

OXYGEN SURFACE EXCHANGE AND DIFFUSION IN FAST IONIC CONDUCTORS

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The rate of oxygen surface exchange on selected bulk oxides exhibiting enhanced oxygen ion conductivity has been derived by measuring ^{18}O penetration profiles using a high sensitivity dynamic SIMS technique. These values for the oxygen surface exchange coefficient (K) were used to derive the steady-state oxygen fluxes through the oxide surface for conditions when the bulk oxide was in equilibrium with 1 atm. of oxygen at 500 and 700°C. The oxygen fluxes were transformed into current fluxes and compared with available exchange current densities (i_0) measured using electrochemical techniques. The two sets of current densities exhibited large differences for zirconia based electrolytes which confirmed the important role of platinum as an electro-catalyst. However for bismuth based electrolytes good agreement was noted between the two sets of i_0 values. It was concluded therefore that the dissociative adsorption of oxygen occurred predominately on the surface of the Bi_2O_3 based electrolyte and that the presence of a metal electrode (Pt or Au) had little effect upon the overall exchange current kinetics.

1. INTRODUCTION

A significant and largely unexplored phenomenon in the performance of oxides used in electrochemical devices is the oxygen exchange mechanism operative at the relevant gas/solid interface. The rate of exchange of oxygen between the gas phase and the surface of an oxide electrolyte or electro-catalyst can be the rate determining step in the overall electrode kinetics. It is possible to determine the rate of oxygen surface exchange on bulk oxide surfaces by measuring ^{18}O penetration profiles using a high sensitivity dynamic SIMS technique¹. Values for the oxygen surface exchange coefficient (K) derived from these measurements can be transformed into current fluxes and compared with parameters derived from standard electrochemical techniques. The performance of oxide electro-catalytic materials can also be dependant upon the rate of oxygen surface exchange as the overall catalytic process may involve

lattice oxygen. An example is provided by partial oxidation reactions² and other reactions such as the oxidation of CO ³.

2. EXPERIMENTAL

2.1. Preparation of samples

Yttria stabilised zirconia (YSZ) single crystals containing 16 mole % Y_2O_3 prepared by the skull melting technique (Ceres Corp., Waltham, Mass., U.S.A.) were oriented by back reflection Laue to give $\langle 100 \rangle$ surfaces. The oriented crystals were prepared as thin ($\sim 2\text{mm}$) square ($10 \times 10\text{mm}$) slices and the $\langle 100 \rangle$ surface was polished with successive diamond abrasives down to $1/4 \mu\text{m}$. The slices were subjected to a variety of annealing procedures prior to the isotopic exchange experiments.

Details of the preparation of the polycrystalline ceramic samples in Tables 1 and 3 fabricated at the University of Twente (UT) have been reported elsewhere^{3,4}. The $\text{Bi}_2\text{O}_3\text{-Er}_2\text{O}_3$

(or Y_2O_3) ceramic samples referred to in Table 2 were prepared by mixing Bi_2O_3 and Er_2O_3 (or Y_2O_3) powders, followed by a calcination at $700^\circ C$. The agglomerated powders were milled in isopropanol, isostatically pressed, and the samples sintered at temperatures between 750 and $800^\circ C$. All the ceramic samples had a density greater than 95% of the theoretical value. Investigations by Auger electron spectroscopy (AES) indicated that surface segregation did not occur on zirconia based materials if a freshly prepared surface (e.g. fracture surface or polished surface) was annealed at temperatures lower than $600^\circ C$ for 60 hours⁶. Preliminary measurements suggest that a similar situation prevails for the bismuth based materials heated for 10 hours at $600^\circ C$.

2.2. Dynamic SIMS experiment

Details of the experimental technique involving ^{18}O isotopic exchange and subsequent determination of the ^{18}O penetration profile in oxide samples has been described elsewhere¹. All the oxide samples were annealed in pure oxygen ($^{16}O_2$) at the temperature used for the isotopic exchange measurements. The oxide sample was quenched by rapid removal of the surrounding furnace and the $^{16}O_2$ oxygen gas pumped away. Enriched $^{18}O_2$ (typically 70-90%) was then introduced into the reaction tube and the furnace, already maintained at the appropriate temperature, was rapidly placed in position around the reaction tube thus initiating the $^{18}O/^{16}O$ exchange reaction. After an appropriate diffusion anneal (usually 30-60 mins) the exchange reaction was terminated by removal of the furnace. The sample was transferred to the high vacuum chamber of the dynamic SIMS apparatus and the profile determined by measuring the $^{18}O/^{16}O + ^{18}O$ ratio as a function of depth. A quadrupole equipped Atomika A-DIDA R-2010 instrument was used for the profile measurements which involved analysing the isotopic concen-

tration of the ^{18}O tracer using negative ion SIMS and simultaneous bombardment with a low energy electron beam to provide charge compensation¹. The depth scale on the profile is obtained by measuring the crater after analysis using an optical interferometer or Talystep instrument. The sputter rate is then assumed to be constant throughout the analysis which is an appropriate assumption for single crystals and for cubic isotropic polycrystalline materials.

3. RESULTS

Under the conditions used for the exchange anneal, the solution to the diffusion equation corresponds to a semi-infinite medium, however, the boundary conditions are related to the rate of transfer of the diffusing species across the surface. The assumption made is that the rate of exchange is proportional to the difference between the concentration in the gas C_g and the concentration in the surface C_s at any time. This boundary condition is expressed by,

$$-D(dC/dx)_{x=0} = K(C_g - C_s), \quad (1)$$

where D denotes the self diffusion coefficient. The solution to the diffusion equation in this case is as follows

$$C_x \equiv (C - C_{bg}) / (C_g - C_{bg}) = \text{erfc} [x/2(Dt)^{1/2}] - \exp(hx + h^2Dt) \text{erfc} [x/2(Dt)^{1/2} + h(Dt)^{1/2}] \quad (2)$$

where C is the isotopic concentration at depth x , C_{bg} is the background isotopic concentration, K is the surface exchange coefficient, t is the diffusion time and $h=K/D$. Note that for large values of $h(Dt)^{1/2}$ then the rhs of eqn. (2) can be simplified to:

$$C_x = \text{erfc} [x/2(Dt)^{1/2}] \quad (3)$$

All the oxide samples examined in the present investigation were oxygen ion conductors exhibiting relatively high oxygen ion diffusion coefficients. Accordingly the rate of $^{18}O/^{16}O$ exchange between the gas phase and solid oxide was

limited by the kinetics of the surface exchange process and not the diffusion coefficient of oxygen within the solid.

A typical profile obtained for a sample of $\text{Nd}_2\text{Ce}_2\text{O}_7$ is shown in Fig. 1. The change in the ^{18}O concentration in the gas phase ($\sim 90\%$) to that in the oxide surface ($\sim 2\%$) is clearly evident and indicative of surface exchange control. Accordingly the data were analysed using equation 2 and values derived for K , the surface exchange coefficient, and D , the oxygen self diffusion coefficient. These values are summarised in Tables 1, and 2.

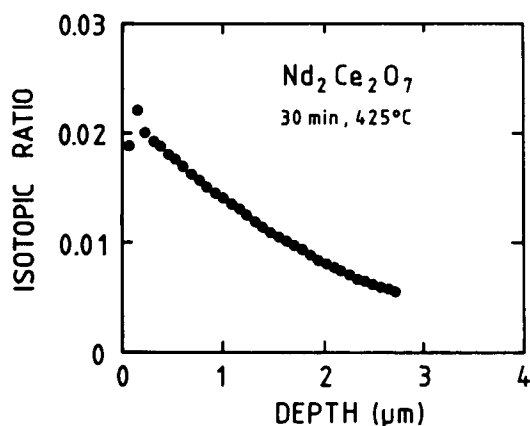


FIGURE 1
Experimental SIMS data.

4. DISCUSSION

4.1. Comparison with electrochemical kinetics

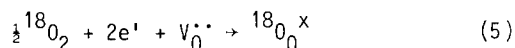
The flux of ^{18}O from the gas to the solid oxide surface is given by the expression,

$$J = -K(C_g - C_s), \quad (4)$$

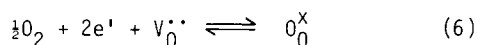
where K is the oxygen surface exchange coefficient, and C_g , C_s are the concentrations of ^{18}O in the gas and solid phases, respectively.

Many steps, e.g. adsorption, dissociation, surface diffusion, charge transfer, incorporation into lattice anion vacancy, etc. are associated

with the surface exchange of oxygen and in principle, at least, any one of these steps can be rate controlling. The overall mechanism can be represented by the equation,



The present isotopic exchange experiments were conducted under conditions when the oxide surface was believed to be in thermodynamic equilibrium at the anneal temperature with oxygen gas at 1 atm. The value of the surface exchange coefficient (K) therefore refers to the equilibrium situation.



In the absence of any driving force (e.g. chemical or electrochemical potential gradient), equal but opposite oxygen fluxes between the gas and solid oxide maintain the equilibrium situation. This situation could correspond to i_0 , the exchange current density, if the presence of the electrode material did not influence the kinetics of reaction⁶. This assumption would imply that the electrode is functioning as a current collector only (i.e. source and sink of electrons) but has no catalytic role. It is appropriate, therefore, to compare the current fluxes derived from the present oxygen exchange measurements with exchange current densities obtained from electrochemical investigations. Accordingly oxygen fluxes were calculated using a simplified version of eqn.

$$(4), \text{ i.e.} \quad J = K C_g, \quad (7)$$

As C_g is approximately 10^{26} atoms/ m^3 and C_s has values around 10^{28} atoms/ m^3 it is acceptable for this preliminary analysis to neglect C_g .

The relevant current fluxes are then calculated using the expression,

$$i \text{ (A/m}^2\text{)} = 2.e.J. \quad (8)$$

Typical values obtained are discussed in the following sections.

4.1.1. Zirconia based electrolytes

TABLE 1

Selection of oxygen surface exchange (K) and oxygen diffusion (D) data for zirconia based electrolytes

Specimen	Source	Temp(°C)/Time(mins)	k(m/s)	D (m ² /s)
(ZrO ₂) _{0.84} (Y ₂ O ₃) _{0.16}	IC (SC)	500/30	2 x 10 ⁻¹¹	7 x 10 ⁻¹⁵
(ZrO ₂) _{0.84} (Y ₂ O ₃) _{0.16} (Pt coated ref. 5)	IC (SC)	500/30	4 x 10 ⁻¹¹	1.4 x 10 ⁻¹⁴
(ZrO ₂) _{0.84} (Y ₂ O ₃) _{0.16}	IC (SC)	700/30	3 x 10 ⁻¹¹	2 x 10 ⁻¹³
YSZ	UT (PC)	700/30	6 x 10 ⁻¹¹	2.5 x 10 ⁻¹³
(ZrO ₂) _{0.84} (Y ₂ O ₃) _{0.16} (Bi implant ref. 5)	IC (SC)	700/30	1.6 x 10 ⁻¹⁰	1.4 x 10 ⁻¹²
YSZ	UT (PC)	700/30	3.2 x 10 ⁻¹¹	4.0 x 10 ⁻¹⁴
(Fe implant [*])				
YSZ	UT (PC)			
(Fe implant ^{**})		700/30	3.4 x 10 ⁻¹⁰	3.3 x 10 ⁻¹³

IC - Imperial College, UT - University of Twente, SC - single crystal, PC - polycrystalline.

^{*} 10 μA at 110KV - total dose 18 x 10¹⁶ Fe^{**} 4.5 μA at 15 KV - total dose 18 x 10¹⁶ Fe (less damage .'. more effect on K and D not lowered so much).

Reference to Table 1 indicates that at 700°C (973°K) typical values derived for K for zirconia based electrolytes are 10⁻¹¹m/s. This value would indicate an i₀ value of approximately 3 x 10⁻²A/m² (i.e. 3 x 10⁻⁶A/cm²). Inspection of the electrochemical measurements performed by Verkerk et al⁴ suggests that this i₀ value is approximately 10³ times too low to account for the observed I-V characteristics which involved platinum electrodes. This conclusion is in accordance with the analysis of Verkerk et al⁴ who suggested that at high oxygen partial pressures oxygen molecules are dissociately adsorbed onto the platinum electrode. The rate controlling step for reaction (6) was believed to be the diffusion of the adsorbed oxygen ions on the platinum surface to sites where

they could be incorporated into the oxide lattice.

It would appear therefore that the presence of porous platinum electrodes on zirconia electrolyte increases the rate of oxygen exchange in the absence of external driving forces by about a factor of 1000 at 700°C compared to the magnitude of the flux calculated using values for the oxygen surface exchange coefficient derived from the isotopic exchange measurements. Accordingly the oxygen surface exchange coefficient has been measured on <100> surfaces of (ZrO₂)_{0.84}(Y₂O₃)_{0.16} single crystals which had been sputtered with platinum. These experiments have already been reported⁵ and it was noted that the presence of platinum did enhance the value of K, the oxygen exchange coefficient, by a small fac-

tor (~ 2) but no dramatic increase was noted as expected from the electrochemical measurements⁴. The relatively small increase of K noted in the isotopic exchange experiments needs further investigation, in which particular attention is paid to the role of segregation which is known to influence electrode kinetics^{6,7}.

Additional surface exchange experiments were also conducted on YSZ samples ion implanted with Fe. Reference to Table 1 indicates that the presence of iron at the surface can influence the surface exchange coefficient values at 700°C. The magnitude of the effect appears to be dependant upon the experimental conditions associated with the implantation procedure, and further work is in progress to determine the role of the various parameters. It appears that at high oxygen pressures (1 atm p_{O_2}), at least, the presence of iron at this concentrations would have little effect upon the electrode kinetics. However further investigations are necessary as it is possible to obtain higher Fe concentrations by ion implantation, and it is also important to study the influence of the radiation damage associated with the ion implantation process⁸.

4.1.2. Bismuth oxide based electrolytes

Values for K and D derived from isotopic exchange experiments on polycrystalline Bi_2O_3 - Y_2O_3 and Bi_2O_3 - Er_2O_3 samples are reported in Table 2. Examination of these data immediately reveals the significantly higher ($10^2 - 10^4$) values for the oxygen surface exchange coefficient on surfaces of Bi_2O_3 based electrolytes compared to zirconia based electrolytes (see previous section). For example at 700°C on

$Bi_{0.775}Er_{0.225}O_{1.5}$ samples a value of 10^{-7} m/s was derived for K . This value corresponds (see section 4.1.) to an exchange current density of 32 mA/cm² assuming charge-transfer to be the rate determining step. Using the electrochemical results of Verkerk et al⁴ for a single experiment it is possible to derive a value of

15-25 mA/cm² for an apparent exchange current density assuming that 100% of the geometric electrode surface is electro-active. The exchange current densities derived from the surface exchange measurements and electrochemical data are in good agreement. Verkerk et al⁴ also observed that replacing platinum by gold electrodes had little effect upon the electrode kinetics, and that the electrochemical results were best interpreted by assuming that the active site for adsorption was associated with the presence of Bi^{3+} ions on the surface of the Bi_2O_3 - Er_2O_3 solid electrolyte. The metal electrode (Pt or Au) was not principally responsible for the dissociative adsorption of oxygen which predominately occurs on the surface of the Bi_2O_3 based electrolyte. The isotopic oxygen exchange results are in accordance with this interpretation and suggest that the role of any metal electrode is mainly confined to that of current collection. Clearly the optimum electrode configuration is likely to be different for Bi_2O_3 and ZrO_2 based electrolytes in view of the different sites proposed for dissociative adsorption.

As the presence of Bi^{3+} ions appeared to have a very significant influence upon the rate of oxygen exchange some preliminary experiments⁵ were conducted in which Bi^{3+} ions were implanted into the surface of yttria stabilised zirconia (YSZ) electrolytes. A typical depth profile of ^{209}Bi implanted ions as determined by SIMS is reproduced in Fig. 2 and it will be noted that a surface concentration of approximately 0.1 - 0.5% Bi was obtained. The oxygen surface exchange coefficient values determined for these samples (Table 1) show a significant increase of about one order of magnitude compared to the untreated YSZ samples. These results appear to confirm that the presence of Bi^{3+} ion at oxide surfaces increases the rate of oxygen exchanges. This observation is very important for catalytic processes.

TABLE 2

Selection of oxygen surface exchange (K) and oxygen diffusion (D) data for bismuth oxide based electrolytes.

Specimen	Source	Temp(°C)/Time(mins.)	K (m/s)	D (m ² /s)
Bi _{0.75} Er _{0.25} O _{1.5}	UT (pc)	500/30	3 × 10 ⁻¹⁰	5 × 10 ⁻¹²
Bi _{0.775} Er _{0.225} O _{1.5}	UT (pc)	500/30	3 × 10 ⁻¹⁰	4 × 10 ⁻¹²
Bi _{0.75} Y _{0.25} O _{1.5}	UT (pc)	500/30	9 × 10 ⁻¹⁰	-
Bi _{0.775} Er _{0.225} O _{1.5}	UT (pc)	700/30	1 × 10 ⁻⁷	4 × 10 ⁻⁹
Bi _{0.75} Y _{0.25} O _{1.5}	UT (pc)	700/30	5 × 10 ⁻⁹	9 × 10 ⁻¹²

UT - University of Twente, pc - polycrystalline.

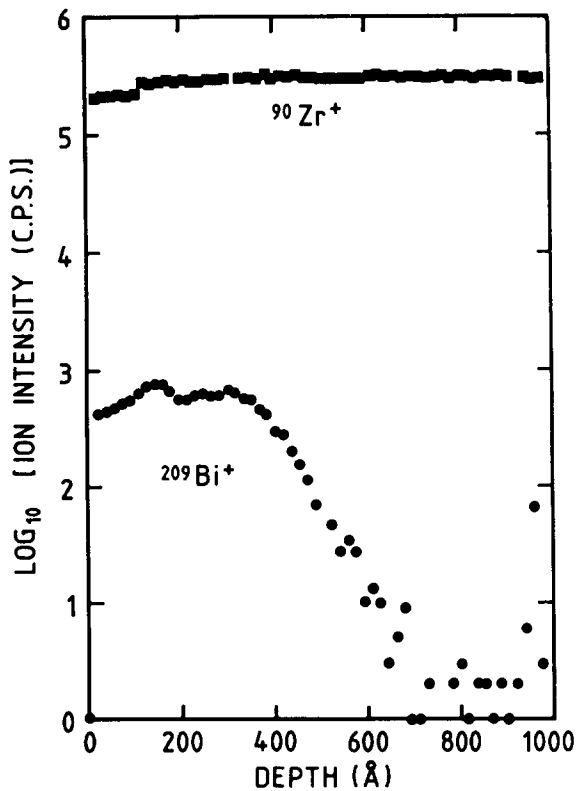


FIGURE 2

The depth profile of ²⁰⁹Bi implanted into YSZ at an energy of 150 keV and a dose of 5 × 10¹⁵/cm². Shown here are the intensities of the ²⁰⁹Bi⁺ and ⁹⁰Zr⁺ ions.

5. CONCLUSIONS

The steady state oxygen flux across selected gas/solid oxide electrolyte interfaces derived from isotopic penetration profiles (using SIMS) and exchange current densities (using electrochemical measurements) have been compared. The two sets of data were very different for zirconia based electrolytes which confirmed the important role of platinum as an electrocatalyst. In contrast good agreement was noted between the two sets of data for bismuth based electrolytes. It was concluded therefore that the dissociative adsorption of oxygen occurred predominately on the surface of the Bi₂O₃ based electrolyte and that the presence of a metal electrode (Pt or Au) had little influence upon the electrode kinetics. The measurement of oxygen surface exchange coefficients can therefore provide additional insight into the rate controlling mechanism associated with the oxidation and reduction of oxygen on oxide electrolyte surfaces. Determination of the surface exchange coefficient using SIMS can also often provide information about 'near surface' anomalies such as segregation and surface damage. This information can also be used to assist in the interpretation of electrochemical electrode kinetic data.

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