Impact of Initial Reduction and H2/H2O Contents on the Performance and Microstructure of Ni Cermets

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Impact of initial reduction and H_2/H_2O contents on the performance and microstructure of Ni cermets

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A direct relation between microstructural properties and degradation of Ni cermets in solid oxide cells (SOCs) has been well established. Usually related to changes that occur in the initial microstructure during operation, degradation, such as agglomeration of Ni [1,2] and poisoning from contaminants [3], has a known dependence on temperature [1] and water partial pressure [2] amongst other operating parameters.

Although some degradation issues can be tackled by improved stack designs, system solutions, and improved quality control [4], design and stabilisation of a Ni cermet microstructure that exhibits adequate performance throughout the envisaged lifetime of a SOC remains somehow elusive and only further understanding can help solve the pressing degradation issues. So being, this work presents a systematic assessment of how parameters such as initial microstructure, temperature, time and H_2/H_2O contents impact the performance of different Ni cermet electrodes and supports with technological interest for Risø DTU anode supported SOCs.

The impact of electrode composition, initial microstructure and operating parameters, such as temperature and steam content, on performance and degradation was determined using symmetric cells. The latter were manufactured only by tape-casting or by combination of tape-casting and spraying methods. All cells contained either Ni/YSZ or Ni/ScYSZ anodes, Ni/YSZ anode supports with varying microstructures and YSZ or ScYSZ electrolytes. Different cell designs were also used, from the more common thick electrolyte to cells with thin electrolytes and two or one anode support. 6 mm x 6 mm sintered pieces were tested in a specially designed rig [5]. The cells were heated up in air, with the initial reduction temperature varied between 1000 °C and 850 °C and then tested in H_2 atmospheres, with varying contents of H_2O, between 850 and 650 °C. Degradation studies were mainly performed at high steam contents (between 50 % and 70 % H_2O) for varying periods of time, following initial fingerprinting of the cells.

The performance and impact on degradation were assessed by electrochemical impedance spectroscopy (EIS) and the impedance spectra analysed by a combination of distribution of relaxation times (DRT) [6] and complex nonlinear least-squares (CNLS). Microstructural analysis was performed on pre-tested and post-tested cells using scanning electron microscopy (SEM) and low-voltage SEM, and will be used to explain the observed electrochemical behaviours.

Figure 1 shows two very different degradation behaviours for two distinct symmetric cells with single anode-support and Ni/ScYSZ or Ni/YSZ electrodes. In addition to different electrodes, both support structures also exhibited distinct microstructures. Both cells were simultaneously tested at 850 °C, 72 % H_2O for a period exceeding 100 h. As can be seen, most of the increase in resistance occurs on the series resistance (R_s) in the ScYSZ based cell, whereas in the case of the YSZ based cell the highest increase was seen for the polarisation resistance (R_p). LV-SEM micrographs revealed significant different levels of Ni agglomeration between the two cells, but also a different impact on the two electrodes for the same ScYSZ cell, depending on whether they were interfacing or not with the anode support.

This type of information can enable further understanding of the mechanisms and conditions for degradation, simultaneously providing valuable guidelines for the design of electrode microstructures and full cells that exhibit adequate levels of performance and stability for long term operation.

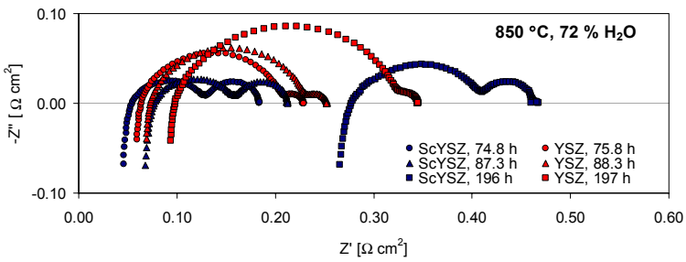

Figure 1: Nyquist plot of impedance data for a ScYSZ and a YSZ based cell, with different supports, obtained at different times during a degradation test performed at 850 °C, 72 % H_2O. Time shown corresponds to time elapsed from the start of the test.

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