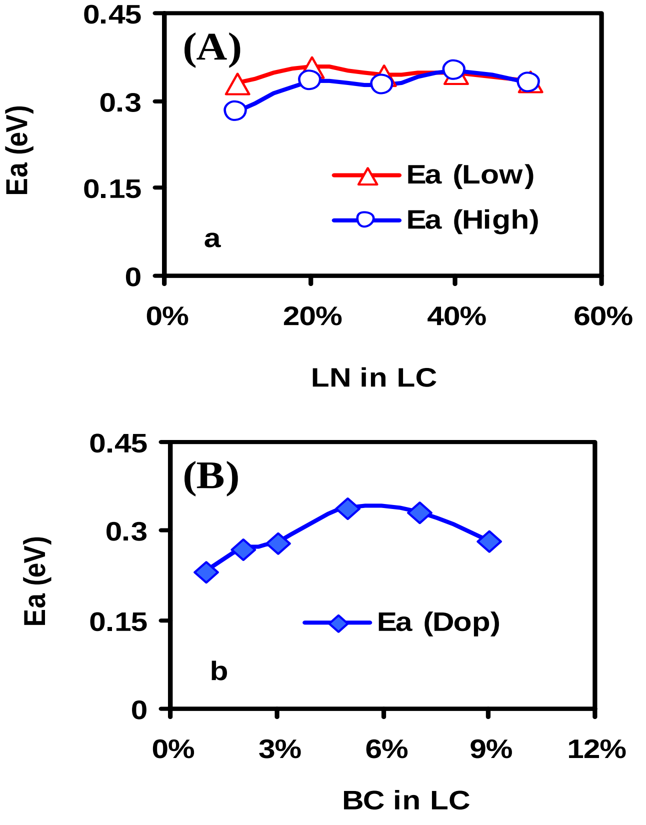

Fig. 4. Comparison of activation energies of ion migration in $Li_2CO_3:LiNbO_3$ composite (a) with $BaCO_3$ doped Li_2CO_3 system (b) (LN: $LiNbO_3$, LC: Li_2CO_3, BC: $BaCO_3$).

Conduction in divalent cation doped systems is through the vacancies incorporated by aliovalent cation substitution. This indicates that the surface interaction of Li_2CO_3 with $LiNbO_3$ grains is of the type (I) given above. This interaction predominates at lower temperatures, a well-known effect for heterogeneous composites.

The values of capacitances, C_∞ and $C_b^{\perp}$ are calculated from the peak frequency values obtained for the two semicircles in impedance plots. The high frequency capacitance C_∞ for the present composite was found varying from 22-50pF whereas the low frequency capacitance $C_b^{\perp}$ varies from 55-85pF for the maximum conducting composition, $50Li_2CO_3:50LiNbO_3$ with variation in temperature.

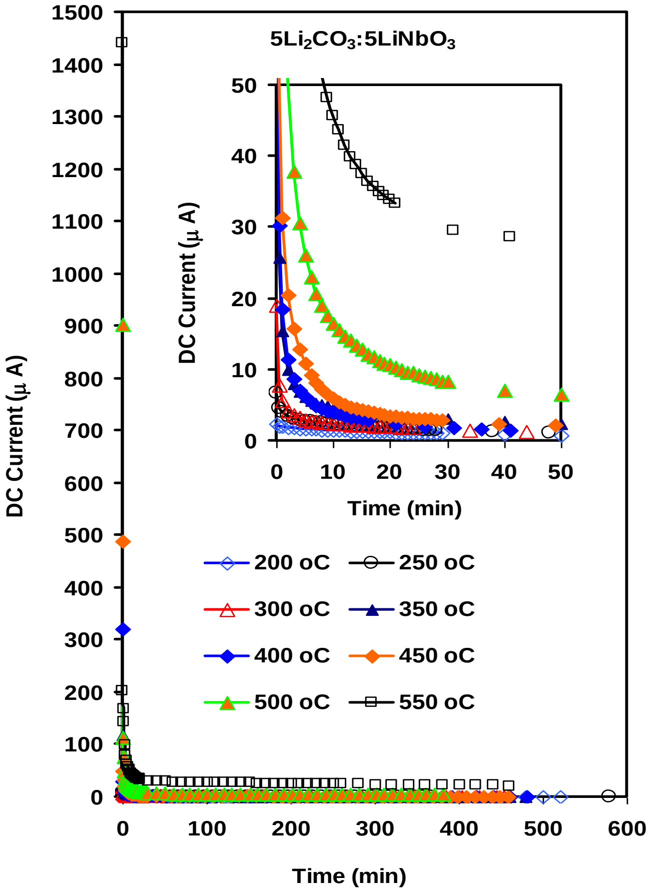

Fig. 5. Wagner's DC polarization curves indicating zero and infinite time currents with an inset showing magnified view.

Wagner's dc polarization technique was used for determination of ionic and electronic transport number of the electrolyte. A dc electric field of small magnitude was applied across the sample having both blocking electrodes. Complete polarization of Li^+ ions at very fast rate was observed in the temperature range 200 to 550 °C as shown in **Fig. 5**. The zero time conductivity drops by a magnitude of more than three decades as soon as dc potential is switched on, indicating availability of large number of low enthalpy Li^+ ions in the sample which gets mobilized with application of electric field. The electronic transference number (t_e) of the composite obtained from infinite time conductivity was found to be very low ~10^{-7}. t_e was found decreasing with increase in temperature and attains almost a steady value in the temperature range 300-500°C, and increases slightly above 500°C.

From the sensor response shown in **Fig. 6**, it is seen that the alumina dispersed composite electrolyte system is slow compared to that of the sensors made using ferroelectric dispersed composite electrolytes as sensing surface / electrode, evidently suggesting the fact that, the ferroelectric dispersed composites have better kinetics at the sensing surface to adsorb the O_2 and CO_2 gas molecule, setting fast equilibrium than other. The response and recovery times of different sensors are listed in **Table 1**. A close scrutiny reveals that the response time of the alumina and barium titanate dispersed electrolytes exhibit relatively slower kinetics (35-55 sec).

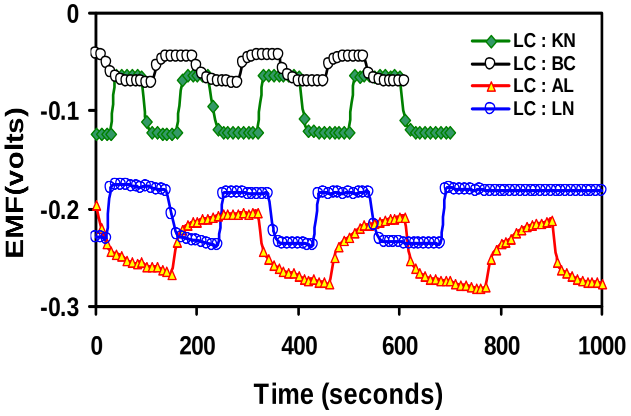

Fig. 6: The response of sensors with different sensing electrodes on toggling P_{CO2} between 260- 2600 *ppm* at 400^{o}C. (LC: Li_2CO_3, KN: $KNbO_3$, AL: Al_2O_3, LN: $LiNbO_3$).

Table 1. Response and recovery times for the sensors with different sensing electrode/electrolytes at 400^{o}C (LC: Li_2CO_3, AL:Al_2O_3, LN: $LiNbO_3$, KN: $KNbO_3$, BT: $BaTiO_3$).

Electrolyte/ test electrode	Reference Electrode	Response time (sec)	Recovery time (sec)
Li_2CO_3	$Li_2Ti_6O_{13}$	<120	>200
LC:LN	$Li_2Ti_6O_{13}$	<10	>20
LC:KN	$Li_2Ti_6O_{13}$	<20	>20
LC:BT	$Li_2Ti_6O_{13}$	<40	>50
LC:AL	$Li_2Ti_6O_{13}$	<60	>150

Whereas, the sensors with the lithium niobate and the potassium niobate dispersed composite show faster response time (5-15 sec). From which it is concluded that the electric field of ferroelectric phase helps in gas adsorption and charge transfer reaction at the test and reference electrodes. Faster electrode kinetics in the $LiNbO_3$ dispersed cell than $KNbO_3$ could only be due to small mass and ionic radius of the Li^+ ion which results into relatively greater ionic mobility through the electrolyte and faster reactions at test as well as reference electrode.

Quick dc polarization and fast electrode kinetics whereas no significant difference in capacitances C_∞ and $C_b^{\perp}$, indicates major role played by the spontaneous electric field of ferroelectric phase in improving characteristics of composite solid electrolyte.

Conclusion

Spontaneous polarization of ferroelectric $LiNbO_3$ phase plucks Li^+ ions at the interface from Li_2CO_3 grain results into generation of Li^+ vacancies. Which, intern enhances the ionic conductivity of the composite. The high polarizability and small size of Li^+ ion are responsible for the high mobility and fast electrode kinetics of gas adsorption as well as desertion. Hence the ferroelectric dispersed composites are potential candidates for electrolyte and/or sensing electrode of the EC gas sensors.

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