

## Quantifying and Correlating the Composition and Conductivity of Grain Boundaries in Ca-doped CeO<sub>2</sub> Electrolytes, an AC-STEM EELS Study

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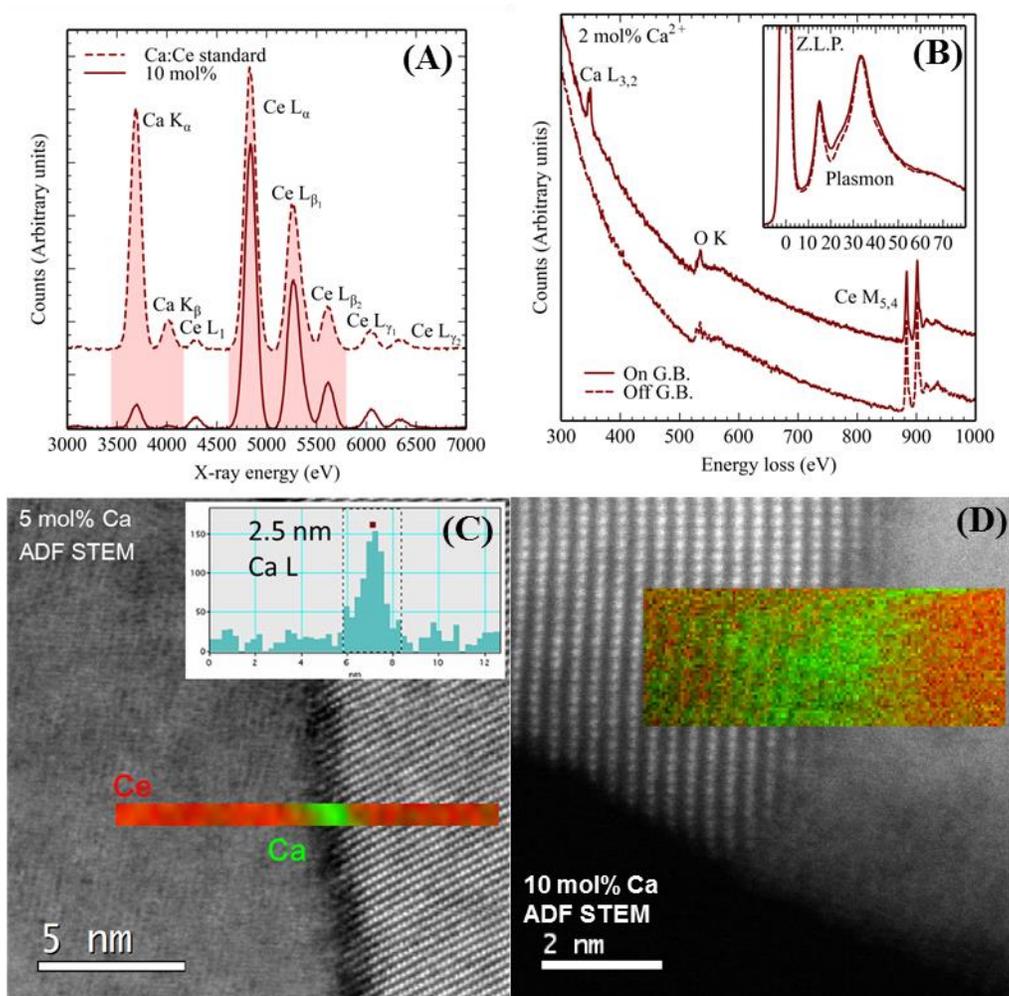
Grain boundaries in polycrystalline oxygen ion conductors such as Y-stabilized ZrO<sub>2</sub> (YSZ) and doped CeO<sub>2</sub> are highly resistive at low and intermediate temperatures (<550 °C), which degrades the total ionic conductivity of the bulk material [1-3]. High resistivity relative to grain interiors is widely believed to be the result of an intrinsic space charge potential barrier which emanates from grain boundary cores several nanometers into grains, creating a region of charge carrier depletion—in this case oxygen vacancies [1,2]. The magnitude of the potential barrier, and thus the width of the affected *space charge zone* are thought to be closely related to the atomic structure and elemental composition within nanometers of the boundary core. However, it is well known that there is significant diversity in the interfacial atomic structure of grain boundaries in a given material, and recent AC-STEM EELS measurements by our group suggest that there is also considerable variation in boundary core composition. Here, we employ AC-STEM imaging and nanospectroscopy to quantify elemental composition of grain boundaries in a series of Ca-doped cerias, and correlate these findings with electrical conductivity data.

Imaging and nanospectroscopy were performed using a probe-corrected JEOL ARM200F S/TEM. Atomic resolution ADF STEM images were correlated with core-loss EELS near-edge fine structure to characterize electronic structure and to quantify the local ionic concentrations in the vicinity of grain boundaries in a series of Ca<sub>x</sub>Ce<sub>1-x</sub>O<sub>2-δ</sub> with 0.02 ≤ x ≤ 0.10. Ceria nanopowders—prepared in the authors' lab using a spray drying (rapid solution evaporation) technique, underwent traditional ceramic processing to yield bulk polycrystalline samples from which electrical conductivity data and TEM specimens could be extracted. Quantitative nanospectroscopy was aided by the use of standard specimens used to experimentally determine proper Ca:Ce and O:Ce *k-factors* (scattering cross-section ratios, [4]). For instance, a Ca:Ce EELS *k-factor* was determined from simultaneous EELS/EDX measurements whereby the Ca:Ce EDX *k-factor* (derived from Ca:Ce standard, see fig. A) was used to identify the Ca:Ce molar concentration ratio. To address plural scattering, EELS spectral integration windows of 80 eV were used. AC-STEM data were correlated with macroscopic electrical conductivity measured using AC impedance spectroscopy, which discerns grain interior and boundary conductivities.

As seen in fig. B, energy-loss spectra acquired at grain boundary cores differed significantly from those acquired away from the boundary in grain interiors. The boundary core Ca concentration was typically greater than twice that of the grain interior, indicating Ca segregation to grain boundaries which was accompanied by Ce depletion. Figures C and D show representative 2D elemental maps derived from EELS spectrum images, and illustrate the very significant variability in cation concentration in the vicinity of the boundary. The relative intensity of the Ce-M<sub>4,5</sub> white lines was also found to vary within several nanometers of boundary cores, indicating local reduction of Ce<sup>4+</sup> to Ce<sup>3+</sup>. The O-K near edge fine structure was also variable with distance and contained features indicative of the presence of oxygen vacancies in and around boundary cores. These electronic structure data, the quantification of ion concentrations, and correlation with grain boundary electrical conductivity will be discussed.

## References and acknowledgements

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**Fig. A:** Background-subtracted EDX spectra acquired from Ca:Ce standard and 10 mol% Ca with highlighted integration windows.

**Fig. B:** Unprocessed EELS data acquired on and off a grain boundary in 2 mol% Ca. Inset are corresponding low-loss plasmon signals.

**Fig. C & D:** AC-STEM ADF images of grain boundaries in 5 mol% and 10 mol% specimens with overlaid cation maps derived from 2D EELS spectrum images. Fig. C inset shows the Ca signal profile across the boundary.