# First results on a $(La,Sr)CrO_3$ anode fed with methane

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Strontium doped lanthanum chromite (LSC) appears as a promising anode material due to its satisfactory electronic conductivity, its thermal expansion coefficient close to that of YSZ, and its stability under reducing environment. Moreover, if the anode is directly fed with methane, LSC is known to have an extremely low activity towards carbon deposition. In this work electrochemical characterizations of LSC anodes tested under a steam-methane mixture are presented. Their objective is to verify the absence of carbon deposition and to estimate the amount of steam reforming occurring without catalyst.

Cells used in this work have a geometry specific of the electrochemical test bench with a thick electrolyte substrate made of $ZrO_2$ powder stabilized with 8%mol $Y_2O_3$ (YSZ). The cathode material is a $(La,Sr)MnO_3$ perovskite The two processes used to deposit electrode layers, i.e. plasma spraying and wet spraying, are detailed. Electrochemical characterizations of these cells have been performed at 900°C under air (1 Atm) on the cathode side and either hydrogen and argon or a mixture of methane-steam and argon at the anode side with a C/S ratio of 1.5 and a total pressure of 1 Atm.

- Polarization curves obtained under hydrogen on both type of anodes, appear to be rather similar. Their analysis leads to very close values of overvoltages, activation resistances and exchange currents. These values are found disappointing.
- Electrochemical impedance spectra recorded under methane have been analyzed in order to determine kinetic parameter values (fig. 1). Plasma sprayed electrodes show a stable behavior with no significant evolution of activation resistance nor exchange current upon time. This result, unless it is validated by appropriated analysis, tends to indicate that no severe carbon deposition occurs within the anode while operating with methane.
- Chemical composition of anodic exhaust gas has been followed according to the time and to the value of imposed current density through the cell. The obtained results show that, in these conditions, only a small fraction of the incoming methane undergoes steam reforming. As expected, the higher the operation temperature the higher the reformed fraction. The CO electro-oxidation reaction would have a significant contribution in the current production.
- Overvoltage curves ($\eta(I)$ deduced from polarization curves V(I)) are found to have a very specific and reproducible shape. A limiting $CH_4$ adsorption mechanism allows to propose a good modeling of the experimental data.

The microstructures of both types of anodic layer, wet sprayed or atmospheric plasma sprayed (fig.2, 3), appear to be rather different in terms of grain size and porosity distribution. The main common point is the brittle nature of the interface between LSC and YSZ. This brittle interface could explain the high and similar activation resistances measured on both cells and could hide any other effect that should have normally be expected from microstructures having different specificities.

In order to improve the interfacial toughness of LSC on YSZ, some authors suggest introducing an intermediate layer. In this work, an attempt is made to enhance directly the reactivity of the two ceramics by modifying the oxygen stoechiometry within the LSC powder. After deposition, upon thermal annealing, oxygen vacancies would diffuse to restore a continuous gradient across the interface generating the expected reactivity between LSC and YSZ. Some first samples exhibit promising adhesion properties.

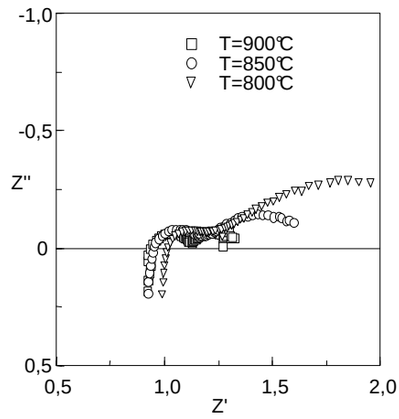


*Figure 1: Impedance spectra for a plasma cell fed with water/methane mixture. Ratio $CH_4/H_2O=1.5$.*

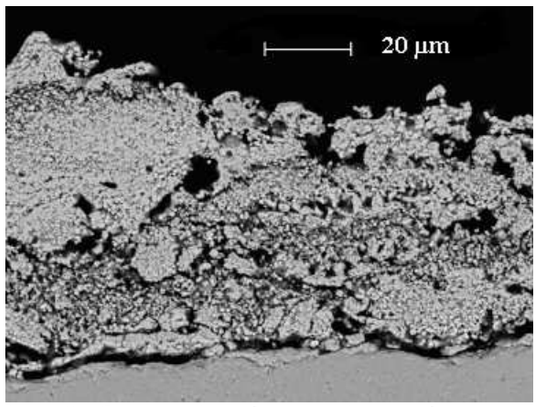


*Figure 2 : Cross section of the anodic layer from the cell elaborated by plasma deposition.*

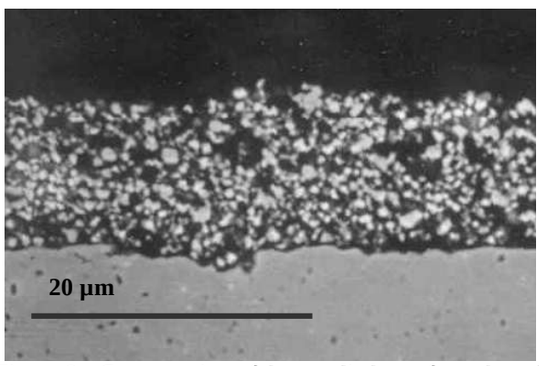


*Figure 3 : Cross section of the anodic layer from the cell elaborated by spray deposition.*