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Structure and chemistry of CeO_2/YSZ interfaces investigated by TEM/STEM

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Ceria (CeO_2) and yttria stabilized zirconia (YSZ) are two typical candidates for electrolyte materials in solid oxide fuel cells attributed to their high ion conductivities. However, the conductivities of these materials are closely connected with high temperatures.Therefore, it is important to develop electrolyte materials which can conduct oxygen ions at lower temperatures. Recent experiments have shown that heterostructures consisting of alternating layers of Gd-doped CeO_2 and Y-doped zirconia (YSZ) exhibit higher ionic conductivity compared to either of the bulk materials[1]. However, the mechanism for the high ionic conductivity of the CeO_2/YSZ hetero structures is still unclear and under debate until now. Theoretical calculations indicate that the oxygen vacancy formation energy is considerably reduced at the interfaces and oxygen vacancies expected to segregate to the interfaces might provide highways for rapid ion conduction[2]. The aim of our work is to obtain insights into the structure and chemistry of interfaces between CeO_2 and YSZ by scanning transmission electron microscopy (STEM) combined with electron energy-loss spectroscopy (EELS).

Epitaxial CeO_2 films were grown on YSZ (111) substrates using pulsed laser deposition (PLD). TEM samples in cross-sectional geometry were prepared by the tripod polishing technique followed by Ar^+ ion-milling while cooling the specimen with liquid nitrogen. Investigations were carried out at 200 kV in an analytical TEM/STEM microscope (JEOL-ARM 200F) equipped with cold field-emission gun (C-FEG) and CEOS probe Cs-corrector. A post-column imaging energy-filter (GATAN GIF Quantum ER) attached to this system is used for EELS spectroscopy and electron spectroscopic imaging (ESI).

A bright-field (BF) STEM image of the cross-sectional view is presented in Figure 1a, showing the CeO_2/YSZ interface. The CeO_2 film epitaxially deposited on the (111) surface of YSZ is approximately 30 nm thick and continuous. Figure 1b shows a high-resolution, high-angle annular dark-field (HAADF)-STEM image of the interface. From the image it can be seen that the CeO_2 film and YSZ substrate have a cubic on cubic orientation relationship ((111) $<1\text{-}10>_{CeO2}$ // (111) $<1\text{-}10>_{YSZ}$). No reaction layers or other phases can be observed at the interface. Periodical misfit dislocations were observed at the interface with extra atomic planes appearing in YSZ. It is well known that the Ce-$M_{4,5}$ edges are valence sensitive to the ionic oxidation state. Since the possible presence of Ce^{3+} is seen as evidence of oxygen vacancy formation, oxygen states of cerium ions near the interface were investigated by electron energy-loss spectroscopy (EELS). Intensity ratios of Ce-$M_{4,5}$ white-lines as observed in energy-loss near-edge structures (ELNES) were used to determine the valence states of cerium. Measured spectra were compared with known reference spectra acquired from compounds containing cerium in Ce^{3+} or Ce^{4+} oxidation state. In addition, quantitative analysis has been performed on the Ce-$M_{4,5}$ edges to study the ratio of Ce^{3+} to Ce^{4+} as function of the distance from the interfaces.

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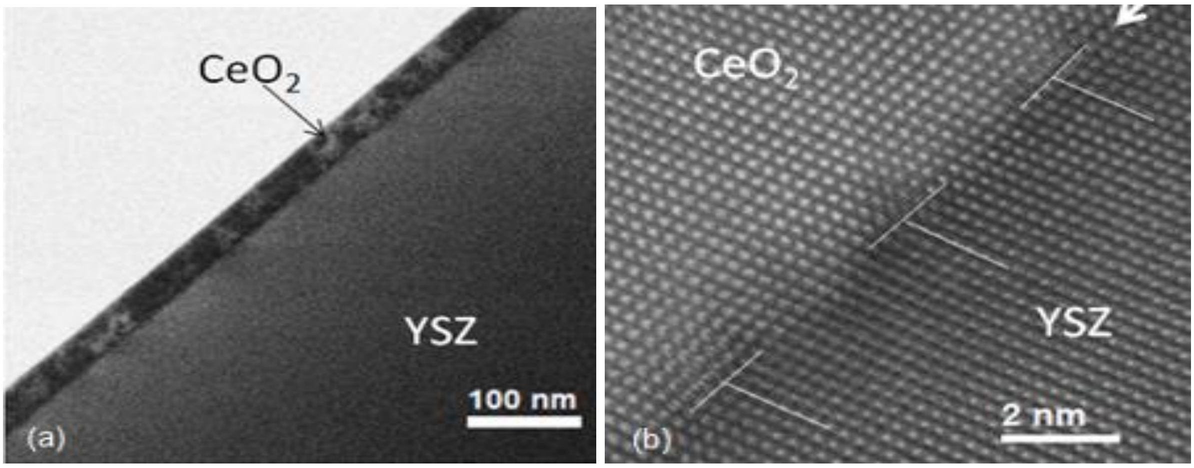

Figure 1.(a)Bright-field STEM image of CeO_2/YSZ interface. (b) High-angle annular dark-field (HR)STEM image of CeO_2/YSZ acquired along $(1\text{-}10)_{YSZ}$ direction. White arrow indicates the position of interface. Lattice mismatch is accommodated by periodically spaced misfit dislocations as indicated in (b).