

Growth of Nano-Domains in Gd-CeO₂ Mixtures: Hybrid Monte Carlo Simulations

Due to growing concern about global warming and dwindling supplies of fossil fuels, increasing interest is being directed towards alternative sources of energy. Popular and promising alternatives are fuel cells, and a substantial amount of research and development has been undertaken to improve the materials used in, and the design of, these devices. For example, in solid oxide fuel cells (SOFCs) the oxidant (e.g. air, O_2) is reduced at the cathode. The oxide ions produced from this process are then transported through the solid electrolyte material, ideally a purely ionic conductor, to the anode where the fuel (e.g. H_2 , hydrocarbons) is oxidised. Electrons generated by this process then flow from the anode to the cathode, completing the circuit and generating power. Lowering the operating temperature of SOFCs to an intermediate temperature range of 600 °C - 800 °C is an ongoing area of intense research and gadolinium doped ceria (CeO_2) is a key material suggested as a suitable electrolyte for this purpose [1].

The efficiency of a solid electrolyte material is linked to how freely the oxide ions can move through it and thus the ionic conductivity. The conductivity of CeO_2 can be enhanced by doping with a cation with a charge that is different from that of Ce. In gadolinium doped ceria (GDC) a Gd^{3+} ion replaces a Ce^{4+} and to maintain charge neutrality an oxygen vacancy is created for every two Gd^{3+} dopants. Thus the formula of the solid solution can be written as $Gd_xCe_{1-x}O_{2-x/2}$ where x can take values from 0 to 1. This implies the ionic conductivity should increase steadily with the number of dopant ions. But it does not, the experimental behaviour is considerably more complex and the ionic conductivity is not a simple function of dopant concentration, but passes through a pronounced maximum at $x_{Gd} = 0.1$ [2]. In addition, the conductivity is very sensitive to the thermal history of the sample and is observed to degrade if the sample is exposed to elevated temperatures [3].

In order to investigate the thermodynamic and structural properties of materials containing large numbers of defects (either dopants and/or vacancies) it is absolutely vital to sample a large number of different configurations of atoms. In conventional Monte Carlo (MC) it is possible to exchange the position of ions chosen at random in order to sample multiple configurations. Unfortunately, in Gd doped CeO_2 sampling of different configurations will be very poor due to the different size and charge of the cations and it is essential to resort to a different approach, i.e. some sort of relaxation is required to allow the atoms move when ions are exchanged and take account for the very different immediate local environments of the Gd and the Ce.

We have developed a computational strategy in which a short molecular dynamics (MD) simulation provides the necessary relaxation. This method improves the efficiency of the simulation dramatically and makes simulations on these systems feasible.

The structural properties of $Gd_xCe_{1-x}O_{2-x/2}$ can be determined over the entire solid solution and allows our simulations to be compared with powder diffraction and EXAFS experiments. For example, figures 1 and 2 display calculated bond lengths determined from EXAFS and diffraction data.

The conductivity can be calculated [4] for atomic configurations determined from the HMC simulations and compared to configurations in which the cations are randomly distributed. We have assumed that the sintered samples in reference [3] can be represented by a random configuration of cations (and vacancies) and the aged samples by configurations obtained from the HMC simulations. Our results are in good agreement with the experimental results in reference [3] and the calculated conductivity of the HMC configurations is greatly reduced for $x \geq 0.15$ (figure 3). This is the composition at which we observe the formation of a network of Gd-rich ions (figure 4). Our results suggest that the growth of Gd-rich domains have significant impact on the conductivity of GDC, preventing the passage of oxide ions through the electrolyte. Indeed, we attribute the ageing of GDC electrolytes to the growth of these domains.

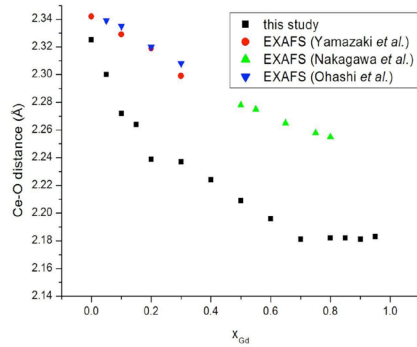


Figure 1. Ce-O distances as a function of composition for $Gd_xCe_{1-x}O_{2-x/2}$. The experimental data are from Ohashi *et al.* [5], Nakagawa *et al.* [6], and Yamazaki *et al.* [7].

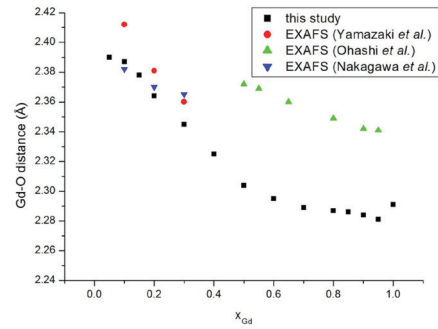


Figure 2. Gd-O distances as a function of composition for $Gd_xCe_{1-x}O_{2-x/2}$. The experimental data are from Ohashi *et al.* [5], Nakagawa *et al.* [6], and Yamazaki *et al.* [7].

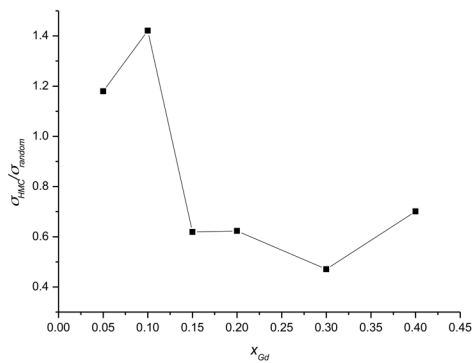


Figure 3. The ratio of ionic conductivity obtained from HMC starting configurations, σ_{HMC} , and those obtained from random configurations of cations, σ_{random} . The ionic conductivity is assumed to be entirely from oxygen ion diffusion.

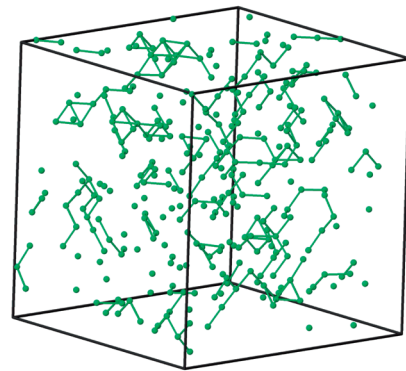


Figure 4. The distribution of Gd ions in GDC for $x_{Gd} = 0.15$. Only the Gd ions are shown and where a next-nearest neighbour interaction exists a "bond" has been inserted (this "bond" is only for graphical purposes and there is no other inference as to physical interaction).

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