I J R B A T, Issue (X) Vol (III) Sept 2022: 55-60
A Double-Blind Peer Reviewed & Refereed Journal
OPEN ACCESS
e-ISSN 2347 – 517X
Original Article

Reg. No. : MH-NGP/00001
INTERNATIONAL JOURNAL OF RESEARCHES IN BIOSCIENCES, AGRICULTURE AND TECHNOLOGY
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ELECTRICAL TRANSPORT WINDOW FOR Li2ZrO3 AS AN OPEN REFERENCE MATERIAL FOR SOLID STATE ELECTROCHEMICAL GAS SENSORS

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Communicated :21.05.2022
Revision : 20.06.2022 & 01.07.2022
Accepted :25.07.2022
Published: 30.09.2022

ABSTRACT: The electrical characterisation of Alkali Oxide of Transition Metal, Li2ZrO3 is presented in this study. In-situ impedance spectroscopy measurements were carried out in different partial pressures of oxygen embedded in dry Argon in temperature range 300-500oC. Impedance analysis was done by formulating equivalent RC circuits. Wagner's approach was employed to the material in pallet form for DC measurements, where blocking electrodes were kept under comparable atmospheric conditions.

A mixed conducting window best suited for the sensor's open reference electrode functioning at roughly 300oC has been identified using electronic and ionic conductivities and transport numbers.

Key words: - Electrochemical gas sensor, open reference electrode, transport number, impedance spectroscopy.

INTRODUCTION :

Electrochemical gas sensor is an electrode concentration cell. The three basic components of an electrochemical cell being an electrolyte, sensing electrode and reference electrode, it is necessary to check their individual contribution in electrochemical cell performance and their validity for being used in the cell (Schettler H.et al, 1993; Ambekar P. et al, 2004). The electrolyte being predominantly ionic conductor and the other two components being mixed conductors (ionic-electronic) at cell working temperature, all the three materials must show apt performance for efficient functioning of the sensor. The performance of these materials is governed by the chemical kinetics and types of defects at the electrode and interfaces (Ibrahim S.G. et al, 2015) The notable feature of the point defects is that they are in thermal equilibrium within the solid and may be treated as chemical species in terms of equilibrium constant and mass action law. To determine the effect of nonmetal activity of the surrounding atmosphere on the concentration of different types of defects, Kroger and Vink considered the various combinations of defects in a compound MX and applying the mass action law, made detailed calculation to find out the variation of the concentration of individual defects as a function of nonmetal activity of the surroundings under an isothermal condition (Kroger F. A. and Vink H. J., 1956). Also, the concentration of the defects' changes in a different manner in the different ranges of nonmetal activity with various combinations of defects. Since the conductivity is directly proportional to the concentration of the defect, the variation of the electrical conductivity with the nonmetal activity indicates the behavior of the predominant defect and has often been used to predict the defect structure of ionic solids, by comparing the experimental results with the theoretical calculated slopes of conductivity Vs nonmetal activity plots. Thus, effect of surrounding gases on the electrical conductivity of solid electrolyte must be evaluated in order to understand the sensor functioning completely. Apart from these, the gas kinetics at the sensing surface in presence of the catalyst must be understood before checking the performance of the sensor cell at workable temperature and gas concentration (Ambekar P. and Randhawa J. 2021). In the electrochemical sensor, all three components are of great importance viz. reference electrode: where the chemical potential is kept constant: the sensing electrode: where the chemical potential changes with partial pressure of gas under test and the electrolyte: which is an purely ionic bridge between the two electrodes.

In the present study, one of the major components, the reference electrode material, in this case Lithium Zirconate, Li_2ZrO_3, is studied for its conductivity measurements (Burghate P. D., et al 2015) which was carried out using both ac complex impedance technique by keeping the samples under different atmospheric conditions and DC measurements which are carried out using Wagner's DC polarization method under similar atmospheric conditions. Lithium zirconate is a known cathode material for electrochemical battery application having large solid solubility for Li+-ions (Nair B. N. et al 2004). A three-phase mixture of Li_2ZrO_3 +ZrO2 + electrolyte fixes the chemical activity of Li+-ion according to Gibb's Phase Rule (Faghri A. and Zhang Y., 2006). Fixed activity of conducting ion gives a stable potential at reference electrode with respect to which changing potential at the test electrode is measured

MATERIALS AND METHODS:

Materials Preparation: The sensor's reference electrode material lithium zirconate (Li_2ZrO_3) has been procured by Aldrich Sigma with a purity of 99.9% for the study with a CAS No. 12031-83-3 with a particle size of 80 mesh. The procured powder is heated at around 110oC for about 6 hours and then used for making pellets of 9 mm diameter and 1-3 mm thick. So obtained pellets were sintered at the temperature of 600°C for 24 hours under natural atmospheric conditions. The pellets were subjected to electrode formation using platinum sputtering under argon atmosphere for 20 minutes. The film thickness was maintained so as to get proper electrical contact and triple point area using gradient sputtering technique (Ambekar P. et al 2014).

AC Conductivity Measurement: The pellets of Li_2ZrO_3 as obtained above were used for impedance analysis using HP4192A Impedance Analyzer with frequency range from 5Hz to 13MHz. Gas atmosphere was maintained by passing constant gas compositions of different partial pressures of Oxygen in embedded Argon. Partial pressure of O_2 gas is changed by mixing it with inert gas Argon. The atmospheric conductivity measurements were done at three different temperatures viz., 300, 400 and 500oC.

DC Conductivity Measurement: The samples were then subjected to DC conductivity measurements i.e. transport number determination using Wagner's dc polarization technique, in open atmospheres at elevated temperatures from 200-500oC. The schematic of the measurement set up is shown in Figure-1 (Ambekar P. et al 2022).

Sensor Characterisation: This reference material so tested was used in an electrochemical CO_2 gas sensor. An optimized electrolyte with maximum conducting composition $7Li_2CO_3:3CaCO_3$ of was selected for above sensor study. The schematic of sensor cell with cell configuration - A is shown in Figure 2.

Ar, CO_2, O_2, Pt/ZrO_2+ Li_2ZrO_3/ $7Li_2CO_3:3CaCO_3$ / Pt, CO_2, O_2, Ar ---- (A)

The test electrode was also prepared using gradient sputtering technique mentioned earlier so as to nullify the errors due to diffusion during sensor characterization.

RESULT & DISCUSSION:

The Arrhenius plots shown in Figure-3 depicts the effect of O_2 gas concentration on the ac electrical conductivity of Li_2ZrO_3 in the temperature range 200-600 ^oC. Excluding the predominant effect of O_2 partial pressures at low and high temperature ends, conductivity of lithium zirconate is least affected by variation in pO_2 in the temperature range 300-500oC. The activation energy for conduction is found to be 0.245eV as calculated from the linear portion of the graph by fitting a straight-line having equation as shown in figure-3. This magnitude of activation energy confirms the presence of ionic conduction phenomenon in the reference electrode.

The contribution of ionic and electronic type of charge carriers to the electrical conductivity is determined from the zero time and infinite time conductivities of the material when subjected to a small amount of dc polarizing voltage. Figure 4 shows the polarization readings for the sample at different temperatures ranging from 200-500oC under open atmosphere conditions. With increase in temperature the zero-time conductivity was found increasing by an order of magnitude, whereas infinite time conductivity which is due to electronic type of charge carriers was found remaining almost unaffected Figure 5(B). This suggest the increase in ionic conduction with increase in temperature, as it is seen in the increase in ionic transport number value Figure 5(A).

The performance of sensor cell with configuration A stated above is shown in Figure 6. The graph shows sensor emf measured at 400^oC for CO_2 partial pressure variation from 261ppm to 1.8%. The value of theoretical cell emf was calculated from the data of Gibbs free energy of formation of Li_2ZrO_3 and ZrO_2 at 400 ^oC (Barin I., 1993). Even though a significant change in the magnitude of emf is seen, the sensitivity of the sensor 29mV/atm i.e. emf produced for a one decade change of test gas partial pressure is found to comparable with the theoretical value 23 mV/atm

CONCLUSION:

A three-phase mixture of Lithium Zirconate with ZrO_2 makes a steady reference electrode for an electrochemical gas sensor at elevated temperature, producing nearly theoretical sensitivity. The ac electrical conductivity measurement suggests the temperature range of 300-500^oC for reference electrode to produce fixed activity under O_2 gas variation.

ACKNOWLEDGEMENTS:

The authors are thankful to the Department of Physics, Nagpur University for providing experimental support.

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Figure-1: The schematic of the set-up for DC measurement

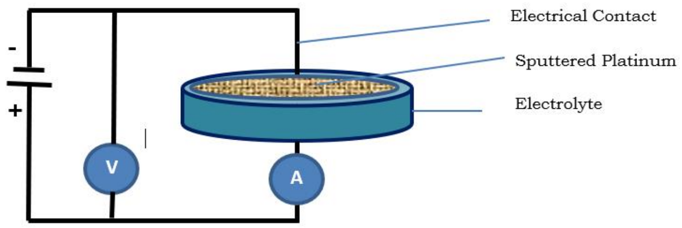

Figure-2: The schematic of an electrochemical gas sensor with open connection

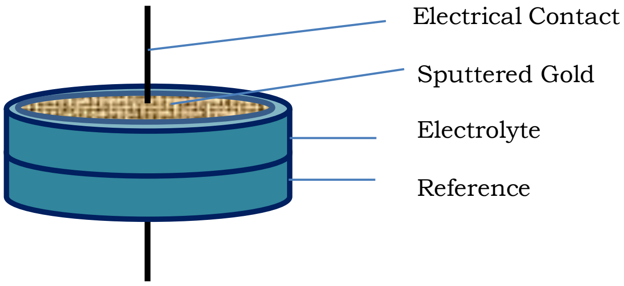

Figure-3: Arrhenius plots for Li2ZrO3 under different atmospheric conditions depicting oxygen stability window

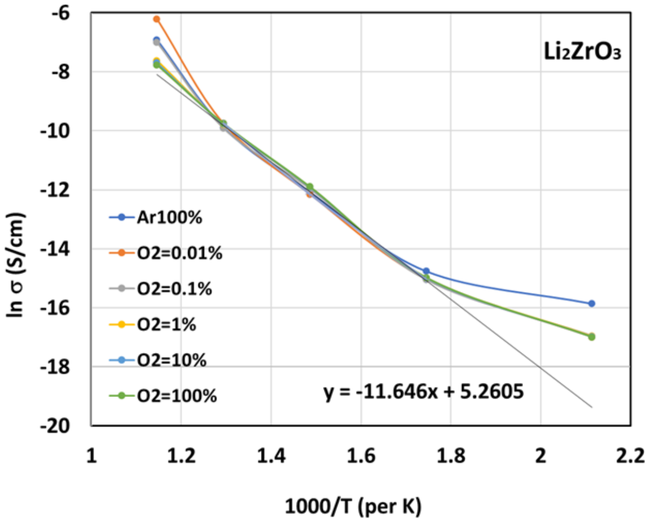

Figure-4: Transport number measurement shows the zero time and infinite time current readings for the sample at different temperatures ranging from 200-500°C

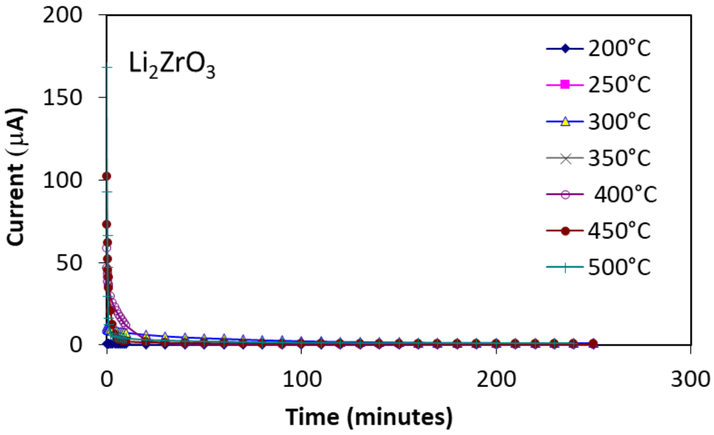

Figure-5: Ionic and Electronic transport number of the material with temperature is depicted in Fig. 5A & the zero and infinite time conductivities are depicted in Fig. 5B.

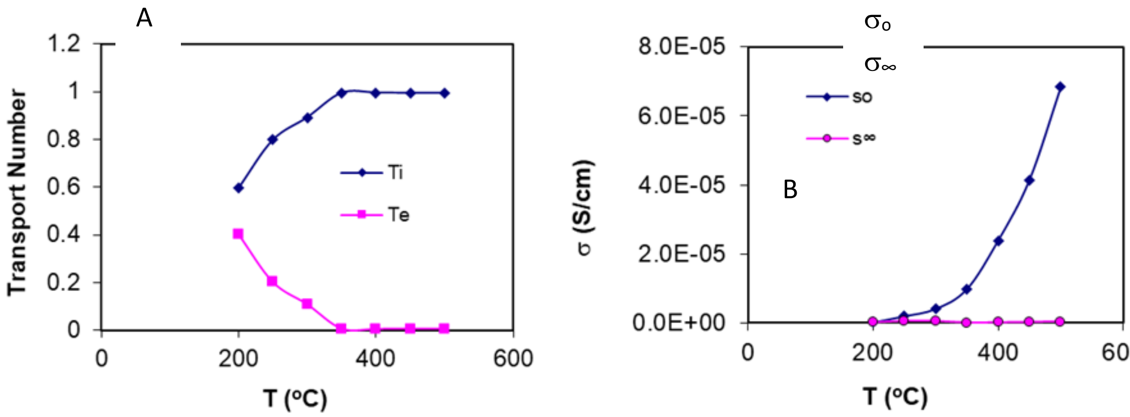

Figure-6: Comparison of experimental and theoretical behaviour of the sensor cell is depicted wherein due to loading effect cell emf with different partial pressures of CO2 embedded in air is seen deviated.