

# *Influence of SO<sub>2</sub> on the electrolytic domain of yttria stabilized zirconia*

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The influence of SO<sub>2</sub> in gas environments on the electronic transference number of a partially stabilized zirconia (PSZ: ZrO<sub>2</sub> + 4.5 mol% Y<sub>2</sub>O<sub>3</sub>) was investigated. The total conductivity for PSZ was measured in air and in an SO<sub>2</sub>-O<sub>2</sub> gas mixture of identical  $P_{O_2}$  for temperatures in the range of 500-1000°C. The conductivity increased measurably with the presence of SO<sub>2</sub>. This increase is attributed primarily to the addition of electronic carriers in the presence of SO<sub>2</sub>. Two methods for estimating and measuring transference numbers in the SO<sub>2</sub> environment gave electronic transference numbers ranging from  $\approx 0.05$  to  $\approx 0.33$  for the temperature range of 500-1000°C. These results indicate that zirconia electrolytes may be mixed conductors for other environments containing sulphur species and the Nernst equation may not be valid.

## 1. Introduction

Zirconia base electrolytes are used extensively as oxygen sensors for a wide range of applications, particularly to monitor exhaust gases in combustion systems. Ideally, these electrolytes operate under conditions of selective oxide ion conduction, with an ionic transference number,  $t_i \geq 0.99$ . This region of operation is referred to as the electrolyte domain. Under these conditions, the Nernst equation may be used to relate the open circuit emf to the difference in the oxygen chemical potential at the two electrodes. It has been shown that the electrolytic domain of solid oxide electrolytes depends upon the ambient oxygen partial pressure [1-12]. At high and at low oxygen pressures, respectively, electron holes or electrons are introduced in significant concentrations as a result of oxygen incorporation reactions. This partial electronic conduction causes internal shorting and deviation from the ideal Nernst emf. For most oxide electrolytes, the electrolytic domain has been determined as a function of  $P_{O_2}$ , temperature, and dopant concentration [13]. The influence of other gaseous species are often present in systems of interest. The oxides of sulphur, for example, are frequently present in combustion processes.

In another application described in recent publications [1, 2], zirconia was used in an electrochemical chain cell for a solid state sulphate detector for sulphur oxides. These cells are proposed for the direct determination of partial pressures of SO<sub>2</sub> and SO<sub>3</sub> in the gas phase surrounding the surface of contact between the two electrolytes (YSZ yttria stabilized zirconia, and sulphate). In these studies, however, only the oxygen partial pressure was considered as the important variable in determining the electrolytic domain; the influence of SO<sub>2</sub> and SO<sub>3</sub> was not considered.

The present study was undertaken to establish whether sulphur containing species in the gas mixture might influence the electrolytic properties of oxide in electrolytes. We describe the results of a study of the influence of SO<sub>2</sub> on the ionic conductivity of partially stabilized yttria-zirconia.

## 2. Experimental procedures

The conductivity of PSZ samples (4.5 mol% Y<sub>2</sub>O<sub>3</sub> in ZrO<sub>2</sub>\*) was measured using an a.c. technique with the following symmetrical cell:

\* Purchased from Zircoa Inc., Solon, Ohio.

atmosphere, Pt|PSZ|Pt, atmosphere

Sintered disc samples (12.7 mm in diameter and 1.6 mm thick) were polished to produce flat plane parallel faces and porous platinum electrodes were deposited on the discs using successive applications of platinum paste<sup>†</sup> followed by annealing at 850° C in air. The edges of the discs were subsequently removed to avoid a short circuit between the electrodes. The disc samples were placed in a conductivity cell, with the samples spring-loaded between two platinum foil contacts. The assembly was placed in a controlled atmosphere system in a tube furnace, with provisions for control and uniformity of the temperature and electrical shielding to minimize stray voltage effects. The a.c. conductivity was measured using Lissajous figures [14] with frequencies in the range of 2 Hz to 100 kHz and the results plotted as a complex admittance diagram (CAD) (conductance as the real part [abscissa] and susceptance [ordinate] as the imaginary part). The CAD allows the separation of the conductivity into contributions from the bulk, the electrode, and grain boundaries. Further details of this apparatus and experimental techniques are given elsewhere [15–17].

The a.c. conductivities of PSZ were measured first in air, with the ionic (bulk) conductivity for different temperatures obtained from the high frequency intercept of the CAD's. The a.c. conductivities were then measured on the same specimen in SO<sub>2</sub>-O<sub>2</sub> mixtures, using a system of flowmeters, blenders and traps to establish the desired gas mixture. The flow rates of SO<sub>2</sub> and O<sub>2</sub> were adjusted so that P<sub>O<sub>2</sub></sub> = 0.21 atm. in the mixture, namely O<sub>2</sub>/SO<sub>2</sub> = 0.266, or, for a total flow rate of 80 cm<sup>3</sup> min<sup>-1</sup>, f<sub>O<sub>2</sub></sub> = 16.8 cm<sup>3</sup> min<sup>-1</sup> and f<sub>SO<sub>2</sub></sub> = 63.2 cm<sup>3</sup> min<sup>-1</sup>. (Note the formation of SO<sub>3(g)</sub> based on reaction SO<sub>2(g)</sub> + 1/2 O<sub>2(g)</sub> = SO<sub>3(g)</sub> is neglected because ΔG<sub>1000° C</sub> = +70.09 kJ mol<sup>-1</sup>, thus P<sub>O<sub>2</sub></sub> does not change appreciably because of this equilibrium.)

The electronic transference number, *t<sub>e</sub>*, for the electrolyte was determined by two methods. The first method assumed that any increase in total conductivity arising from the presence of SO<sub>2</sub> in the atmosphere is an electronic contribution, thus, the transference number is directly related

<sup>†</sup> No. 6926, Engelhard Industries, Murray Hill, NJ.

to this increase:  $t_e = (\sigma' - \sigma)/\sigma'$ , where  $\sigma'$  is the conductivity in the SO<sub>2</sub>-O<sub>2</sub> mixture and  $\sigma$  is the conductivity in air. The second method compared the reversible emf of an oxygen concentration cell with that predicted by the Nernst Equation, with  $E_{\text{obs}} = t_i E_N$ , where  $E_{\text{obs}}$  and  $E_N$  are the observed and Nernst values of the emf, respectively, and  $t_i$  is the ionic transference number, with  $t_i + t_e = 1$ .

### 3. Results and discussion

The influence of SO<sub>2</sub> in the ambient gas on the conductivity of PSZ is shown in Fig. 1. As is seen from this figure, the total conductivity of PSZ is higher in the SO<sub>2</sub>-O<sub>2</sub> atmosphere than in air, even though the P<sub>O<sub>2</sub></sub> is identical in both environments. The effect is larger at high temperature: Δσ/σ' ≈ 0.05 at 500° C and 0.33 at 1000° C.

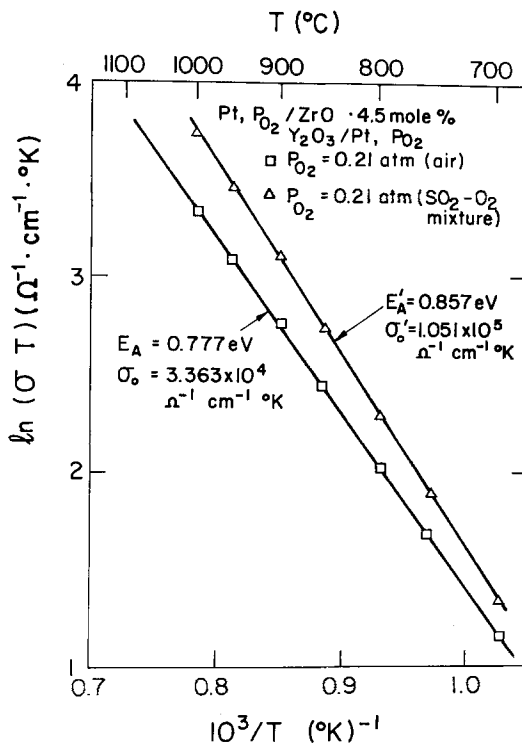
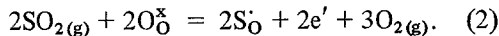
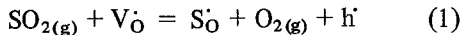


Fig. 1. Influence of SO<sub>2</sub> on the electrical conductivity of Y<sub>2</sub>O<sub>3</sub>-PSZ electrolytes. An increase in conductivity in SO<sub>2</sub>-O<sub>2</sub> mixture is observed compared to air, for a constant P<sub>O<sub>2</sub></sub> = 0.21 atm. A change in activation energy is also observed.

This increase in total conductivity might arise from several causes, but the principal reasons to be expected would be an increase in the concentration and/or mobility of oxide ion vacancies or interstitials or the incorporation of components from the vapour that introduce electronic defects in the electrolyte. Since the external oxygen chemical potentials are essentially constant in the two cases ( $P_{O_2} = 0.21$ ), it seems most probable that a sulphur containing species is incorporated in the electrolyte introducing electronic species. Many different incorporation reactions may be proposed, and the following are only some reasonable proposals. A sulphur atom may be incorporated on oxygen substitutional sites, however, the larger size of sulphur ions and the lower electronegativity value may cause a preference for a singly ionized species  $S^{*}$ . If one now considers either filling existing oxide ion vacancies  $V_O$ , or replacing oxygen in normal lattice sites  $O_O$  with  $S^*$  species, the following two incorporation reactions may be written:



The first incorporation reaction would decrease the ionic conductivity and introduce holes as electronic species. The combined influence of the decrease in ionic charge carriers and increase in electronic charge carriers would cause a small increase in the conductivity. The second incorporation reaction would produce a larger increase since electrons are introduced without any significant change in the ionic charge carriers. It will be noted, however, that both mechanisms would increase the electronic contribution to the conductivity, leaving the ionic conductivity relatively unchanged, because a high  $V_O^{\cdot}$  concentration is fixed by the  $Sc_{Zr}$  stabilizer concentration. Thus, the increase in the conductivity arises primarily from the introduction of electronic carriers. Several other defect models may be proposed and lead to similar conclusions. Assuming, that the PSZ is initially a pure ionic conductor and that the increase in conductivity is due to an electronic component, the electronic transference

\* The traditional defect notation is employed here [18, 19], where  $\cdot$ ,  $'$  and  $\times$  indicate effective positive, negative or neutral charges, with the perfect ionic crystal taken as the base of reference.

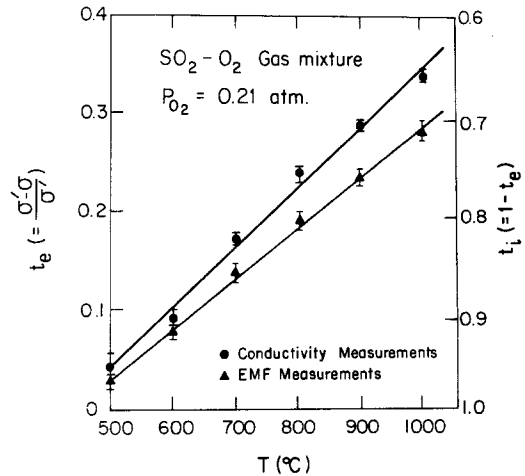


Fig. 2. Electronic transference number of  $Y_2O_3$ -PSZ (4.5 mol %) solid electrolytes in the  $SO_2$  atmosphere. The results of both conductivity and reversible emf measurements are shown.

number may then be calculated as:

$$t_e = \frac{\sigma' - \sigma}{\sigma'} = \frac{\Delta\sigma}{\sigma'} \quad (3)$$

where  $\sigma'$  and  $\sigma$  are the conductivities in the  $SO_2$ - $O_2$  and air environments, respectively, with  $\sigma = \sigma_i$  and  $\sigma' = \sigma_i + \sigma_e$ , with  $\sigma_i$  and  $\sigma_e$  the ionic and electronic conductivities, respectively. The respective calculated values for  $t_e$  are given in Fig. 2. As noted from this figure, the value of  $t_e$  ranges from  $\approx 0.05$  to  $\approx 0.33$  over the temperature range of 500–1000° C, a temperature range of interest in the application of this electrolyte. These values are sufficiently high to cause problems in the use of this electrolyte in such environments. It will be noted that the assumptions made in this estimate might lead to a value of  $t_e$  that is larger than the actual value if some of the increase in the conductivity arises from an increasing concentration of a mobile oxide ion species.

In order to obtain values of  $t_e$  by another method, reversible emf measurements were performed using an oxygen concentration cell and the results compared to the Nernst equation. Tubes of PSZ were used with a flowing  $O_2$ -Ar mixture (0.054 %  $O_2$  in Ar) on the outside of the electrolyte and air inside. The measured emf for this case was very close to values calculated from the Nernst equation:

$$E_{rev} = \frac{RT}{4F} \ln \left( \frac{P_{O_2}^{air}}{P_{O_2}^{SO_2-Ar}} \right) \quad (4)$$

where  $P_{O_2}^{air} = 0.21$  atm.,  $P_{O_2}^{O_2-Ar} = 5.4 \times 10^{-4}$  atm. The air on the inside of the tube was then replaced by a  $O_2$ - $SO_2$  mixture with the ratio of  $O_2/SO_2 = 0.26$  ( $P_{O_2} = 0.21$  atm) and after equilibration, the new emf,  $E'$ , was lower than the value calculated from the Nernst equation. Since  $P_{O_2}^{SO_2-O_2} = 0.21$  atm.,  $P_{O_2}^{O_2-Ar} = 5.4 \times 10^{-4}$  atm. and  $P_{O_2}^{air} = 0.21$  atm, the decrease in emf for the  $SO_2$ - $O_2$  case must be due to a decrease in  $t_i$  in accord with Equation 5. The ionic transference number can be obtained from Equations 4 and 5:

$$E' = \bar{t}_i \frac{RT}{4F} \ln \left( \frac{P_{O_2}^{SO_2-O_2}}{P_{O_2}^{O_2-Ar}} \right) \quad (5)$$

The ionic transference number can be obtained from Equations 4 and 5:

$$\bar{t}_i = \frac{E'}{E} = 1 - \bar{t}_e \quad (6)$$

The results of  $t_e$  versus  $T$  obtained from these reversible emf measurements are shown in Fig. 2 along with the results of the conductivity measurements. The agreement between the two approaches is reasonable and indicates a significant mixed conductivity of PSZ in these environments at elevated temperatures.

In order to test whether the change in conductivity arises from a reversible incorporation reaction, the atmosphere was cycled back and forth from air to  $SO_2$ - $O_2$ . After a few hours in each respective atmosphere, a conductivity characteristic of the ambient atmosphere was observed.

The  $SO_2$  partial pressures in our test environment were much higher than encountered in typical combustion environments. However, the extent of sulphur incorporation, in accord with Equations 1 or 2, is controlled by the  $P_{SO_2}/P_{O_2}$  ratios. Since combustion environments are often low in oxygen, relatively low  $SO_2$  concentrations may produce substantial sulphur incorporation. As a consequence, even if the electrolytic domain normally is inside the  $P_{O_2}$  values for the electrolyte in question, the concurrent presence of  $SO_2$  may produce mixed conductivity for the electrolyte.

#### 4. Summary

An investigation of the influence of  $SO_2$  on the electrolytic properties of partially stabilized

zirconia (PSZ:  $ZrO_2 + 4.5$  mol %  $Y_2O_3$ ) led to the following conclusions:

1. Replacement of air by an  $O_2/SO_2 = 0.266$  gas atmosphere measurably increases the total conductivity of PSZ.

2. This increase may be explained by the incorporation of partially ionized sulphur on the oxide sublattice, with compensating electronic defects.

3. The conductivity increase, with  $SO_2$  in the environment, appears to be principally an electronic component.

4. Estimates of the  $t_e$  (the electronic transference number) assuming the entire conductivity increase is electronic, leads to  $t_e$  values of  $\approx 0.05$  to  $\approx 0.33$ , for temperatures between 500 and  $1000^\circ$  C.

5. Experimental values of  $t_e$ , obtained by comparing the observed cell emf to the Nernst value, are in good agreement with the above estimates.

6. The increase in conductivity when  $SO_2$  is in the atmosphere is reversible.

7. In reducing (low  $P_{O_2}$ ) environments that contain  $SO_2$ ,  $ZrO_2$  electrolytes may be mixed conductors, and the oxygen potentials calculated from the Nernst equation may be in error.

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