

Interpreting Cation Displacements and Image Motifs Associated with the Oxygen Exchange Reaction on Ceria 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 CeO₂(ceria)-based nanoparticles. Here we explore how possible theoretical structural motifs evolve on 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 with Buckingham pair potentials [1, 2]. Image simulations were performed using JEMS, a commercialized software package for HRTEM image simulation [3].

Initial structural models were derived from HRTEM images to investigate possible surface structural changes which may occur when oxygen vacancies are introduced. **Figure 1a-b** are two simulated HRTEM images which could be extrema for the oxidation-reduction reaction taking place on the (111)-(110) step-edge of ceria surfaces. A HRTEM image of a similar step-edge is shown in **Figure 1c**. The structures were iteratively compared with experimental data and refined using MD. This methodology 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 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.

[1] R. A. Buckingham, Proc. Royal Soc. A, **168** (1938) p. 264-283.

[2] S. Plimpton, Journal of Computational Physics, **117** (1995) p. 1 - 19.

[3] P. A. Stadelmann. JEMS - EMS java version, 2004.

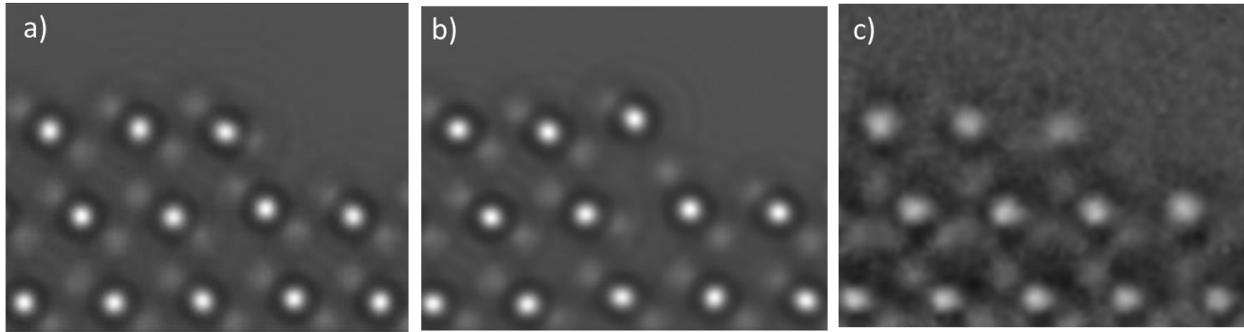


Figure 1. Simulated HRTEM images of the **a)** (111) surface with a fully oxidized (110) step-edge and **b)** the (111) surface with a (110) step-edge where a column of oxygen atoms are removed along the (110) step-edge. **c)** A HRTEM image of a ceria nanoparticle step-edge. The sub-surface oxygen column has moved into a "bridging oxygen" column located at the step-edge.

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