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ABSTRACT:

Electrochemically Driven Redox Phenomena in Oxide Ion Conducting Solid Eletrolytes

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Fuel cells have gained particular interest due to the demands for sustainable energy sources. Solid oxide fuel cells (SOFC) have reached a mature state of development, in the case of solid state electrolysis cells (SOEC) there are still challenges in materials engineering. In electrolysis mode, i.e. if an external electric current is driven, degradation effects due to electrochemical redox processes can occur, which may limit the lifetime. Electric current induced redox phenomena also gain importance for the preparation of ceramic materials using field-assisted flash sintering (FAST) and spark plasma sintering (SPS) techniques. Intermediate reduction during the sintering process was recently reported. [1]

In the first part of this contribution, different electrochemical redox processes that can generally take place in an oxide ion conducting solid electrolyte will be highlighted. Electroche-mical redox phenomena will occur if the transference number of the electronic charge carriers is changing at an interface. This includes reduction phenomena at electrode interfaces as well as a (oxidative) pore formation at interfaces between solid electrolytes and mixed conductors. [2, 3] Electroreduction phenomena will lead to a reaction front of the reduced material moving to the anode side, as reduced solid electrolytes are usually much better electronic conductors. Metallic inclusions/particles in solid electrolytes can be regarded as internal electrodes, acting as an electric “short circuit”. This will also lead to reduction phenomena on one particle side and in an oxide ion conductor to the built-up of a high oxygen pressure on the other particle side.

In the second part the nature of blackened zirconia is focused, formed by electroreduction of yttria-stabilized zirconia (YSZ). In contrast to the solid electrolyte YSZ, (reduced) blackened YSZ is a good electronic conductor and has been the subject of various studies in recent decades. New investigation on YSZ single crystals reveal strong strain fields leading to the formation of checkerboard like structures on the surface above highly oxygen defi¬cient regions below the surface. Transmission electron microscopy and x-ray photoelectron spec¬troscopy have been employed to understand their physical nature. [4] Zr^{4+} is reduced to lower valences, Zr^{2+} and even Zr^{0} has been found. Zr (II) suboxides are formed, leading to the enhanced electronic conductivity.

The change of the molar volume leads to a structural distortion. This may be the origin of the strain fields and an explanation of the often reported deterioration of the mechanical properties.

[1] T. P. Mishra, R. R. I. Neto, G. Speranza, A. Quaranta, V. M. Sglavo, R. Raj, O. Guillon, M. Bram and M. Biesuz, Scripta Materialia 179, 55 (2020)
[2] J. Janek and C. Korte, Solid State Ionics 116(3-4), 181-195 (1999)
[3] F. Tietz, D. Sebold, A. Brisse and J. Schefold, J. Power Sources 223, 129-135 (2013)
[4] Chr. Rodenbücher, K. Szot, D. Wrana, B. R Jany, F. Krok and C. Korte, J. Physics: Energy 2(3), 034008 (2020)