Predicting the Electronic Structure of CeO$_2$ Grain Boundaries for Comparison with Atomic Resolution EELS

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Intermediate temperature solid oxide fuel cells are an attractive energy source for converting hydrocarbon fuels into electrical energy. However, the highly resistive grain boundaries (GB) in these polycrystalline electrolytic materials leads to a significant decrease in the overall ionic conductivity. One of the most popular theories for the origin of this increased resistivity across electrolytic GB's is an intrinsic resistance arising from a so-called space charge potential region surrounding the GB core. Recent electron energy-loss spectroscopy (EELS) analysis on doped CeO$_2$ shows that grain boundary dopant segregation may also be a significant factor influencing oxygen migration energy [1,2]. To gain a fundamental understanding of the underlying GB charge transport mechanisms in ceria-based oxides, we are modelling the relationship between GB character, composition, electronic structure and conductivity. Initially, density functional theory was employed to determine the bonding for a select number of stoichiometric CeO$_2$ symmetric tilt boundaries. Preliminary calculations are compared with experimentally determined EELS from CeO$_2$.

All computations were performed using the local density approximation (LDA) exchange-correlation functional with spin-polarization considered. Within LDA formalism, the Kohn-Sham equations were solved through the implementation of projector augmented wave (PAW) method using a plane-wave basis set as implemented in VASP [3]. The energies were converged within 1 meV with k-point sampling during all optimization carried out on a Monkhorst-Pack grid of 8x8x8 for bulk calculations and 1x5x5 for the GB supercells with a plane-wave cut-off of 400 eV. For a more accurate representation of the Fermi level and partial occupancies, the tetrahedron method with Blöchl corrections and the Davidson-block iteration scheme was used.

To validate the choice of pseudopotential, a comparison of simulated and experimental EELS oxygen K-edge was carried out for bulk CeO$_2$. Figure 1 shows a good qualitative match between experiment and theory. The first peak in the simulated oxygen energy-loss spectrum is due to the 1s➔4f type transition. Our current DFT model fails to correctly cancel out the self-interaction energy leading to delocalization of the Ce 4f electrons which shifts the 4f levels down in energy. The simulate edge shape matches most of the predictions from other DFT methods seen in literature which show similar relative peak height trends [4]. Grain boundary structures were modelled using the method proposed by Braithwaite et al [5]. Our study has focused on the $\Sigma 3(210)/[001]$ symmetric tilt GB of stoichiometric CeO$_2$ and the system was allowed to relax in three dimensions. Significant restructuring of the GB core was observed with atoms moving as much as 1 Å, as shown in Figure 2. To understand the electronic and local bonding changes associated with the GB, angular momentum site-projected density of states (DOS) was calculated for oxygen atoms at the bulk, the GB core and the GB side as depicted in Figures 2 and 3. The DOS calculation suggests that it should be possible to detect significant variations in electronic structure at different oxygen sites within the GB. In future work, more computationally efficient methods will be initially employed to investigate a wider number of GB configurations. These results will be discussed during the presentation

[6].

References:

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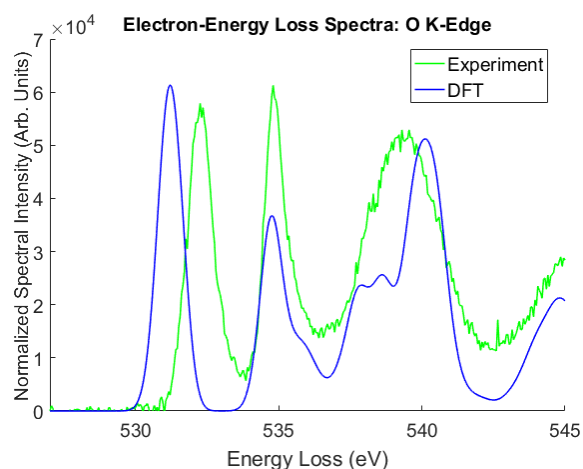
Figure 1. Simulated EELS obtained for bulk CeO_2 overlaid with experimental EELS. A Gaussian broadening function was used to match the DFT calculations to EELS.
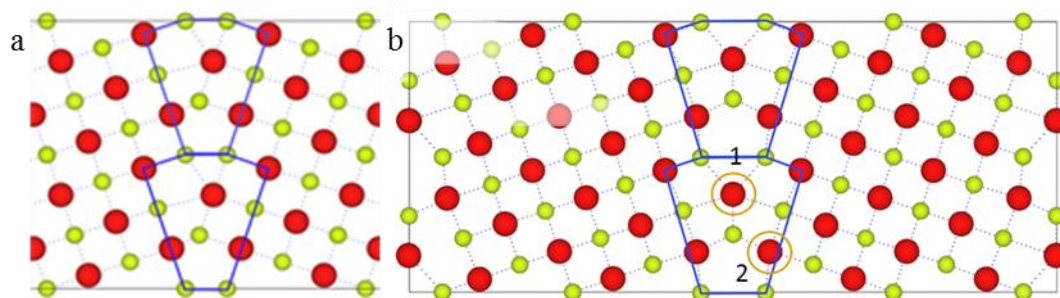

Figure 2. (a) Pre-relaxed GB structure. (b) Relaxed $\Sigma3(210)/[001]$ GB structure. The red circles are oxygen, green circles are cerium. The orange circles indicated by 1 and 2 correspond to the core and side oxygen sites, respectively.
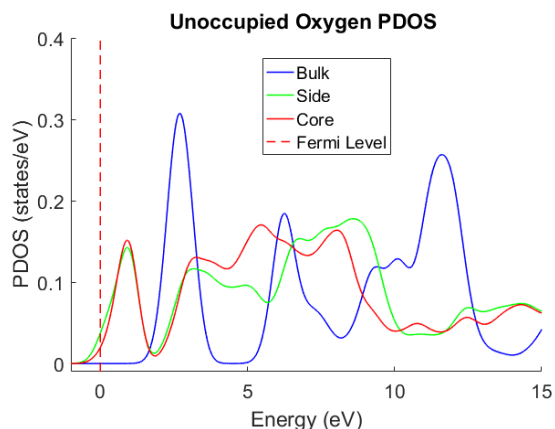

Figure 3. The angular momentum site-projected DOS for GB oxygen sites of CeO_2 as compared to the bulk. Zero corresponds to the Fermi level.