

Preparation and characterization of ceramic materials for cathodes of intermediate temperature solid oxide fuel cells

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Solid oxide fuel cells (SOFCs) are energy conversion devices that produce electricity with high efficiency and negligible pollution. Other advantages such as multi-fuel capability, a modular construction design and environmental compatibility make them to be considered as one of the most promising future power generation devices. YSZ (yttria stabilized zirconia with 8 mol.% of Y₂O₃) represents the state of the art electrolyte for high temperature (800–1000 °C) SOFCs. This material possesses an adequate level of oxygen-ion conductivity combined with excellent mechanical properties and stability in both oxidizing and reducing atmospheres. However, many problems related to the correct use of the other components (anode, cathode, and interconnector) of the SOFC are to be present during service at the above operating conditions which also leads to many disadvantages in the selection of interconnects and sealing materials. Therefore, a lower operating temperature becomes necessary to reduce manufacturing costs and to increase their durability. For that purpose, new materials are required demand for materials that can efficiently operate a lower temperature, *i.e.* electrolytes with higher conductivity such as Gd-doped Ceria (GDC) (1) or La(Sr)Ga(Mg)O₃ (LSGM) (2) and also is crucial the development of more effective cathode materials with increased electrocatalytic. This is the main purpose of this work.

The cathode materials should be characterized by increased oxide ion transport in addition to high electronic conductivity. $La_{1-x}Sr_xFeO_3$ (LSF) has demonstrated higher electrical and ionic conductivity than the conventional $La_{1-x}Sr_xMnO_3$ (LSM). In this same way, $La_{1-x}Sr_xCoO_3$ (LSC) can be considered as a promising cathode for intermediate temperature SOFCs with high values of conductivity. However, the good electrocatalytic performance of this Cobalt-based-cathode is somehow limited by a thermal expansion coefficient (TEC) mismatch with other components of the SOFC and also low stability. TECs of both the electrolyte and electrode layers should be well matched to ensure long-term operational stability of the SOFCs. Considering all the above aspects, alternative materials could be ferrite/cobaltite cathodes as $La_{0.6}Sr_{0.4}Fe_{1-y}Co_yO_{3-x}$ (LSFC). The electronic conductivity of these samples in air is characterized by the higher values at increasing Co contents and besides, the presence of Fe helps to minimize mechanical stresses as it can reduce the TEC mismatch.

However, substitution of Co as a major B-site cation in the perovskite air electrode is highly desirable due to potential disruptions in the cobalt supply chain as early as 2030, as well as its related high price and risks to health. Moreover, its presence (Co) in electrochemical cells is associated with high thermal expansion coefficient as mentioned before. Other phases, as Ruddlesden-Popper phases, must be considered as air electrodes (or cathodes). Doped $Sr_3Fe_2O_7$ (SF) (n=2 R-P phase) with Ni (Sr_3FeNiO_7) increased the conductivity by a 3x factor. The substitution in A position of the structure with Pr or La, (Pr/La)_{0.2} $Sr_{2.8}FeNiO_7$, allow to stabilize the phase and have better mechanical performance. Also, the conductivity has reached over 200 S cm⁻¹ and over 100 S cm⁻¹ at all times (100-1000°C).

The solid state reaction of the corresponded oxides is an easy synthesis process to obtain ceramic powders of different materials. However, the homogeneity of the final synthesized powder is poor. The compositional complexity of the materials above mentioned due to the number of cations involved require a synthesis method that ensures optimal chemical homogeneity to determine its final properties. Here we show a low cost and simple alternative, with excellent results, based on the chelation of complex cations leading to the formation of an intermediate resin, which, on charring and calcining, leads to a sinterable powder. In this work we present two alternatives, one is substituting citric acid with EDTA and ethylene glycol with glycerol for producing (Pr/La)_{0.2}Sr_{2.8}FeNiO₇. And other based on the auto-combustion of an ethylene glycol-metal nitrate polymerized gel precursor that can be efficiently used to easily produce a range of La_{0.6}Sr_{0.4}Fe_{1-y}Co_yO_{3-x} (LSFC) at moderate temperatures. This method generates less carbon residues than other similar techniques of synthesis as that based on the Pechini method. The results here presented are important not only for the synthetic route itself but also because they establish practical cathode operational parameters on sintered samples for the selection of the most suitable composition, considering the TECs of the electrolyte utilized and the operating temperature of the cell.

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References

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