New Na⁺-glass -Na₂CO₃ composites for solid state electrochemical CO₂ gas sensor

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Ionic conductivity of the Na⁺-glass-Na₂CO₃ composites prepared by liquid phase sintering technique is investigated using complex impedance analysis. The conductivity maximum is obtained for 50wt% glass added to Na₂CO₃. An enhancement in conductivity is discussed in the light of space charge layer at glass-crystal interface (hetero-junction). Whereas, the maximum is understood to be due to optimum dispersion of glass, i.e., percolation threshold. The galvanic sensor utilising optimised composition along with open reference electrode exhibit good reversibility. The response time is found to be 1 minute. Sensor shows long term stability and negligible cross interference to SO₂ and moisture.

1 Introduction
Recently, there has been a strong incentive to engineer the materials which are thermodynamically stable and exhibit appreciably high ionic conductivity due to their usefulness in electrochemical gas sensors. The polycrystalline ion conductors rather than their single crystal counterparts and glasses have been preferred in such applications due to the following advantages: (i) ease of fabrication in required shape and size, (ii) isotropy in physical and mechanical properties (iii) thermodynamic stability. However, the greatest drawback associated with them is the presence of in-built micropores which hinders the mobility of ions. In addition to this, during the sensor operation at high temperatures, cooling and heating cycles, these materials develop micro-cracks leading to permeation of the gas towards the reference. On the other hand, in general, high ionic conducting glasses possess low glass transition temperature (T_g) which restricts their use in the sensors operating at moderately high and very high temperatures. Additionally, there is a major problem in achieving good electrode(solid)-electrolyte(glass) interface contact. Interestingly, when the glass dispersed crystalline samples are sintered just above the glass transition temperature (T_g), (liquid phase sintering) there is an increase in conductivity as well as sinterability.

In recent past, development of CO₂ gas sensor has gained much of attention due to their potential industrial applications. CO₂ is very difficult to detect by conventional gas sensors for the reason of high stability at ambient temperature. Most of the sensors reported earlier have been required to be operated at high temperature (973 K).

In 1986, Maier et al.², for the first time have demonstrated CO₂ gas detection utilising open reference. Since then many types of devices have been investigated using metal oxides, Zeolites and polymers with carbonate solution. Recently, the sensors based on Na⁺ conductors, β-Alumina and NASICON coated with Na₂CO₃ auxiliary electrode have been reported to respond well to change in concentration. However, the response time has been seen to be several minutes at 773 to 973K.

The selection of apt carbonate based material, as either solid electrolyte or auxiliary electrode, became crucial from sensitivity, response time and long term stability view points. A detailed literature survey, however, reveals that so far very less attention has been paid towards the development of carbonate based solid electrolytes. All above factors prompted us to synthesise a polycrystalline-glass composite solid electrolyte system from CO₂ gas sensor point of view.

2 Experimental Details

The 40Na₂O·60B₂O₃ (NB)-glass was prepared by melting together appropriate mole fraction of Na₂CO₃ and B₂O₃ (99.99% purity, E Merck, Germany) followed by quenching it in an aluminium mould kept at room temperature³. The Na₂CO₃ (99.99% purity, E Merck, Germany) and the prepared glass, used as a dispersoid,
were crushed separately and sieved (400 mesh) to get in the form of fine powders. The Na₂CO₃ with 10 to 90 wt% of NB-glass was mixed thoroughly under acetone. Later, each mixture was pressed uniaxially to get a pellet of the dimensions approximately 1-2 mm in thickness and 9 mm in diameter. The pellets were finally sintered at 550°C for an hour (liquid phase sintering). The sintering temperature was selected slightly above the glass transition temperature (Tg). Thus, prepared samples were characterised by X-ray powder diffraction (Philips PW 1700) using CuKα radiation and scanning electron microscope (Cambridge Mark-III stereoscan electron microscope).

For electrical conductivity measurement, ohmic contact was ensured by applying silver paint onto both the parallel surfaces of the pellet followed by baking at 473 K for two hours. Before measurements, the samples while spring loaded, were heated in an electric furnace at 623 K for two hours so as to homogenize the charge carriers in them. The real and imaginary parts of the complex impedance were measured as a function of frequency from 10 Hz to 13 MHz at various temperatures in the range from 623 to 423 K during the cooling cycle using computer controlled HP 4192A LF impedance analyser. The ionic transport number, in the temperature range from 373 to 573 K, was determined by Wagner's dc polarisation technique using Keithley 617 programmable electrometer.

A few galvanic cells were constructed using optimised solid electrolyte and open reference electrode as discussed earlier. The sensor was characterised at 670 K. The test gas of pre-decided partial pressures (CO₂ in a 21% O₂ and remaining Ar gas) was obtained using electronic mass flow meters-cum controllers (Teledyne Hestings, USA). The response time and reversibility of sensor are tested by toggling the concentration of CO₂ in O₂ and Ar between 1% to 500 ppm, and simultaneously recording the cell emf as a parametric function of time. The long term stability of the sensor at a fixed CO₂ partial pressure along with the cross sensitivity with other gases was investigated.

4 Results and Discussion

A detailed X-ray powder diffraction and scanning electron microscopy studies suggest the dispersion of unreacted glass in the Na₂CO₃ matrix.

The transference number measurement showed a negligible contribution of the electronic component (σₑ) to the total electrical conductivity (σT = σ⁺ + σₑ) in the temperature range from 373 to 573 K.

The bulk conductivity of each samples is obtained by following a complex impedance analysis as discussed elsewhere. The plots of log(σT) versus 10²T, for Na⁺-glass-Na₂CO₃ composite system (Fig. 1), obey the Arrhenius law:

\[ \sigma T = \sigma T₀ \exp\left(-\frac{E_a}{kT}\right) \]

... (1)

where, \(E_a = E_f + E_m\), \(E_f\) and \(E_m\) being the energies of defect formation and migration respectively. A close look at Fig. 2 reveals that the conductivity initially increases with the increase in glass concentration and attains a maximum value for 50 wt%, and decreases thereafter.

The system under consideration is a heterogeneous, and so, there exists more or less sudden structural changes. Heterogeneity involves distinct interfaces between phases of different chemical composition. Now, redistribution of the ionic and electronic constituents
take place causing formation of a diffused space charge layers across the interface. The total conductivity of such heterogeneous system is due to contributions form: (i) the LB-glass, (ii) the crystalline Na$_2$CO$_3$, (iii) homo-junction (Na$_2$CO$_3$- Na$_2$CO$_3$ interface) and (iv) hetero-junction (Na$_2$CO$_3$-glass interface).

The dispersion of glass by LPS technique not only fills the voids present in Na$_2$CO$_3$ matrix but also glues the grains together. Thus, as the concentration of glass into Na$_2$CO$_3$ matrix increases, the total conductivity enhances due to: (i) decreased voids, (ii) positive contribution from high conducting glassy phase and (iii) formation of highly conducting pathways across the crystal-glass interface. The decrease in conductivity after attaining maximum for 50 wt% glass is due to the percolation threshold concentration i.e, onset of disruption of surface percolating paths. At this composition, according to Bunde et al.\textsuperscript{7}, the conductivity of this sample is governed by ion percolating paths across the sample\textsuperscript{7}.

The variation of sensor emf as a function of time after toggling the CO$_2$ partial pressure from 1% to 500 ppm (at a fixed 21% O$_2$ concentration and argon as carrier gas) is shown in Fig. 3. As seen, the emf of sensor initially increases rapidly and attains a saturation value. A close look of the Fig. 3 also reveals a perfect reversible behaviour of the sensor. Even after a few thermal cycling (heating and cooling), sensor show a similar trend. The time required to attain 90% of saturation value is defined as the response time. The response time for the present sensor is found to be around 60 seconds.

The variation of sensor emf with time at a fixed CO$_2$ partial pressure is shown in Fig. 4. As seen there is no change in the emf value with time indicating a good long term stability. The cross sensitivity to SO$_2$, H$_2$ and moisture was determined by introducing these gases along with the known partial pressure of CO$_2$ and recording the emf with time. The cross sensitivity of present sensor to other gases e.g., SO$_2$, H$_2$ and moisture is found to be negligible.

4 Conclusion

The dispersion of Na$_2$O:B$_2$O$_3$ glass enhances the ionic conductivity of pure Na$_2$CO$_3$ by about an order of magnitude, at temperature 523 K. The study would provide a new route for the development of the composite solid electrolytes for gas sensor application.

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**References**