Abstract

The present work aims at the development of an ageing-resistant and sulfur-tolerant high-performance anode for the metal supported solid oxide fuel cell (MSC). As a starting point, the current MSC concept of Plansee with an Ni/YSZ cermet as anode material, which is already established in the fuel cell technology, is used. The work’s main innovation is the replacement of the purely ionic conducting YSZ phase by a mixed ionic/electronic conducting oxide Ce$_{1-x}$Gd$_x$O$_{2-δ}$ (GDC).

In the first part of the work, a comparison of the sintering behavior between GDC and the reference material YSZ was made. The results from studies on powder compacts and by means of dilatometry indicate that the sintering atmosphere (air/hydrogen) does not affect the shrinkage of YSZ, whose maximum sintering rate is reached at $T_{\text{max}} = 1330$ °C. In contrast, GDC’s shrinkage is strongly increased in reducing hydrogen atmosphere compared to the shrinkage in air. The maximum sintering rate $T_{\text{max}}$ is noted at 1100 °C for GDC in hydrogen. In reducing atmospheres and at high temperatures, the enhanced solid state diffusion of GDC is caused, according to literature, by the following factors: (i) an increased quantity of oxygen vacancies, (ii) a change of valence from Ce$^{4+}$ to Ce$^{3+}$ and (iii) a reduced Gd/Ce lattice mismatch induced by the valence change of Cerium.

Based on these findings, a series of cermet anode layer samples with different Ni/GDC ratios and sintering conditions was prepared and characterized, from which a set of Best Choice manufacturing parameters (sintering at 1100 °C, +3 K/min, 3 h, H$_2$) with a cermet ratio 60/40 wt.% for Ni/GDC was derived.

An impedance spectroscopical characterization of symmetrical cells for partial decoupling of particular electrode processes was performed in a single-compartment system. The Ni/GDC anode stands out both by a much lower polarization resistance and a small temperature dependence as compared to the Ni/YSZ anode. For both anode types two electrode processes could be decoupled, which differ in their relaxation times. One of the processes is associated with a limitation due to gas diffusion and the second process is linked to a hydrogen surface reaction. The entire polarization of the Ni/GDC anode is dominated by a gas diffusion limitation, which additionally is superimposed by a further unknown electro-catalytic process. The greatest optimization potential of the Ni/GDC anode, according to conducted experiments, lies therefore within the optimization of the anode microstructure.

Single cell measurements served to demonstrate the functionality of the Ni/GDC anode within the real MSC system, with comparing of the cell performance to the Plansee MSC. At 700 °C, the MSC based on a Ni/YSZ anode (with an anode layer thickness of $d = 3$ µm) reached a current density of 0,55 A/cm$^2$ at the operating point of 0,7 V. A subsequent variation of the Best Choice Ni/GDC-based MSC with an increased anode layer thickness of $d = 8$ µm led to an improvement of performance by more than 100 %, by achieving $j_{0,7V} = 1,12$ A/cm$^2$ at 700 °C.

Concluding from those results: (i) compared to the Plansee Ni/YSZ anode, the electrochemical reaction zone of Ni/GDC extends an electrode layer thickness of 3 µm, (ii) the cell voltage of Ni/GDC based MSC is only slightly reduced by an activation overvoltage, what presumably can be attributed to a high catalytic activity and a low temperature dependence of the Ni/GDC system, (iii) the anode performance of Ni/GDC anodes is clearly limited by gas diffusion, what was shown by means of symmetrical cells as well as single cell measurements, which is why a high optimization potential in terms of improved microstructure, with attention to high porosity and enhanced catalytic surface, is on hand.