Research Article

Development of Glass Dispersed Electrolyte and Electrode for Solid State SO$_2$ Gas Sensor

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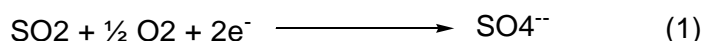Department of Physics, AmolakchandMahavidyalya, Yavatmal(Maharashtra)India.

Abstract: Electrochemical SO$_2$ gas sensor fabricated using Ag$^+$-glass dispersed Ag$_2$SO$_4$as an electrolyte. A sensor was prepared by depositing a thin layer of ferroelectric dispersed composite as an auxiliary phase. Modified the working electrode improves the sensor response due to presence of large number triple point (gas, Pt, electrolyte interface). The sensor was found responding to various test gas concentrations, showing Nernstian behavior (two-electron reaction) in limited range of gas partial pressure.

Keywords: Glass dispersed solid electrolyte, auxiliary electrode, gas sensor.

INTRODUCTION

SO$_2$ gas sensors has been currently in demand due to serious concern over acid rain (environmental pollution) and public health considerations resulting from tremendous growth of industrialization. Concurrently, there have been continuous efforts to obtain sensors with improved performance. In fact, the performance of any solid state electrochemical gas sensors has always been rated on its response time, thermodynamic stability, operating temperature, gas sensing ability and sensitivity. All these parameters are by and large governed by two basic components, solid electrolyte and reference electrode, of sensors. Thus, in recent past they have become the focus of interest. The chief objects of the present investigation to improve the sensitivity, stability and fast response time of a sensor.

Electrochemical sensors for detecting SO$_2$/SO$_3$ gas are prepared using sulphate based solid electrolytes, since the gas equilibrates with SO$_4{}^{--}$ ion:

$$SO2 + \tfrac{1}{2} O2 + 2e^- \longrightarrow SO4^{--} \qquad (1)$$

As the most sulphate are hygroscopic and have poor sinter ability, moisture cross sensitivity and development of micro cracks are their disadvantages. Hence conductingglasses are preferred in such application due to certain advantages; especially ease of fabrication in requiring shape and size, isotropy in

physical and mechanical properties, good response time and thermodynamic stability. Additionally, there is a major problem in achieving a good electrode (solid)-electrolyte (glass) interface contact. Alternatively, the glass dispersed electrolytes have been reported less porous as well as highly conducting[1, 2.]The use of metal/metal sulphate (Ag + Ag_2SO_4) as a solid reference electrode overcomes the tedious process of maintaining stable reference gas concentration. For the Ag-O-S system, Ag and Ag_2SO_4 coexist as an equilibrium phase, giving reversible reaction at the reference electrode and fixing the chemical activity of Ag^+- ion. This also results into better long term stability of the cell[3]. In the present study, the composition belonging to Ag^+ glass ($25Ag_2O:65B_2O_3:10SiO_2$) dispersed Ag_2SO_4as an electrolyte and a thin layer of Al_2O_3 fused with Ag_2SO_4 as an auxiliary electrode are synthesized following LPS (liquid phase sintering) technique and also modified the working electrode. A few electrochemical SO_2 gas sensors are fabricated

EXPERIMENTAL DETAILS

The composition $25Ag_2O:65B_2O_3:10SiO_2$ glass with high Tg was prepared by melting (at 1000^0C) together appropriate molar fractions of the initial ingredients; Ag_2NO_3, H_3BO_3 and SiO_2 (Aldrich, USA with purity greater than 99.5%) followed by quenching it in an aluminiummould kept at room temperature. The details preparation and characterizations of glass system are discussed elsewhere[4]. The Ag_2SO_4 (99.99% purity) and Ag glass were crushed separately and sieved to get fine power of average size < 40 micron followed by preparation of composite solid electrolyte[5].Composition, with 10- Wt% of Ag glass dispersed in Ag_2SO_4 was employed as an electrolyte and a thin layer of Al_2O_3fused with Ag_2SO_4 at 600^0 C as an auxiliary electrode (prepared by LPS technique).Homogeneous mixture of Ag (powder) + electrolyte was used as the reference electrode. It was hermetically sealed from test gas.

A couple of electrochemical SO_2 gas sensors with the following configurations were fabricated.

Pt, Ar, O_2, SO_2, Rf sputtered Pt. film /Ag- glass+$Ag_2 SO_4$ (electrolyte)/Ag+ electrolyte/Pt   **Cell-A**
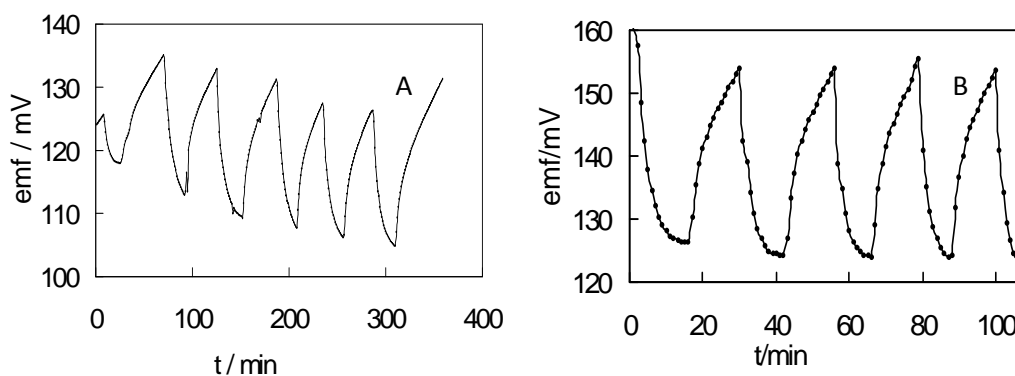
Pt, Ar, O_2, SO_2, Rf sputtered Pt. film / Ag_2SO_4-Al_2O_3/ Ag -glass+$Ag_2 SO_4$ (electrolyte)/Ag+ electrolyte/Pt **Cell-B**

Were constructed employing the cold press technique, i.e. palletizing reference and electrolyte separately and then stacking together[5].

The cell was maintained at 500^0C in a specially designed quartz tube probe assembly with the help of Eurotherm 810 PID temperature controller. The OCV of the cell was measured using computer controlled Solatron 1287 electrochemical interface. The blend of SO_2,O_2 and Ar gases with predetermined concentrations ranging from 200 ppm to 6% of SO_2 at fixed 21% O_2 was   obtained by using electronic mass flow controllers/ meters (Teledyne Hastings, USA). In order to determine the response time of sensor, SO_2 gas concentration was toggled between 1300ppm to 2600 ppm and subsequent OCV was measured. Test gas with different SO_2 concentrations was passed for fixed duration and the stabilized OCV was recorded.
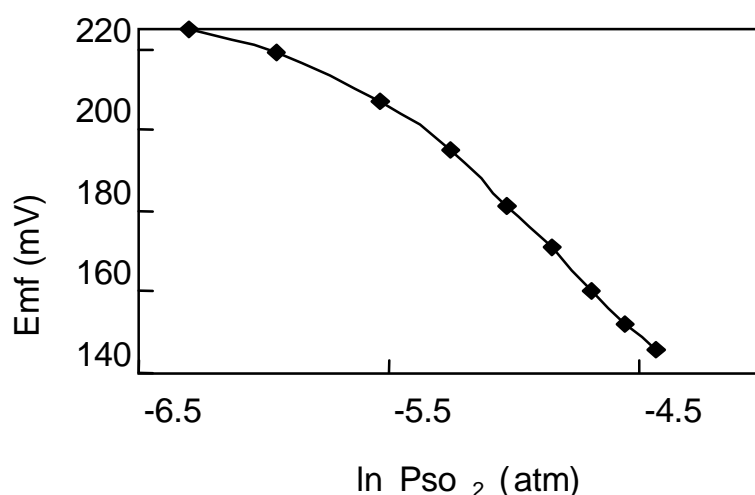
RESULT AND DISCUSSION

Fig.1. A and B depicted the variation of emf with time after switching the SO_2 gas partial pressure in the test gas for cell A and cell B, respectively. Evidently, perfectly reversible cell emf is obtained for both the cells A and B. Furthermore, a considerable improvement in the response time is also observed by the use of composite electrolyte as an auxiliary phase (cell-B) compared to without silver sulphate based auxiliary electrode (cell-A). The marked reduction in the sensor response time is attributed to considerably enhanced reaction rate due to the Al_2O_3 dispersion in Ag_2SO_4. This clearly indicates that, besides enhanced defect concentration at the grain-boundary interface on the surface according to space charge theory [6], the oxy-ion activity of the disperse solid plays active role in the reaction kinetics. The inclusion of inert phase necessarily increases the number of reaction triple points (SO_2+O_2+Pt) at Ag_2SO_4 grains by modifying the surface topography.
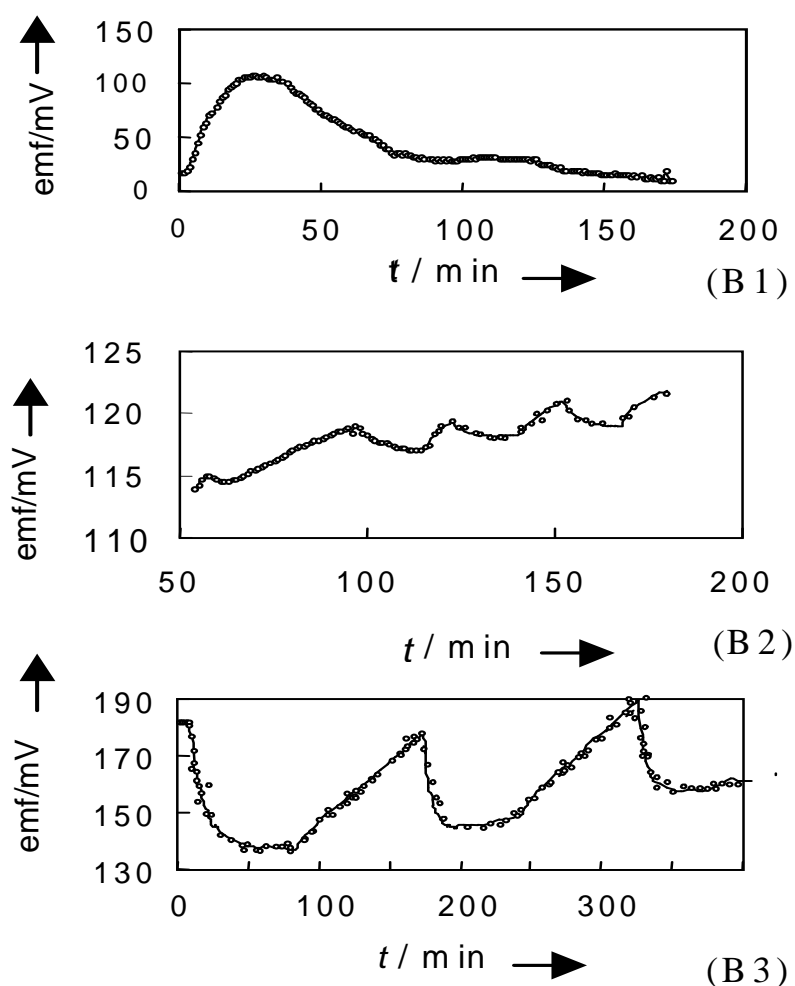
Fig. 1: Response of the cells with configurations A and B for two different
SO$_2$/SO$_3$ partial pressure at 500°C.

The variations of emf as a parametric function of SO$_2$ gas concentration in depicted in F**ig.2.**Response time of electrochemical sensor is governed by the reaction kinetics at the test electrode. The equilibrium electrode reaction includes adsorption of SO$_3$ and O$_2$ on the platinum surface and their diffusion towards the three phase line with e$^-$ transfer reaction giving O$^-$ which on reaction with SO$_3$ gives SO$_4^-$ and formation of Ag$_2$SO$_4$ after transport of Ag$^+$ to the surface[7]. Furthermore, it is reported that ac measurements show different rate limiting steps of the electrode reaction, at low and high temperatures. In the high temperature region (T>550°C) charge transfer is the rate limiting step, while in the lower temperature region (T<490°C) the surface diffusion of oxygen atom is rate determining. A similar study has been conducted in the SO$_2$ sensor by using a known oxy-ion conductor YSZ as a microelectrode on the K$_2$SO$_4$ surface in SO$_3$ atmosphere[8].
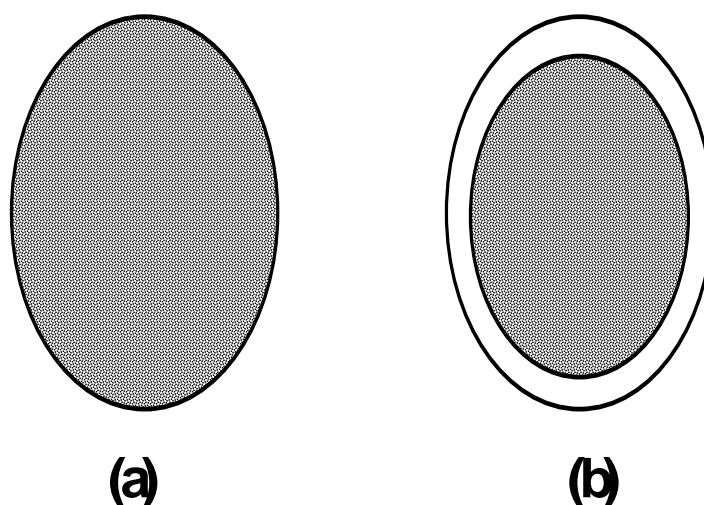

Fig 2: Response of the cell–B for different SO$_2$partialpressure at 500^{0}C

The optimization of working electrode is very crucial thus, porous film of various thickness, obtained on the cell-B by changing sputtering time, and subsequently characterized. **Fig.3** clearly indicates that the cell-(B1) as working electrode obtained by sputtering for 10 m, does not respond at all to the change in gas concentration. On the other hand, the response time of the cell (B3), sputtered for 20m is very large. These results indicate that the porosity of the pt-film should be optimized to obtain fast response time. The pt-film obtained by 10m sputtering time is discontinuous at many places leading to erroneous sensor response. Whereas, for longer sputtering time more than 18m, the sensor responds very fast (1-2m) for the pt-film that is obtained by sputtering for 15mporosity of the film reduces considerably, thereby impeding the permeation of test gas to and from the reaction triple points (gas + pt + electrolyte). Thus, sensor responds sluggishly. A close look at the **Fig.3.**reveals a drift in the value of saturated emf for cell B2 suggesting lack of chemical equilibrium. In order to overcome this, the porous pt-film (15m sputtering time) was obtained on partial surface of sensing side as indicated in F**ig.4.**
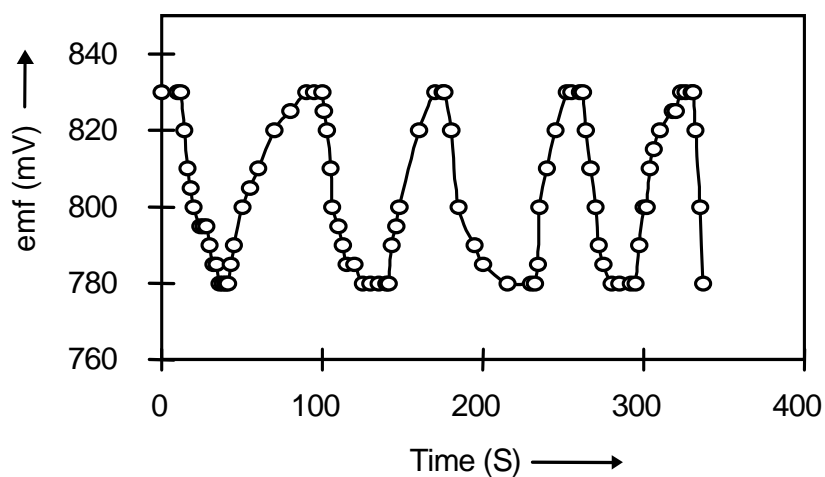

Fig.3:Variation of emf with time on switching SO$_2$ partial pressure in 21% O$_2$ and remaining Ar for sensors with sputtering time (B1) 10 (B2) 15, and (B3) 20 m to optimize Pt working electrode.

Fig. 4: Pt-porous film at sensing side (a) covered entire surface (b) covered partially.

The response of the modified sensor is shown in F**ig. 5**.Evidently; the emf of the sensor initially increases rapidly and attains a saturation value. The time required to attain 90% of saturation value, which we define as the response time, is found to be 45 seconds. A close look at the **Fig.5**.alsoreveals that the sensor attains the same saturation value (emf) after each change in gas concentration showing perfect reversibility. The reproducibility of the above results was confirmed by repeating the experiments on a new identical sensor.

Fig. 5: Variation of sensor emf with time after changing test gas concentration for modified sensing side.

CONCLUSION

Electrochemical SO_2 gas sensor with glass dispersed Ag_2SO_4 as an electrolyte and inert practical dispersed Ag_2SO_4 was employed as an auxiliary electrode and also modified working electrode gives large number of triple points (gas^+ Pt^+ electrolyte interface) to improve the sensor performance and also reduces the response time.

ACKNOWLEDGEMENTS

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