Impedance Behavior of LSCF/YDC/LSCF Symmetrical Half Cell Prepared by Plasma Spray

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Abstract
Impedance studies of electrolyte supported symmetrical half cells La0.6Sr0.4Co0.2Fe0.8O3-/Ce0.85Y0.15O2-/La0.6Sr0.4Co0.2Fe0.8O3- with electrodes deposited by atmospheric plasma spraying (APS) show that the applied technique influences reversibly the substrate properties, introducing additional contribution to the interface substrate/electrode. After thermal treatment in temperature range 100-800°C during the impedance measurements, an annealing effect is observed. It eliminates the additional increase of the electrolyte resistivity and increases slightly the polarization resistance. The observed effect could be related to thermally and/or mechanically induced local microstructure defects, caused by the APS procedure. The obtained results show that for stabilization of the cell’s performance, annealing should be performed after the APS deposition. It can be supposed that an appropriate annealing atmosphere may prevent the electrodes deactivation.

Keywords: electrochemical impedance spectroscopy; atmospheric plasma spraying; cathode performance; symmetrical half cells; relaxation

1. Introduction
The power of SOFC is knowingly limited by the cathode performance. For improving the oxygen electrode in the so called IDEAL-Cell design, based on application of three independent chambers for hydrogen, oxygen, and water [1,2], symmetrical half cells were fabricated using several techniques and tested by impedance spectroscopy. This paper presents results obtained on electrolyte supported half cells La0.6Sr0.4Co0.2Fe0.8O3-/Ce0.85Y0.15O2-/La0.6Sr0.4Co0.2Fe0.8O3-. They were produced in two steps: (1) cold pressing and sintering of YDC electrolyte at 1350°C for 5h; (2) atmospheric plasma spraying (APS) of thin porous electrodes on both sides of the YDC pellet [3].

2. Experimental
The electrolyte powder was prepared by Marion Technologies. The electrode material was supplied by HC Stark and agglomerated by Marion Technologies. This procedure ensures partial melting of the particle surface and conservation of the porous inner side of the particle for better gas distribution and specific surface area. While plasma spraying, several parameters have influence on the resulting microstructure. For example surface roughness and substrate temperature
influence the deposition. Therefore the pre-sintered substrates were sandblasted in order to increase the roughness. In addition to that particle velocity and temperature in flight was monitored continuously to avoid the complete melting of the splats. All these parameters were systematically modified to achieve high gas permeability rates and high deposition efficiency in the resulting layers. Plasma sprayed porous layers along with the YDC pre-sintered substrate are presented in Fig. 1. Partially melted agglomerated particles can be seen within the coating. Sufficient porosity was successfully achieved in the resulting oxygen electrode functional layers. The substrate was heated from the back side in order to reduce the temperature difference between the partially melted particles and the impact surface. This temperature difference may lead to thermal shocks that result in cracks in the sintered ceramic substrate.

![Fig.1. Microstructure of the cathodic symmetrical half cell: (a) and (b) - cathode/electrolyte interface; (c) and (d) - zoom in the porous electrode.](image)

The impedance measurements were performed on Solartron 1260 FRA over frequency range 10 MHz - 0.1Hz with density 5 points per decade in temperature interval 100- 800°C. Both potentiostatic and galvanostatic regimes were applied, depending on the cell impedance, which is governed by the temperature. For lower temperatures, where the sample resistance is in the MΩ range, the studies were carried at amplitude 200 mV, which was reduced to 50 mV above 200°C. At temperatures above 700°C the impedance data quality was increased by applying galvanostatic regime with amplitude 5 - 20 mA. Configuration of the cell with thick electrolyte support (about 2 mm) avoids distortions in the impedance measurements coming from the misalignment of the working and counter electrodes [4-6].
The performance of impedance measurements in a wide temperature range ensures characterization of both the electrolyte and the electrode, which was used for investigating the effect of the more severe plasma spraying conditions on the ceramic substrate. For this purpose an electrolyte supported half cell prepared by tape casting (TC) of the electrodes was used for comparative analysis.

3. Results and Discussion

The first observations of the APS sample at low temperatures, where the electrolyte bulk resistivity can be separated from that of the grain boundaries, show drastic increase of the grain boundary contribution and its frequency dispersion (semicircle II in Fig. 2). Those results could be attributed to some changes in the substrate/interface microstructure caused by the APS procedure. Measurements with another APS sample (Fig. 2b) confirmed the observed behavior, which was the reason for the performance of a more detailed investigation.

At 300°C semicircle II splits into two strongly depressed arcs (IIA and IIB in Fig 3a). The next measurement cycles (from 100°C to 800°C) give stable and reproducible results, which, however, differ from those obtained during the first measurement (Figs.3b, 4).

Fig. 2. Complex plane impedance diagrams of symmetrical half cells with electrodes deposited by TC (□) and APS (○).

Fig. 3. Complex plane impedance diagrams of symmetrical half cell with electrodes deposited by APS: (a) first measurement cycle; (b) first (○) and second (□) measurement cycles.
The comparison of the data obtained from the first and from the second measurement cycles identifies step IIA as the grain boundaries contribution (Figs. 3a, 4). Obviously the impedance described with segment IIB is connected with the plasma spraying. Its position is in favor of the hypothesis for microstructure changes at the interface electrode/electrolyte, which disappear after the first measurement cycle, i.e. after thermal treatment up to 800°C.

At temperatures above 500°C, where the electrode reaction is well pronounced, two separated frequency dependent steps are observed (Fig. 5). The resistivity of the second (low frequency) process, with impedance shape typical for transport limitations [6-8], increases after the first measurement cycle.

The impedance diagrams, as well as the Arrhenius plots for the polarization resistance of TC and APS half cells show comparable results in the temperature range 600°C - 700°C with slightly lower polarization resistance of the TC sample above 650°C (Fig. 6).

For a deeper inside into the observed phenomena, Differential Impedance Analysis [7, 8] will be performed.
Fig. 6. Complex plane impedance diagrams of symmetrical half cells with electrodes deposited by TC (□) and APS (○) - second measurement cycle: (a), (b), (c); (d) - corresponding Arrhenius plots: (■) TC sample with $E_a= 1.97$ eV; (▼) APS sample - first measurement cycle with $E_a= 0.97$ eV; (●) APS sample - second measurement cycle with $E_a= 1.34$ eV.

4. Conclusions

Impedance studies of LSCF/YDC/LSCF electrolyte supported half cells show increase of the electrolyte resistivity after APS deposition, combined with good performance of the electrodes. This phenomenon could be related to thermally and/or mechanically induced local microstructural defects at the interface substrate/electrode. After the first measurement, performed in the range 100-800°C, which can be regarded also as an annealing cycle, the electrolyte resistivity decreases to its values before the APS treatment, while the polarization resistance slightly increases. For stabilization of the cell’s performance after the APS deposition, an annealing step is offered. It can be supposed that an appropriate annealing atmosphere may prevent the observed electrodes deactivation. This conclusion should not be generalized, but attributed to the investigated samples and preparation technology for electrodes deposition.

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