MANGANESE DIFFUSION IN SINGLE CRYSTAL AND POLYCRYSTALLINE YTTRIA STABILISED ZIRCONIA

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ABSTRACT

A key factor in predicting the long term performance of a Solid Oxide Fuel Cell (SOFC) is a knowledge of the transport and reactivity properties of the various component materials in a stack. Dynamic Secondary Ion Mass Spectrometry (SIMS) was used to determine the diffusion coefficients of manganese in single crystal and polycrystalline yttria stabilised zirconia (YSZ), in the temperature range of 1100 to 1400°C. The activation energies for manganese diffusion in these materials was found to be 5.36 and 7.34 eV, respectively.

INTRODUCTION

The successful commercialisation of SOFC’s will depend on their ability to produce power over a period of years, with only a small, but predictable loss of efficiency. A key factor in achieving this goal is a knowledge of how the constituents of the various components in an SOFC stack react and inter-diffuse under the elevated temperatures envisaged during their operation. This may lead to changes in the stoichiometry of phases, modifying their physical properties or the formation of interfacial phases possessing undesirable properties.

A candidate SOFC system, for high temperature operation (950 to 1000°C), is based upon a YSZ electrolyte with a La$_{1-x}$Sr$_x$MnO$_{3±δ}$ (LSM) cathode and a Ni / YSZ cermet composite anode. It is well known that LSM may react with YSZ to form lanthanum and strontium zirconates in the interfacial region (1, 2), and that manganese has an appreciable solubility within YSZ (3). There have been, to date, very few studies of manganese diffusion into YSZ in which the manganese diffusion coefficient has been...
explicitly calculated. Lau and Singhal carried out such a study using electron microprobe analysis (EMA) to measure the diffusion profiles of manganese in both single crystal (110 orientation) and polycrystalline YSZ (4). Due to the long profile required for EMA, only very long anneals at a single high temperature, 1400°C, were carried out.

This aim of this study is to determine the diffusion coefficient of manganese in both single crystal and polycrystalline YSZ in the temperature range of that covers the maximum temperature that an electrolyte and electrode structure will encounter (i.e. during electrode sintering). The determination of diffusion coefficients over a range of temperatures will allow the manganese transport properties, at SOFC operating temperatures, to be assessed by extrapolation to lower temperatures.

A comparison between the lattice diffusion coefficients of manganese in single crystal YSZ and the effective diffusion coefficients of manganese in polycrystalline YSZ will give an insight into the relative importance of the cation transport processes leading to fuel cell degradation.

EXPERIMENTAL PROCEEDURE

Materials

The YSZ single crystals, with a [100] orientation, had an yttria (Y2O3) content of 9.5 mol.% and were obtained from Pi-Kem. They were supplied with one surface electrochemically polished, with an Ra of < 15 nm.

Pellets of polycrystalline YSZ were made from a commercial YSZ powder, with an yttria content of 7.5 mol. % (Tosoh TZ8Y). The pellets were iso-statically pressed at a pressure of 350 Mpa, and sintered at 1550°C for 4 hours. The density of the pellets exceeded 99% of the theoretical density of the YSZ. One face of each pellet was polished through a range of silicon carbide and diamond abrasives, finishing with a 0.25μm grade. Pellets of Mn2O3 (Ventron-Alpha) were iso-statically pressed at 350 Mpa, and were sintered at 1400°C for 12 hours.

The diffusion of manganese was studied by annealing a YSZ sample in air, with its polished face in contact with manganese oxide. The subsequent manganese diffusion profile in the YSZ was determined, using Dynamic SIMS.

Anneals

Two methods of carrying out this procedure were investigated. Firstly, the polished face of the YSZ was contacted with a polished face of a manganese oxide pellet (Materials given this treatment will be referred to as oxide couples or OC). An alternative
method was by depositing a 0.5μm thick, dense layer of manganese oxide onto the polished surface of YSZ, using a Pulsed Laser Ablation (PLD) with a Nd-YAG laser (λ = 266nm and power = 0.5 to 4.0J.cm⁻²) technique (5, 6). The aim of this method was to produce a uniformly thick layer of oxide in very intimate contact with the YSZ (Materials treated thus, will be referred to as PLD). Anneal temperatures and times for the single crystal and the polycrystalline YSZ materials are shown in Table 1.

Characterisation Techniques

After the anneals, any changes in the crystallographic structure of the YSZ, were investigated using X-ray diffraction (XRD), using a Philips PW1710 diffractometer with Cu-Kα radiation. Changes in the morphology of YSZ surface, after anneals were investigated using Atomic Force Microscopy (AFM), using a Quesant Resolver instrument.

The diffusion profiles of manganese in the YSZ, after anneals, were determined by dynamic SIMS, using an Atomika 6500 instrument, with a 5keV ¹²³Xe⁺ primary ion beam. Positive secondary ion fluxes with mass/charge ratios of 55 (⁵⁵Mn⁺), 89 (⁸⁹Y⁺) and 90 (⁹⁰Zr⁺), were monitored as a function of sputter time. Depth calibration of the SIMS profiles was carried out by the subsequent analysis of the sputtered crater depth using a profilometer.

RESULTS

Manganese diffusion into polycrystalline YSZ

X-Ray Diffraction. XRD of the annealed polycrystalline YSZ pellets are shown in Figures 1 and 2. Although XRD is generally considered to be a bulk technique, information about the surface region may be obtained from materials, even when, as in this study, the Bragg-Brentano geometry is used. For the low angle peak at 2θ ≈ 31° (YSZ (111) reflection), 50% of the diffracted information is from within the first 9μm of the surface, and 10% of the information is from the first 2μm of the surface (7).

The oxide couple YSZ samples, which were given long anneals, showed marked modification of the YSZ diffraction pattern. Above an anneal temperature of 1250°C, there is a marked shift in the pattern consistent with the formation of an Mn/YSZ solid solution, containing up to ~ 9.5 % Mn to a depth of at least 15μm. Only for oxide couple samples annealed below 1150°C do we observe a diffraction pattern consistent with a shallow Mn diffusion profile.
The diffraction patterns of the polycrystalline YSZ with PLD layers, are consistent with shallow Mn diffusion profiles (i.e. little modification of the diffraction pattern of the YSZ). This is expected as the anneal times for the PLD samples were, at a given temperature, shorter than for the oxide couple samples.

Atomic Force Microscopy. AFM of manganese free polycrystalline YSZ, and YSZ annealed with a manganese oxide PLD layer are shown in figures 3 and 4, respectively. We observe that the presence of manganese has induced significant grain growth and a change in the YSZ surface topography. The Mn coated area exhibits a rippled surface, which is identical to that observed in Mn / YSZ solid-solutions (3). However, the surface roughness ($R_a = 70$nm) is still acceptable for the SIMS measurement as the profile lengths exceeded this value by at least an order of magnitude. AFM of the polycrystalline YSZ/oxide couple samples, shows that the surface topography is unsuitable for the SIMS analysis. The longer anneal times used in the oxide couple preparations led to significant grain growth of the YSZ.

Manganese diffusion into polycrystalline and single crystal YSZ

Concentration profiles within the range of 0.1 to 10µm may be readily analysed using dynamic SIMS. Shorter profiles are problematic, due to the attainment of equilibration of the sputtering process, and longer profiles lose depth resolution due to roughening of the crater bottom.

From the XRD measurements of polycrystalline YSZ in contact with manganese oxide pellets, it was clear that the samples given long anneals, at high temperature, that Mn diffusion had proceeded to considerable depth. Therefore, SIMS analysis was carried out on the YSZ samples with PLD layers of manganese oxide, which had been given shorter anneal times.

A solution for Fick’s second law in one dimension, for a semi-infinite source and a constant surface concentration, is

$$c(x,t) = \text{erfc} \left( \frac{x}{\sqrt{4Dt}} \right)$$  \[1\]

where, $c$ is the concentration of the diffusing ions, $x$ the diffusion distance, $t$ the anneal time and $D$ the diffusion coefficient. This may be rearranged to give,

$$\text{erfc}^{-1} (c(x,t)) = \frac{x}{\sqrt{4Dt}}$$  \[2\]

Therefore, a plot of the inverse complementary error function, $\text{erfc}^{-1} (c(x,t))$, against $x$ should be linear, with a slope of $(2\sqrt{Dt})^{-1}$. A typical diffusion profile of Mn into polycrystalline YSZ is shown in Figure 5.
The effective diffusion coefficients of manganese in polycrystalline YSZ, against reciprocal temperature, are shown in Figure 6. The effective diffusion coefficient is the sum of the contributions of lattice, grain boundary and defect diffusion processes of manganese in YSZ. The activation energy for manganese diffusion in polycrystalline YSZ, derived from this plot, is $7.34 \pm 0.32 \text{eV}$ ($708 \pm 31 \text{kJ.mol}^{-1}$).

It was found that with the single crystal YSZ samples in contact with the manganese oxide couples, the manganese oxide adhered very strongly to the YSZ. In some cases, the adhesion was so strong that the YSZ crystal cracked on cooling, due to the lattice expansion mismatch between the manganese oxide and the YSZ. The annealed single crystal samples were washed with concentrated hydrochloric acid to remove manganese oxide adhering to the YSZ surface (8). The lattice diffusion coefficients of manganese in the single crystal YSZ are also plotted against reciprocal temperature in figure 6. The activation energy for Mn diffusion in the single crystal YSZ is $5.36 \pm 1.09 \text{eV}$ ($517 \pm 105 \text{kJ.mol}^{-1}$).

**DISCUSSION AND CONCLUSIONS**

By extrapolation of the Arrhenius plot of manganese diffusion coefficients in single crystal YSZ to lower temperatures, and extrapolation of the diffusion data of manganese in polycrystalline YSZ, to higher temperatures, we may compare the two sets of data directly. The effective diffusion coefficient of manganese in polycrystalline YSZ, is far higher than for single crystal YSZ. Ignoring the slight difference in the composition of the single and polycrystalline materials, this indicates that grain boundary diffusion is the dominant transport process of Mn in polycrystalline YSZ.

The absolute values for the lattice diffusion coefficient of Mn in single crystal YSZ is 1 to 1.5 orders of magnitude higher than self-diffusion data for Y$^{3+}$ and Zr$^{4+}$ in YSZ (9-12), which are also shown in figure 6. The activation energies of Mn, Y and Zr diffusion in YSZ are shown in Table 2. We observe that the activation energy of lattice diffusion of Mn in single crystal YSZ, is close to the literature values of the activation energies of yttrium and zirconium self-diffusion.

The similarity of the lattice diffusion behaviour of Mn$^{2+}$, Y$^{3+}$ and Zr$^{4+}$ may not be surprising if we consider that their ionic radii in 8-fold coordination are not too dissimilar; 0.96, 1.019 and 0.84 Å, respectively (13). The oxidation state of manganese oxide in YSZ is reported to be a mixture of 2+ and 3+ (3 and 14). Examination of the L$_2$ and L$_3$ absorption edges of Mn / YSZ solid-solutions using Electron Energy Loss (15) and Soft X-ray Absorption Spectroscopies (16), supports the idea of mixed valence manganese oxidation states. Although they were not reported in reference 13, one would anticipate that the ionic radii of Mn$^{3+}$ and Mn$^{4+}$ would be smaller than Mn$^{2+}$. Therefore,
the small ionic radii of the manganese with high oxidation states, may explain the fact that the diffusion coefficient of manganese in YSZ is higher than the $\text{Y}^{3+}$ and $\text{Zr}^{4+}$ self-diffusion coefficients.

It is apparent that in polycrystalline YSZ, the predominant transport process for manganese diffusion is via the grain boundary. The high activation energy for Mn diffusion in polycrystalline YSZ is surprising. The activation energy of grain boundary diffusion of $\text{Y}^{3+}$ and $\text{Zr}^{4+}$ in YSZ is reported to be lower than interior diffusion (10). More diffusion data, over a wider temperature range, is required to confirm that the apparent high activation energy is not a result of a limited number of data points over a narrow temperature range.

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Table 1. Anneal Conditions for Single Crystal and Polycrystalline YSZ

| Single Crystal YSZ                          | Polycrystalline YSZ                          |
|---------------------------------------------|---------------------------------------------|
| Oxide Couple                               | Oxide Couple                               |
| PLD layer                                  | PLD layer                                  |
| Temp / °C                                  | Temp / °C                                  |
| Time / hours                               | Time / hours                               |
| -----                                      | -----                                      |
| -----                                      | -----                                      |
| -----                                      | -----                                      |
| 1250                                       | 1250                                       |
| 400                                        | 100                                        |
| 1300                                       | 150                                        |
| 200                                        | 300                                        |
| 1400                                       | 50                                         |

Table 2. Activation Energies for Cation Diffusion in YSZ

| Cation  | Y₂O₃ mol.% | Method | State                | Temperature range / °C | Activation energy / eV | Ref. |
|---------|-------------|--------|----------------------|------------------------|------------------------|------|
| Zr⁴⁺    | 9.5         | SIMS   | Single crystal (111) | 1200 - 1500            | 4.78±0.17              | 9    |
| Y³⁺     | 9.5         | SIMS   | Single crystal (111) | 1300 - 1500            | 4.79±0.23              | 9    |
| Zr⁴⁺    | 16          | SIMS   | Polycrystalline      | 1600 - 2100 lattice    | 4.05                   | 10   |
| Zr⁴⁺    | 16          | SIMS   | Polycrystalline      | 1600 - 2100 grain boundary | 3.20                   | 10   |
| Y³⁺     | 16          | SIMS   | Polycrystalline      | 1600 - 2100 lattice    | 4.38                   | 10   |
| Y³⁺     | 16          | SIMS   | Polycrystalline      | 1600 - 2100 grain boundary | 3.03                   | 10   |
| Y / Zr  | 20          | Creep  | Polycrystalline      | 1400 - 1600 lattice    | 5.83                   | 11   |
| Y / Zr  | 9.4         | Creep  | Single crystal       | 1300 - 1550 lattice    | 5.5±0.5                | 12   |
| Mn      | 9.5         | SIMS   | Single crystal (100) | 1250 - 1400            | 5.36±1.09              | This study |
| Mn      | 7.5         | Polycrystalline | 1150 - 1300          | 7.34±0.32              | This study |

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Figure 1. XRD of polycrystalline YSZ / Mn-oxide couples

Figure 2. XRD of an annealed Mn-oxide PLD layer on polycrystalline YSZ
Figure 3. AFM image of Mn-free polycrystalline YSZ

Figure 4. AFM image of polycrystalline YSZ after an anneal of Mn-oxide PLD layer (1300°C for 1.5 hours)
Figure 5. Diffusion profile of Mn oxide PLD layer / Polycrystalline YSZ (1150°C for 30 hours)

Figure 6. Arrhenius Plot of Manganese and Cation Diffusion in YSZ

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