Nanoscale Probing of Electronic Structure in Reducible Oxides with Monochromated Electron Energy-Loss Spectroscopy

William J. Bowman, Qianlang Liu, and Peter A. Crozier

School for the Engineering of Matter, Transport and Energy, Arizona State University, Tempe, AZ, USA

Electroceramic oxides such as cerias, titanias and tantalates can show a wide range of electrical, optical and catalytic properties which make them potentially attractive in many energy and environmental technologies. For example, doped ceria is attractive as both an electrolyte and an anode material for intermediate temperature solid oxide fuel cells. Titania has attracted considerable attention because of its high stability and unique photocatalytic properties. The critical functionalities of these reducible oxides are often related to local oxygen vacancy concentrations and electronic structure. Recent developments in both aberration corrected scanning transmission electron microscopy (AC-STEM) and electron energy-loss spectroscopy (EELS) allow electronic structure to be locally probed with high spatial and energy resolution [1]. Here these tools are employed to investigate electronic structure in Pr doped ceria with a goal of understanding the origin of enhanced electrical conductivity at grain boundaries. We also show that monochromated EELS can be employed to probe localized bandgap states on the surfaces of titania nanoparticles.

A spray drying approach was employed to prepare cerias with a wide range of composition. The grain and grain boundary (GB) electrical conductivities were determined using AC impedance spectroscopy. Ceria co-doped with Gd and Pr show grain boundary conductivities that were 2 orders of magnitude greater than doping with only Gd [2]. STEM orientation imaging and EELS were used to investigate GB character and composition. Typical STEM data show strong segregation of Pr and Gd to grain boundaries (FIG. 1) with the Pr concentration increasing from 4% in the grain to 13 % at high-angle GB. It has been suggested that electrical conductivity may arise from a polaron hoping mechanism which relies on the presence of Pr *4f* levels within the bandgap region. To explore the sensitivity of EELS for detecting Pr *4f* bandgap states, we fabricated a doped CeO_2 containing 10% Pr. Monochromated EELS was employed to investigate the electronic structure. Pure CeO_2 shows a bandgap of about 3.3 eV whereas the Pr doped sample shows significant intensity within the bandgap region in the form of a plateau starting at about 1.5 eV (FIG. 2). Spectral modelling shows this to arise from a sharp state lying 1.4 eV above the top of the valence band corresponding to the Pr *4f* level. Future work will repeat these measurements on the GB phase and correlate with electrical properties.

TiO_2 and Ta_2O_5 are ideal model systems for exploring structure-property relations for solar water splitting. Prior work shows that functionalizing with Ni and NiO co-catalysts dramatically increases their activity for water splitting [3]. FIG. 3 shows a typical energy-loss spectrum from a titania nanoparticle taken in aloof-beam mode, wherein the electron beam is positioned a few nanometers away from the nanoparticle surface. This dramatically reduces electron beam damage and allows fragile electronic surface structure to be probed. The spectra show a series of peaks within the bandgap region, revealing the presence of bandgap states at the surface of the nanoparticles. These features will be interpreted in terms of oxygen vacancies near the surface.

References

[1] Krivanek, O.L., et al., Nature, 2014. 514: p. 209-212.
[2] Bowman, W.J., et al., Solid State Ionics, 2015. 272: p. 9-17.
[3] Liu, Q., et al., Applied Catalysis B: Environmental, 2015. 172: p. 58-64.
[4] We acknowledges financial support of the US NSF Graduate Research Fellowship Program (grant DGE-1311230), NSF DMR-1308085 and US Department of Energy (DE-SC0004954) and the use of John M. Cowley Center for HR Microscopy at Arizona State University is gratefully acknowledged.

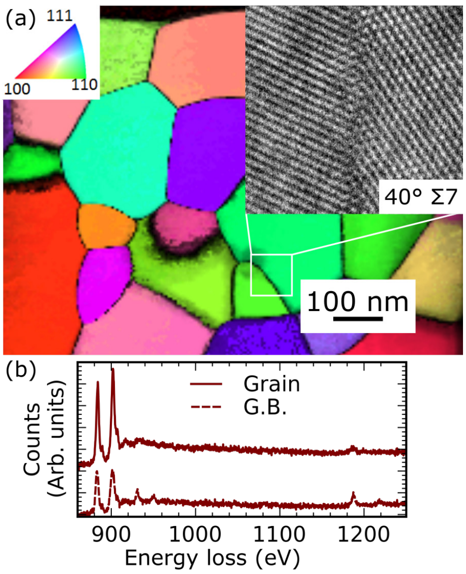

FIG. 1. a) STEM orientation image with high resolution images (insert) and b) EELS from grain and GB.

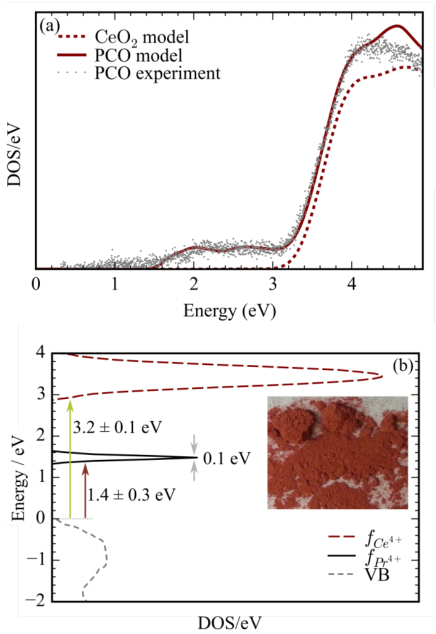

FIG. 2. a) Monochromated valence-loss EELS and b) modelled density of states showing Pr *4f* bandgap state.

FIG. 3. a) Transmission (black) and aloof-beam EELS (blue) from TiO_2 nanoparticle (insert shows ADF image of TiO_2 particle and small Ni metal particle). b) Density of states showing surface states (black) that gives best fit to experimental spectra.