Chemical instability as reason for degradation of ionic conductivity in the system Y_2O_3-ZrO_2

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Y_2O_3-doped ZrO_2 with 8.5 mol% yttria (8YSZ) is well-known as electrolyte for fuel cell applications since the ionic conductivity is maximal at this dopant content [1]. The considerable degradation of the ionic conductivity of 8YSZ at temperatures of about 1000 °C is undisputable [2, 3]. This degradation is accompanied by the coarsening of nanoscaled regions containing the tetragonal YSZ phase that are coherently embedded in the cubic matrix of the grains [3]. Understanding the reason for the degradation has become an important issue for the last 25 years. However despite numerous studies in the zirconia-rich region of the YSZ phase diagram degradation is not well understood. A suitable method to analyze the tetragonal phase is transmission electron microscopy (TEM) combined with energy-dispersive x-ray spectroscopy (EDXS) and electron energy loss spectroscopy (EELS) which were applied to analyze the local composition of as-sintered and aged 8YSZ on the nanoscale.

Polycrystalline 8YSZ electrolytes (TOSOH, Japan) were studied before (as-sintered) and after heat treatment in air (950 °C, 2000 h). The distribution of the tetragonal phase was investigated by dark-field imaging according to Butz et al. [3]. A C_s-corrected 300 keV FEI Titan was used for analytical experiments. In order to study the local oxygen and yttrium content EELS/EDXS line scans (step size 1 nm) were simultaneously recorded in thin sample regions with homogeneous thickness t ($5\ nm \leq t \leq 30\ nm$).

In addition to the ‘simple’ detection of the nanoscaled tetragonal precipitates (Figure 1a) [3, 4] the temporal instability was discernable in as-sintered 8YSZ. The contrast fluctuation in dark-field imaging is interpreted in terms of the local phase transition between the cubic and a tetragonal phase. In contrast, the tetragonal precipitates in the coarsened regions in aged 8YSZ as depicted in figure 1b remain statically. No chemical inhomogeneities were detected in as-sintered 8YSZ within the EDXS and EELS detection limits (Figure 2a). Analytical experiments clearly demonstrate the decomposition of 8YSZ on the nanoscale during the heat treatment. Quantitative EDXS shows that the coarsened tetragonal regions in aged 8YSZ are strongly depleted of Y ions (solid lines in figure 2b), whereas oxygen vacancies appear to accumulate close to those regions as marked by small arrows in figure 2b.

The observed microstructural fluctuation of nanoscaled regions of the tetragonal phase strengthens the assumption of a phase transition between the cubic and the metastable t’’ phase in as-sintered 8YSZ as proposed by Yashima et al. [5]. The interpretation of the observed microstructural features in the heat treated 8YSZ is more complex since the degradation is accompanied by the decomposition of the material on the nanoscale which is discussed to be of spinodal nature. This decomposition leads to strong variations of dopant ions and oxygen vacancies and is discussed as reason for the degradation of ionic conductivity in 8YSZ since the maximum of ionic conductivity is at 8.5 mol% Y_2O_3.

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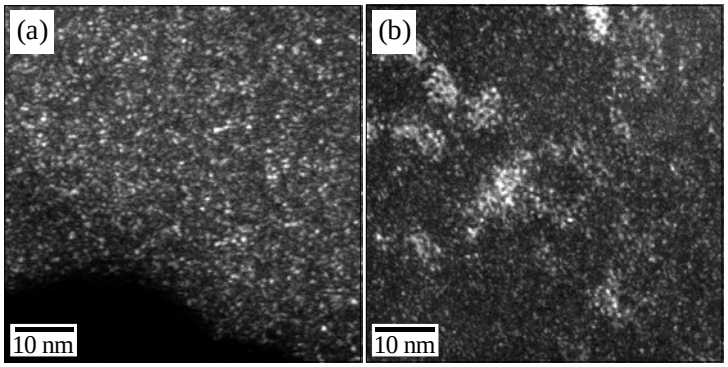

Figure 1. Dark-field images of (a) as-sintered 8YSZ and of (b) heat-treated 8YSZ: tetragonal precipitates appear bright while the cubic matrix is dark.

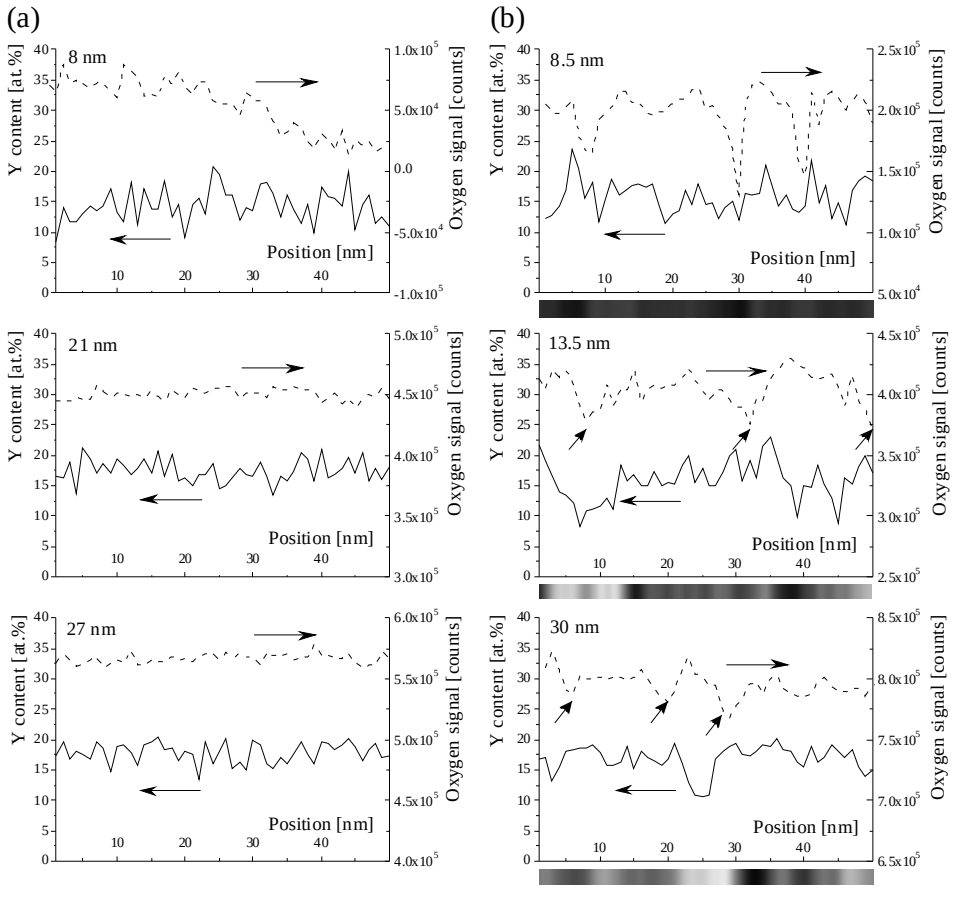

Figure 2. Analytical data of representative line scans: solid lines depict the Y content on the cationic sub-lattice (quantitative EDXS), dashed lines represent thickness-normalized oxygen net signal of EEL spectra of (a) as-sintered 8YSZ and (b) heat treated 8YSZ. In (b) the intensity of HAADF STEM images along the line scans is presented to correlate local chemistry with the position of coarsened tetragonal regions (bright contrast).

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