Application for a TSM-DTC funded PhD studentship

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by Friday January 8, 2010

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Please complete the following:

1. Project title

Optimisation of Yttria Stabilized Zirconia Surfaces for renewable energy applications.

2. Project abstract (≤ 200 words please and please add 1 or 2 key references)

Yttria Stabilised Zirconia (YSZ) is a functional ceramic material with multiple applications in energy related technologies: e.g. as an electrolyte material in high temperature electrochemical devices such as the Solid Oxide Fuel Cell (SOFC) and more recently in Solid Oxide Electrolyser Cells (SOEC's) for hydrogen production from renewable sources. The aim of this project is to understand the processes involved in the electrochemical reactions taking place during device operation to further improve and optimize the performance of this material. The key topic is the mechanism of exchange of lattice oxygen at the surface of the material with molecular species in the gas phase. Of these species, O_2 is of major interest in SOFC applications and H_2O is of major interest for electrolyser applications. We propose

to study surfaces and interfaces of YSZ by *ab initio* thermodynamics, to determine the surface defect structure and then to study the interaction of surface defects with molecules in the gas phase. Having established this methodology for planar single crystal surfaces, the effects of micro-crystallinity, grain boundaries, and triple points will be included in the calculations of gas interchange and diffusion in real microstructures, in close collaboration with experiment.

3. What is the multi-scale nature of the project? (≤ 100 words please)

We'll study the ionic current with Kinetic Monte Carlo (KMC), in the manner Lau et al [1, 2]. Their model did not consider interactions between defects or incorporate data systematically from DFT calculations. On the other hand, the need for including the interaction between oxygen vacancies was pointed out by the atomic scale calculations of Pietrucci et al.[3]; we shall build on their results, since they do not address the length and timescales accessible to KMC. The KMC model will be developed at Imperial, while the DFT work will be done at UCL.

4. How do the expertises of the supervisors complement each other? (≤ 100 words please)

Profs. Finnis and Shluger have extensive experience in the modeling of bulk and surface properties of zirconia based materials[4-9]. Prof. Finnis was one of the pioneers of using ab initio thermodynamics for studying non-stoichiometric interfaces, and introduced an accurate approach to calculating the chemical potential of oxygen[10]. He has also studied the thermodynamics of water adsorption on an oxide (magnetite)[11]. Prof. Kilner is currently involved in the characterization of zirconia surfaces and has had extensive experience in the measurement of the kinetics of oxygen exchange with ceramic materials.

5. Is there a self-contained 12-week MSc project that would usefully initiate this PhD project? (If the answer is no the project will not be offered as an MSc project)

Yes. The project will involve writing a computer code for determining the positions of Y ions and compensating vacancies in the cubic zirconia corresponding to different models of their distribution in the lattice. This will be followed by studying the geometric and electronic structures of this system using atomistic (static and molecular dynamics) and DFT methods and analysing its phonon spectra.

References

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3. Pietrucci, F.; Bernasconi, M.; Laio, A.; Parrinello, M., Vacancy-vacancy interaction and oxygen diffusion in stabilized cubic ZrO2 from first principles. *Physical Review B* **2008,** *78* (9), 7.

4. Finnis, M. W.; Paxton, A. T.; Methfessel, M.; van Schilfgaarde, M., The crystal structure of zirconia from first principles and self consistent tight binding. *Physical Review Letters* **1998,** *81*, 5149-5152.
5. Fabris, S.; Paxton, A. T.; Finnis, M. W., Relative energetics and structural properties of zirconia using a self-consistent tight-binding model. *Physical Review B* **2000,** *61*, 6617-6630.
6. Ostanin, S.; Craven, A. J.; McComb, D. W.; Vlachos, D.; Alavi, A.; Finnis, M. W.; Paxton, A. T., Effect of relaxation on the oxygen K-edge electron energy loss near-edge structure in yttria-stabilised zirconia. *Physical Review B* **2000,** *62*, 14728-14735.
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