SYNTHESIS AND CHARACTERIZATION OF STRONTIUM AND IRON-DOPED LANTHANUM COBALTITE NANOCRYSTALLINE POWDERS FOR SINGLE CHAMBER SOLID OXIDE FUEL CELLS

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ABSTRACT

Different sets of perovskite-type oxides of general formula La₀.₈Sr₀.₂Co₁₋ₓFeₓO₃ (0.0 < x < 1.0) were successfully prepared by the amorphous citrate method. Simultaneous thermogravimetric and differential thermal analysis (TG-DTA) was carried out on the precursor gels to determine the minimum temperature of the oxide formation, which was found to be 600°C. After thermal treatments, samples were characterized by using Induced Couple Plasma (ICP) spectroscopy, X-ray diffraction (XRD) and Scanning Electron Microscope (SEM). Single-phase nanocrystalline powders were obtained with controllable grain size from 10 to 20 nm as a function of the iron ratio. ICP results indicate that for the prepared samples the actual metal contents were nearly equal to the nominal values. XRD results showed that La₀.₈Sr₀.₂Co₁₋ₓFeₓO₃ compounds possess a rhombohedral to orthorhombic structure, depending on the iron content. Moreover, the perovskite-type nano-powder oxides were characterized as electrodes on Ce₀.₅Sm₀.₅O₂₋ₓ pellets in symmetrical cells, and the electrochemical properties of the electrode/electrolyte interfaces were investigated using electrochemical impedance spectroscopy (EIS).

INTRODUCTION

In the last twenty years, the world energy demand increased almost linearly for automotive or stationary applications and world electricity consumption grew an average of 3% per year. In the same time, the world population and carbon dioxide emissions grew at an average annual rate of 1.6% and 1.2%, respectively. Most important contributors to the growth in energy consumption and carbon dioxide emissions were motor vehicle ownership and stationary energy production (1).

New Energy Devices (NEDs) that use environmental-friendly technologies as alternative to oil combustion for energy production are not yet widely used due to the economic and technological restrictions. Among various types of NEDs, fuel cells are rapidly growing as a technology to cope with the problems induced by shortage of fossil fuels, increase of energy demand in the society and global warming. Among various types of fuel cells, solid oxide fuel cell (SOFC) technology has shown considerable promise for a variety of applications, providing a low environmental impact option for the society’s ever-
increasing energy needs. In fact, SOFC technology is the most efficient, cleanest and versatile electrochemical system for chemical to electrical energy conversion for the low emission vehicles (LEV) and low emission stationary system (LESS) applications (2).

To encourage their general utility in this regard, as well as to increase efficiencies and reduce costs, there has been an important level of research focused on lowering the operating temperature of these electrochemical devices. The high operating temperatures (800–1000°C) of conventional SOFCs give rise to economic and technical problems related with materials cost and long-term stability (3). A considerable quantity of studies is currently directed towards decreasing operating temperatures below 800°C, by using doped ceria electrolytes (e.g. SDC - Sm2O3 doped CeO2) as an alternative to yttria-stabilized zirconia (YSZ - Y2O3 doped ZrO2) used in the traditional high temperature SOFCs (4).

For most economic applications, it is desirable to have fuel cells that directly utilize hydrocarbon fuels instead of hydrogen, without reforming of available hydrocarbon fuels to hydrogen. Single-chamber solid oxide fuel cells (SC-SOFCs) are the most fuel-flexible of the various SOFC types because, at low temperatures, they can directly oxidize hydrocarbon fuels (5,6).

Reducing the SOFC operating temperature, however, causes an increase in the ohmic losses across the electrolyte and electrodes, and this becomes a critical problem for application. Reducing the thickness of the solid oxide electrolyte (using films) decreases the electrolyte ohmic losses, while polarization loss at the electrode/electrolyte interfaces can be minimized using mixed ionic electronic conducting (MIEC) materials, such as lanthanum cobaltite for the cathode, with high specific surface area to increase the triple phase boundary (TPB), by using nanocrystalline oxides (7-9). In fact, there has been a considerable amount of experimental work on MIEC materials with perovskite-type structure for application in intermediate temperature SC-SOFCs. For example, LnCoO3 perovskite-type (with Ln = La, Ba, etc) has been found to exhibit a significant oxygen ionic conductivity with a MIEC behavior at intermediate temperatures. Strontium and iron-doped rare-earth cobaltite oxides in the (LaSr)(CoFe)O3 system (10), and strontium and iron-doped alkaline-earth cobaltite oxides in the (BaSr)(CoFe)O3 system (11) have been widely investigated in recent years as possible cathodes, due to their high catalytic activity towards the oxygen reduction reaction, high oxygen self-diffusion coefficients, and high electrical conductivity with mixed conduction.

Various preparation routes have been proposed including solid state reactions and wet chemical methods, such as amorphous citrate method and Pechini process. The wet chemical synthesis are known to show advantages because they allow high product purity, fine and constant grain-size powders, low processing temperature, and low cost. We selected the amorphous citrate method to prepare highly homogeneous electrode nanocrystalline powders at a lower temperature than that needed for solid-state reaction. Using this chemical synthesis route, it is possible to easily control the microstructure of the powders, which, in turn, can affect the electrochemical cell efficiency, durability, and the operating temperature of cathode for intermediate temperature applications.

Different sets of perovskite-type mixed oxides of general formula La0.8Sr0.2Co1-xFexO3 (0.0<x<1.0) were successfully prepared. The synthesized nanocrystalline powders were
characterized as electrodes on SDC using electrochemical impedance spectroscopy (EIS) measurements as a function of temperature and of the metal ratio.

EXPERIMENTAL

Powders were prepared by the so-called amorphous citrate process, where citric acid is used as a chelating agent of metal cations. $La_{0.8}Sr_{0.2}Co_{1-x}Fe_xO_3$ powders were synthesized using lanthanum (III) nitrate hexahydrate (99.99%; Aldrich), strontium (II) nitrate (99+%; Aldrich), cobalt (II) nitrate hexahydrate (98+%; Aldrich), and iron (III) nitrate 9-hydrate (98+%; Aldrich) as sources of La, Sr, Co and Fe, respectively, and deionized pure water as a solvent, with the addition of citric acid ($C_6H_8O_7H_2O$, Iso - for analysis, Carlo Erba reagents). All reagents were used without further purification.

Appropriate amounts of the metal cation nitrates were dissolved in distilled water. The nitrate solution was mixed with an aqueous citric acid solution. A pale colored solution was obtained without any suspension, agglomeration or precipitation. The color depended on the chemical nature of the transition-metal in the oxides: yellowish gel for the Fe-rich compositions or violet gel for the Co-rich samples. The mixed solution was evaporated on a hot plate at 120°C for 3 h under stirring. NOx gas gradually evolved and the volume of the solution was slowly reduced. At this point, the viscosity increased rapidly. After obtaining a transparent metal-organic gel, evaporation was continued and then the gel was completely dried overnight in an oven at 90°C. The evolved gases caused the gel to expand to more than three times of the original volume, forming a weak, soft but feeble mass. The bulk showed a complex three-dimensional structure.

Simultaneous thermogravimetry and Differential Thermal Analysis (TG-DTA) was carried out on the dried metal-organic precursor complex to compare the thermal effects as a function of the metal content, by means of a Netzsch Analyser (model STA 409), on ca. 60 mg samples, with a temperature ramp of 5°C/min from room temperature up to 1200°C in air flow (100 ml/min), with Al2O3 as a reference.

The metal content in the sintered samples was determined by Induced Couple Plasma (ICP) spectroscopy (Model SPS4000 Plasma Spectrometer, SII Seiko Instruments Inc.). The phase identity, crystal structure, and lattice constants of the material were investigated using X-ray diffraction (XRD) analysis (Model PW-1700, Philips) with CuKα radiation at 30 kV and 40 mA. XRD data were collected between 20 and 80° of 2θ angles with a step interval of 0.02°. After comparing the experimental patterns with the theoretical patterns obtained by JCPDS, the lattice constants were determined by a least-squares refinement of the d-spacing with the ASPO program (12). Micrograph images of the calcined samples were obtained using Scanning Electron Microscopy (SEM, Model S-4500, Hitachi Co., with 4855 Digital Beam Control Interface). Particle size was determined and cross-referenced by XRD Scherrer analysis and SEM observations.

Perovskite-type oxides were characterized as electrodes on $Ce_{0.8}Sm_{0.2}O_{2-x}$ ceramic pellets (diameter < 1 cm; thickness < 0.3 cm) using electrochemical impedance spectroscopy (EIS) measurements. Dense electrolyte pellets were obtained by ball-milling $Ce_{0.8}Sm_{0.2}O_{2-x}$ powders, forming the powders by uniaxially pressing, and then sintering at 1600°C for 10 h. The pellet density was estimated to be around 85-90% of the theoretical
density. Symmetrical electrodes of nanocrystalline powders were deposited on SDC ceramic pellets \((\text{La}_{0.8}\text{Sr}_{0.2}\text{Co}_{1-x}\text{Fe}_x\text{O}_3)/\text{SDC}/\text{La}_{0.8}\text{Sr}_{0.2}\text{Co}_{1-x}\text{Fe}_x\text{O}_3)\) by screen printing. Perovskite powders were mixed with the same volume of polyethylene glycol and ethyl alcohol and then applied to the electrolyte by painting. The painted slurries were then fired at 900°C in air for 1 h.

EIS measurements were performed using a Solartron SI 1260 Impedance/Gain-Phase Analyzer and a 1255 Solartron Frequency Response Analyzer in the frequency range from 13 MHz to 0.1 - 0.01 Hz (5 points per decade) with a 10 mV signal amplitude, in the 600 to 800°C temperature range, in air atmosphere. Electrical connections were made by gold net at the both sides of the pellet. The impedance spectra and data sets were fitted and deconvoluted using the EQUIVCRT software. Interfacial resistance and activation energy of nano-sized \(\text{La}_{0.8}\text{Sr}_{0.2}\text{Co}_{1-x}\text{Fe}_x\text{O}_3\) powders were measured in the two-electrode symmetric cell configuration and cell performance was evaluated using an in-house built test station.

RESULTS AND DISCUSSION

TG-DTA curves of the precursor powders were different depending on the metal content (x). DTA curves of the samples showed a three-step decomposition, as shown in Fig. 1 where TG-DTA curves of the \(x = 0.3\) citrate precursor powder are reported as an example, together with the TG-DTA curves of pure citric acid (AC). Several weight loss regions ended at approximately 200°C, 350°C, and 540°C, while above the last temperature there is no further weight loss.

The TG curve of perovskite precursor gel showed three decomposition steps, as also described by other authors (13). The exothermic peak about 140°C appears to be related with the nitrate decomposition. The first weight loss is mostly due to dehydration, decomposition, and evaporation of volatile inorganic components. The two peaks at about 400°C correspond to the decomposition of citric acid, as shown by the comparison of the DTA curves of the precursor and of citric acid (see Fig. 1). The weight loss of the citric acid ended at about 440°C, with the liberation of gases. The second large weight loss between 180 and ca. 500°C can be ascribed to the decomposition and burnout of most of the organics trapped in the powder precursor, or burnout of the residual carbon and decomposition of citric acid. The small exothermic kink with the onset temperature at ca. 400°C is probably due to direct crystallization of perovskite compounds from the amorphous component (14). In fact, the TG analysis showed that the major part of the weight loss associated with the decomposition and oxidation of the precursor started at about 500°C and, in the same time, the formation reaction of perovskite phase was continued up to higher temperatures. Above 600°C, there was no further weight loss and heat variation on TG/DTA curves. Moreover, the TG curve shows about 86.8% weight loss occurring between 200 and 300°C, correlated with a strong DTA endothermic peak. A minor weight loss (10.8%) was observed between 300 and 450°C which can be correlated to the strong DTA exothermic peak at the same temperature range due to the combustion of either acid derivations or residual carbon.

Fig. 2 summarizes the temperature shifts of the main thermal effects (endothermic at low temperature, exothermic, extrapolated onset and extrapolated endothermic at high
temperature) of the powder precursors obtained by amorphous citrate method as a function of the iron content, as measured from the DTA curves. Only the second exothermic decomposition temperature changed as a function of the metal ratio. The reactions were completed at about 600°C, and this temperature was selected for the thermal treatment of the samples.

Figure 1. TG-DTA curves of the La$_{0.8}$Sr$_{0.2}$Co$_{0.7}$Fe$_{0.3}$O$_3$ citrate precursor (x=0.3) and of pure citric acid (AC).

Figure 2. Temperature of the maximum or minimum corresponding to the main thermal effects obtained from the DTA curves of the prepared La$_{0.8}$Sr$_{0.2}$Co$_{1-x}$Fe$_x$O$_3$ precursors, determined with a temperature ramp of 5°C/min. (solid lines guide the eyes).

After a mild thermal treatment (2h-600°C), chemical, structural and morphological characterization showed that all the samples were perovskite-type single-phase. ICP results indicated that the actual metal content for the fired samples was practically equal to the nominal values.
XRD analysis was carried out on the heated powders. Fig. 3 shows the XRD patterns at room temperature of all the compositions tested after thermal treatment at 600°C for 2 h. All the powders were single-phase La_{0.8}Sr_{0.2}Co_{1-x}Fe_{x}O_{3} oxides with a perovskite structure, but a systematical shift of the peak position towards smaller angles with increasing the iron content was observed. XRD studies confirmed earlier works, indicating that La_{0.8}Sr_{0.2}Co_{1-x}Fe_{x}O_{3} may have a rhombohedral to orthorhombic structure as a function of the metal content (15,16). At room temperature the structure transition from rhombohedral to orthorhombic symmetry takes place from La_{0.8}Sr_{0.2}Co_{0.3}Fe_{0.7}O_{3} to La_{0.8}Sr_{0.2}Co_{0.2}Fe_{0.8}O_{3}, respectively. For x < 0.7-0.8, the perovskite had a rhombohedral structure (Space-group number = 166; Space-group symbol = R3m), while for x > 0.8 an orthorhombic structure (Space-group number = 62; Space-group symbol = Pbnm) was observed. In La_{0.8}Sr_{0.2}Co_{1-x}Fe_{x}O_{3} structures, a modest Fe substitution, which means large x-values, could lead to the formation of the rhombohedral system (17) with good agreement with JCPDS 28-1229.

Crystalline size of the heated powders was calculated from the XRD peak broadening of two diffraction peaks (at 33° and 58° of 2θ) using the Scherrer analysis. The crystal size of La_{0.8}Sr_{0.2}Co_{1-x}Fe_{x}O_{3} powders linearly increased with increasing the iron content. The morphology of powders was investigated by SEM, confirming the XRD results. In fact, typical grain dimensions of the samples were below 20 nm.

![XRD Patterns](image)

**Figure 3.** XRD patterns of La_{0.8}Sr_{0.2}Co_{1-x}Fe_{x}O_{3} products obtained by heating all the powder precursors at 600°C for 2 h.

(*r* = rhombohedral symmetry; *o* = orthorhombic symmetry).

EIS was used to characterize the variation of the cell performance as a function of temperature and metal contents. In fact, to optimize the performance of the cathode in the SC-SOFCs, it is important to gain knowledge about all physical and chemical processes occurring at the cathode/electrolyte interface. EIS can be helpful to discriminate the resistance associated with each single process and calculate the total resistance by the sum of single processes. From EIS data, the activation energy (Ea) of each process and
area-specific resistance (ASR) of the interface can be calculated, to understand oxygen reduction reaction mechanisms.

Fig. 4 shows the complex impedance spectra measured using a two-probe configuration for the sample with x = 0.9, at 600°C (Fig. 4a) and 800°C (Fig. 4b). The EIS set data for samples at high temperatures showed that the width of the high-frequency semicircle was nearly dependent on the composition. Fig. 4 shows a decrease in resistance with increasing the temperature. The arc at low frequencies is due to the interfacial resistance of the electrode, and depends on the chemical compounds. An additional depressed semicircle appeared at very low frequency and at low temperatures. Moreover, the highest frequency real-axis intercept is related to the cell ohmic resistance (R_0) and thus, in an approximate hypothetical equivalent circuit models, the lowest frequency real-axis intercept provides a measure of the total cell resistance (R_t). The experimental data are well represented by the distributed-element “ZARC” impedance expression as the combination of the resistance in parallel with the CPE impedance (Z_{cpe}). Many authors agree that different responses are attributed to the presence of inhomogeneities in the electrode samples, and this can be described in terms of a distribution of relaxation times (18).

To separate the number of processes hidden in the experimental impedance spectra, the data presented were deconvoluted by EQUVCRT program using the complex equivalent circuit shown in Fig. 4(c). The equivalent circuit, that most closely reproduces the experimental impedance characteristics, was expressed with combinations of parallel resistance and capacitance circuit elements and, from the electrochemical equivalent circuit models point of view, the spectra could be deconvoluted into two (high temperature) or three semicircles (low temperature) where each semicircle represents a single theoretical reaction step with a different relaxation time. Ohmic resistance, high frequency arc resistance, low frequency arc resistance and additional low frequency arc resistance at low temperatures, are indicated by R_0, R_1, R_2 and R_3 respectively. Furthermore, such as high frequency arc constant phase elements (CPE_1), low frequency arc constant phase element (CPE_2), and additional low frequency arc constant phase element at low temperature (CPE_3) are indicated in figure by Q_1, Q_2 and Q_3, respectively.
Appreciable discussion of the circuit from an electrochemical viewpoint appears in Macdonald (19) and, more recently, in Leng et al. (20). Ostergård and Mogensen found three limiting processes at high temperatures for the La$_{0.88}$Sr$_{0.15}$MnO$_3$/YSZ interface (21) and, in particularly, the high frequency impedance was tentatively attributed to a charge transfer electrode/electrolyte cross section of oxide ions from the La$_{0.88}$Sr$_{0.15}$MnO$_3$/YSZ interface to vacancy in the YSZ, while the low frequency arc was ascribed to a diffusion of oxide ions to the electrode/electrolyte interface. At the same time, the medium frequency process was ascribed to a dissociation of adsorbed oxygen molecules.

\[ \log(\sigma T) \text{[K/Ohm cm}^2\text{]} \]

Figure 5. (a) x = 0.5 samples and (b) La$_{0.8}$Sr$_{0.2}$Co$_{1-x}$Fe$_x$O$_3$ nano-powders in symmetrical cells: ASR associated at each single resistance and at each partial electrochemical process (left axis). Arrhenius plots of single electrochemical processes associated to $R_0$, $R_1$, $R_2$ and $R_3$ (right axis).

In general, the study of the electrochemical behavior of La-Sr-Co-Fe-O systems on electrolyte pellets clearly showed that many equivalent circuit models and numerous fundamental level of description with nano- or microscopic models attempt to provide description of the movement of charge-carrying oxide ions in the systems or in the electrolyte/electrode interface. The present study brings another view to this frame, with the help of EIS measurements to systematically investigate the reactions of the nanocrystalline La$_{0.8}$Sr$_{0.2}$Co$_{1-x}$Fe$_x$O$_3$ phases, including a tentative to discriminate between electrochemical parameters associated at the single process and the total resistance calculated by the sum of single processes, between medium-high temperatures and medium-low temperatures. Fig. 5(a) illustrates the evolution of resistance for x = 0.5 electrodes as a function of temperature. In this way the temperature dependence of each single process was obtained. For all the perovskite-type oxides, $R_0$ increased slowly with increasing the temperature, in comparison with the other resistances ($R_1$, $R_2$, $R_3$). A reduced effect of $T$ on $R_0$ was expected since $R_0$ is associated with ohmic resistance. At low operating temperatures ($T < 600°C$), the effect of the electrode resistance ($R_0$) dominates the total cell impedance.

$E_a$ values were evaluated according to the Arrhenius equations, for partial resistance electrode reactions, and reported in Fig. 5 for selected samples. In particular, Fig. 5(a) shows the temperature dependence of resistance associated at each single process for x =
0.5 electrodes, which gives $E_a$ values of 0.68, 1.67, 1.51 and 1.74 eV, associated with resistors $R_0$, $R_1$, $R_2$ and $R_3$, respectively. Moreover, Fig. 5(b) shows the ASR values as a function of temperature, and the Arrhenius plots of the global electrochemical process for the samples with high iron concentration ($x = 0.9, 0.7$ and $0.5$). The measured $E_a$ values are 1.52, 1.72 and 1.60 eV for the samples with $x = 0.9, 0.7$ and 0.5, respectively.

Various authors have found different values of activation energy and the nature of the individual process is not completely clear. In conclusion, results of the present work are in general agreement with those of a recent study (22).

CONCLUSIONS

Nanocrystalline La$_{0.8}$Sr$_{0.2}$Co$_{1-x}$Fe$_x$O$_3$ single phase perovskite-type oxides, prepared by amorphous citrate process, were characterized as electrodes on Ce$_{0.8}$Sm$_{0.2}$O$_{2-x}$ electrolyte using electrochemical impedance spectroscopy (EIS) measurements. The electrochemical properties of the interfaces between the porous electrode and the electrolyte were investigated from 600°C to 800°C under an uniform air atmosphere. Impedance measurements demonstrated that the direct oxidation of oxygen is achievable at temperatures between 600 and 800°C using SDC-based SOFC and La$_{0.8}$Sr$_{0.2}$Co$_{1-x}$Fe$_x$O$_3$.

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REFERENCES

1. J. L. Hallock Jr., P. J. Tharakan, A. S. Hall Charles, M. Jeerson and W. Wu, Energy, (2005), in press.
2. K. Frenken, M. Hekkert, P. Godfroij, Technol. Forecast Soc., 71, 485 (2004).
3. C. K. Wincewicz, S. J. Cooper, J. Power Sources, 140, 280 (2005).
4. T. Hibino, S. Wang, S. Kakimoro and M. Sano, Solid State Ionics, 127, 89 (2000).
5. T. Hibino, K. Ushiki and Y. Kuwahara, Solid State Ionics, 91, 69 (1996).
6. C. S. Ionel, C. P. Jacobson, S. J. Visco, and L.C. De Jonghe, Electrochem. Solid-State Lett., 7, A198 (2004).
7. C. M. Schaldach, W. L. Bourcier, P. H. Paul, and W. D. Wilson, J. Colloid and Interface Sci., 275, 601 (2004).
8. J. Fleig, J. Power Sources, 105, 228 (2002).
9. H. Hu, M. Liu, Solid State Ionics, 109, 259 (1998).
10. B. C. H. Steele, Solid State Ionics, 86-88, 1223 (1996).
11. Z. Shao and S. M. Haile, Nature, 431, 170 (2004).
12. V. Buscaglia and M. Leoni, in ICFAM Report, Genoa, Italy, (1991).
13. M. S. G. Baythoun and F. R. Sale, J. Mater. Sci., 17, 2757 (1982).
14. H. M. Zhang, Y. Teraoka, N. Yamazoe, Chem. Lett., 665 (1987).
15. L.-W. Tai, M. M. Nasrallah, H. U. Anderson, D. M. Sparlin, R. R. Sehlin, Solid State Ionics, 76, 273 (1995).
16. L.-W. Tai, M. M. Nasrallah, H. U. Anderson, D. M. Sparlin, R. R. Sehlin, Solid State Ionics, 76, 259 (1995).
17. C. Chieh, Acta Cryst., A40, 567 (1984).
18. J. R. Macdonald and M. K. Brachman, Rev. Mod. Phys., 28, 393 (1956).
19. J. R. Macdonald and D. R. Franceschetti, Impedance Spectroscopy - Emphasizing Solid Materials and Systems, J. R. Macdonald, Editor, p. 90, John Wiley & Sons, New York, (1987).
20. Y. J. Leng, S. H. Chan, S. P. Jiang, K. A. Khor, Solid State Ionics, 170, 9 (2004).
21. M. J. L. Ostergård, M. Mogensen, Electrochim. Acta, 38, 2015 (1993).
22. H. Ullmann, N. Trofimenko, F. Tietz, D. Stover, A. Ahmad-Khanlou, Solid State Ionics, 138, 79 (2000).