COMPARING THE ELECTRICAL AND PROTONIC CONDUCTIVITY OF MESOPOROUS AND NANOCRYSTALLINE THIN FILMS OF CERIA-ZIRCONIA SOLID SOLUTIONS

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Due to the redox activity of the redox couple Ce^{3+}/Ce^{4+}, ceria-based solid solutions are typical mixed electronic and ionic conductors (MIECs) which are used e.g. as solid electrolytes in oxygen membranes or as electrode material in solid oxide fuel cells. $Ce_xZr_{1-x}O_2$ (CZO) solid solutions not only show an increased thermal and mechanical stability compared to the corresponding binary oxides, but also exhibit an improved oxygen storage capacity making CZO a prominent material system for heterogeneous catalysis. Besides the control over composition, the defect chemistry of CZO may be optimized by nanostructuring. Here we present investigations of the electrical properties of mesoporous $Ce_{0.8}Zr_{0.2}O_2$ thin films prepared by solution phase coassembly of salt precursors with an amphiphilic diblock copolymer using an evaporation-induced self-assembly (EISA) process. The mesoporous thin films exhibit a regular pore network with a high surface to volume ratio making them an ideal model system to study the influence of surface effects on the transport properties. Structural characterization using SEM, WAXD, XRD, XPS and Raman spectroscopy reveal the high structural quality of the thin films with 24 nm diameter pores which are surrounded by a crystalline wall structure consisting of 3 to 15 nm grains. Nanocrystalline thin films were prepared using pulsed laser deposition and characterized by SEM and XRD. Using electrochemical impedance spectroscopy, the electrical properties of the mesoporous and nanocrystalline thin films were investigated in a temperature range from room temperature to 500 °C and under different oxygen partial pressures between 1 and 10^{-4} bar. Measurements under varying humidity show large differences between the mesoporous and nanocrystalline thin films. While a significant increase in the conductivity is observed for the nanocrystalline thin films at temperatures below 250 °C and high humidity conditions, the mesoporous samples show no contribution of protonic conductivity. As will be discussed, these results indicate that the high surface area of the mesoporous samples has either no or very little effect on the protonic transport properties in CZO.

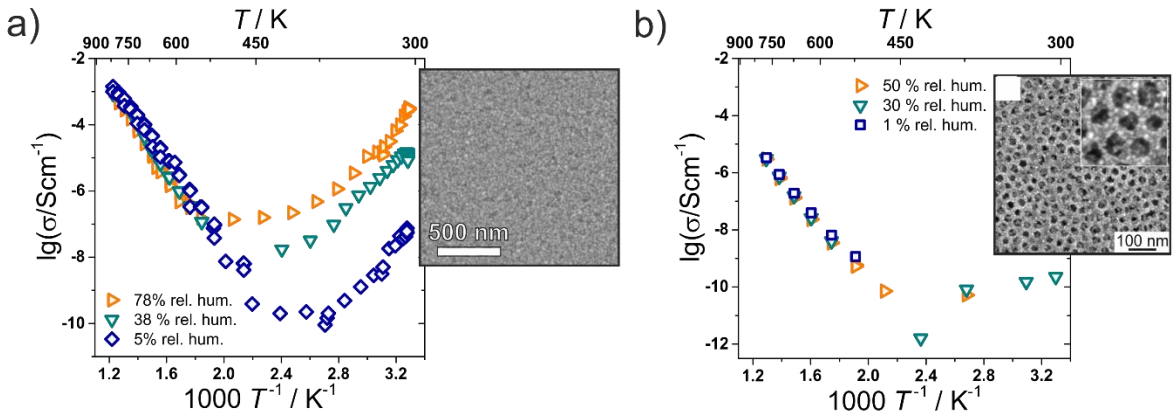

Figure 1: Temperature-dependence of the total conductivity for (a) nanocrystalline and (b) mesoporous $Ce_{0.8}Zr_{0.2}O_2$ thin films for varying humidity. Significant proton conduction at low temperatures can only be observed for the nanocrystalline thin films.