Interpreting Cation Displacements and Image Motifs Associated with the Oxygen Exchange Reaction on CeO2 Nanoparticles

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Oxygen exchange is a critical reaction that controls the functionality of many oxide-based electrochemical processes. Understanding the key structural defects which impact the oxygen exchange reaction at the surface is essential to integrate and adopt the next generation of renewable energy technologies. To study the atomic-level variations which occur during the oxygen exchange reaction, *in situ* aberration-corrected transmission electron microscopy was employed on ceria-based nanoparticles. Here we explore how possible theoretical structural motifs evolve on CeO_2 (ceria) surfaces using first principles and atomistic simulations. Initially we investigate the cation displacement which takes place when surface oxygen vacancies are introduced. The theoretical structural motifs provide an avenue to interpret how oxygen vacancies may manifest in high-resolution transmission electron microscope (HRTEM) images.

To gain fundamental insights into the factors which regulate the oxygen exchange mechanism at various surfaces of ceria nanoparticles, molecular dynamics (MD) simulations were performed. Atomistic calculations were performed based on a rigid ion model as part of the LAMMPS simulation package. The short-range Coulombic interactions were described by parameterized Buckingham pair potentials with a cut-off radius of 10 Å. The long-range forces were summed using Ewald's method [1, 2]. Image simulations were performed using JEMS, a commercialized software package for HRTEM image simulation with an optimum negative C_s condition [3].

Initial structural models were derived from HRTEM images to investigate possible surface structural changes which may be occur when oxygen vacancies are introduced [4]. Various surface vacancy configurations and concentrations were explored. **Figure 1** illustrates two models which could be extrema for the oxidation-reduction reaction taking place on the (111)-(110) step edge of ceria surfaces. For comparison, a HRTEM image of a similar step edge is shown in **Figure 2c**. The models were used as input for image simulations and compared with the experimental data. The method described above serves two purposes: 1) to make refinements to the model suggesting a more realistic approximation to the physical structure and 2) provide an understanding of the dynamics which might occur near step edges and terrace sites during the oxygen exchange reaction. **Figure 2** gives a side-by-side comparison of the experimental data alongside the images of the simulated model structures presented in **Figure 1**. Using MD simulations in this manner provides a framework from which we can correlate cation displacement with the release and uptake of oxygen ions. Simulations show that Ce atomic columns are displaced approximately by 0.3 Å. The analogous quantity which we can extract from the HRTEM images is the root-mean square displacement (RMSD) of surface atoms. This value was also determined to be approximately 0.3 Å. The direction of the cation displacement will depend on the location of the oxygen vacancy which will change during the time taken to record the experimental image. However, the general agreement between the predicted cation displacement and the experimental observation suggests that step edges have the potential to be active sites for oxygen exchange. To further validate

this interpretation, it is necessary to obtain activation energies using density functional theory. This methodology is a more rigorous theoretical framework for interpreting experimental images and should provide a deeper insight on the oxygen exchange kinetics [5].

References:

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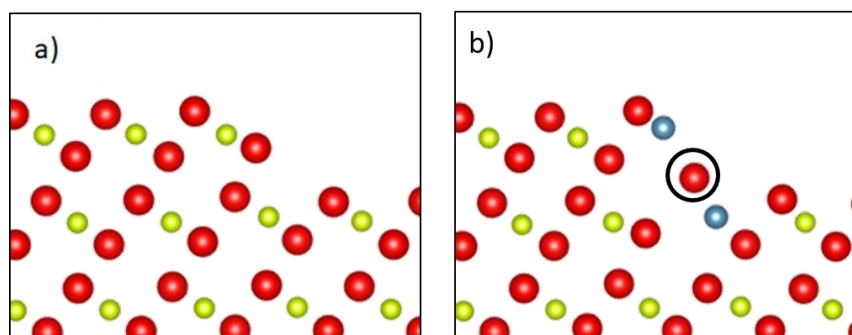

Figure 1. a) The (111) surface, fully oxidized, with a (110) step edge. b) The (111) surface with a (110) step edge where the column of oxygen atoms are removed, in projection, and the sub-surface oxygen column moves into a bridging oxygen column indicated by the black circle. Red circles indicate oxygen atoms, yellow circles indicate Ce^{4+} atoms and blue circles indicate Ce^{3+} atoms. c) Experimental HRTEM image with a negative C_s coefficient. The model structures are relaxed using molecular statics.
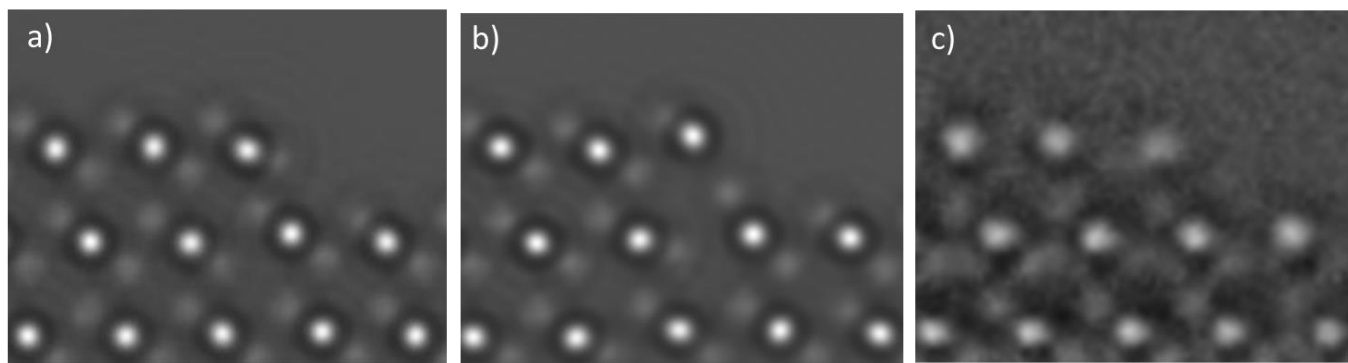

Figure 2. Simulated HRTEM images of a) an oxidized, and b) a reduced (111)-(110) step edge of ceria. c) HRTEM image of a ceria particle, showing the same (111)-(110) step edge area as in the simulations.