Yttria-stabilized Zirconia (YSZ) has been widely used as structural and functional ceramic in harsh chemical environments or at high operating temperatures. For most applications its long-term stability is of importance. As the system \( \text{Y}_2\text{O}_3-\text{ZrO}_2 \) exhibits a miscibility gap, spinodal decomposition occurs depending on the \( \text{Y}_2\text{O}_3 \) content and the applied conditions. This also holds for 8.5 mol% YSZ [1] one of the most common electrolytes for solid oxide fuel cells (SOFC). During operation at 950 °C the spinodal decomposition of 8YSZ, which is characterized by the microstructural coarsening of metastable \( \text{t}'' \)-YSZ precipitates (Fig. 1a) and the accompanied evolution of chemical variations (Fig. 1b), leads to a significant degradation of the oxygen-ion conductivity (40% within 5000 h). Besides the fact that the decomposition rate depends on the temperature, it can also strongly be enhanced by \( \text{pO}_2 \)-sensitive trace elements possessing strongly different solubility for 8YSZ in oxidizing or reducing atmosphere. Here, the accelerated decomposition of Ni-containing 8YSZ in reducing atmosphere, which proceeds more than 50 times faster than for pure 8YSZ (Fig. 1c), is investigated [2]. To understand the underlying mechanisms, the fundamental processes like Ni indiffusion (oxidizing atmosphere) and Ni exsolution/precipitation (reducing atmosphere) are investigated. The study comprises the local analysis of the oxidation state of the dissolved Ni by EELS. Therefore, an optimized procedure has been established to quasi-in situ prepare ideal metallic reference samples (Fig. 2a). It comprises the preparation of purely metallic Ni nanoparticles on Lacey carbon using a \( \text{H}_2 \)-reactor (thermal treatment: 1 mbar \( \text{Ar/H}_2 \), 650 °C). Such samples are directly transferred into the microscope utilizing an inert-gas glove box plus a transfer holder. The high quality of such metallic Ni particles is shown in Fig. 2b. It has to be mentioned here, that organic residuals are pyrolyzed upon treatment in \( \text{Ar/H}_2 \) (Fig. 2b, graphitic microstructure around the particles) solving the common contamination problem. Figure 2c shows the obtained Ni-L\(_{2,3}\) reference spectra for metallic Ni and NiO that were already used to determine the composition of Ni precipitates (distribution of Ni\(^{2+}\), Ni\(^0\)) that are typically found at 8YSZ grain boundaries after the annealing in reducing atmosphere. The introduced procedure is applicable to preserve the state of almost any TEM sample and will prospectively be extended even to prepare the principal diffusion couples.


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Fig. 1: a) Spinodal decomposition of 8YSZ at 950 °C: a) coarsening of t''-YSZ precipitates within single 8YSZ grains and b) chemical variations across a Y-depleted region. c) Accelerated degradation of Ni-containing 8YSZ in reducing atmosphere (red data points) vs. oxidizing atmosphere (black data points).

Fig. 2: a) Ideal metallic reference particles for oxidation-state analysis: reduction in H2 and subsequent inert-gas transfer (reactor → glove box → transfer holder → microscope). b) Microstructure and structure of metallic Ni particles. c) Obtained Ni-L3 reference spectra. d) Oxidation-state analysis of Ni precipitates at 8YSZ grain boundary.