

Electrochemically Driven Redox Phenomena in Oxide Ion Conducting Solid Electrolytes

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Solid oxide fuel cells (SOFC) have gained interest due to the demands for sustainable energy sources and reached a mature state of development, but there are still challenges in materials engineering for solid state electrolysis cells (SOEC). In electrolysis mode, degradation effects due to electrochemical redox processes caused by the opposite current direction can occur. Electric current induced intermediate redox phenomena also gain importance for techniques like field-assisted flash sintering (FAST) and spark plasma sintering (SPS). [1] Generally, when considering two mixed electronic and ionic conductors, such phenomena will occur, if the transference number of the electronic charge carriers is changing at the interface. This includes reduction phenomena at electrode interfaces as well as oxidative pore formation in the interface between solid electrolytes and mixed conductors. [2, 3]

We want exemplarily focus on the formation of blackened zirconia, known since the first reports by Casselton [4] and subject of various studies in recent decades. In future low temperature SOECs, ceria-based electrolytes are even more prone to reduction phenomena. The electroreduction of yttria-stabilized zirconia (YSZ) leads to a dendrite-shaped reaction front of a reduced phase moving to the anode. In contrast to the pristine YSZ, reduced YSZ is a good electronic conductor, leading to an interface with a large change of the electronic transference number. The composition and structure of the oxygen deficient phases is still not cleared in detail. It is reported that the mechanical properties of single crystal or ceramic material degrades significantly.

New investigations on YSZ single crystals reveal that electroreduction lead to the formation of checkerboard-like structures on the surface above an oxygen deficient region in the surface. Transmission electron microscopy (TEM) have been employed. [5] In this region a (presumably) cubic phase with a composition of $(Zr,Y)_2O$ can be found. In addition, an even higher reduced, non-cubic phase with a composition of approximately $(Zr,Y)_9O$ exists, forming belts close to the surface. The lattice constants have strongly shrunk. There are many stacking faults in the strongly reduced phase and misfit dislocations in the interface to the less reduced phase. The strong change of the molar volume may be the origin of strain field, resulting in the checkerboard-like surface structure and for the deterioration of the mechanical properties.

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