Microwave assisted self-combustion synthesis and electrochemical performance of LSCF-SDC composite cathodes

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The improvement of the electrochemical performance of cathodes has become one of the driving forces in the development of intermediate temperature solid oxide fuel cells (IT-SOFCs). To that end, a widely used strategy has been to synthesize composite cathodes by adding oxide-ion conducting phases such as samarium doped ceria (SDC) to $La_{1-x}Sr_xCo_{1-y}Fe_yO_{3-\delta}$ (LSCF) perovskites. These materials usually show an improvement of the electrochemical performance which has been associated to the enhancement of the three-phase boundaries (TPB) from the cathode-electrolyte interface to the whole cathode surface [1].

Composite cathodes are usually prepared by conventional mechanical mixing. In this process, both cathode and electrolyte powders are previously synthesized, calcined to promote the crystallization of the target phases and then mixed by ball milling. Nonetheless, this conventional method strongly depends on the characteristics of the starting particulate materials and processing conditions, often yielding a non-uniform distribution of elements that results in nonhomogeneous microstructures and poor cathode performance. Therefore, the development of novel synthesis approaches to attain composite cathodes with uniform distributions of elements in order to improve cathode performance and durability is essential.

Although LSCF-doped ceria composites have been widely used as SOFC cathodes, very little information has been reported regarding the preparation of such materials by one-step synthesis. In a recent paper published by Shen et al. [2], authors reported the one-step synthesis of homogeneous mixtures of CGO and LSCF nanopowders using induction plasma by axial injection of a solution. According to the authors, this method provides an efficient way to synthesize uniformly distributed composite nanopowders and avoids long sintering times and contaminations associated with any mechanical mixing process.

In the present work, a novel microwave-assisted self-combustion method to achieve high-performance LSCF-SDC composite cathodes by one-step synthesis is reported. Special emphasis is given to the electrochemical characterization of symmetrical cells, in which the cathode performance for oxygen reduction is evaluated by impedance spectroscopy. LSCF-SDC composite powders of composition $La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O_3$–$Ce_{0.8}Sm_{0.2}O_{1.9}$ (50 wt.% SDC) were prepared by microwave-assisted self-combustion using nitrates as cation sources and urea as fuel and reducing agent. Stoichiometric amounts of these chemicals were dissolved in distilled water. The resulting solution was heated up to 70 ºC under constant stirring aiming at obtaining a viscous gel. Afterwards, the gel was placed in a microwave oven set to 900 W and 2.45 GHz. Under these conditions, self-ignition took place after about 2 minutes.

The as-prepared powder was calcined between 800 and 1000 °C for 4 h in air. Powder characterization was carried out by XRD and TEM. The powder calcined at 900 °C was planetary milled at 500 rpm for 1 h and ball milled at 50 rpm for 1 h, in order to break agglomerates. The milled powder was mixed with a commercial organic vehicle (Quimiceram, Portugal), and the resulting slurry was screen-printed on both sides of dense CGO pellets, resulting in LSCF-SDC/CGO/LSCF-SDC symmetrical cells then used for electrochemical measurements. The cathode layers were sintered between 1150 and 1200 °C in air for holding times varying from 1 to 4 h, in order to assess the effects of the sintering conditions on the microstructure, evaluated by SEM, and electrochemical performance. Impedance spectroscopy was carried out in a two-probe configuration over the frequency range from 1 MHz to 0.1 Hz, at OCV as a function of temperature (600 – 800 °C) and oxygen partial pressure (N_2/O_2 mixed atmosphere) at 750 °C.

Fig. 1 shows a typical impedance spectrum at 700 °C, in air, for the LSCF-SDC cathode sintered at 1150 °C for 1 h. Two semicircles are clearly observed within the frequency range studied, suggesting that at least two different electrode processes limited the oxygen reduction reaction. From the inset in Fig. 1, there is a significant reduction in the area specific resistance (ASR) of the cathodes at different sintering conditions. This suggests that ASR can be adjusted by microstructural design. The optimum microstructure resulted in 0.18 ohm.cm^2 ASR at 750 °C in air.

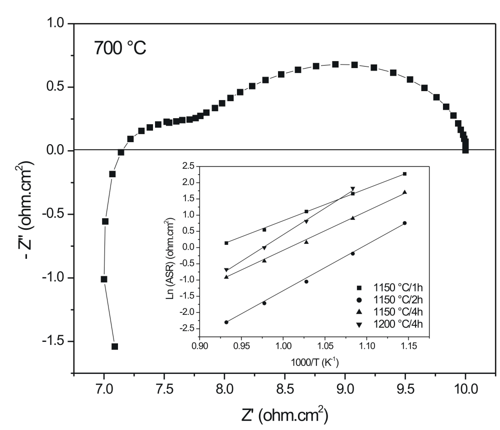

Fig. 1. Typical impedance spectrum at 700 °C, in air, for the LSCF-SDC cathode sintered at 1150 °C for 1h. Inset shows Arrhenius plot of the area specific resistances.

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References

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