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Determination of transport properties of gadolinia doped ceria powders from SIMS profiles

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1. Introduction

Gadolinia doped ceria is an excellent oxygen ion conductor at intermediate temperatures. In addition to that, introduction of nanocrystalline grains in gadolinia doped ceria may significantly improve the surface exchange and diffusion. However, conventional processing of nanocrystalline powders such as cold compaction followed by sintering at high temperatures may result in large grain sizes. It would therefore be ideal to perform oxygen exchange experiments on as-prepared or as-received nanocrystalline powders at temperatures below 400º C, avoiding grain growth. In addition, such experiments would eliminate the influence of grain boundaries in the process of oxygen exchange, as is usually present in the bulk polycrystalline materials. Oxygen surface exchange experiments on powder samples, to our knowledge, have not been done so far on gadolinia doped ceria powders. Typically, oxygen uptake measurements are done on powder samples using techniques such as thermo gravimetric analysis (TGA). Alternatively, as demonstrated here, one may use Secondary Ion Mass Spectrometry (SIMS), to obtain the same information and extract surface exchange coefficients. The objective of the present study is to obtain oxygen surface exchange coefficient in gadolinia doped ceria powders, below the grain growth temperatures, using SIMS.

2. Experimental

Gadolinia doped ceria powder ($Ce_{0.9}Gd_{0.1}O_{1.95}$), GDC10, was purchased at Nextech Materials. X-ray diffraction (XRD) and Transmission electron microscopy (TEM) were done on the as-received powder to obtain the microstructural information. XRD was done on Siemens machine with Cobalt K_α radiation (wavelength, $\lambda=0.1789$ nm), using powders in the form of pressed pellets. Oxygen exchange experiments were done with GDC10 powders at temperatures from 150 to 350º C, for times up to 20 hours at each temperature and under ^{18}O concentration of 96.3% and pressure of 200 mbar. The oxygen exchanged powders were analyzed using SIMS (VG Lab) using the following procedure. The powders were pressed with fingers between two Indium foils each of nominal dimension $10\times10\times1$ mm^3. The two foils were then peeled apart and the remaining loose powder was blown off. The residual powder, embedded in one of the foils was introduced into the SIMS. The secondary ion signals monitored as a function of time were: ^{16}O, ^{18}O, In, Ce and Gd.

3. Results and discussion

XRD and TEM measurements indicate that the powder consists of spherical particles with a diameter of 25 nm. From the flat SIMS profiles (concentration of ^{18}O independent of depth), it appeared that the powder particles were uniformly filled with ^{18}O even at the shortest annealed times. The ^{18}O content increased with increasing time, approaching the outside gas concentration, at all temperatures, however with different rate constants. Oxygen surface exchange and diffusion are sequential processes. If surface exchange is rate controlling, the solution for the concentration of ^{18}O as a function of time is given by [1],

$$C(t) = \left[{}^{18}O\right] = C_\infty (1 - e^{-\frac{t}{\tau}}) \tag{1}$$

where C_∞ is the surrounding gas concentration (96.3%) and

$$\tau = \frac{r_0}{3k} \tag{2}$$

Here r_0 is the radius of the particle and k is the exchange coefficient. On the other hand, when both k and the diffusivity D are taken into consideration, the solution for concentration as a function of time is given by [2],

$$\frac{C(t)}{C_\infty} = 1 - \sum_{n=1}^{\infty} \frac{6L^2 e^{-\frac{\beta_n^2 Dt}{r_0^2}}}{\beta_n^2(\beta_n^2 + L^2 - L)} \tag{3}$$

where

$$L = \frac{kr_0}{D} \tag{4}$$

Here β_n is such that $\beta_n \cot\beta_n + L + 1 = 0$. The β_n values are tabulated in Crank [2] up to n=6.

Equation (3) was used for numerical fit, using first six terms. The surface exchange coefficient calculated from eqn. (1) was used as input at each temperature. The Arrhenius expressions for the k and D values are,

$$k = 1.3\times10^{-7} \exp\left(\frac{-0.5\text{eV}}{kT}\right)\text{cms}^{-1} \tag{5}$$

$$D = 6\times10^{-15} \exp\left(\frac{-0.3\text{eV}}{kT}\right)\text{cm}^2\text{s}^{-1} \tag{6}$$

References

[1] W. Jost, Diffusion in Solids, Liquids and Gases, Academic Press, New York, 1960.

[2] J. Crank, The Mathematics of Diffusion, Oxford University Press, Oxford, 1975.