SO_x solid state gas sensors: A review

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Abstract. The performance of any solid state electrochemical gas sensor is always rated on its response time, thermodynamic stability, operating temperature, gas sensing ability, sensitivity and gas concentration range which is sensed. Here, we have reviewed the factors contributing towards a gradual development of electrochemical solid state SO_x sensor in terms of a continuous tailoring of its two basic components, i.e. solid electrolyte and reference electrode with high ionic and mixed (ionic + electronic) conductivities, respectively.

Keywords. Solid electrolytes; sensor; electrodes; anodic reaction; pollution.

1. Introduction

Atmosphere, which makes up the largest fraction of the biosphere, is a dynamic system that continuously absorbs a wide range of solids, liquids and gases from both natural and man made sources. Clean dry air contains 78.09% nitrogen by volume and 20.94% oxygen. The remaining 0.97% is composed of gaseous mixture of carbon dioxide, carbon monoxide, helium, argon, krypton, nitrous oxide, as well as very small amounts of other organic and inorganic gases whose amount in the atmosphere varies with time and place. The portion of these substances, which interacts with environment to cause toxicity, diseases, aesthetic distress, psychological effects or environmental decay, has been labelled by man as a pollutant. Today the whole world is in the grip of global warming, ozone layer depletion, acid-rain and toxicity resulting from various chemical pollutants (table 1) released by tremendously grown industries, automobiles and homes. In this context, sulphur dioxide causes hazardous effect in many different ways. For environmental pollution monitoring and control, there is a need for the device that can measure the *in situ* concentration of SO_x ($x = 2, 3$) gas.

2. Sulphur dioxide: A hazardous pollutant

The oxides of sulphur are produced during coal combustion, burning of fossil fuels and melting of non-ferrous sulphide ores. This gas is injurious to plants. Exposure to high levels of gas (> 100 ppm) causes destruction of leaf tissue (leaf necrosis) and damage of edges of leaves and the area between leaf veins. Chronic pressure of SO₂ leads to chlorosis, i.e. bleaching or yellowing of

the normal green portions of leaves. As relative humidity increases plant injury is also increased. Such injury becomes maximum when the stomata (small opening in the surface tissue, which provides for interchange of gases with atmosphere) are open, i.e. during daytime. The long-term low-level exposure to SO₂ is more dangerous for crops than short-term high dose exposure. Some past incidents responsible to fatalities (table 2) alerted the man. There are four possible routes along which sulphur dioxide may react: (i) photo-chemical reactions, (ii) photo-chemical and chemical reactions in the presence of nitrogen oxides and/or hydrocarbons, (iii) chemical process in water droplet containing metal salts and ammonia and (iv) reaction on solid particles in the atmosphere.

3. Electrochemical gas sensors

New electrochemical methods of sensing various gases present in the environment/atmosphere have attracted many scientists and engineers due to inherent simplicity, direct readout and scope for miniaturization (Worrell and Liu 1983). They have been classified into three types (Weppner 1992) depending on whether the electrochemically active species, derived from the gas in question, is the mobile ion (type-1), the immobile ion (type-2), or neither mobile nor immobile (type-3) ion of solid electrolyte (figure 1). The last type needs to have sensitive auxiliary phase which itself is solid electrolyte, in combination with the sensing electrode, forms a half cell of type 1 or 2. The use of electrochemical gas sensors is based upon the fundamental physical properties associated with the sensing species, which develop the cell emf in logarithmic proportion of the concentration of the particular gas in parts per million (ppm).

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3.1 Kinetics and thermodynamics of SO_x gas sensor

Extending the analogy of Nernst equation for potential difference between the two similar electrodes dipped into two different solutions, with of course one reference gas (') electrode and another test gas (''), one can arrive at an equation for SO₃ gas sensor as;

$$E = RT/2F \ln \frac{P''SO_3 \cdot P''O_2^{1/2}}{P'SO_3 \cdot P'O_2^{1/2}} \quad (1)$$

The experimental evidences (Jacob *et al* 1987) indicate that the half-cell reaction at the electrolyte–gas interface is the equilibration of SO₄²⁻ ions in the sulphate electrolyte with the electrochemically active SO₃ gas,

The conversion of SO₂ to electroactive SO₃ (in presence of catalyst) follows the reaction

where K is the equilibrium constant given by

$$K = P(SO_3)/[P(SO_2) \cdot P(O_2)^{1/2}]. \quad (4)$$

Table 1. Pollutant gases and related global environmental problems.

Gases	Related problem
SO _x , NO _x , HCl	Acid rain
CO ₂ , CH ₄ , Fluorocarbon, N ₂ O, O ₃	Global warming
Fluorocarbon, halocarbon	Ozone layer depletion
CO, NO _x , Hg, Pb	Toxicity

The value of K for platinum and V₂O₅ catalysts can be obtained by following equations (5) and (6), respectively (Worrell and Liu 1983; Rao *et al* 1991):

$$\ln(K) = 11783/T - 11.15, \quad (5)$$

in the temperature range 327–827°C,

$$\ln(K) = 5106/T - 4.845. \quad (6)$$

The knowledge of oxygen partial pressure in gas is crucial. In environmental applications, where small SO₂ and SO₃ concentrations are present, the oxygen partial pressure is essentially considered as constant to 0.21 atm. So the theoretical SO₂ partial pressure (Inlet) can be obtained by the relation,

$$P_{SO_2}(\text{Inlet}) = P_{SO_2} + P_{SO_3} = P_{SO_3}(1 + 1/K(P_{O_2})^{1/2}). \quad (7)$$

The half-cell reaction encountered at Ag + Ag₂SO₄ solid reference electrode–electrolyte interface is;

Thus a complete redox reaction for the cell configuration

can be obtained by combining reactions (2) and (8)

Consequently, Nernst equation takes the form;

$$E = \frac{-\Delta G^\circ(T)}{2F} + \frac{RT}{2F} \ln \frac{P_{SO_3} P_{O_2}^{1/2}}{a_{Ag_2SO_4}}, \quad (10)$$

where R is the gas constant; P_{SO_3} and P_{O_2} are the partial pressures of SO₃ and O₂ gases, respectively.

Table 2. Reported hazardous incidents in past.

Year	Country	Effects/remarks
Dec 1930	Meuse River Valley, Belgium	Thermal inversion trapped SO ₂ -38 ppm level 60 deaths – several cattle killed
Oct 1948	Donora, Pennsylvania USA	40% population affected – 20 deaths 2 ppm SO ₂
Dec 1952	London	Temperature inversion – smog – 1.3 ppm SO ₂ approx. 3500–4000 deaths in excess of normal
Jan 1956	London	0.4 ppm SO ₂ – 180–200 deaths
Dec 1957		Major victims (60%) in age group 70 + years

^aAg₂SO₄ is the activity coefficient of Ag₂SO₄. The Gibbs free energy $\Delta G^\circ(T)$ at T (K) can be expressed as (Rao *et al* 1991):

$$\Delta G^\circ (600 \text{ K} < T < 703) = -312148 + 227.36 \times T \text{ (J/mol)}, \quad (11)$$

$$\Delta G^\circ (703 \text{ K} < T < 933) = -290016 + 196.10 \times T \text{ (J/mol)}, \quad (12)$$

$$\Delta G^\circ (933 \text{ K} < T < 1100) = -261600 + 165.52 \times T \text{ (J/mol)}. \quad (13)$$

3.2 Development of sensor

It is well known that the quality performance of any solid state electrochemical gas sensor, henceforth abbreviated as SSEGS, is always rated on its response time,

thermodynamic stability, operating temperature, gas sensing ability, sensitivity, gas concentration range that is sensed and obeying Nernst's law behaviour. The efficiency, with which the three basic constituents of sensor, i.e. the solid electrolyte, the reference electrode and the working electrode (figure 1) function, solely governs its performance. The magnitude of ionic and electronic conductivity, chemical and thermodynamic stability, phase and form of solid electrolyte and reference electrode are the determining factors of the efficiency. It is worth mentioning here that the solid electrolytes should possess high ionic conductivity whereas, reference electrode should be a very good mixed conductor (ionic and comparable electronic conductivity) at the operating temperature.

Before designing of any SSEGS with stringent specifications, a hunt for advance materials along with deeper understanding of properties and performance is necessary as the cost and workability can be resolved by new materials and processing techniques. Thus, it is thought imperative to review the materials aspect of SSEGS to benefit scientists working in this particular area by looking at its tremendous potential in today's technology. To do this more systematically, the existing literature is first viewed through the problems posed by solid electrolyte as well as the reference electrode during gradual development of SSEGS on the basis of the phase and the form of materials used therein, and then considering the factors responsible for giving improved performance of SSEGS in terms of engineered solid electrolytes and reference electrodes.

In the very first attempt of making a SO₂ sensor, the electrolyte Li₂SO₄-K₂SO₄-Na₂SO₄ system in the molten form has been used (Flood and Boye 1962; Boxall and Johnson 1971; Salzano and Newman 1972). The cell developed by Salzano and Newman (1972) using SO₂, SO₃, Pt electrode and (Li, Na, K)SO₄ melt separated by ion permeable glass for monitoring SO₂/SO₃ in gases up to ppm range is depicted in figure 2. The use of molten salt electrolyte, however, posed certain difficulties like: (i) quite high operating temperature 925°C, (ii) corrosion of cell due to high reactivity and (iii) need of periodic change to compensate evaporation losses and maintenance of reference gas electrode (Gauthier and Chamberland 1977; Gauthier *et al* 1977, 1981; Jacob and Rao 1979).

The use of electrolytes in solid phase obviates the above-cited problems due to their following known characteristics: (i) imperious barrier to liquids and gases, however, allows one or more ions to migrate through its lattice when tendency of such migration exists, (ii) it facilitates the measurement of chemical potential difference of migrating species on either side in terms of emf in a properly constituted cell combination, (iii) execute thermal and chemical stability at high temperatures and (iv) corrosion resistance.

Figure 1. Three types of solid electrolyte gas sensors.

Gauthier and Chamberland (1977) in their pioneer work, have used K_2SO_4 solid electrolyte in the pellet form with the gas reference electrode for detecting and measuring SO_2/SO_3 concentrations. They have obtained a reliable open circuit potential with the gas flow rate and surface area of the catalysts, sufficient to establish an equilibrium concentration of SO_3 (in the unknown gas) in the temperature range 650–930°C (Gauthier *et al* 1981). Following this work, many attempts have been made to use single-phase alkali sulphates (table 3) like Na_2SO_4 (Jacob and Rao 1979; Saito *et al* 1983, 1984a, b; Maruyama *et al* 1985; Imanaka *et al* 1987a) and K_2SO_4 (Demuyser and Bele 1983; Jacob *et al* 1987; Akila and Jacob 1988), possibly with a view to further reduce the operating temperature and achieve other merits like chemical and thermodynamic stability, sinterability, etc leading to quality performance of sensor. Sensor with single-phase solid electrolyte and gas reference is shown schematically in figure 3 (Jacob and Rao 1979).

Gauthier and Chamberland (1977) have observed the transformation of K_2SO_4 into liquid rich $K_2S_2O_7$ at high SO_3 partial pressures destroying the mechanical integrity of sensor. Similarly, Jacob and Rao (1979) and Jacob *et al* (1987) in their sensor with solid Na_2SO_4 as electrolyte and reference gas electrode, have reported the formation of sodium pyrosulphate salt at higher partial pressure of SO_3 in the vicinity of electrolyte interface exposed to test gas mixture. Additionally, transient cell potential have been seen due to micro-cracks formed in

the electrolyte during thermal cycle of heating and cooling, as a result of volume change which occurs during phase transition in Na_2SO_4 at about 247°C. The connectivity of micro-cracks throughout the electrolyte led to gas permeation, which in turn decreased the cell voltage. Similar difficulties have also been associated with the other single-phase sulphate electrolytes, e.g. K_2SO_4 , Li_2SO_4 etc exhibiting analogous phase transitions (Saito *et al* 1983, 1984a, b). Although, no results with a solid reference electrode in a Na_2SO_4 based sensor have been reported, Jacob *et al* (1987) have achieved improved performance with Na_2SO_4 as solid electrolyte and gas reference electrode at higher pressures of SO_3 due to greater polarizing power of Na^+ than of K^+ . To overcome this problem, 1% Ag_2SO_4 doped K_2SO_4 has been used (Gauthier *et al* 1981). However, drift in the cell voltage has been observed, presumably due to cation concentration gradients. An extensive cation inter-diffusion between Ag_2SO_4 and K_2SO_4 has been reported at temperatures in the range from 650 to 950°C (Flood and Boye 1962; Haaland 1980; Saito *et al* 1984a). However, recent phase diagram of Ag_2SO_4 – K_2SO_4 (Kumari and Secco 1985) predicts solid solubility in the entire compositional range above the transition temperature (417°C) of Ag_2SO_4 and thus, the reported drifting cell voltage can not be attributed to inter-diffusion of ions between Ag_2SO_4 and K_2SO_4 but rather caused by the poor sinterability, hygroscopic nature and micro-cracks. Saito *et al* (1983) have also reported the lowering of emf for the large differences in SO_x partial pressures between anode and cathode due to permeation of the gases through macroscopic defects such as pores and the cracks in the electrolyte.

The above findings generated enough ground to look for the two-phase systems based on alkali sulphates. In this regard, a good number of multiphase sulphate systems with high ionic conductivity have been developed to quench the growing thirst for searching new appropriate materials (table 4). The Li_2SO_4 – Ag_2SO_4 binary system has been reported comparatively more conducting amongst the other binary sulphates (Lunden and Olsson 1968; Lunden *et al* 1985, 1987, 1988).

The single-phase solid electrolyte sensors with gas reference electrodes, on one hand, have been found reliable about the cross sensitivity but on the other hand, they show voltage instabilities. The year 1981 has seen a remarkable change when Liu and Worrell in their outstanding investigation added a new dimension to the work going on so far pertinent to the development of SSEGS not only by selecting a polycrystalline two-phase composition 77 Li_2SO_4 –23 Ag_2SO_4 , having ionic conductivity of the order of 0.02437 S/cm at 530°C but also making use of $Ag:Ag_2SO_4$ as a reference electrode in the solid form as shown in figure 4 (Liu and Worrell 1981a, b, 1986; Worrell and Liu 1982, 1983, 1984; Worrell 1988). In spite of exceptional selectivity, reliability

Figure 2. Schematic diagram of experimental cell used to study the behaviour of SO_3 , O_2 , Pt/SO_4^{2-} electrode (Salzano and Newman 1972).

Table 3. A comparison of reported SO_x sensors.

Sl. #	Reference electrode	Electrolyte	T_0 (°C)	t_r (minute)	R	Reference
Single-phase solid electrolytes (Type-II)						
1. Gas		K ₂ SO ₄	600–900	—	10 ppm–1%	Gauthier and Chamberland (1977)
2. Gas		Na ₂ SO ₄ –I	700	1	10 ppm–1%	Jacob and Rao (1979)
3. Gas		K ₂ SO ₄	820	few	1–10%	Gauthier <i>et al</i> (1977, 1981)
4. Gas		Na ₂ SO ₄	647–847	few	10–2000 ppm	Saito <i>et al</i> (1984a)
5. Ag : Ag ₂ SO ₄		Ag ₂ SO ₄ : BaSO ₄ 0.66 m%	597	1	3 ppm–1%	Liu <i>et al</i> (1990)
6. Ag : Ag ₂ SO ₄		Ag ₂ SO ₄	500	5	10–11 ⁴ ppm	Singh and Bhoga (1997)
Multi-phase solid electrolyte (Type-II)						
7. Gas		Na ₂ SO ₄ –Y ₂ (SO ₄) ₃ –Al ₂ O ₃ (48.2 : 11.6 : 40.2)	700	~ 60	30 ppm–1%	Imanaka <i>et al</i> (1987a)
8. Gas		Na ₂ SO ₄ : Y ₂ (SO ₄) ₃ : SiO ₂	700	—	200 ppm–20%	Imanaka <i>et al</i> (1985b)
9. Gas		Na ₂ SO ₄ –La ₂ (SO ₄) ₃ –Al ₂ O ₃ (48.2 : 11.6 : 40.2)	700	~ 60	30 ppm–1%	Imanaka <i>et al</i> (1986)
10. Solid CoSO ₄ –Co ₃ O ₄		Na ₂ SO ₄ –Y ₂ (SO ₄) ₃ –Al ₂ O ₃ (48.2 : 11.6 : 40.2)	700	~ 60	200 ppm–1%	Imanaka <i>et al</i> (1987a)
11. Ag : Ag ₂ SO ₄		Ag ₂ SO ₄ : Li ₂ SO ₄	530		5 ppm–1%	Worrell (1988)
12. Ag : Ag ₂ SO ₄		25Li ₂ SO ₄ : 75Ag ₂ SO ₄	545	1	3–2000 ppm	Mari <i>et al</i> (1990)
13. Ag : Ag ₂ SO ₄		70Ag ₂ SO ₄ : 30SrSO ₄	500	5	10–11 ⁴ ppm	Singh and Bhoga (1997)
14. Ag : Ag ₂ SO ₄		70Ag ₂ SO ₄ : 30 (glass)	500	50 S	10–11 ⁴ ppm	Singh and Bhoga (1999)
Auxiliary sulphate electrode (Type-III)						
15. Gas		CaO : ZrO ₂ /K ₂ SO ₄ auxiliary electrode	780	—	5 ppm–1%	Gauthier <i>et al</i> (1981)
16. Gas		NASICON electrolyte Na ₂ SO ₄ auxiliary electrode	780	3.3	50 ppm–1%	Maruyama <i>et al</i> (1985)
17. Gas		CaF ₂ CaF ₂ + CaSO ₄ auxiliary electrode	927	60	10–106	Jacob <i>et al</i> (1987)
18. Gas		NASICON electrolyte Na ₂ SO ₄ auxiliary electrode	447–807	3.3	10 ppm–1%	Akila and Jacob (1988)
19. Gas		Na ⁺ –β–alumina with Na ₂ SO ₄ auxiliary electrode	513	30	10–1%	Akila and Jacob (1989)
20. Ag		Ag ⁺ –β′–alumina with Ag ₂ SO ₄ auxiliary electrode	500	5–10	1–1%	Rao <i>et al</i> (1991)
21. Ag		Ca–β/β′–alumina CaSO ₄ auxiliary electrode	700	—	2–20%	Rog <i>et al</i> (1991)
22. Gas		Na ⁺ –β′′–alumina Na ₂ SO ₄ auxiliary electrode	927	1	10–1000 ppm	Rao <i>et al</i> (1992)
23. Gas		MgO : ZrO ₂ Li ₂ SO ₄ : CaSO ₄ auxiliary electrode	700	—	20–200 ppm	Yan <i>et al</i> (1993)
		Li ₂ SO ₄ : CaSO ₄ : SiO ₂ auxiliary electrode	650	10S	2–200 ppm	Yan <i>et al</i> (1994)
Temperature gradient						
24. Gas		Na + –β′′–alumina Na ₂ SO ₄ auxiliary electrode	476	—	10–1000 ppm	Rao <i>et al</i> (1994)

T_0 , Operating temperature; t_r , response time; R , sensitivity range.

and chemical stability of two-phase $\text{Li}_2\text{SO}_4\text{-Ag}_2\text{SO}_4$ system it is discarded due to considerably narrow temperature range of operation (520–550°C). Additionally, polycrystalline $\text{Li}_2\text{SO}_4\text{-Ag}_2\text{SO}_4$ disintegrated after three to five days, due to chemical reaction at the grain boundaries, with traces of water vapour in the gas atmosphere. Liu *et al* (1990) have utilized BaSO_4 doped Ag_2SO_4 electrolyte in three different configurations so as to protect the solid reference from test gas as depicted in figure 5. The silver wire type reference along with Pt-coated quartz fibre exhibited better performance (shortest response time) over other types (plate type and embedded type). Now it can be concluded that, in the cases of polycrystalline sulphates, the micro-cracks associated with the volume change on heating and poor sinterability are the major problems to be tackled.

In one of the approaches, to overcome the difficulty associated with the polycrystalline sulphates, several Japanese investigators have fabricated sensors (type-3) using thin film sulphate electrolyte on NASICON (Saito *et al*

1983, 1984a, b; Maruyama *et al* 1985), $\text{Na}^+\text{-}\beta''\text{-alumina}$ (Itoh *et al* 1984) and $\text{Ag}^+\text{-}\beta''\text{-alumina}$ (Imanaka *et al* 1987a; Itoh and Kozuka 1984). These oxides have been employed to avoid the above mentioned problems because in addition to good sinterability, no structural phase transition takes place during heating from room temperature to their melting point (Jacob *et al* 1987; Akila and Jacob 1988, 1989). The sulphate-based electrolyte is physically or electrochemically coated on the surface exposed to test gas acting as an auxiliary electrode. The relation between emf and SO_2 partial pressure is given by (Yamazoe and Miura 1994),

$$E = E_0 + (RT/2F) \ln (P\text{SO}_x). \quad (14)$$

But, a standard gas reference with a known SO_x partial pressure has been found necessary while using a galvanic cell with such configuration. Considering the ion exchangeability of $\text{Na}^+\text{-}\beta''\text{-alumina}$, Meng *et al* (1989) have prepared polycrystalline $\text{Ag}^+\text{-}\beta''\text{-alumina}$ as the solid electrolyte and used it with Ag metal solid reference to obtain a complete solid state SO_x sensor. Itoh *et al* (1984) have used $\text{Ag}^+\text{-}\beta\text{-alumina}$ in the form of disks. Whereas, Rao *et al* (1991, 1992) and Rao and Schoonman (1992) have prepared a galvanic sensor using tubular $\text{Ag}^+\text{-}\beta\text{-Al}_2\text{O}_3$ as solid electrolyte in conjunction with Ag metal reference and porous platinum working electrode with the cell configuration

A novel SO_x sensor using a temperature gradient has been reported by Rao *et al* (1994). In their design a temperature gradient of 100°C has been maintained between the inner sensing and the outer reference gas electrodes (figure 6). The $\text{Na}^+\text{-}\beta''\text{-alumina}$ in the tubular form has been used as a solid electrolyte. The response time of this thermal gradient $\text{Na-}\beta\text{-alumina}$ (TGNB) sensor is found to be about 10 min. Additionally, even though the experimental results were consistent with the theoretical predictions, the reference electrode complexity still persists. Hence the concept of temperature gradient sensors has not inspired research activity any further to take up.

The unique concept of using metal-metal sulphate $\text{Ag:Ag}_2\text{SO}_4$ as a solid reference electrode has removed the complexity of maintaining and circulating the stable concentration of reference gas which has been found quite cumbersome and impracticable for the field applications because they require a reliable method to maintain a constant reference gas composition and an external calibration technique to monitor the reference gas composition. Moreover, the problem of isolation of the reference and test gases has been solved, to some extent, with additional advantage of miniaturization of the sensor in the complete solid state form (as its performance depends on the chemical potential difference of the

Figure 3. Sensor using single-phase Na_2SO_4 and gas reference (Jacob and Rao 1979).

electrode). In furtherance with this, Gauthier *et al* (1981) have attempted oxide-sulphate (MgO, MgSO₄) reference electrode. The need of well-controlled temperature in this case has made their efforts go in vain. Imanaka *et al* (1985a) have investigated sensors using metal oxide/metal sulphate (MgO/MgSO₄, Mn₂O₃ and Ni/NiSO₄) reference with either Na₂SO₄ or Na₂SO₄-Y₂(SO₄)₃-SiO₂ as solid electrolyte. The sensors, in general, exhibited higher emf than the theoretical value. The drifting cell potential has been attributed to (i) the formation of solid solution of sulphate present in electrolyte and reference electrode and or (ii) change in oxidation states of transition metal (Mn, Ni). Later, they have achieved (Imanaka *et al* 1987b) experimental emf in agreement with that of theoretical one using Na₂SO₄-La₂(SO₄)₃-Y₂(SO₄)₃-SiO₂

or Na₂SO₄-Y₂(SO₄)₃-Al₂O₃ electrolyte and NiO-NiSO₄ or Co₃O₄-CoSO₄ solid reference.

A clear-cut view of the gradual development of existing sulphate materials and the cited merits of the solid reference electrode for SO_x sensor evoked interest to re-look at the comparative conductivity data and phase stability of the alkali sulphates before setting a march to examine the newly developed sulphates in conjunction with the solid reference electrode for fabricating a sensor.

In any sensor development activity, the optimization of response time, sensitivity and stability are the crucial stages. Hence, most of the recent investigations have been directed to achieve (i) minimum response time, (ii) sensitivity over large concentration range and (iii) long-term stability. These aspects are discussed below.

Table 4. Conductivity data of sulphate based multi-phase systems.

System	σ (S/cm)	Temp. (°C)	Reference
50Li ₂ SO ₄ -50Li ₂ WO ₄	1.72	540	Kvist (1965)
60Li ₂ SO ₄ -40Na ₂ SO ₄	8.5×10^{-2}	773	Josefson and Kvist (1969)
Li ₂ SO ₄ -K ₂ SO ₄	7.0×10^{-4}	530	Natarajan and Secco (1975)
90Li ₂ SO ₄ -10ZnSO ₄	2.6×10^{-6}	280	Singh and Deshpande (1984)
90Li ₂ SO ₄ -10Na ₂ SO ₄	3.59×10^{-5}	282	Singh and Deshpande (1984)
90Li ₂ SO ₄ -10K ₂ SO ₄	2.66×10^{-6}	282	Singh and Deshpande (1984)
90Li ₂ SO ₄ -10MgSO ₄	6.69×10^{-8}	282	Singh and Deshpande (1984)
45Li ₂ SO ₄ -55Ag ₂ SO ₄	1.17	530	Liu and Worrell (1986)
82.5Li ₂ SO ₄ -17.5CaSO ₄	2.1×10^{-3}	500	Dissanayake and Careem (1988)
78Li ₂ SO ₄ -22MgSO ₄	3.6×10^{-3}	500	Dissanayake and Careem (1988)
Na ₂ SO ₄ : Na-glass			Singh and Salodkar (1989)
90Li ₂ SO ₄ -10Sm ₂ (SO ₄) ₃	3.40×10^{-6}	300	Chaklanabish <i>et al</i> (1992)
30Li ₂ SO ₄ -70La ₂ WO ₄	1.0×10^{-4}	400	Dissanayake <i>et al</i> (1990)
Li ₂ SO ₄ -Li ₃ VO ₄	-		Touboul <i>et al</i> (1990)
80Na ₂ SO ₄ -20MgSO ₄	5.0×10^{-2}	540	Bandaranayake and Mellander (1990)
65Na ₂ SO ₄ -35Ce ₂ (SO ₄) ₃	1.5×10^{-4}	200	Secco (1990)
(50Li ₂ O : 39B ₂ O ₃ : 10ZrO ₂)	6.6×10^{-6}	220	Singh and Bhoga (1990)
90LiNaSO ₄ : 5LiCl : 5Na ₂ MoO ₄	3.6×10^{-4}	370	Prabaharan <i>et al</i> (1992)
60Li ₂ SO ₄ -40MO (MO=CeO ₂ : Y ₂ O ₃ : Yb ₂ O ₃ : LaO ₃)	$\sim 10^{-6}$	300	Uvarov <i>et al</i> (1992)
60Li ₂ SO ₄ -40BaTiO ₃	$\sim 10^{-6}$	300	Uvarov <i>et al</i> (1992)
90Ag ₂ SO ₄ -10Rb ₂ SO ₄	1.0×10^{-5}	180	Wachasunder (1992)
50Ag ₂ SO ₄ -50Na ₂ SO ₄	1.3×10^{-5}	180	Singh <i>et al</i> (1992)
Li ₂ SO ₄ : MSO ₄ -Al ₂ O ₃ (M=Zn, Ag, Na)	$\sim 10^{-2}$	400	Liu <i>et al</i> (1995)
80Ag ₂ SO ₄ -20BaSO ₄	5.6×10^{-4}	300	Singh <i>et al</i> (1995b)
20Ag ₂ SO ₄ -80K ₂ SO ₄	1.076×10^{-6}	180	Singh <i>et al</i> (1995c)
90Li ₂ SO ₄ -10Al ₂ O ₃	4.6×10^{-6}	300	Singh and Bhoga (1995)
80Li ₂ SO ₄ -20BaTiO ₃	2.3×10^{-6}	300	Singh and Bhoga (1995)
90Li ₂ SO ₄ -10LiNbO ₃	1.3×10^{-6}	300	Singh and Bhoga (1995)
90Li ₂ SO ₄ -10K ₂ NbO ₃	5.7×10^{-6}	300	Singh and Bhoga (1995)
80Li ₂ SO ₄ -20BaTiO ₃	2.3×10^{-6}	300	Singh and Bhoga (1995)
50(Li ₂ SO ₄ : Na ₂ SO ₄)-50Al ₂ O ₃	10^{-2} - 10^{-5}	500	Liu <i>et al</i> (1995)

3.3 Response time and sensitivity

A typical variation of sensor emf as a parametric function of time with changes in gas concentration is shown in figures 7a-c. The response time of sensor, as a rule, is defined as the time required to reach 90% of the steady state value. In another approach, Akila and Jacob (1988) have expressed it by

$$\frac{(E_t - E_0)}{E_\infty - E_0} = 1 - \exp(-t/\tau)^{1/2}, \quad (16)$$

where E_t , E_0 , and E_∞ have been defined as sensor voltage at $t = 0$, $t = t$ and $t = \infty$, respectively, and τ is characteristic time constant. A careful look at figures 7a and b reveals a shorter response time when the SO_x concentration changes from low to high *vis-à-vis* high to low. Moreover, it follows a Arrhenius' law (Akila and Jacob 1989). A close scrutiny of literature reveals similar behaviour not only for SO_x sensor (Akila and Jacob 1989; Rao *et al* 1991), but also for O_2 (Fouletier *et al* 1974), CO (Miura *et al* 1990), H_2 (Tan and Tan 1994), NO_x (Yamazoe and Miura 1996) etc. Yang *et al* (1996) have attributed

the longer response time (when SO_2 concentration changes to a smaller value) to the difficulty in SO_2/SO_3 gas desorption and diffusion from Pt electrodes as well as additional catalysts, if any. The response time of sensor has also been seen to be dependent on operating temperature, in general and longer response time at relatively low temperature, in particular (Jacob *et al* 1987; Akila and Jacob 1989; Yang *et al* 1996). The shorter response time at relatively higher temperature may be correlated with an increased rate of the electro-

Figure 6. Temperature gradient sensor (Rao *et al* 1994).

Figure 4. Sensor with solid reference electrode (Worrell and Liu 1984).

Figure 5. Three types of sulphate sensors (Liu *et al* 1990).

Figure 7. emf response after changes in composition of test gas (a) for $\text{Ag} + \text{Ag}_2\text{SO}_4$ reference (Mari *et al* 1990) and (b) gas reference (Akila and Jacob 1989).

chemical reaction as well as faster adsorption and de-adsorption of the gas (Akila and Jacob 1989).

Mari *et al* (1990) have studied SO₂ sensor with cell configuration

where, 25Ag₂SO₄:75Li₂SO₄, a two-phase system has been used as solid electrolyte at the operating temperature of 550°C. The different configurations of the measuring electrodes have been tried along with the optimization of electrolyte thickness to minimize the sensor response time. Figure 8 represents the schematic diagram of solid state galvanic cells with three different platinum measuring electrode configurations (i) a platinum sheet with holes drilled in about 50% area, (ii) a platinum mesh and (iii) a platinum layer directly sputtered onto the sintered sulphate electrolyte. The presence of a large number of gas-phase/electrode/electrolyte triple points favours the kinetics of electrode reaction. Thus, platinum sputtered on sulphate electrolyte configuration, having the largest number of triple points due to the porous structure of platinum film, presents the shortest response time. Moreover, the response time of the gauge has been reported to be dependent on electrolyte thickness. In the best case of platinum sputtered (2 mm thick) on electrolyte, a minimum response time but not shorter than 20 min has been observed. In order to reduce the response time further, Worrell and Liu (1984) have used additional catalyst V₂O₅ in the upstream of gas system. Later, Liu *et al* (1990) in their study have used three different additional catalysts, V₂O₅, Pt-coated alumina single bore tube and Pt-coated quartz with a view to achieve faster equilibrium between SO₂, SO₃ and O₂ gas mixture and ultimately fast response. Interestingly, the response time has been seen (to a first approximation) to be independent of gas concentration and its flow rate (Liu and Worrell 1981a; Akila and Jacob 1989).

Figure 8. Schematic of SSEGs, (A) platinum sheet with holes drilled in about 50% area, (B) platinum mesh and (C) platinum layer directly sputtered onto the sintered sulphate electrolyte.

The operating temperature of most of the SSEGS discussed above has been found to be slightly higher than 500°C with the SO₂ gas sensing ranging between 10 and 1000 ppm (figures 9a and b) in accordance with the Nernst's law (10). Accordingly, the sensor emf changes a few hundreds of mV. However, at higher SO₂ concentrations (> 1%), the change in emf may be insignificant due to its logarithmic dependence. Further, a close look at figure 9a reveals a large deviation from theoretical value for high and low SO₂ concentrations at low (curves 1 and 2) and high (curve 3) operating temperatures,

Figure 9. Variation of emf with (a) SO₂ concentration at three temperatures (Belanger *et al* 1984) and (b) with log P_{SO₃PO₂)^{1/2} at regular intervals of temperature (Akila and Jacob 1989).}

respectively. Differential of (10) with respect to PSO_3 , yields

$$dE = (RT/2F) (dPSO_3/PSO_3). \quad (18)$$

Evidently the sensitivity ($dE/dPSO_3$) of the sensor can be increased with increase in operating/working temperature. The commensurable results for sensors, particularly, with gas reference have been observed (Saito *et al* 1984a; Jacob *et al* 1987; Akila and Jacob 1989; Rao *et al* 1992). Figure 9b, as an example, illustrates this behaviour.

On the other hand, since the sensor emf is chiefly linked with the partial pressure of electrochemically active SO_3 ions, it can be correlated with the SO_2 to SO_3 conversion reaction constant K (3). The variation of K with temperature depicted in figure 10 suggests a considerable decrease in electro-active SO_3 partial pressure with temperature, thereby a decrease in sensor emf is envisaged (figure 9a) for solid reference electrode (Belanger *et al* 1984). Rao *et al* (1991) and Yang *et al* (1996) have also reported a similar behaviour. From above discussion one can infer that the sensitivity for SO_2 gas may be extended further in higher/lower concentration range by increasing/decreasing the operating temperature (curves #1 and #3 of figure 9a). The response time and the sensitivity of various sensors have been compared in table 3. The chemical stability and electronic conductivity of solid electrolyte, discussed in the following sections, have been seen to influence greatly the stability of sensor.

3.4 Chemical stability of cell components

The reliability and accuracy of solid electrolyte sensor critically depend on the chemical stability of the cell

Figure 10. Variation of K (SO_2 to SO_3 conversion reaction constant) with temperature for platinum and V_2O_5 catalysts.

components in the environment of operating conditions. For example, an undesirable cell reaction within the electrode mixture or between electrolyte and its environment results in the drifting of cell potential. Thermodynamic data of the lithium–oxygen–sulphur system has been depicted in a phase stability diagram (figure 11, Liu and Worrell 1981a). The figure illustrates the sulphur and oxygen pressures in which various solid phases Li_2O , Li_2S , Li_2SO_4 are stable at 527°C. The areas represent regions of one phase stability and solid lines represent two-phase equilibria. The intersection point of three solid lines represents the unique value of the sulphur and the oxygen pressure where three condensed phases are in equilibrium. The diagram further indicates that lithium metal does not coexist with Li_2SO_4 . The cross-hatched region (A) represents the exit gas environments from typical combustion processes in which the oxygen and SO_2 partial pressures vary from 0.01 to 0.21 and 10^{-6} to 10^{-2} atm respectively. Thus, figure 11 exhibits that the lithium sulphate remains stable in typical combustion gas environments. Furthermore, lithium sulphide has a stable phase in the oxygen sulphur pressure environments encountered in coal gasification, shown as cross-hatched region (B). Liu and Worrell (1981b, 1986) have installed lithium sulphate based sensors in a coal gasification environment, where the sulphate electrolyte decomposed into Li_2S .

3.5 Influence of electronic conductivity

The electronic conductivity in a solid electrolyte has two harmful effects during the sensor/cell operation. One is,

Figure 11. Phase stability diagram for Li–O–S at 527°C (Liu and Worrell 1981a).

the short circuit effect, which simply lowers the actual open circuit potential than that expected from Nernst's equation (Worrell 1988). The decreased potential (due to short circuit effect), however, has been calculated by incorporating the electronic transference number for the given electrolyte in Nernst's equation. It has been a more common approach to establish a calibration curve for the sensor, which has been determined experimentally by measuring the sensor potentials with known concentrations of SO₂ and/or SO₃.

A more indigenous effect of electronic conductivity has been shown in figure 12 for sulphate-electrolyte cell of the configuration:

With any electronic current, electrons migrate from the negative to the positive (gas) electrode, and the mobile lithium cations move in the same direction to maintain electrical neutrality throughout the sulphate electrolyte. The half-cell reactions, which occur at the gas and the reference electrodes, are:

and

The Ag₂SO₄ formed at the reference electrode-electrolyte interface, by interjection of silver cations into the Li₂SO₄ electrolyte, results in the unstable transient cell potentials.

The silver sulphate based solid electrolytes, in view of high ionic conductivity, invariance over SO_x partial pressure and chemical stability, offer additional advantages, and thus have become the base to provide experimental evidences. All these factors prompted us to engineer new silver sulphate based composite electrolytes through two approaches: (i) silver ion conducting glass dispersed silver sulphate and (ii) insulating particle dispersed silver sulphate. Through these approaches the problem associ-

ated with micro-cracks and inter cation diffusion could be avoided (Singh *et al* 1999). The salient features responsible for the selection of Ag₂SO₄ as electrolyte are given below.

3.6 Salient features of Ag₂SO₄ solid electrolyte

The Ag-Ag₂SO₄ mixture seems to be the most attractive alternative for reference gas electrode in a sulphur dioxide gas sensor (Liu and Worrell 1981a, b). In addition, the Ag-O-S system is unique in which Ag and Ag₂SO₄ co-exist as the equilibrium phases in contrast to the usual situations depicted in figure 11 where, Li₂O separates from Li₂SO₄. Ag-Ag₂SO₄ reference electrode is compatible to give reversible reaction (8). The open circuit cell voltage must be related to the cell reaction to determine the concentration of SO₂ or SO₃ in the gas mixture. Concurrently, all the available experimental evidences indicate that SO₄²⁻ of the Ag₂SO₄ electrolyte equilibrates with SO₂/SO₃ in accordance with the reaction (2) (Gauthier *et al* 1977, 1981; Saito *et al* 1984a; Akila and Jacob 1989; Mari *et al* 1990).

In spite of the better performance of Li₂SO₄:Ag₂SO₄ in SSEGS reported by Liu and Worrell (1986), the solid electrolyte has posed the following three major problems:

- (I) In single-phase composition, in lithium rich region, Li₂SO₄ decomposes to Li₂S in low oxygen pressures that hampers cell reaction and the performance thereby,
- (II) The hygroscopic nature of Li₂SO₄ that predominates in lithium rich region disintegrates polycrystalline Li₂SO₄ within 2 to 5 days. Although, the short-term test of sensor has been successful, the disintegration causes failure of sensor during long term tests.
- (III) The cation inter-diffusion in between the electrolyte and Ag₂SO₄ belonging to reference electrode affects the long-term stability, analogous to that observed in K₂SO₄ electrolyte.

Hence, the Ag₂SO₄ based solid electrolytes opted for, have been quite successful in offering the following additional advantages when compared with the

Figure 12. Schematic diagram of the effect of electronic conductivity.

Figure 13. Phase stability diagram for Ag-O-S.

Figure 14. Long-term stability after five thermal cycling of sensor with glass dispersed Ag_2SO_4 and inset for pure Ag_2SO_4 .

$\text{Li}_2\text{SO}_4 : \text{Ag}_2\text{SO}_4$ solid electrolyte: (i) the Ag–O–S system (presented in the phase diagram of figure 13) is unique where, Ag and Ag_2SO_4 co-exists as an equilibrium phase in contrast to the usual situation that occurs in Li_2SO_4 . Moreover, Ag– Ag_2SO_4 reference electrode exhibits reversible reaction, (ii) Ag_2SO_4 is not hygroscopic and so the cell disintegration problems are ruled out leaving margin to offer better long-term stability, (iii) a major problem of cationic inter-diffusion between electrolyte and reference electrode does not remain valid for creating concentration gradients and hence the better long-term test, (iv) moreover, the Ag_2SO_4 based systems exhibit low activation enthalpy and thereby the high conductivity in general, as compared to the $\text{Li}_2\text{SO}_4 : \text{Ag}_2\text{SO}_4$ system. High conductivity/mobility helps in getting a fast equilibration of the cell reaction, which is one of the meritorious key points for achieving a shorter response time, (v) better mechanical integrity of Ag_2SO_4 based solid electrolytes with Ag : Ag_2SO_4 solid reference electrode and (vi) the sinterability of Ag_2SO_4 is much better than Li_2SO_4 . Thus, a good number of silver sulphate based electrolytes have been tailored for the development of SSEGS with a view to reduce operating temperature, response time and obtain long term stability (Singh and Bhoga 1996). Various approaches adopted include: (i) classical isovalent doping in Ag_2SO_4 (Singh *et al* 1996a; Secco and Usha 1994), (ii) aliovalent doping in Ag_2SO_4 (Singh 1988; Singh *et al* 1996b, 1998a; Singh and Bhoga 1998), (iii) new binaries of Ag_2SO_4 with CaSO_4 (Singh *et al* 1995a), BaSO_4 (Singh *et al* 1995b; Bhoga *et al* 1999) and Me_2SO_4 where, Me = Cs, Gd_2 and La (Singh *et al* 1999), and (iv) dispersion of the second insoluble insulating phase (Anwane 1998) and Ag^+ conducting glass (Singh and Bhoga 1999).

The cell response and sensitivity of sensor utilizing silver conducting glass dispersed Ag_2SO_4 have been seen to be stable on subjecting it to a number of thermal cycling (heating and cooling between room temperature and 525°C). On the other hand the cell with pure Ag_2SO_4 has degraded (figure 14) only on fifth cycle of heating and cooling (Singh and Bhoga 1999). The response time < 30 sec has been achieved due to multi-component nature of electrolyte. The dispersion of silver conducting glass into polycrystalline Ag_2SO_4 matrix has not only been seen to give enhanced ionic conductivity but also provide improved mechanical integrity and sinterability leading to better operating life and thermal stability *vis-à-vis* pure one. There is enormous scope to develop new materials, novel techniques, sensor designing, interfacing, etc to meet stringent industrial specifications.

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