Solid oxide cells for steam electrolysis

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Solid oxide cells for steam electrolysis

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Introduction
An alternative design of the planar cathode supported cells (SOFC) for steam electrolysis is meant to overcome the high degradation rates experienced on the traditional SOC with electrodes from Ni-YSZ and LSM-YSZ cermet, when running at intermediate temperatures, 750–850°C, and current densities above -1 A/cm² [1-3], which are an interesting regime for operation in large-scale hydrogen production and energy storage.

In order to avoid Ni as the electron conductor in the cell support and Ni-grain growth in the cathode, both the cell and the cathode are supported by an electrically conductive ceramic based on porous strontium titanate and the cathode is then deposited as nano-sized particles on this conductive backbone [4]. Further, both electrodes are based on ceramic oxides that exhibit mixed electrical and ionic conductivity.

Experimental
The half-cell was produced by simultaneously tape casting the electrolyte from Sc2O3-doped zirconia and the cathode backbone from donor-doped strontium titanate, Sr0.95Ti0.9Nb0.1O3 (STN). After drying, the cell support from STN was cast on top and the half-cell was further processed through binder removal in air and firing in 5%H2/N2 atmosphere at 1300°C for 4 hours. The steam electrode (cathode) of nano-crystalline Ce0.8Gd0.2O1.9 (CGO) with 10wt% Ni was applied to the porous backbone by impregnation and drying of a nitrate-based precursor solution. Subsequently, a CGO-protective layer was applied to the anode face by spin-coating and the cell was dried and fired in N2 at 750°C for 2 hours. By screen printing the oxygen electrode (anode) of an LSCF-CGO composite and subsequently the current collector (LSM-LSC) the cell was completed.

The cell (5x5 cm) was sandwiched between layers of Pt-mesh and mounted with a boron-aluminosilicate glass sealing in an aluminia test fixture before being subjected to initialisation at 750°C in 5%H2/N2 for 2h and subsequently in H2 for 1h.

The cell was characterized by electrochemical impedance spectroscopy (EIS) at OCV, in fuel cell and in electrolysis modes and by IV-curves with 4–50% H2O in H2 to the cathode and O2 to the anode. Electrochemical impedance spectra were recorded from 0.06 Hz to 82 kHz with 12 points per decade during the electrolysis tests and analysis of the difference in impedance spectra (AdIS) was performed [5]. From the impedance spectra, the ohmic or serial resistance (Rs) can be found as the value of the real part of the impedance measured at 82 kHz. The polarization resistance (Rp) can be calculated as the difference in real part of the impedance at 0.38 Hz and at 82 kHz.

Performance testing was run at 850°C during 500h at constant load conditions of 0.5 A/cm² in 50% H2O2H2 mixture. Oxygen was swept over the oxygen electrode.

Results and Discussion
The porous STN-structures showed overall porosities of 29% and 14%, and average pore sizes of -3 μm and -0.5 μm for the cell support and the electrode backbone, respectively. Figure 1, which shows the electrode backbone less open than desired. The barrier layer sintering temperature was 180 MPa. The electrolyte often exhibited few pinholes after sintering, which usually disappeared after application of the CGO-barrier layer. However, such pinholes may open again, when the cells are heated for testing. The barrier layer sintering temperature was lower than usually employed.

The result of cathode impregnation is illustrated in Figure 2, and it can be observed that the final CGO/YSZ composite preferably filled up cavities in the electrode backbone. Direct measurements on the ceria concentration showed that [Ce] = 5.8 wt% and 9.2 wt% in the cell support and electrode backbone, respectively. The cell performed promising after initialisation at 750°C, particularly the polarisation resistance was low, Rp < 0.15 Ωcm² for 50% H2O/H2 at 750°C. The serial resistance, Rs, varied reversibly at 750°C from 0.22 Ωcm² to 0.28 Ωcm² by varying the steam concentration from 4% to 50% but later, during the performance testing at 850°C and 50% H2O/H2, Rs increased irreversibly from 0.12 Ωcm² at a rate of 1 mΩcm² per hour. Simultaneously, Rp increased by 0.4 mΩcm² per hour, which rates are orders of magnitude above the threshold for industrial interest. Measurement of the cell EMF and the oxygen partial pressure, pO2, in the feed and off gases revealed that a cross-over leak at about 5% of the nominal feed flow likely explains the high degradation rates of the electrode performance, almost from the very beginning. The so-called gas shift analysis, cf. Figure 3, also supports this by showing degradation at both electrodes after the performance test.

The mechanisms for the irreversible change of Rs has not been identified in detail, but redistribution during test of the elements, eg. titanium, that were shown to diffuse between the STN and the ceria phases during half cell sintering, have been observed and may be linked to this.

Conclusion and outlook
Made and tested in a limited number only, the STN-based solid oxide electrolysis cells nevertheless showed an interestingly high initial performance at 750°C, as the ASR was between 0.37–0.45 Ωcm² at 4-50% steam, and they also compare well to highly optimized cells, based on the Ni-YSZ and LSM-YSZ cermet where typical ASR-values at 750°C are 0.39–0.45 Ωcm². As the serial resistance, Rs, was a significant contributor to the overall ASR in the STN-based cells, further optimisation of the cell processing route is likely to reduce the ASR.

In spite of the high degradation rates observed at 850°C and in high steam concentration, the cell architecture may still be an interesting option for an efficient low-temperature cell if the degradation mechanisms can be understood.

References

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