

Unveiling the Atomistic Processes of the Accelerated Decomposition of 8.5 mol% Y_2O_3 -stabilized ZrO_2 by Environmental TEM

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Yttria-stabilized Zirconia (YSZ) has been widely used as a structural or functional ceramic in harsh chemical environments and/or at high operating temperatures. For applications, its long-term stability has significance.

As the ternary Y_2O_3 - ZrO_2 system exhibits a miscibility gap, spinodal decomposition occurs depending on the Y_2O_3 content and the applied conditions. This particularly holds for 8–8.5 mol% YSZ, a common electrolyte material, e.g., for solid oxide fuel cells (SOFC) [1,2]. During operation around 900 °C, the spinodal decomposition of 8YSZ, which is characterized by microstructural coarsening and accompanying evolution of large chemical variations (Fig. 1b,c), leads to a significant degradation of the oxygen-ion conductivity (Fig. 1a, e.g., 40% within 5000 h at 950 °C) [1,2]. The decomposition rate is highly dependent on temperature, and may be strongly enhanced by the presence of trace elements, which possess different solubility in 8YSZ under oxidizing or reducing atmospheres.

Here, the accelerated decomposition of Ni-containing 8YSZ, as it commonly forms during SOFC manufacturing, is investigated in detail (Fig. 1a,d). It proceeds more than fifty times faster than the degradation of pure 8YSZ [3]. In order to elucidate the underlying mechanisms, the fundamental processes like Ni in-diffusion (oxidizing atmosphere) and Ni ex-solution/precipitation (reducing atmosphere) are investigated (Fig. 1d). The comprehensive investigation is based on the local analysis of the behavior of the dissolved Ni, meaning the evolution of its oxidation state and atomic configuration at different oxygen partial pressures, by *in situ* electron energy-loss spectroscopy (EELS, Fig. 1e) in an environmental transmission electron microscope (ETEM). Those measurements are complemented by global *in situ* X-ray absorption spectroscopy.

This study demonstrates that *in situ* ETEM experiments under application-relevant conditions are extremely useful to clarify complex phase transformation and solid-state diffusion processes on the nm-scale such as those here.

References:

[1] B Butz *et al*, SSI **177** (2006), pp. 3275

[2] B Butz *et al*, Acta Materialia **57** (2009), pp. 5480

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[4] B Butz acknowledges provision of sample materials by the IWE at KIT, Germany and the IEK-1 at FZ Jülich, Germany. The research is funded by the German Research Foundation, DFG grant no. BU 2875/2-1. Part of this work was performed at the Stanford Nano Shared Facilities.

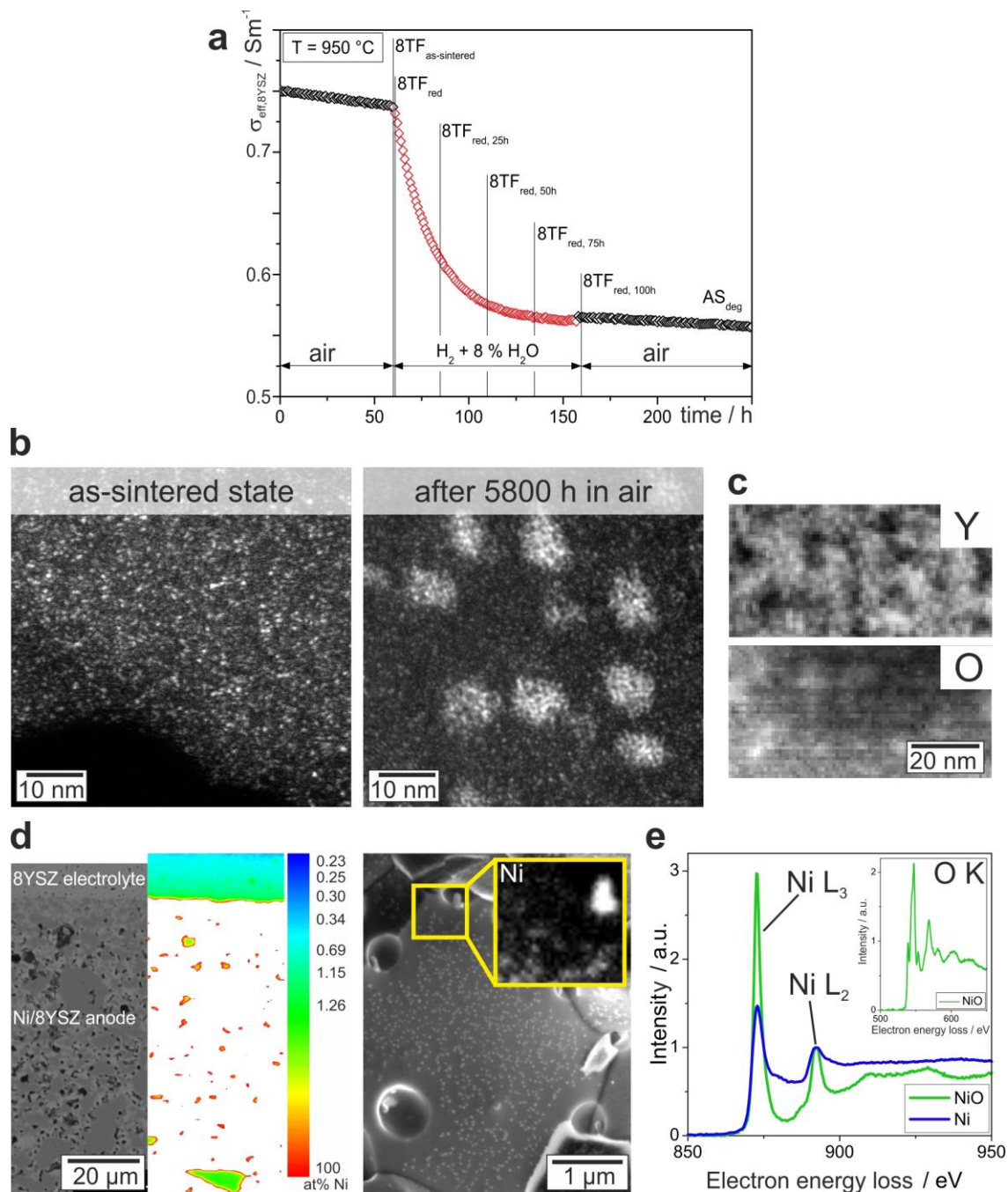


Figure 1. Accelerated degradation of oxygen conductivity of Ni-containing 8YSZ in H_2 (red), degradation rate in air (black) is similar to that of pure 8YSZ, b) microstructural (DF imaging) and c) chemical (STEM-EDXS/EELS) decomposition of pure 8YSZ after 5800 hrs at $950\text{ }^{\circ}\text{C}$, oxygen variations in c) are of the order of a few at%, d) in-diffusion of Ni into an 8YSZ electrolyte upon sintering of a solid oxide fuel cell (left, WDXS) and precipitation of dissolved Ni at 8YSZ grain boundaries upon annealing in H_2 (right), which drastically enhances cation mobilities within the 8YSZ and causes the acceleration of the decomposition (cf. 1a), e) EEL spectra of metallic and oxidized Ni species; near-edge structure clearly indicates the electronic configuration, while extended edge structures are used to determine atomic configuration.