LSCFO/CGO CATALYST FOR O₂ REDUCTION IN IT-SOFCs AND ELECTROCHEMICALLY DRIVEN OXYGEN GENERATOR CELLS

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ABSTRACT

Composite cathodes have been investigated for operation in ceria-based electrolyte cells for operation at intermediate temperatures. Composites based on LSCFO/CGO and LSMO/CGO were studied. LSCFO-based oxides were found to be the best candidates giving the lowest cathodic overpotential. Structural morphology and electrochemical properties are discussed. An air separation electrochemical device based on ΔV driving force was constructed using LSCFO material. The device based on an electrode-supported architecture showed 1 Acm⁻² at 0.15 V at the operational temperature of 800°C. Furthermore, the O₂ production was measured directly showing a flow rate of 3.5 ml min⁻¹ cm⁻² which is about four times higher than the minimum value acceptable for practical applications. The high electrochemical performance of the present device indicates good opportunities to significantly decrease the O₂ production costs as well as to produce small and light weight portable devices.

INTRODUCTION

Solid oxide fuel cells (SOFCs) offer a clean pollution-free technology for the electrochemical generation of electricity with high efficiency (1). A typical SOFC is operated near 1000°C; it utilises yttria-stabilised zirconia (YSZ) as the electrolyte, which exhibits an oxide-ion conductivity at 1000°C of about 0.1 Scm⁻¹. Lowering the operation temperature to 700-800°C would enhance the reliability, lifetime, and operating cost of the cell; but, with conventional membranes of YSZ the reduction in temperature results in poor performance (2). Two approaches were developed for operation at temperatures <800°C: i) reduction of the thickness of the YSZ electrolyte membrane to less than 10 μm; and ii) use of alternative electrolytes having an oxide-ion conductivity at or below 800°C that is comparable to that of YSZ at 1000°C. Ceₓ₋ₓGdₓO₂₋₄⁺ₓ/₂ (CGO) is a very promising electrolyte for intermediate temperature solid oxide fuel cell (IT-SOFC) applications.

The electrodes for IT-SOFC should have high electrical conductivities, adequate porosity for gas transport, good compatibility with the electrolyte and long-term stability. Performance is governed by the electronic resistivities of the electrocatalysts, overpotentials associated with charge-transfer at the electrocatalyst–electrolyte gas-phase
boundaries, the ionic resistivity of the electrolyte, and rates of transport of gases through the porous electrodes.

The rate of charge transfer is known to be a function of microstructural variables such as the particle size and surface area of the electrocatalyst. Hence, there is a need to understand the behaviour of electrodes in terms of microstructural and electrochemical parameters in order to optimise performance. More particularly, because of the large cathode polarisation at these low operating temperatures, the necessity for considerable improvements of cathode materials and microstructures has arisen. Large interest is currently being expressed in porous ceramic development fabricated from perovskite oxides with high electronic conductivities referred to as Mixed Electronic and Ionic Conductors (MIEC) together with pure Ionic Conductor oxides. Thus, $La_xSr_{1-x}Fe_yCo_{1-y}O_3$ (LSCF) and $La_{1-x}Sr_xMnO_3$ (LSM) mixed with CGO have been studied. Then, LSCF/CGO/LSCF+CGO cells have been investigated. These show low cathodic electrochemical resistance and could be applied for oxygen generation for practical applications (so-called oxygen pumps).

There are a large number of commercial processes that need pure oxygen, oxygen-enriched or oxygen-depleted streams. Examples of industrial uses of oxygen enriched atmospheres include glass making, the petrochemical industry, bleaching for the pulp of paper in the paper industry, and for cutting and welding in the metallurgical industry. Oxygen is also used in small quantities for critical tasks of life support for military, aerospace and medical applications. Oxygen can be obtained from air by one of the three conventional processes: the distillation of cryogenic air (for large scale production), pressure swing adsorption, and vacuum swing adsorption. The cost of the process depends on the purity required and the production scale. In the present work, a separation process based on an electrochemical ceramic oxygen generation (ECOG) device has been investigated by using the low overpotential cathodes developed for IT-SOFCs. The method of operation is similar to an electrolysis cell and more properly to an electrochemically driven-oxygen pump in which air and electrical power are used to generate pure oxygen. The flux of oxygen produced by an ECOG is directly proportional to the current passing through the cell upon application of a certain voltage. The objective is to achieve maximum current (oxygen generation) with the minimum applied voltage at temperatures as low as possible ($\leq 800^\circ$C). This approach has distinct advantages compared to the conventional technologies mentioned above. The ECOG devices produce oxygen of high purity (i.e. 100%) in a single operation and, as a consequence, the production costs may be significantly decreased as well as small and light weight devices for portable uses may be possible.

**EXPERIMENTAL DETAILS**

The synthesis of all the powder components was carried out by the acrylamide polymerisation technique (3). The acrylamide polymerization gel consists of long polymeric chains, cross-linked to create a tangled network, soaked with an aqueous liquid. Polymerization of the gel proceeds in a first step with the combination of an initiator (e.g. thermo-initiator with the acrylamide monomer which is thereby activated) and as the chain of polyacrylamide grows up, the active site shifts to its free end. Bis-acrylamide (i.e., N,N'-Methylenebisacrylamide), includes two acrylamide units joined through their-CONH$_2$ groups via a methylene group. It can link two growing chains.
Hence, bis-acrylamide enables the formation of cross-linked chains resulting in a complex topology with loops, branches and interconnections.

The process starts with the dissolution of La(NO$_3$)$_3$·6H$_2$O (Aldrich 99.99%), Sr(NO$_3$)$_2$ (Aldrich 99.99%), Co(NO$_3$)$_3$·6H$_2$O (Aldrich 99.99%) and Fe(NO$_3$)$_3$·9H$_2$O (Aldrich 99.99%) separately in H$_2$O for the synthesis of the La$_{1-x}$Sr$_x$Fe$_{1-y}$Co$_y$O$_3$-$\delta$, the same way with La(NO$_3$)$_3$·6H$_2$O (Aldrich 99.99%), Sr(NO$_3$)$_2$ (Aldrich 99.99%), and Mn(NO$_3$)$_2$·6H$_2$O (Aldrich 99.99%) for the La$_{1-x}$Sr$_x$MnO$_3$-$\delta$ and the also the same way with Ce(NO$_3$)$_3$·6H$_2$O (Aldrich 99.99%) and Gd(NO$_3$)$_3$·6H$_2$O (Aldrich 99.99%) for the Ce$_{1-x}$Gd$_x$O$_2$-$\delta$.

The polymerisation process started with the chelation of the Co$^{3+}$ and Fe$^{3+}$ separately, which has been carried out by the addition of the EDTA powder (Flucka, 98%) adjusting the pH with NH$_4$OH (20%, Carlo Erba) up to complete dissolution (4<pH<6). The EDTA amount corresponds to the molar stoichiometric ratio 1 mol (EDTA) : 1 mol (cation). This chelation was used to prevent the possible reaction of the acrylamide monomers with the cations which inhibits the polymerisation reaction. However, not all cations react with the acrylamide monomers such as La$^{3+}$, Gd$^{3+}$, Mn$^{2+}$ and Sr$^{2+}$ (4). Once all the solutions were chelated and/or dissolved, they were mixed. Subsequently, acrylamide (Fluka, 99%), bis-acrylamide (i.e. N,N'-Methylenebisacrylamide, Fluka, 99%) and the initiator AIBN (i.e. 2,2'-Azobis 2-methylbutyronitrile, Fluka 98%) were added. The solution was vigorously stirred and heated up to the monomers dissolution and the gel was formed when the solution reached ~80°C. After that, the gel was dried obtaining the xerogel at 200°C for 2 h and finally was calcined at 500-800°C for 2-5 h obtaining the desired single phase.

To study different cathode compositions, an electrolyte-supported cell was used. The cell membrane was fabricated by compacting the CGO powders, previously ball milled for 2 h, by uniaxial pressing (300 MPa). The green pellet is treated at 1450°C for 6 h in static air obtaining a disk supported electrolyte membrane ($\rho_{rel} > 95\%$) The cathode was deposited by spraying. A suspension of cathode formulation powders was prepared in an ultrasonic bath using ethanol as a solvent. The solution was sprayed by an aerograph device on a heated electrode substrate (300°C). Then, the system was sintered at 1100°C for 2 h. Finally, a counter electrode and a reference one were deposited on the other side of the electrolyte membrane.

The manufacturing of the electrochemical cells based on an electrode supporting architecture is carried out by using the synthesized powders. The electrode supporting element is made by mixing LSCFO with CGO (70 / 30% wt.). The cell has a cylindrical shape ($\phi = 16$ mm, $d = 1$ mm). The supporting electrode and the deposited electrolyte membrane assembly is made by a proprietary process. Finally, a LSCFO counter-electrode is deposited on the electrolyte membrane by the same process.

Gold paste (Hereaus) was used to form the current collector. An Autolab electrochemical apparatus equipped with a FRA was used for the electrochemical analysis. The structural and compositional analyses were made by XRD in a Bragg-Brentano configuration (Philips Xpert, Netherlands) and XRF (Bruker AXS, Germany) with CuK$\alpha$ anode. The microstructural analyses were carried out by SEM (Philips XL30, Netherlands) and TEM (Philips CM12, Netherlands).
RESULTS AND DISCUSSION

Cathode Element Study

The XRD analysis of the fabricated raw powders showed CGO, LSMO and LSCFO pure phases. Morphological analyses were carried out by BET for the surface area and TEM for the microstructural characterization. The BET analysis showed values of 6-8 m$^2$/g for all components. The TEM imaging (Fig. 1) revealed medium particle size of 100-150 nm for the LSCFO and LSMO and 40-50 nm for the CGO.

![TEM images (a) LSCFO mixed conductor, (b) CGO ionic conductor, and (c) LSMO mixed conductor.](image)

As described in the experimental part, the study of the cathode overpotential was carried out by using a membrane supporting element of CGO with a thickness of 300-400 μm.

The electrochemical analysis of the cathodic overpotential of the LSMO/CGO and LSCFO/CGO cathodes is shown in Fig. 2. It was observed that the lower overpotential

![Cathode overpotential values of the different oxide composites as a function of current density.](image)
corresponds to the cathode based on LSCFO. Taking into account the trend of those curves, it could be observed that at 800°C the electrode kinetics is controlled by the electrochemical process (5). Moreover, the dependence between the cathode composition (i.e. mixed conductor/ionic conductor) and the cathodic overpotential value at 1 A/cm² at 800°C is shown in Fig. 3.

From this plot it can be observed that the LSMO/CGO shows typical percolation behaviour as a function of the composition (6). There is an optimal composition that gives the lowest overpotential corresponding to 70/30 wt% of LSMO/CGO. However, a different behavior was observed for the LSCFO/CGO, and in the latter case there is no percolation effect. Therefore, there is no influence of the ionic conductivity component on the cathode at this temperature. In fact, LSCFO has enough ionic conductivity that makes unnecessary the addition of CGO. However, a percolation effect appears at lower temperature (7).

Finally, the cathode morphology of LSCFO and the 70/30 wt% of LSMO/CGO was analyzed. The SEM imaging of the both cathodes is showed in Fig. 4. An optimal porosity and particle interconnection for LSCFO was observed. However, the morphology of LSMO and CGO is very different. The LSMO underwent an important grain growth while the CGO remains as small grains. Therefore, it is very difficult to achieve the homogeneity in distribution and porosity formation due to different grain growth features between both materials.

It can be concluded that LSCFO gives the best cathodic overpotential and better morphology for use as a cathode at temperatures around 800°C. Therefore, this cathode system was applied to fabricate an electrochemical ceramic oxygen generation cell for air separation using the cell potential as the driving force. In the following, the fabrication and electrochemical properties of this kind of a device are described.
Electrochemical Oxygen Generation Cell Study

As was mentioned in the experimental part, the electrode supporting compound powders were sintered at 900°C after pellet formation in a cylindrical shape. Then, the electrolyte membrane was sprayed on the substrate and treated at high temperature to obtain a full density membrane. However, it is convenient that the electrode substrate remain with certain porosity to provide suitable gas diffusion. Moreover, the counter electrode should be porous for the same reason.

The SEM cross-section analysis was carried out after prolonged cell operation (Fig. 5). Electrode support and the full density membrane are shown. The supporting anode shows low degree of porosity due to the high pressure treatment and firing procedure. The porosity of the anode needs to be ameliorated by introducing appropriate pore formers.

From Hg porosimetry anode porosity was measured to be only 10-12%. Indeed, the counter-electrode showed high porosity together with an optimal intergrain connectivity which might provide a good electronic percolation path as was shown in the Fig. 5 in the cathode element section study.

Figure 4. SEM images a) LSMO mixed with CGO, and b) LSCFO mixed conductor.

Figure 5. SEM cross-section images of an ECOG device after prolonged operation.
In Fig. 6, the AC polarization measurement at 800°C in air at the cathodic side and 100 cc/min of He at the anodic side is shown. He was used as a carrier for the gas composition analysis by microgas chromatography. The electrochemical configuration of this sample consists of the supporting element acting as an anode (e.g. $2\text{O}_2 \rightarrow \text{O}_2 + 4\text{e}^-$) and the thinner counter electrode as a cathode (e.g. $\text{O}_2 + 4\text{e}^- \rightarrow 2\text{O}_2^2$). It can be observed that the current density of 1 Acm$^{-2}$ corresponds to about 0.10 V and the power consumption of 100 mWcm$^{-2}$. There is some negative potential from 0-0.2 Acm$^{-2}$. It means that the electrochemical cell works spontaneously using the oxygen differential pressure between the cathodic and anodic chambers as a driving force. At current densities above 0.2 Acm$^{-2}$ the electrochemical cell does not work spontaneously and an external potential is applied.

Figure 6. Polarization measurement at 800°C using static air in cathode (thinner electrode) and 100 cc min$^{-1}$ of He in the anode (supporting electrode).

Moreover, the O$_2$ flow produced at the anode was measured directly. The anodic gas was analyzed by a microgas chromatography using a 100 cc/min of He as a gas carrier and fixing the electrochemical cell current density to 1 Acm$^{-2}$ and 800°C. This measurement showed that the Faradaic efficiency is 98 ($\pm$ 2)%.$^3$ It means that all the current density is associated with O$_2$ evolved. It was measured 3.4 ml min$^{-1}$ cm$^{-2}$ that corresponds to about 4 times greater than the target amount needed for practical applications using an applied voltage lower than 0.15 V.$^3$

A cyclic voltametry study was carried out after the life-time test to identify the limiting processes. The measurement was performed at 800°C with a sweep rate of 5 mV/s (Fig. 7). In this experiment, it was observed that the overpotential is lower when the cathodic reaction occurs in the thinner layer electrode. When the supporting electrode was used as a cathode, some gas diffusion resistance appeared, as accounted by the trend to reach a limiting diffusion current density and the presence of the hysteresis loop.
A chronopotentiometry experiment was carried out for 15 days at a constant current density of 4 A/cm$^2$ (Fig. 8). This high current density was selected to make an accelerated test since the practical current density suitable for real applications is lower than 1 A/cm$^2$.

Moreover, the cell behavior was monitored during the stability test experiments by impedance spectroscopy (Fig. 9). The cell performance was better at the beginning of the test up to 60 hrs; afterwards it remains constant. It was observed that the serial resistance (e.g. $R_s$) does not change with time indicating that the ohmic losses remain constant for all measurements. However, the total resistance changed after the first working day up to reaching the steady state. It could be observed that the variation of the total resistance is due to polarization (e.g. $R_p$). This might be attributed to an enhancement of the catalytic properties with the operational time up to a certain level. Therefore, it can be assumed that the initial improvement of the electrochemical cell performance may be related with the improvement of the initial electrocatalytic activity which affects the kinetic processes.

CONCLUSIONS

It was shown that the composites of LSCF and CGO-based oxides are good candidates to be cathode materials with CGO electrolyte. The LSCFO/CGO electrodes are compatible both chemically and mechanically with CGO electrolytes. The rate of charge transfer is known to be a strong function of microstructural features such as the grain size of the
electrocatalyst, porosity of the electrode mixtures composite. The LSMO is a poor ionic conductor, and the electrochemical reactions are limited to the region close to the triple phase boundary with the CGO. However, LSCFO is a MIEC with appreciable ionic conductivity, and exchange of oxygen occurs at the electrode surface with diffusion of oxygen ions through the mixed conductor. Therefore, it is unnecessary to add CGO when the cathode is operated at 800°C and corresponds to 0.08 V at 1 A cm\(^{-2}\). An air separation process using this cathode material and based on an electrochemical ceramic oxygen generation (ECOG) is discussed. The present device with an electrode supported architecture showed 1 A cm\(^{-2}\) at 0.15 V at 800°C. Also, the \(O_2\) production showed 98 (±2)% of Faradaic efficiency and a flow rate of 3.5 ml min\(^{-1}\) cm\(^{-2}\) which is about four times higher than the minimum value acceptable for practical applications. It was also observed that the cell needs a certain time of operation to reach a steady state. The high performance of the present device indicates good possibilities to decrease \(O_2\) production costs significantly. Small and light weight devices for portable uses are also envisaged. Future efforts will address decrease in operating temperature while maintaining similar performances.

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