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Characterization of Structure and Grain Boundary Composition in Undoped and Doped Ceria Synthesized by Spray Drying for Solid Oxide Fuel Cells

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High-resolution imaging and spectroscopy are vital tools for investigating nanoscale structural and compositional features of electroceramic materials for solid oxide fuel cell (SOFC) applications. Acceptor cation-doped ceria has demonstrated significant electronic and ionic conductivity in the temperature range of approximately 350 °C to 700 °C and is therefore a promising material for both SOFC electrolytes—which demand high ionic conductivity, and SOFC anodes—whose efficacy depends on sufficient electronic and ionic conduction pathways in contact with fuel or exhaust gasses (i.e. large three phase boundary (TPB) area). By utilizing a mixed ionic/electronic conductor at the anode, it is possible to expand the catalytically active TPB region over the entire electrode surface. Electron energy-loss spectroscopy (EELS) and energy dispersive x-ray spectroscopy (EDX) provide high spatial resolution chemical information, and are thus ideal for investigating nanoscale structural and compositional irregularities pertinent to the engineering of grain boundaries – structural features shown to influence electrical conductivity.

We have prepared a series of undoped and doped ceria electrolytes for characterization of electrical conductivity by AC-impedance spectroscopy, as well as structural and chemical analysis by analytical electron microscopy. Electrolyte preparation for impedance measurements is performed using mixed oxide powders synthesized by spray-drying: a simple and inexpensive powder synthesis method [1]. Nitrate salts of ceria and various rare-earths were used as precursors to synthesize powders which were then die-pressed in uniaxial compression at 180 MPa in a hardened steel piston/cylinder assembly at room temperature to yield electrolyte discs. Discs were sintered for 24 hrs at 1350 °C and Pt contacts were applied for impedance measurements. Following electrical characterization, TEM samples were prepared by sonic cutting, mechanical grinding, polishing, and argon ion milling of the oxide electrolytes. High resolution imaging and microanalysis were performed using a variety of microscopes operating between 200 kV and 400 kV.

The compositional homogeneity of the spray-dried electrolytes, as well as the effect of doping on grain size has been investigated for (nominally) CeO_2, $Ce_{0.8}Gd_{0.2}O_{1.9}$ ("GDC"), and $Ce_{0.75}Gd_{0.1875}Pr_{0.0625}O_{1.875}$ ("GPDC"). As the presence of an amorphous grain boundary phase and/or dopant segregation to grain interface regions is expected to affect intergranular ionic transport, TEM EDX and high spatial resolution STEM EELS chemical analyses have been performed at and near grain boundary regions. EELS analysis of the CeO_2 and GDC has indicated enhancement of Si at grain boundaries in both samples, likely indicating the segregation of residual precursor impurities to the grain interface during heat treatment. Grain boundaries and triple grain junctions observed in GPDC and GDC (see figs. 1 and 2) appeared to

be free of any amorphous phase. However, EELS linescans performed across grain boundaries in GDC suggested the enhancement of both Gd and Si. For example, composition profiles like the one presented in Fig. 2 indicate Gd segregation to a grain boundary in GDC. Structural and compositional grain boundary widths measured at full width half maxima (minima) have been investigated. Correlations between composition, structure, and electrical properties measured via AC impedance spectroscopy will also be presented.

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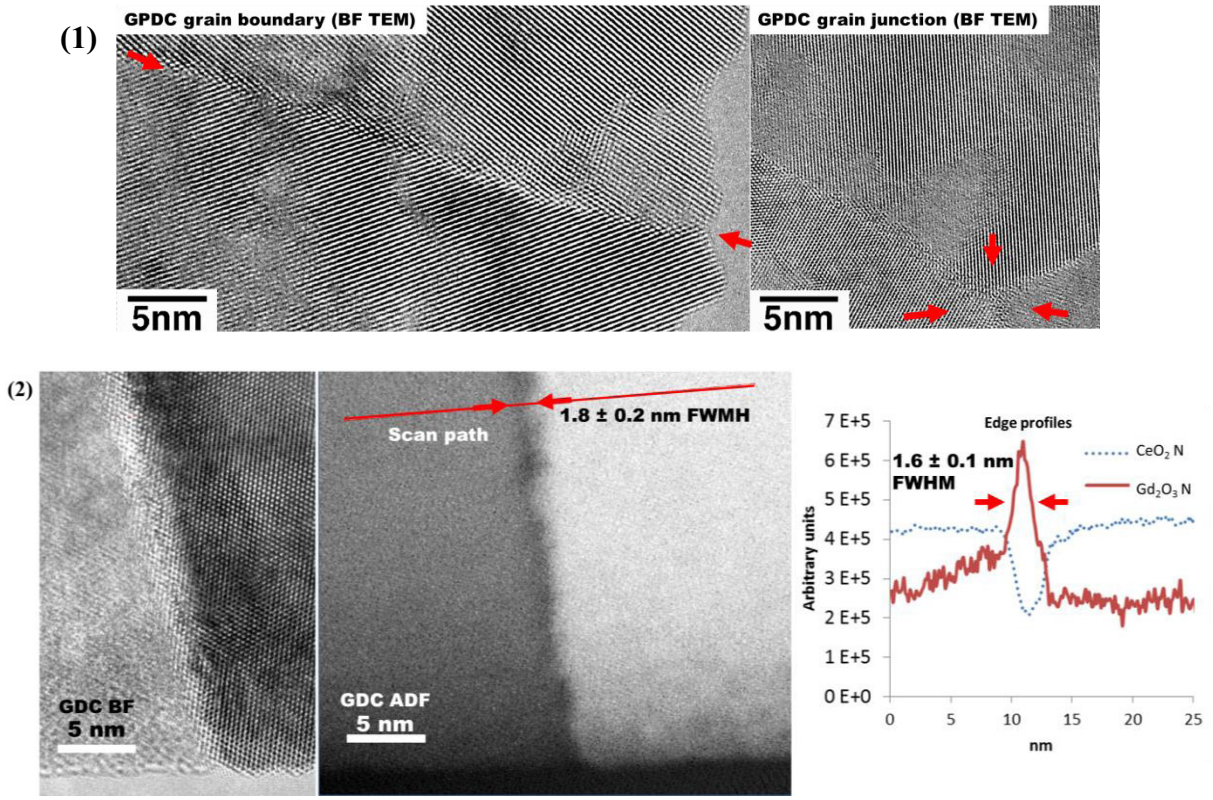

Fig. 1) Typical grain boundary [L] and junction [R] in GPDC shows structurally abrupt interfaces free of amorphous material. Data collected with JEOL-4000EX
Fig. 2) Grain boundary in GDC imaged in BF TEM [L] and ADF STEM [M] with corresponding EELS line-scan profiles for Ce and Gd N-edges [R]. The indicated width in [R] corresponds to the FWHM of the Gd_2O_3 EELS N-edge profile. Data collected with JEOL-4000EX, JEOL-2010F

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