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THE FORMATION FEATURES OF A SOLID OXIDE FUEL CELL AND ITS INFLUENCE ON THE PERFORMANCE

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Solid oxide fuel cell (SOFC) is a promising electrochemical source of electricity presenting high efficiency, tolerance to various types of fuel, and low pollution. At the moment, the most commercialized electrochemical cells are based on zirconium dioxide stabilized by yttrium (YSZ) or other rear metal. The demand for new materials to apply as SOFC electrolytes or electrodes is increasing as well. However, the impact of the microstructure is often left out of the SOFC related research. Currently, the majority of studies involving SOFCs are carried out on cells with a thin-film electrolyte instead of a bulk supporting electrolyte. This approach is meant to reduce the internal resistance of the cell and to enhance performance. There are several different ways to produce thin oxide films and among them, dip-coating and tape casting are ones of the most prominent. These techniques require relatively simple equipment and could produce films of a thickness of around 10 μm. Although dip-coating and tape casting are used frequently in oxide electrochemical cell manufacturing, the results are often controversial. This happens because small adjustments in those methods could lead to drastic differences in microstructure and performance.

In this work, we investigate electrochemical properties and the long-term durability of a SOFC with supporting Ni-YSZ anode, SSZ electrolyte, LNF cathode, and an extremely thin protective SDC layer. We describe a convenient way to prepare the SOFC and discuss the influence of synthesis and sintering properties on its performance and long-term durability.

Here we produced supporting current collector layer of Ni-YSZ (50 wt.% of YSZ) anode by tape-casting technique and deposited thin AFL using the deep coating method. After the sintering of the supporting layer at 1550 °C, the porosity was found to be around 30 %. An obvious solution would be the lowering of the temperature, but the sintering at lower temperature does not allow us to obtain dense electrolyte film, hence the cell must bee eventually undergo high-temperature sintering. Thus, starch was added to the suspension prior to the casting as a pore former. The desired porosity window of 50 – 60 % was achieved with 30 wt.% of the pore former (see Fig. 1).

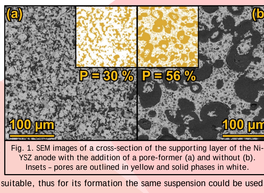


Fig. 1. SEM images of a cross-section of the supporting layer of the Ni-YSZ anode with the addition of a pore-former (a) and without (b). Insets – pores are outlined in yellow and solid phases in white.

For the functional layer, the porosity of 30 % is suitable, thus for its formation the same suspension could be used, but without pore former.

This work focuses on the influence of formation factors of SOFCs. The supporting Ni cermet anodes produced by the tape-casting technique and the anode functional layer, electrolyte, and two cathode layers are obtained using dip-coating. The most advantageous composition of a dispersive medium is developed for each level of a cell. One of the most challenging parts of obtaining a ceramic multilayer cell is co-sintering of the layers. To adjust all of the parameters of the process heating microscopy was used, as it is shown in Fig. 2.

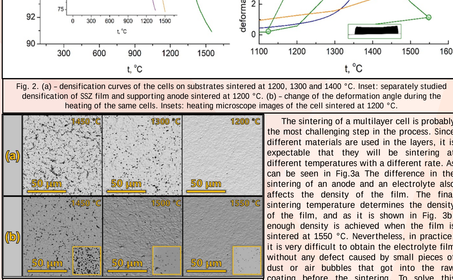


Fig. 2. (a) – densification curves of the cells on substrates sintered at 1200, 1300 and 1400 °C. Inset: separately studied densification of SSZ film and supporting anode sintered at 1200 °C. (b) – change of the deformation angle during the heating of the same cells. Insets: heating microscope images of the cell sintered at 1200 °C.

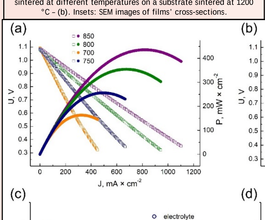


Fig.3. SEM images of the SSZ film surface sintered for 5 hours at 1550 °C on substrates sintered at 1200, 1300 and 1450 °C – (a); the film sintered at different temperatures on a substrate sintered at 1200 °C – (b). Insets: SEM images of films' cross-sections.

The sintering of a multilayer cell is probably the most challenging step in the process. Since different materials are used in the layers, it is expectable that they will be sintering at different temperatures with a different rate. As can be seen in Fig.3a The difference in the sintering of an anode and an electrolyte also affects the density of the film. The final sintering temperature determines the density of the film, and as it is shown in Fig. 3b, enough density is achieved when the film is sintered at 1550 °C. Nevertheless, in practice, it is very difficult to obtain the electrolyte film without any defect caused by small pieces of dust or air bubbles that got into the raw coating before the sintering. To solve this problem, coatings were deposited twice, so the small defects were canceled out by the next layer and the resulting film become gas-tight.

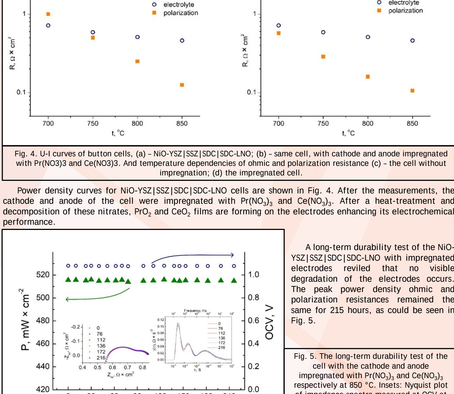
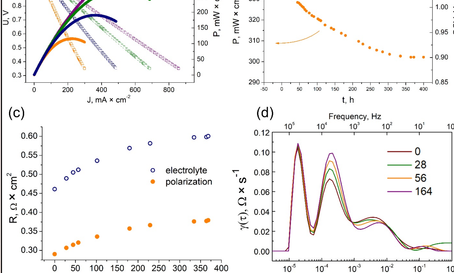


Fig. 4. U-I curves of button cells, (a) – NiO-YSZ|SSZ|SDC-LNO; (b) – same cell, with cathode and anode impregnated with Pr(NO3)3 and Ce(NO3)3. And temperature dependencies of ohmic and polarization resistance (c) – the cell without impregnation; (d) the impregnated cell.

Power density curves for NiO-YSZ|SSZ|SDC-LNO cells are shown in Fig. 4. After the measurements, the cathode and anode of the cell were impregnated with $Pr(NO_3)_3$ and $Ce(NO_3)_3$. After a heat-treatment and decomposition of these nitrates, PrO_2 and CeO_2 films are forming on the electrodes enhancing its electrochemical performance.



A long-term durability test of the NiO-YSZ|SSZ|SDC|SDC-LNO with impregnated electrodes reviled that no visible degradation of the electrodes occurs. The peak power density ohmic and polarization resistances remained the same for 215 hours, as could be seen in Fig. 5.

Fig. 5. The long-term durability test of the cell with the cathode and anode impregnated with $Pr(NO_3)_3$ and $Ce(NO_3)_3$ respectively at 850 °C. Insets: Nyquist plot of impedance spectra measured at OCV at different times and corresponding DRT curves.

To evaluate the influence of the barrier SDC layer on the SOFC's performance, the cell without the SDC layer was tested. The peak power density of the NiO-YSZ|SSZ|SDC-LNO was found to be 337.3 mW×cm-2 which is already 29% lower than the peak power density of the same cell with the barrier layer (see. Fig.6). Long-term measurements have shown that the degradation continued even after the sintering stage, despite that the sintering of the cathode was carried out at 1200 °C and durability test at 850 °C, so one could suggest that the most of the degradation should have happened during high-temperature sintering, the cell continued to lose performance for almost 400 hours (see Fig.6 (b) and (c)).

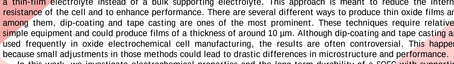


Fig. 6. (a) – U-I curves of the NiO-YSZ|SSZ|SDC-LNO; (b) – long-term durability of this cell at 850 °C; the evolution of the ohmic and polarization resistances during the durability test; (c) – corresponding DRT curves

Cells with and without the barrier layer were studied by SEM and EDX after 200 hours of exposure to the SOFC operation conditions. Even though the performance of the cell without the SDC layer was lower by 28.7 % after sintering and 200 hours of the exposure, the EDX maps of La and Zr does not show a distinguishable difference, as shown in Fig 7. However, the zirconium profile across the cathode and electrolyte layers changes differently for the cells with and without the SDC barrier layer. It can be seen In Fig. 7. (b), that zirconium distribution in the cell with the SDC barrier layer consists of a plateau and in case of the cell without the barrier layer zirconium content increases linearly with distance. This means that the thin barrier layer prevents interlayer diffusion, and its absence leads to Zr atoms in the cathode layer, which probably complicates the oxygen ions diffusion from the cathode to the electrolyte.

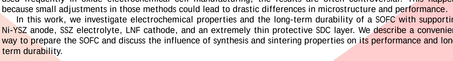


Fig. 7. SEM images and EDX maps of (a) - NiO-YSZ|SSZ|SDC-LNO (without barrier layer); (c) - NiO-YSZ|SSZ|SDC|SDC-LNO (with barrier SDC layer); (b) Profile of zirconium distribution in these cells on the cathode/electrolyte boundary.

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