Modelling of Anion Transport in YZrON

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1. Introduction

Despite there are many materials, which show high oxygen ion diffusion, there are no materials with high, and predominating, nitrogen diffusion. Nevertheless, finding such materials would make it possible to design new devices like direct nitrogen sensors, or making it also possible to produce ammonia electrochemically.

One recent idea to get such materials was the use of nitrogen-doped cation-stabilised zirconias: The base oxide, zirconia can itself incorporate many lower-valent metal oxides; most prominent are yttria and calcia, while creating a large amount of oxygen vacancies. Incorporation of nitrogen should it make possible to even increase the amount of anion vacancies. Since a N^{3-} anion is only 0.1 Å bigger than an O^{2-} anion, it can be assumed that the nitrogen diffusion in a (Me,Zr)-(N,O) system might be fast.

To check this hypothesis, the nitrogen diffusion was recently investigated in YZrON [1]. It is the goal of this paper to check these experimental results by modelling the anion diffusion in YZrON using molecular dynamics.

2. Computer simulation

Molecular dynamics calculations were performed using the program DL_POLY [2]. Cubic supercells with 20 mol % yttria and 6 mol% nitrogen were setup by randomly placing cations, oxygen vacancies and nitrogen anions on an initially perfect cubic ZrO_2 lattice. Each supercell consists of 256 ZrO_2 units. Parameters for Buckingham potentials are reported elsewhere [3]. After performing the molecular dynamics run, anion diffusion coefficients were obtained from the trajectory of the respective anions. Radial distribution functions, lattice constants and other parameters were obtained as well.

3. Results and discussion

The anion trajectories were in all cases along the (100) direction, both for the oxygen and the nitrogen diffusion; there is no evidence for anion transport along (110) or (111). Furthermore, the trajectories are linear, no curvature was observed. This is despite that during the linear jumping the anions came close to the cations at half of the migration pathway.

Radial distribution functions did show that the distance between cations and nitrogen anions on the one hand and between cations and nitrogen anions on the other hand are practically identical. The Y^{3+}-anion distance is 0.25 Å higher than the Zr^{4+}-anion distance. The minimum N-N distance is higher than the minimum O-N and O-O distance,

respectively; the latter two are very similar (see Fig. 1). It is also observed that the nitrogen anion is more likely to be close to yttrium, while oxygen is preferably close to zirconium cations. This is in contrast to the formal defect chemistry equation 1:

(1)　$Y_{Zr}' + N_O'$　--->　$[Y_{Zr}'+N_O']^{2'}$
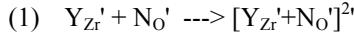
A reaction between nitrogen anion and stabiliser cation would lead to a doubly charged species, but can be rationalised by ionic size effects (Y^{3+} is 0.2 Å bigger than Zr^{4+}, N^{3-} is 0.1 Å bigger than O^{2-}).
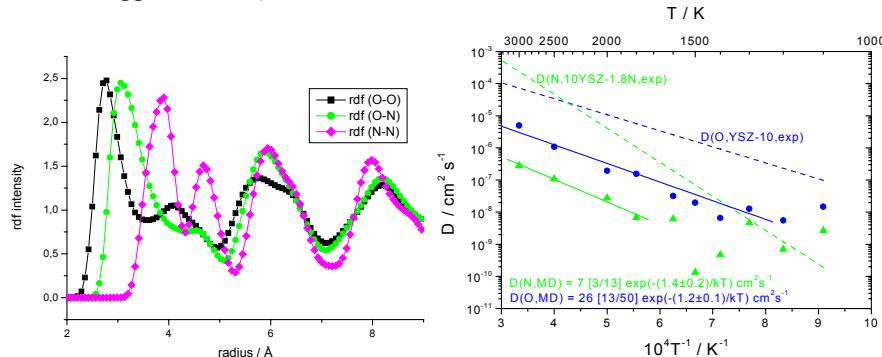

Fig. 1: Radial distribution functions for the anions in YZrON (left, at 1300 K) and plot of the anion diffusion coefficients (right; enclosed are also experimental values for anion diffusivities, taken from [1] and [4]).

Anion diffusivities are also included in Fig. 1. It can be seen that for all temperatures the nitrogen diffusion is higher than the oxygen diffusion. The activation enthalpy is 1.2 or 1.4 eV for the two anions, much smaller than experimentally observed for nitrogen diffusion (2.2 eV, [1]). Nevertheless, the diffusion coefficients agree within less than two orders of magnitude with the (extrapolated) experimentally determined diffusion coefficients.

4. Conclusion

Nitrogen and oxygen diffusivities were calculated for YZrON using molecular dynamics. The nitrogen diffusion is slower than the oxygen diffusion. There is some evidence for the association of nitrogen with yttrium stabiliser cations, indicating that ionic size effects are more relevant in YZrON than ionic charge effects.

References

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