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L'OXYDE SOLIDE REVERSIBLE ET A L'OXYDE SOLIDE

(54) Title: MIXED METAL OXIDE ELECTRODE MATERIAL FOR SOLID OXIDE AND REVERSIBLE SOLID OXIDE FUEL
CELL APPLICATIONS

(57) **Abrégé/Abstract:**

Novel mixed-conducting perovskite oxides, including $\text{La}_{0.3}\text{Ca}_{0.7}\text{Fe}_{0.7}\text{Cr}_{0.3}\text{O}_{3-\delta}$, useful as electrodes for solid oxide fuel cells (SOFCs) and reversible solid oxide fuel cells (RSOFCs) applications. The electrochemical activity of an exemplary perovskite, screen-printed on a doped ceria electrolyte, towards both the oxygen reduction (ORR) and oxygen evolution (OER) reactions, was examined at 600-800 °C in stagnant air using a symmetrical RSOFC configuration. Under open circuit conditions, the exemplary perovskite showed a very low polarization resistance (R_p) of only 0.07 $\Omega \text{ cm}^2$ at 800 °C, comparable to some of the best-performing oxide materials. An air electrode made with the exemplary material was also found to be very stable, with very little loss in performance and no interfacial damage observed, even after 100 hr at a 0.4 V (OER) and -0.4 V (ORR) overpotentials.

ABSTRACT

Novel mixed-conducting perovskite oxides, including $\text{La}_{0.3}\text{Ca}_{0.7}\text{Fe}_{0.7}\text{Cr}_{0.3}\text{O}_{3-\delta}$, useful as electrodes for solid oxide fuel cells (SOFCs) and reversible solid oxide fuel cells (RSOFCs) applications. The electrochemical activity of an exemplary perovskite, screen-printed on a doped ceria electrolyte, towards both the oxygen reduction (ORR) and oxygen evolution (OER) reactions, was examined at 600-800 °C in stagnant air using a symmetrical RSOFC configuration. Under open circuit conditions, the exemplary perovskite showed a very low polarization resistance (R_p) of only $0.07 \Omega \text{ cm}^2$ at 800 °C, comparable to some of the best-performing oxide materials. An air electrode made with the exemplary material was also found to be very stable, with very little loss in performance and no interfacial damage observed, even after 100 hr at a 0.4 V (OER) and -0.4 V (ORR) overpotentials.

MIXED METAL OXIDE ELECTRODE MATERIAL FOR SOLID OXIDE AND REVERSIBLE SOLID OXIDE FUELL CELL APPLICATIONS

BACKGROUND OF THE INVENTION

Solid oxide fuel cells (SOFCs) are electrochemical devices that can convert chemical energy into electrical energy with very high efficiency. SOFCs also have several other advantages over combustion-based technologies, such as fuel flexibility (H_2 , hydrocarbon-based fuels such as CH_4 , CO , etc.), low emission of pollutants (SO_x and NO_x), and serve to capture CO_2 from the anode exhaust stream in high purity form, already separated from N_2 .

A typical SOFC consists of a dense electrolyte and two porous electrodes, the anode and the cathode. As part of the efforts to develop new energy conversion systems, there is great interest in reversible fuel cells, particularly reversible solid oxide fuel cells (RSOFCs). RSOFCs are single-unit, all-solid-state, electrochemical devices that can operate in both the fuel cell (SOFC) and electrolysis (SOEC) mode, thus acting as flexible energy conversion and storage systems, particularly to store intermittent renewable energy, such as wind or solar. The most common degradation and cell failure issue for RSOFCs arises at the air electrode when the cell is operating in the electrolysis mode (oxygen evolution at the air electrode). This is due to delamination of the electrocatalytic material from the electrolyte. Although the delamination mechanism is not fully understood, several processes have been postulated, including high oxygen pressure development, morphological changes in air electrodes, and electrolyte grain boundary separation [1-5]. Therefore, in this work, one of the main emphases is the development of a mixed conducting oxide (MIEC) that can withstand electrolysis conditions without delamination, while also exhibiting superior oxygen evolution and reduction activities.

To date, the most common materials used in RSOFCs are essentially the same as those used for SOFC, namely yttria stabilized zirconia (YSZ) as the electrolyte, a Ni-YSZ cermet as the fuel electrode, and a $La_{1-x}Sr_xMnO_3$ (LSM)-YSZ composite as the air electrode. The search for higher performance electrode and electrolyte materials for RSOFCs has been a key focus of research in recent years, with a particular emphasis on the development of new air electrodes. This has included the development of mixed ionic-electronic conductors (MIECs), such as Fe-based perovskites e.g., $SrFeO_{3-\delta}$, and

the use of a variety of cation dopants in both the A and B-sites [6-9]. As an example, LaCrO_3 and its doped variants are good candidates for application as interconnect materials and cathode materials in SOFCs [10]. Other high performance air electrode materials include $\text{La}_{0.6}\text{Sr}_{0.4}\text{Co}_{0.2}\text{Fe}_{0.8}\text{O}_{3-\delta}$ (LSCF), which has exhibited a low polarization resistance (R_p) of $0.18 \, \Omega \, \text{cm}^2$ at $800 \, ^\circ\text{C}$ [11], $\text{La}_{0.6}\text{Sr}_{0.4}\text{Fe}_{0.8}\text{Cu}_{0.2}\text{O}_{3-\delta}$ (LSFCu), which has demonstrated a very low R_p of $0.07 \, \Omega \, \text{cm}^2$ [12], and $\text{La}_{0.8}\text{Sr}_{0.2}\text{Cr}_{0.5}\text{Mn}_{0.5}\text{O}_3$ (LSCM) (2), which has exhibited a polarization resistance of $0.3 \, \Omega \, \text{cm}^2$ at $800 \, ^\circ\text{C}$ [13].

Recently, Chen et al. [14] have shown very good catalytic activity for both H_2/CO oxidation and O_2 reduction using the same MIEC material at both electrodes, i.e., $\text{La}_{0.3}\text{Sr}_{0.7}\text{Fe}_{0.7}\text{Cr}_{0.3}\text{O}_{3-\delta}$ (LSFCr), used for the first time as an SOFC electrode. The selected stoichiometry of the material was based on increasing the electronic and ionic conductivity of a Fe-based perovskite by heavy A-site substitution of La by Sr. As well, the partial substitution of Fe at the B site by Cr was done to stabilize the orthorhombic perovskite and its associated high level of vacancy disorder [15].

Usually, MIECs are synthesized by solid-state reactions, where the process involves multiple heating ($\geq 1200 \, ^\circ\text{C}$) and regrinding steps to help overcome the solid-state diffusion barrier [16]. Some of the traditional methods by which MIECs have been prepared include the sol-gel method [6], the EDTA citrate complexing process [12], the auto-ignition process [7], the Pechini method [9], and most commonly, by using combustion methods [14].

SUMMARY OF THE INVENTION

In the present study, the performance of derivatives of LSFCr containing calcium, i.e., $\text{La}_{0.3}\text{Ca}_{0.7}\text{Fe}_{0.7}\text{Cr}_{0.3}\text{O}_{3-\delta}$ (LCFCr), synthesized by the combustion method is examined. Several previous studies [17, 18] have shown that the thermal expansion coefficient (TEC) of perovskite materials decreases as the A-site cation size is decreased. Herein, the A-site of the perovskite was doped with Ca instead of Sr, to decrease the thermal expansion coefficient of the MIEC to more closely match that of the gadolinium doped ceria (GDC) electrolyte. While the thermal expansion data for perovskites reflects both physical and chemical expansion processes, the chemical expansion due to oxygen loss should dominate the thermal expansion behavior at high temperatures. The partial substitution of Ca for Sr may also enable the introduction of structural inhomogeneities, as calcium doping of LaFeO_3 is known to promote oxygen-vacancy ordering [19, 20].

However it was uncertain if the excellent electrochemical properties of LSFCr, could be maintained despite the replacement of Sr with Ca.

Consistent with these objectives, LCFCr/GDC/LCFCr symmetrical half cells, operated at 600-800 °C in stagnant air, were assessed herein and have been found to exhibit excellent electrochemical performance and long term durability, similar to that of the previously studied LSFCr material [8]. Electrochemical measurements herein have shown polarization resistances of only 0.07, 0.34, 0.71, 1.6 and 4 $\Omega \text{ cm}^2$ at 800, 750, 700, 650 and 600 °C, respectively.

This invention also provides microwave based methods for making the electrode material of the invention.

The invention further demonstrates the resistance of the electrode materials of this invention to sulfur.

The invention provides electrode material, i.e., electrocatalytic material, having the formula:



where:

M is Ca or a mixture of Ca and Sr where the molar ratio of Ca to Sr ranges from 1:1 to 100:1;

w is 0.2 to 0.4;

x is 0.6 to 0.8;

y is 0.6 to 0.8;

z is 0.2 to 0.4;

and

δ represents oxygen deficiency.

In specific embodiments, M is Ca.

In specific embodiments:

w is 0.27 to 0.33;

x is 0.67 to 0.73;

y is 0.67 to 0.73; and

z is 0.27 to 0.33.

In specific embodiments:

w is 0.29 to 0.31;

x is 0.69 to 0.71;

y is 0.69 to 0.71; and

z is 0.29 to 0.31.

In specific embodiments, w is 0.3; x is 0.7; y is 0.7; and z is 0.3.

In specific embodiments, the electrode material is a perovskite of the above formula.

In a specific embodiment, M is a mixture of Ca and Sr. More specifically in an embodiment, the molar ratio of Ca to Sr is 1:1. Yet more specifically, the molar ratio of Ca to Sr is 10:1.

In a preferred embodiment, in the electrode material M is Ca. In a preferred embodiment the electrode material is $\text{La}_{0.3}\text{Ca}_{0.7}\text{Fe}_{0.7}\text{Cr}_{0.3}\text{O}_{3-\delta}$.

In a specific embodiment, the electrode material of the invention has atomic % composition of;

La (15 ± 0.5)

Ca (34.5 ± 1)

Cr (15 ± 0.5) and

Fe(35 ± 1).

The invention further provides electrodes which comprise an electrode material of this invention. In a specific embodiment, such electrodes are formed as a layer on a solid oxide electrolyte. In a specific embodiment, the electrode is a fuel electrode, particularly for a solid oxide fuel cell or a reversible solid oxide fuel cell. In a specific embodiment, the electrode is an air or oxygen electrode, particularly for an SOFC or a RSOFC.

The invention further provides electrodes which consist of an electrode material of this invention. In a specific embodiment, such electrodes are formed as a layer on a solid oxide electrolyte. In a specific embodiment, the electrode is a fuel electrode, particularly for a solid oxide fuel cell or a reversible solid oxide fuel cell. In a specific embodiment, the electrode is an air or oxygen electrode, particularly for an SOFC or a RSOFC.

The invention further provides electrodes which comprise an electrode material of this invention as the electrocatalytic material of the electrode. Such electrodes may contain other supporting or non-electrocatalytic active materials. In a specific embodiment, such electrodes are formed having at least one layer of electrocatalytic material on a solid oxide electrolyte. In a specific embodiment, the electrode is a fuel

electrode, particularly for a solid oxide fuel cell or a reversible solid oxide fuel cell. In a specific embodiment, the electrode is an air or oxygen electrode, particularly for an SOFC or a RSOFC.

The invention further provides solid oxide fuel cell having an electrode which comprises an electrode material of the invention.

The invention further provides a reversible solid oxide fuel cell having an electrode which comprises an electrode material of the invention.

The invention also provides methods for generating electricity which comprises operating a solid oxide fuel cell having at least one electrode comprising an electrode material of the invention

The invention also provides methods for selectively generating electricity or employing electricity to generate a fuel which comprises selectively operating a reversible solid oxide fuel cell having an electrode of the invention comprising an electrode material of the invention to generate electricity or to generate a fuel.

The invention also provides methods wherein the solid oxide fuel cell or reversible solid oxide fuel cell is efficiently operated in the presence of a fuel containing hydrogen sulfide.

In specific embodiments, electrode materials of the invention are prepared by microwave assisted methods. In particular, electrode materials of the invention are prepared by microwave-assisted combustion, microwave-assisted co-precipitation or a microwave-assisted sol-gel method.

BRIEF DESCRIPTION OF THE DRAWINGS

Figure 1. Rietveld refinement of LCFCr powder (synthesized by the conventional combustion method) X-ray diffraction patterns observed (red dotted lines), refined (black solid lines), and their difference (bottom line). Green vertical bars indicate the X-ray reflection positions.

Figures 2A and 2B. *In situ* high temperature XRD patterns from 25-1100 °C in air (FIG. 2A). Cell parameters a, b and c and unit cell volume as a function of temperature (FIG. 2B).

Figure 3. HRTEM image of LCFCr crystals in a powder sample (prepared by the combustion method) along the [101] zone axis and the corresponding digital diffraction pattern.

Figure 4A and B. Impedance spectra of LCFCr at 800 °C, 750 °C, 700 °C, 650 °C and 600 °C (FIG. 4A). The impedance response was obtained in stagnant air at the OCP. Equivalent circuit used for data fitting (FIG. 4B)

Figure 5. Arrhenius plot of total polarization resistance (R_p) resistance vs. $1/T$ for LCFCr air electrode, screen-printed on GDC electrolyte and measured at the OCP in stagnant air over a temperature range of 600-800 °C.

Figure 6. Potentiostatic response of LCFCr tested at 800 °C and 0.4 V for 100 h in stagnant air. Inset shows the OCP impedance spectra, in air, collected before and after the potentiostatic measurements.

Figure 7. Potentiostatic response of LCFCr tested at 800 °C and -0.4 V for 100 h in stagnant air. Inset shows the OCP impedance spectra collected before and after the potentiostatic measurements in stagnant air.

Figure 8. (a-c) Back-scattered electron (BSE) images of the cross-section of the LCFCr/GDC electrolyte interface after 100 hours of cell testing at 0.4 V anodic and cathodic overpotential at 800 °C (Figures 8a and 8b). Figure 8c is a back-scattered electron (BSE) image of the cross-section of the LCFCr/GDC electrode/electrolyte interface in a cell before electrochemical testing.

Figure 9. Comparison of XRD patterns of LCFCr, synthesized by (a) the regular combustion method (Method 1) and two microwave-related methods, (b) by the microwave-combustion method (Method 2), and (c) by the microwave-assisted sol-gel method (Method 3) and calcined at three different temperatures, 700 °C, 900 °C and 1000 °C.

Figure 10. Rietveld refinement of powder X ray diffraction patterns for LCFCr observed (red dotted lines), refined (black solid lines), and their difference (bottom line). Vertical bars indicate the X-ray reflection positions. The patterns are for LCFCr powder (a) synthesized by the microwave-combustion method (Method 2) and (b) by the microwave-assisted sol-gel method (Method 3).

Figure 11. SEM images of LCFCr powders formed using (a) microwave-assisted combustion synthesis (Method 2) and (b) microwave-assisted sol-gel synthesis (Method 3).

Figure 12. HRTEM images of LCFCr crystals along the [101] zone axis and the corresponding diffraction patterns for powders formed by (a) microwave-assisted combustion synthesis (Method 2) and (b) microwave-assisted sol-gel synthesis (Method 3).

Figure 13. OCP impedance data for symmetrical full cell based on $\text{La}_{0.3}\text{M}_{0.7}\text{Fe}_{0.7}\text{Cr}_{0.3}\text{O}_{3-\delta}$ ($\text{M} = \text{Sr}, \text{Ca}$) electrodes, at 800 °C, showing the Nyquist and Bode (inset) plots, all in wet 30% H_2/N_2 gas mixtures at the fuel electrode and with air exposure at the O_2 electrode.

Figure 14. OCP impedance data for symmetrical full cell based on $\text{La}_{0.3}\text{Ca}_{0.7}\text{Fe}_{0.7}\text{Cr}_{0.3}\text{O}_{3-\delta}$ (LCFCr) electrodes at 800 °C and showing the Nyquist plot, all in wet 30% H_2/N_2 gas mixtures at the fuel electrode and with air or O_2 exposure at the O_2 electrode.

Figure 15. Performance plot for symmetrical full cell based on $\text{La}_{0.3}\text{M}_{0.7}\text{Fe}_{0.7}\text{Cr}_{0.3}\text{O}_{3-\delta}$ ($\text{M} = \text{Sr}, \text{Ca}$) electrodes and operated at 800 °C, all in wet 30% H_2/N_2 gas mixture at the fuel electrode and with air exposure at the O_2 electrode.

Figure 16. OCP impedance data for symmetrical full cell based on LCFCr electrodes, at 800 °C, showing the Nyquist plots in wet 30% H_2/N_2 , 15% H_2 +15% CO , or 30% CO gas mixtures at the fuel electrode and with air exposure at the O_2 electrode.

Figure 17. Performance plot for symmetrical full cell based on LCFCr electrodes, operated at 800 °C in wet 30% H_2/N_2 , 15% H_2 +15% CO , or 30% CO gas mixtures at the fuel electrode and with air exposure at the O_2 electrode.

Figures 18A-D. OCP and polarized EIS response for symmetrical full cell based on LCFCr electrodes at 800 °C, with wet 30% H_2/N_2 with or without 9 ppm H_2S fed to the fuel electrode and air fed to the O_2 electrode, showing the Nyquist plots acquired at (FIG. 18A) the OCP, (FIG. 18B) -100 mV vs the cell voltage at open circuit, (FIG. 18C) -300 mV vs. the cell voltage at open circuit, and (FIG. 18D) the corresponding resistances obtained from the fitted Nyquist plots using the $R_s(R_{\text{HF}}/CPE_{\text{HF}})(R_{\text{LF}}/CPE_{\text{LF}})$ equivalent circuit model and the % R_p change (inset).

Figures 19A and B. Effect of 9 ppm H_2S exposure and removal on LCFCr anode activity as a function of polarization at 800 °C, showing the current versus time (i/t) plots at (FIG. 19A) -100 mV and (FIG. 19B) -300 mV vs. the full cell voltage at open circuit.

DETAILED DESCRIPTION OF THE INVENTION

The invention relates to certain mixed metal oxide materials which are useful as the active material in electrodes of solid oxide fuel cells and particularly in reversible solid oxide fuel cells, either anodes or cathodes, therein. In a specific embodiment, the

electrode materials herein can be used to make symmetrical solid oxide fuel cells where the electrode material of the anode is the same as in the cathode.

As is known in the art fuel cells convert energy in fuels to electrical energy. Fuel cells can be operated in reverse (as an electrolyzer) using electrical energy to convert a molecule, such as water, to a fuel, such as hydrogen. Reversible cells operate in both modes. In a SOFC an oxidizing material, typically air or oxygen, is in contact with the cathode of the cell and the fuel is in contact with the anode of the cell. During fuel cell operation oxygen ions are transported from the cathode to the anode to oxidize the fuel to form water or if carbon monoxide is present to form carbon dioxide. SOFC cells typically operate at temperatures between about 750 to 950 °C. The electrodes are electrically connected and operation generates a current between the electrodes. In reverse mode, electrical energy is used to produce oxidant and fuel. A reversible SOFC cell (RSOFC or Solid oxide electrolyzer cell [SOEC]) can be operated in both modes. The present invention provides electrode materials that can be used as electrodes (anodes or cathodes or both) in SOFC cells, for example as air or oxygen electrodes, or as electrodes in reversible SOFC cells.

US Patent 8,354, 011 relates to reversible electrodes for solid oxide electrolyzer cells (SOEC). This patent provides a description of electrodes for such cells and the operation of such cells. FIG. 1 therein illustrates a schematic planar configuration of such a cell. Such a planar configuration can be employed in SOFC and SOEC of this invention.

Chen, M. et al. (2013) J. Power Sources 236:68-79 describes the use of certain Sr-rich chromium ferrites for symmetrical solid oxide fuel cells. In particular, the use of $\text{La}_{0.3}\text{Sr}_{0.7}\text{Fe}_{0.7}\text{Co}_{0.3}\text{O}_{3-\delta}$ is described.

US Patent 8,617,763 provides a description of certain SOFC cells and in particular a certain type of anode useful in such cells. Anode, cathode and electrolyte materials described therein can be employed in the devices of the present invention.

As is known in the art, a cell of the invention (SOFC or RSOFC) comprises an anode, a cathode and an ionically conductive solid oxygen electrolyte between the anode and the cathode. Optionally, a buffer layer is positioned between the anode and the electrolyte and/or between the cathode and the electrolyte. In an embodiment, the anode and/or the cathode is provided as a layer on one side of a layer of electrolyte. The other of the anode or the cathode being provided on the other side of the layer of electrolyte. Oxygen anions pass through the electrolyte layer from the cathode to anode

or the reverse dependent upon the mode in which the cell is operated. The optional buffer can be provided as a layer between the layer of anode material and the electrolyte and/or between the layer of cathode material and the electrolyte.

Electrode materials of the invention are those of formula:



where:

M is Ca or a mixture of Ca and Sr where the molar ratio of Ca to Sr ranges from 1:1 to 100:1;

w is 0.2 to 0.4;

x is 0.6 to 0.8;

y is 0.6 to 0.8;

z is 0.2 to 0.4;

w = x is 1;

and y = z is 1.

A preferred electrode material is $\text{La}_{0.3}\text{Ca}_{0.7}\text{Fe}_{0.7}\text{Cr}_{0.3}\text{O}_{3-\delta}$. In a particularly preferred embodiment the electrode material is a single phase material having no detectable second or other additional phase. In an embodiment, the electrode material is substantial single phase material with less than 5% by weight of a second or other additional phase or more preferably having less than about 2% by weight of a second or other additional phase. In specific embodiments, the electrode material is a perovskite.

Various methods can be employed to prepare the mixed metal oxide compounds of the invention. For example the following methods can be used:

A. Microwave method combined with a sol-gel methodology.

Microwave method and a sol-gel methodology can be combined to make electrode materials of the invention, for example $\text{La}_{0.3}\text{Ca}_{0.7}\text{Fe}_{0.7}\text{Cr}_{0.3}\text{O}_{3-\delta}$ (LCFC). Equimolar amounts of metal nitrates are dissolved in distilled water and a saturated polyvinyl alcohol (PVA) solution is added as the complexing agent. The amount of PVA added is such that the ratio of the total number of moles of cations to that of PVA is 1:2. Then the final solution is maintained at 80°C for 1.5 h to form a viscous gel solution. This gel is then irradiated with microwaves (up to 30 min) in a porcelain crucible placed inside another larger one filled with mullite. The microwave source operates at 2.45 GHz frequency and 800 W power and is uniquely able to handle the conditions needed. The polymeric and sponge-like-precursor is then calcined in air at

1000°C for 6 h in order to decompose the organic remnants, rendering a black powder as the final product.

B. Microwave-assisted combustion

Metal nitrates are mixed in stoichiometric proportions, and then water and glycine are added. The sample is introduced into the microwave furnace at 2.45 GHz frequency and 800 W power for 30 minutes. When the water is evaporated, combustion occurred and a flame is observed inside the microwave furnace for 10 minutes. Then the sample is calcined in air at 900°C for 6 h in order to decompose the organic remnants, rendering a black powder as the final product.

C. Microwave-assisted co-precipitation

Metal nitrates are mixed in stoichiometric proportion, 25 ml of acetic acid are added, and then the mixture is stirred and heated at 60°C for 2 hours. When the nitrate vapors are evaporated, a gel formed and then it is introduced into the microwave furnace at 2.45 GHz frequency and 800 W power for 30 minutes, followed by calcination at 900°C.

D. Regular combustion method

When synthesized using the regular combustion method (Method 1), the metal nitrates are mixed in stoichiometric proportions and dissolved in deionized water. A 2:1 mole ratio of glycine to the total cation content is used. Solutions are slowly stirred on a hot plate until auto-ignition and self-sustaining combustion occurred. The sample is first ground and then calcined in air at 1200 °C for 12 hours.

The electrode materials of the invention can be employed in any SOFC or RSOFC configurations and are particularly useful in those configurations which employ electrode layers.

Solid electrolytes useful in the invention include stabilized zirconia, including yttrium stabilized zirconia and scandia stabilized zirconia, doped ceria, including gadolinium-doped ceria or samarium-doped ceria, and certain mixed metal oxides such as LSGM (lanthanum strontium gallium magnesium oxide). One of ordinary skill in the art knows how to select solid oxide electrode s appropriate for use in SOFC and RSOFC devices.

In specific embodiments herein, the SOFC and RSOFC cells are symmetric wherein the anode and cathode materials are the same and are electrode materials of this

invention. In alternative embodiments, alternative anode having alternative electrode materials can be used in combination with cathodes having electrode materials of this invention. Alternate anode materials include among others, perovskite mixed metal oxide materials other than those of this invention, e.g., $\text{La}_{0.3}\text{Sr}_{0.7}\text{Fe}_{0.7}\text{Cr}_{0.3}\text{O}_{3-\delta}$; cermets having a metal phase, such as a nickel or nickel oxide phase, and a ceramic phase, such as doped ceria (samaria or gadolinium-doped); and/or stabilized zirconia.

In alternative embodiments, alternative cathode having alternative electrode materials can be used in combination with anodes having electrode materials of this invention. Alternate cathode materials include among others, perovskite mixed metal oxide materials other than those of this invention, e.g., $\text{La}_{0.3}\text{Sr}_{0.7}\text{Fe}_{0.7}\text{Cr}_{0.3}\text{O}_{3-\delta}$; electron conducting phases (e.g., nickel oxide and magnesium oxide).

One of ordinary skill in the art in view of what is known in the art about electrode materials useful in SOFC or RSOFC application can select among known electrode materials for alternative electrode materials that are useful in combination with the electrode materials of this invention.

Anodes and cathodes may be formed a one or more layers on a surface of a solid electrolyte.

Solid electrolyte can be in a planar layer configuration with one side of the electrolyte layer containing a layer of anode material and the other a layer of cathode material. In symmetric cells the electrode layers are the same materials.

SOFC and RSOFC electrodes are prepared by conventional methods by formation of at least one layer of the electrode material on an appropriate substrate. In a specific embodiment, an electrode is formed by application of a layer of electrode material on a surface of a solid oxide electrolyte material. In a preferred method of preparation of electrodes microwave sintering is employed. The electrode material is screen printed onto the solid oxide electrolyte and it is irradiated at 900 °C for 20 minutes in a Milestone MultiFAST-6 sintering microwave. It was found that the best performance was for the sample irradiated at 900 °C and the cell performance is comparable to the electrodes sintered using conventional furnaces at 1200 °C.

The SOFC and RSOFC of the invention can be formed into stacks as is known in the art. Stacks of such cells are provided by this invention. US Patent 8,663,869 provide examples of such fuel cell stacks.

Molero-Sanchez, B. et al. (2015) Int'l J. Hydrogen Energy 40:1902-1910, Addo, P. et al. (2015) ECS Transactions 66(2):219-228; and Molero-Sanchez, B. et al. (2015)

Ceramics Int'l (article in press, available on line at web site science direct.com) provide details of the examples provided herein.

When a Markush group or other grouping is used herein, all individual members of the group and all combinations and subcombinations possible of the group are intended to be individually included in the disclosure. Every formulation or combination of components described or exemplified can be used to practice the invention, unless otherwise stated. Specific names of compounds are intended to be exemplary, as it is known that one of ordinary skill in the art can name the same compounds differently.

One of ordinary skill in the art will appreciate that methods, device elements, starting materials, and synthetic methods other than those specifically exemplified can be employed in the practice of the invention without resort to undue experimentation. All art-known functional equivalents, of any such methods, device elements, starting materials, and synthetic methods are intended to be included in this invention. Whenever a range is given in the specification, for example, a temperature range, a time range, or a composition range, all intermediate ranges and subranges, as well as all individual values included in the ranges given are intended to be included in the disclosure.

Without wishing to be bound by any particular theory, there can be discussion herein of beliefs or understandings of underlying principles relating to the invention. It is recognized that regardless of the ultimate correctness of any mechanistic explanation or hypothesis, an embodiment of the invention can nonetheless be operative and useful.

The terms and expressions which have been employed are used as terms of description and not of limitation, and there is no intention in the use of such terms and expressions of excluding any equivalents of the features shown and described or portions thereof, but it is recognized that various modifications are possible within the scope of the invention claimed. Thus, it should be understood that although the present invention has been specifically disclosed by preferred embodiments and optional features, modification and variation of the concepts herein disclosed may be resorted to by those skilled in the art, and that such modifications and variations are considered to be within the scope of this invention.

THE EXAMPLES

Example 1:

1. Material Synthesis and characterization

$\text{La}_{0.3}\text{Ca}_{0.7}\text{Fe}_{0.7}\text{Cr}_{0.3}\text{O}_{3-\delta}$ (LCFCr) powders were synthesized by the combustion method. The metal nitrate precursors were mixed in stoichiometric proportions and dissolved in deionized water. A 2:1 mole ratio of glycine to the total cation content was used. Solutions were slowly stirred on a hot plate until auto-ignition and self-sustaining combustion occurred. Then the sample was ground and calcined in air at 1200 °C for 12 hours.

Materials were purchased from Alfa Aesar as follows: Glycine (99.5%); $\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ (99.9%); $\text{Sr}(\text{NO}_3)_2$ (99.0%); $\text{Ca}(\text{NO}_3)_2$ (99.0%); $\text{Cr}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ (98.5%); and $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ (98-101%).

X-ray diffraction (XRD) patterns of all of the samples synthesized in this work were collected using a Philips X'Pert PRO ALPHA1 of Panalytical B.V. diffractometer with $\text{Cu K}\alpha_1$ monochromatic radiation ($\lambda = 1.54056 \text{ \AA}$). The diffractometer was equipped with a primary curved Ge111 primary beam monochromator and a speed X'Celerator fast detector, operating at 45 kV and 40 mA. XRD patterns were collected in the 2θ range of $5 - 120^\circ$ at room temperature with a step size of 0.017° and 8 s counting time in order to ensure sufficient resolution for structural refinement.

Powder X-ray Thermodiffraction patterns were collected on an X'Pert PRO MPD diffractometer with a high temperature reactor chamber Anton Paar HTK1200 camera, using $\text{Cu K}\alpha$ radiation. The measurements were carried out at between room temperature and 1100 °C. The standard working conditions were a 2θ range of $10 - 70^\circ$ with an angle step size of 0.033° and a 25 s counting time. Sample was heated to the target temperatures at a ramp rate of 5 °C/min and stabilized in air for 40 min prior to the measurements. After that, the sample was cooled to RT and XRD patterns were acquired again in order to determine the phase stability of the LCFCr material under heating and cooling conditions.

Fullprof Software was employed to carry out structural refinements from conventional XRD patterns using the Rietveld method. This method of refining the powder diffraction data was used to determine the crystal structure. Zero shift, lattice parameters, background, peak width, shape and asymmetry, atomic positions and isotropic temperature factors were all refined. The Thompson–Cox–Hastings pseudo-Voigt convoluted with axial divergence asymmetry function was used to describe the

peak shape. Linear interpolation between set background points with refineable heights was used afterwards. The values were refined to improve the agreement factors.

All samples investigated by scanning electron microscopy (SEM) were first sputter-coated with Au in an EMITECH K550 apparatus. Field-emission SEM (FE-SEM) was performed using a JEM 6335 F electron microscope with a field-emission gun operating at 10 kV. The FE-SEM was also equipped with a LINK ISIS 300 detector for the energy-dispersive analysis of the X-rays (XEDS). SEM imaging of the cells and attached electrode layers was carried out using a Zeiss Sigma VP field emission SEM.

High resolution transmission electron microscopy (HRTEM) analysis of the LCFCr powders was performed using a JEOL 3000F TEM, operating at 300 Kv, yielding information limit of 1.1 Å. Images were recorded with an objective aperture of 70 µm centered on a sample spot within the diffraction pattern area. Fast Fourier Transforms (FFT) of the HRTEM images were carried out to reveal the periodic image contents using the Digital Micrograph package.

2. Cell fabrication and testing

The LCFCr powders obtained from the regular combustion method were milled (high energy planetary ball mill, Pulverisette 5, Fritsch, Germany) in an isopropanol medium at a rotation speed of 300 rpm for 2 h using zirconia balls. The electrolyte-supported symmetrical cell was constructed with a GDC electrolyte (1 mm thick) as the substrate. The electrolyte was fabricated by pressing the GDC powder under 200 MPa pressure and sintering at 1400 °C for 4 h. The ca. 30 µm thick LCFCr electrodes were then screen-printed symmetrically (over an area of 0.5 cm²) onto both sides of the GDC support and fired at 1000 °C for 2 h. Au paste (C 5729, Heraeus Inc., Germany) was painted on both of the electrode layers to serve as the current collectors.

In all of this work, the electrochemical measurements to evaluate the cell performance were performed using the 3 electrode technique in air. Impedance spectra were collected under open circuit conditions, between 600 °C and 800 °C, using an amplitude of 50 mV in the frequency range of 0.01 to 65 kHz using a Solatron 1287/1255 potentiostat/galvanostat/impedance analyzer. Other experiments involved the application of a 0.4 V anodic and -0.4 V cathodic overpotential to the LCFCr working electrode vs. the reference electrode and measuring the current passed through the cell with time. Zview software was used to fit and analyze the impedance data.

3. Results and Discussion

Structural characteristics of LCFCr electrodes formed using the combustion method

3.1 X-ray diffraction and Rietveld refinement of LCFCr powders

XRD analysis of the $\text{La}_{0.3}\text{Ca}_{0.7}\text{Fe}_{0.7}\text{Cr}_{0.3}\text{O}_{3-\delta}$ (LCFCr) powders was performed and structural parameters for LCFCr were obtained from the Rietveld-refined XRD data. The Rietveld refinement indicated that the synthesized LCFCr powders are a pure crystalline phase with an orthorhombic perovskite structure. FIG. 1 shows the Rietveld refinement fits for LCFCr, and a distorted perovskite structure with an orthorhombic symmetry (S.G. *Pnma*, #62) was confirmed. The unit cell vectors can be represented by $\sqrt{2}a_p \times 2a_p \times \sqrt{2}a_p$, where a_p refers to the simple cubic perovskite cell. The cell parameters were found to be: $a = 5.4540(2) \text{ \AA}$, $b = 7.7158(3) \text{ \AA}$ and $c = 5.4544(1) \text{ \AA}$, while the refinement fit parameters for LCFCr were $\chi^2 = 0.96$, $R_p = 3.26$, $R_{wp} = 4.29$, $R_{exp} = 4.37$ and $R_{Bragg} = 4$. Although the orthorhombic unit cell seems to be pseudo tetragonal, refinements were also performed in the *P4/mmm* space group, but these yielded higher R values ($\chi^2 = 4.03$, $R_p = 5.53$, $R_{wp} = 8.76$, $R_{exp} = 4.37$ and $R_{Bragg} = 5.59$), while the lattice parameters when using this tetragonal group were: $a = b = 5.45441(1) \text{ \AA}$ and $c = 7.7092(1) \text{ \AA}$. Thus, the *P4/mmm* space group was not used for the LCFCr electrode material.

In order to determine the phase stability of the LCFCr material under heating and cooling conditions, *in situ* high temperature XRD measurements were performed from room temperature to 1100 °C, and then back to room temperature again, all in air. FIG. 2A shows that the orthorhombic structure is maintained over the full temperature range up to 1100 °C, since peak splitting is not observed. Moreover, a shift of all the characteristics peaks towards lower angles is observed, which may suggest an increase in the cell parameters with temperature. FIG. 2B shows the cell parameters a , b and c , as well as the unit cell volume vs temperature, calculated from XRD data (FIG. 2A).

Table 1-1 shows the average thermal expansion coefficient calculated from the thermal XRD data (Figure 2), using the methods described in ref [26]. The average TEC is $11.5 \times 10^{-6} \text{ K}^{-1}$ for lattice parameter a , and $12.0 \times 10^{-6} \text{ K}^{-1}$ for lattice parameters b and c . These values are comparable to those reported for the well-known cathode material LSM ($12.2 \times 10^{-6} \text{ K}^{-1}$) [21-23] and noticeably lower than the TEC values for LSCF ($16.3 \times 10^{-6} \text{ K}^{-1}$) [21, 24]. The measured TEC values are also considerably lower

than those for the Sr-rich perovskite, $\text{La}_{0.3}\text{Sr}_{0.7}\text{Fe}_{0.7}\text{Cr}_{0.3}\text{O}_{3-\delta}$ (LSFCr), previously developed in our group [14]. More importantly, the measured thermal expansion coefficient (TEC) of LCFCr (Table 1) matches very well with the TEC of ceria ($11.9 \times 10^{-6} \text{ K}^{-1}$) [11, 21, 25-31], which is a critical requirement for minimizing delamination of the electrodes from the electrolyte, thus avoiding mechanical failure of the cell.

Table 1-1. Average thermal expansion coefficient (TEC) for LCFCr material, determined by *in situ* XRD analysis

Thermal expansion parameters	Average TEC ($\times 10^{-6} \text{ K}^{-1}$)
Lattice parameter (a)	11.5 (25-1100 °C)
Lattice parameter (b)	12.0 (25-1100 °C)
Lattice parameter (c)	12.0 (25-1100 °C)

3.2 TEM analysis of LCFCr powder

Transmission Electron Microscopy (TEM) analysis was also performed on the LCFCr powder material. The cation composition, evaluated semi-quantitatively by X-ray energy dispersive spectroscopy in more than ten single crystals, is in good agreement with the theoretical proportions of the elements in LCFCr, indicating the high purity of the powder. High resolution TEM micrographs recorded along the same zone axis [101] show nano-sized twinned domains rotated by 90°. The appearance of these domains can be associated with the pseudo-cubic nature of these materials. The presence of these domains can help to avoid the formation of tetrahedral chains and therefore the formation of brownmillerite-type defects [32]. Typically, raising the temperature leads to a phase transition of brownmillerite to perovskite at high temperatures, accompanied by a conductivity jump [33]. As mentioned earlier, perovskites exhibit a higher ionic conductivity than brownmillerites and hence they are better candidates for air electrodes in RSOFCs.

3.3 Electrochemical performance of LCFCr as a reversible air electrode

3.3.1 Open circuit studies

The electrochemical performance of the LCFCr material, synthesized by the regular combustion method, was then studied, with the impedance spectra of the

LCFCr/GDC/LCFCr symmetrical half cells in air at 800, 750, 700, 650 and 600 °C shown in FIG. 4A, all at the open circuit potential (OCP). From FIG. 4A two separable arcs are visible over the full frequency range. The best-fit equivalent circuit is shown in FIG. 4B, where R_s is the series ohmic resistance, the sum of R_2 (high frequency) and R_3 (low frequency) is the total polarization resistance (R_p), and the CPEs are constant phase elements. R_s corresponds to the intercepts of the impedance arc with the real axis at high frequencies and arises from the resistance to ion migration within the electrolyte, resistance to electron transport within the cell components, and contact resistances [34]. R_p is the difference between the two real axis intercepts of the impedance arcs and CPE is a component that models the behaviour of a an imperfect capacitor [35], with the associated n parameter being 1 for a perfect capacitor, 0 for a pure resistor, and 0.5 for a Warburg element [36]. The high-frequency arc (R_2) corresponds to the charge transfer process and the low-frequency arc (R_3) has been attributed previously in the literature [12, 37, 38] to oxygen adsorption and desorption on the electrode surface, combined with the diffusion of the oxygen ions.

As can be seen in Table 1-2, the R_p values are very small, 0.07, 0.33, 0.73, 1.67 and 4.24 $\Omega \text{ cm}^2$ at 800, 750, 700, 650 and 600 °C, respectively, even lower than what has been reported for the well-known cathode material LSCF (0.18 $\Omega \text{ cm}^2$ at 800 °C) [11, 39]. However, these R_p values are comparable to what was reported for $\text{La}_{0.3}\text{Sr}_{0.7}\text{Fe}_{0.7}\text{Cr}_{0.3}\text{O}_{3-\delta}$ (LSFCr), previously developed in our group and studied using a LSGM electrolyte, giving an R_p value of 0.11 $\Omega \text{ cm}^2$ at 800 °C [14]. In terms of the capacitance values obtained from the cell examined in FIG. 4, the high-frequency arc (R_2) has a CPE-T value of ca. $10^{-1} (\text{F s})^{1-n}/\text{cm}^2$ and an associated CPE-P value of 0.72, while the low-frequency arc (R_3) also has a CPE-T value of ca. $10^{-1} (\text{F s})^{1-n}/\text{cm}^2$, but an associated CPE-P value of 0.86, very close to that of an ideal capacitor.

Table 1-2. Fitting parameters of the impedance data obtained in Figure 4

Temperature	R_{LF} ($\Omega \cdot \text{cm}^2$)	CPE-P (LF)	R_{HF} ($\Omega \cdot \text{cm}^2$)	CPE-P (HF)	R_p ($\Omega \cdot \text{cm}^2$)	Chi-squared
800 °C	0.05	0.86	0.02	0.72	0.07	1.6x10 ⁻⁵
750 °C	0.21	0.52	0.12	0.71	0.33	1.1x10 ⁻⁴
700 °C	0.51	0.32	0.22	0.70	0.73	3.1x10 ⁻⁴

650 °C	1.18	0.27	0.49	0.67	1.67	3.5x10 ⁻⁴
600 °C	2.99	0.22	1.24	0.61	4.24	4x10 ⁻⁴

The Arrhenius plot of the total OCP polarization resistance for the LCFCr material in air, obtained from the data of FIG. 4A, is presented in FIG. 5. According to the fitting parameters shown in Table 1-2, the resistance of the low frequency arc is approximately 90% of the total R_p and thus the activation energy associated with this arc will be dominant. As shown in FIG. 5, good linearity of the plot of the polarization resistance versus the inverse of temperature is obtained. The derived activation energy (E_a) for the ORR is 125 kJ/mol, which is lower than previously reported for well-known cathode materials, such as LSM (173.7 kJ/mol [40, 41]) and LSCF (178.5 kJ/mol [42]) at the OCP in air. The lower E_a indicates that the LCFCr material is a better catalyst for the ORR than these two materials. Furthermore, according to the literature, this range of activation energies may indicate that oxygen diffusion in the gas phase is one of the slow steps of the reaction [36].

3.3.2 Performance of LCFCr under anodic and cathodic polarization

To further investigate the medium-term electrochemical stability of the LCFCr air electrode for RSOFC applications, potentiostatic experiments at 800 °C, at overpotentials of 0.4 V (OER) and -0.4 V (ORR), were performed for 100 h. In FIG. 6, a degradation rate of 0.59 mA h⁻¹ is seen over 100 h at the anodic 0.4 V overpotential. Impedance measurements, however, show that R_p is very similar before (0.35 Ω cm²) and after (0.30 Ω cm²) the 100 h test at 0.4 V, demonstrating very good medium-term stability of the LCFCr air electrode performance under typical OER operating conditions.

These experiments were performed 24 days after commencing cell testing (FIG. 4) and some degradation of the cell performance has clearly occurred, as seen by comparing the results in Figs. 6 and 7 with those in FIG. 4. However, the ohmic resistance (R_s) is the main cause of this degradation, having changed from 0.77 to 0.99 Ω cm², likely due to the sintering of the current collectors. The shift of the summit frequency (41 Hz before testing and 2.58 Hz after testing) may be consistent with the densification of the Au current collector. Thus, the majority of the degradation seen in FIG. 6 is thus due to this increase in R_s . In support of this conclusion, our previously

published WDX elemental map studies did not reveal an incompatibility issue between LCFCr and GDC [43].

The medium-term electrochemical stability of the LCFCr air electrode towards the oxygen reduction reaction (ORR) was then investigated at a -0.4 V overpotential, again at 800 °C for 100 h. In FIG. 7, a loss in current of 0.67 mA h^{-1} is seen over this time period, which suggests that LCFCr experiences a slightly faster degradation as an ORR catalyst than during the OER. Impedance measurements performed before and after the potentiostatic experiment (FIG. 7) show that R_p increases from $0.25 \Omega \text{ cm}^2$ before cathodic polarization to $0.30 \Omega \text{ cm}^2$ after the 100 h test at -0.4 V. However, R_s does not change, and, in fact, has the same value as that before the anodic (+0.4 V) polarization experiment in FIG. 6. These observations show that LCFCr performs more poorly as an ORR catalyst than during the OER. Furthermore, the fact that R_s in FIG. 7 has recovered to its original OCP value before anodic polarization (FIG. 6) demonstrates that LCFCr is an excellent air electrode for the OER, and that the loss in performance in FIG. 6 is not permanent (the losses observed here in R_s appear to be reversible). Sintering of the current collectors remains the most likely reason for the increase of R_s with time. Furthermore, it is evident that, when the polarization was switched from +0.4 V (FIG. 6) to -0.4 V (FIG. 7), R_s fully recovered. Thus, it is plausible that dewetting of the gold current collector, which may have occurred as a result of sintering at +0.4 V, may have reversed upon the change of polarization direction. This is consistent with the known effect of electrical potential on interfacial tensions [44, 45].

Overall, the LCFCr material is seen to be an excellent air electrode, giving R_p values in the range or even lower than the best SOFC cathode materials discussed in the literature in this temperature range. For example, LSCF has exhibited an R_p value of $0.18 \Omega \text{ cm}^2$ at the OCP [11] and LSFCu an R_p of $0.07 \Omega \text{ cm}^2$, both at 800 °C [12].

3.3.3 Cell microstructure

The typical microstructure of the cell, examined by back-scattered SEM, is shown after electrochemical testing in FIGs. 8A and 8B. The cell consists of a 1 mm dense GDC electrolyte layer, with only one of the two LCFCr electrode layers ($\sim 30 \mu\text{m}$ thick) shown. Also, a gold current collector layer is shown in the image (white phase in FIG. 8A, displaying very good porosity at higher magnification (FIG. 8B)). For comparison, FIG. 8C shows a somewhat higher magnification image (vs. FIG. 8A) of

the microstructure and the interface of a cell before electrochemical analysis, for comparison.

The LCFCr/GDC interface after cell testing at both 0.4 V and -0.4 V, each for 100 h, is seen in Figs. 8A and 8B to have retained a continuous good contact between the LCFCr electrodes and the GDC electrolyte, with no delamination or cracking detected. As mentioned earlier, the delamination of the oxygen electrode from the electrolyte is the most common degradation and cell failure issue for high temperature electrolysis cells [2]. Thus, the fact that our LCFCr-based symmetrical cell did not show any electrode delamination (FIG. 8B) after long times under both anodic and cathodic polarization is very encouraging.

3.4. Conclusions

In this example, Ca was substituted for Sr in the A site of $\text{La}_{0.3}\text{Sr}_{0.7}\text{Fe}_{0.7}\text{Cr}_{0.3}\text{O}_{3-\delta}$ (LSFCr), producing a novel mixed conducting perovskite material $\text{La}_{0.3}\text{Ca}_{0.7}\text{Fe}_{0.7}\text{Cr}_{0.3}\text{O}_{3-\delta}$ (LCFCr). These oxides are being developed for application as air electrodes for use in reversible solid oxide fuel cells (RSOFCs). Due to the smaller ionic radius of Ca vs. Sr, we were expecting to decrease the thermal expansion coefficient of the perovskite to more closely match that of commonly employed RSOFC electrolytes.

In this example, LCFCr was prepared by using the combustion method. XRD analysis showed that the LCFCr powders are a pure crystalline phase, also confirmed by TEM analysis, with an orthorhombic perovskite structure. It was also shown that the average TEC values match closely with that of gadolinium-doped ceria (GDC), the electrolyte used here.

Electrochemical measurements showed very good performance, overall, with open circuit potential (OCP) polarization resistances (R_p) comparable to what has been reported for other well-known perovskites, used in air, at 600 - 800 °C. Further, the activation energy of the oxygen reaction at LCFCr, at the OCP, was found to be lower than literature values for other well-known air electrodes. The medium-term electrochemical stability of the LCFCr air electrode towards the OER (0.4 V) and ORR (-0.4 V) was also investigated at 800 °C for 100 h, showing that R_p hardly changes during the OER, but increases by ca. 20 % during the ORR. SEM imaging of the LCFCr/GDC interface showed no delamination or other forms of physical degradation of the cell after 100 hours at both 0.4 V and -0.4 V. Thus, it is clear that LCFCr is a very promising air electrode material for RSOFC applications.

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Example 2: Microwave-assisted synthesis

1. Introduction

In this example, alternative powder processing methods are examined, with a primary focus on microwave-based synthesis, that could both lower material manufacturing costs and further enhance cathode performance for solid oxide fuel cell applications. $\text{La}_{0.3}\text{Ca}_{0.7}\text{Fe}_{0.7}\text{Cr}_{0.3}\text{O}_{3-\delta}$ (LCFCr), formed using conventional solid-state methods, has been shown in earlier work to be a very promising catalyst for the oxygen reduction reaction. To further increase its performance, microwave methods were used to increase the surface area of LCFCr and to decrease the processing time. It was found that the material could be obtained in crystalline form in only 8 hours, with the synthesis temperature lowered by roughly 300 °C as compared to conventional methods. Current research in the solid oxide fuel cell (SOFC) field is moving towards the use of mixed ionic and electronic conducting oxides (MIEC), which have been shown to be more durable as cathodes than conventional $\text{La}_{1-x}\text{Sr}_x\text{MnO}_3$ (LSM) materials. Usually, MIECs are synthesized by solid-state reactions, where the process involves multiple heating (≥ 1200 °C) and regrinding steps to help overcome the solid-state diffusion barrier (1, 2). Some of the methods by which MIECs have been traditionally prepared include the sol-gel method (3), the EDTA citrate complexing process (4), the auto-ignition process (5), the Pechini method (6), and most commonly, by using combustion methods (7).

In order to enhance the diffusion rate of the ceramic precursors by several orders of magnitude, thus shortening the reaction time and potentially lowering the reaction temperature, there has been an interest in the use of microwave-assisted methods. Furthermore, it is possible to induce interesting changes in particle morphology and sizes using microwave methods (8). Also, microwave-assisted techniques are understood to be environmentally friendly, as they require less energy than conventional material processing methods. This makes microwave synthesis an example of “Green Chemistry” or “Sustainable Chemistry” (8, 9).

The main features that distinguish microwave synthesis from conventional methods are faster energy transfer rates, i.e., more rapid heating rates, and the selective heating of materials. This leads to a unique temperature distribution within the material when it is heated in a microwave furnace. During conventional heat treatment, energy is transferred to a material through thermal conduction and convection, creating thermal gradients. However, in the case of microwave heating, energy is transferred directly to

the material through an interaction of the material at the molecular level with the electromagnetic waves (10). The most important contribution in microwave heating may be that the dipoles in the material follow the alternating electromagnetic field associated with the microwave, with its rapidly changing electric field (ca. 2.4×10^9 times per second). The resistance to this movement generates a considerable amount of heat (11, 12), thus leading to more rapid heating rates.

It has been suggested that, the more complex a material is, the more difficult it is to prepare by using microwave-assisted synthesis. In more complex systems, very good diffusion is required to uniformly disperse three or more cations throughout the sample during the synthesis. The usual solution to this problem is to combine microwave irradiation with other methods, such as sol-gel or combustion synthesis, as has been done for the synthesis of complex perovskites, such as $\text{La}_{0.8}\text{Sr}_{0.2}\text{Fe}_{0.5}\text{Co}_{0.5}\text{O}_3$ or $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$ (1, 13).

Previous research in our group has focused on the development of a sulphur and coke tolerant electrode-supported SOFCs, most recently based on $\text{La}_{0.3}\text{Sr}_{0.7}\text{Fe}_{0.7}\text{Cr}_{0.3}\text{O}_{3-\delta}$ (LSFCr) as a mixed ionic-electronic conducting perovskite material. LSFCr has shown very good catalytic activity for both H_2/CO oxidation and O_2 reduction, thus potentially having use in symmetrical SOFCs (7). In order to take advantage of the excellent performance of LSFCr, the A-site of the perovskite was doped with Ca instead of Sr, as Ca has a smaller ionic radius than Sr. The goal was to decrease the thermal expansion coefficient of this derivative of LSFCr, i.e., $\text{La}_{0.3}\text{Ca}_{0.7}\text{Fe}_{0.7}\text{Cr}_{0.3}\text{O}_{3-\delta}$ (LCFCr), to more closely match that of a Gd-doped ceria (GDC) electrolyte. The partial substitution of Ca for Sr may also enable the introduction of structural inhomogeneties, as Ca doping of LaFeO_3 is known to promote oxygen-vacancy ordering (14, 15).

In the present study, we are focused on the synthesis and characterization of LCFCr, formed using three different methods, regular combustion (Method 1), microwave-assisted combustion (Method 2), and microwave-assisted sol-gel synthesis (Method 3). We show that a single phase material can be successfully synthesized using microwave-assisted methods and that we can also lower the calcination temperature by 200-300 °C using this approach. Our recent work on LCFCr, synthesized using Method 1, has shown very good electrochemical characteristics (16). For this reason, parallel comparison studies (17) of the performance of LCFCr-based cathodes, constructed using the three methods described in this paper, are currently being carried out.

2. Material Synthesis

$\text{La}_{0.3}\text{Ca}_{0.7}\text{Cr}_{0.3}\text{Fe}_{0.7}\text{O}_{3-\delta}$ (LCFCr) powders were synthesized using three different methods, the regular combustion method (Method 1), microwave-assisted combustion (Method 2), and microwave-assisted sol-gel synthesis (Method 3). When synthesized using the regular combustion method (Method 1), the metal nitrates were mixed in stoichiometric proportions and dissolved in deionized water. A 2:1 mole ratio of glycine to the total cation content was used. Solutions were slowly stirred on a hot plate until auto-ignition and self-sustaining combustion occurred. Then the sample was calcined in air at 1200 °C.

LCFCr powders were also synthesized by microwave-assisted combustion (Method 2). Here, the metal nitrates and glycine were dissolved in deionized water using the metal cation proportions required to generate the correct oxide stoichiometry. A 2:1 mole ratio of glycine to the total metal content was used. The stirred solutions were introduced into the microwave furnace and exposed to a 2.45 GHz frequency and 800 W power for 30 minutes. When the water had evaporated, combustion occurred. Then the sample was calcined in air at 700 °C, 900 °C and 1000 °C for 8 h in order to decompose the organic remnants, rendering a black powder as the final product.

In Method 3, microwave energy and a sol-gel methodology were combined to produce the LCFCr powders, with the metal cation proportions used based on the desired stoichiometry. Metal nitrates were dissolved in distilled water and a saturated polyvinyl alcohol (PVA) solution was added to serve as the complexing agent. The amount of PVA added was such that the ratio of the total number of moles of cations to that of PVA was 1:2. Then the final solution was maintained at 80 °C for 1.5 h to form a viscous gel. The gel was then microwave irradiated (up to 30 min) in a porcelain crucible placed inside another larger one filled with mullite. The microwave source operated at a 2.45 GHz frequency and 800 W power and was uniquely able to handle the conditions needed in this work. The polymeric and sponge-like-precursor was then calcined in air at 700 °C, 900 °C and 1000 °C for 8 h in order to decompose the organic remnants, rendering a black powder as the final product.

2. Material characterization

X-ray diffraction (XRD) patterns of all samples synthesized in this work were collected using a Philips X'Pert PRO ALPHA1 of Panalytical B.V. diffractometer with $\text{Cu K}\alpha_1$ monochromatic radiation ($\lambda = 1.54056 \text{ \AA}$). The diffractometer was equipped

with a primary curved Ge111 primary beam monochromator and a speed X'Celerator fast detector, operating at 45 kV and 40 mA. XRD patterns were collected in the 2θ range of $5 - 120^\circ$ at room temperature, with a step size of 0.017° and 8 s counting time, in order to ensure sufficient resolution for structural refinement.

Fullprof Software was employed to carry out structural refinements from conventional XRD patterns using the Rietveld method. This method of refining the powder diffraction data was used to determine the crystal structure. Zero shift, lattice parameters, background, peak width, shape and asymmetry, atomic positions and isotropic temperature factors were all refined. The Thompson–Cox–Hastings pseudo-Voigt convoluted with axial divergence asymmetry function was used to describe the peak shape. Linear interpolation between set background points with refinable heights was used afterwards. The values were refined to improve the agreement factors.

All samples investigated by scanning electron microscopy (SEM) were first sputter-coated with Au in an EMITECH K550 apparatus. Field-emission scanning electron microscopy (FE-SEM) was performed using a JEM 6335 F electron microscope with a field-emission gun operating at 10 kV. The FE-SEM was also equipped with a LINK ISIS 300 detector for the energy-dispersive analysis of the X-rays (XEDS).

High resolution transmission electron microscopy (HRTEM) analysis of the LCFCr powders was performed using a JEOL 3000F TEM, yielding an information limit of $1.1 \text{ \AA}$. Images were recorded with an objective aperture of $70 \text{ }\mu\text{m}$, centered on a sample spot within the diffraction pattern area. Fast Fourier Transforms (FFT) of the HRTEM images were carried out to reveal the periodic image contents using the Digital Micrograph package. The experimental HRTEM images were also compared to simulated images using MacTempas software. These computations were performed using information from the structural parameters, obtained from the Rietveld refinement, the microscope parameters, such as microscope operating voltage (300 kV) and spherical aberration coefficient (0.6 mm), and specimen parameters, such as zone axis and thickness. The defocus and sample thickness parameters were optimized by assessing the agreement between model and data.

3. Results and Discussion

3.1 Microwave-assisted synthesis of LCFCr powders: X-ray diffraction and Rietveld refinement

FIG. 9(a) shows the XRD patterns of the LCFCr powders synthesized by the combustion method (Method 1), as well as by microwave-assisted combustion (Method 2), and microwave-assisted sol-gel synthesis (Method 3). The diffraction patterns show that a pure crystalline phase is obtained for all three synthesis methods. Importantly, the temperature used did not exceed 1000 °C, and without the use of microwave methods, the normal temperature that would have been needed to achieve the same result is 1200 °C.

FIG. 9(b) shows the XRD patterns for the material synthesized by the microwave-combustion method (Method 2) and calcined at three different temperatures. It can be seen that, at 700 °C, the phase is already forming and at 900 °C, the crystalline phase for LCFC has formed. FIG. 9(c) shows the XRD patterns for the material synthesized by the microwave-assisted sol-gel (Method 3) and calcined at the same temperatures. It can be seen that, at 700 °C and 900 °C, the desired phase is already forming and similar to Method 2, at 1000 °C, the desired product is present in the pure form.

FIG. 10 shows the Rietveld refinement fits for the LCFCr samples produced by microwave-combustion method (Method 2, FIG. 9a) and synthesized by the microwave-assisted sol-gel synthesis (Method 3, FIG. 9b). The Rietveld refinement for the LCFCr powders synthesized by the regular combustion method (Method 1) has been carried out in our parallel comparison studies (17). A distorted perovskite structure with an orthorhombic symmetry (S.G. *Pnma*, #62) was confirmed for both samples. The unit cell vectors can be represented by $\sqrt{2}a_p \times 2a_p \times \sqrt{2}a_p$, where a_p refers to the simple cubic perovskite cell. The results obtained for both samples concerning the cells parameters and the atomic positions are summarized in Table 2-1.

3.2 Microstructural analysis of LCFCr powders synthesized using microwave-assisted methods

3.2.1 Scanning (SEM) and transmission electron microscopy (TEM)

FIG. 11 shows the SEM images of LCFCr powders formed using microwave-assisted combustion synthesis at 900 °C (Method 2, FIG. 11(a)) and microwave-assisted sol-gel synthesis and (Method 3, FIG. 11(b)). As can be seen, in both cases, the material has a porous morphology, which makes it a good candidate as an electrode material. A sponge-like porous morphology can be observed for the powders formed using Method 2 (FIG. 11(a)), which is the typical morphology found after combustion processes. The

sponge-like porous morphology from Method 2 is quite different from the morphology obtained using the sol-gel method (Method 3, FIG. 11(b)) which consists of quite homogeneous agglomerated particles (approximate size 400nm).

Table 2-1: Structural parameters for LCFCr obtained from Rietveld refined XRD data.

	LCFCr		
	Conventional combustion (method 1)	MW – combustion (method 2)	MW- Sol-gel (method 3)
<i>a</i> (Å)	5.4550 (2)	5.4615 (8)	5.4476(4)
<i>b</i> (Å)	7.7128 (1)	7.7470 (7)	7.7194(2)
<i>c</i> (Å)	5.4552 (2)	5.4619 (7)	5.4504(4)
La / Ca position 4c:			
<i>X</i>	0.0145(6)	0.01959 (7)	0.0151(6)
<i>Z</i>	-0.003(3)	-0.003 (1)	-0.0062(7)
Occ (La / Ca)	0.30(1) / 0.70(1)	0.30(1) / 0.70(1)	0.30(1) / 0.70(1)
U*100 (Å ²)	0.40(3)	0.44(4)	0.52(2)
Fe / Cr position 4b:			
Occ (Fe / Cr)	0.70(1) / 0.30(1)	0.70(1) / 0.30(1)	0.70(1) / 0.30(1)
U*100 (Å ²)	0.35(2)	0.32(3)	0.43(2)
O(1) position 4c:			
<i>X</i>	0.502(2)	0.503(4)	0.501(3)
<i>Z</i>	0.105(2)	0.106(4)	0.106(4)
Occ	1.00(1)	1.00(1)	1.00(1)
U*100 (Å ²)	0.44(2)	0.27(3)	0.41(5)
O(2) position 8d:			
<i>X</i>	0.297(4)	0.256(2)	0.257(3)
<i>Y</i>	0.003(4)	0.005(3)	0.005(2)
<i>Z</i>	-0.254(3)	-0.31(2)	-0.30(3)
Occ	1.00(1)	1.00(1)	1.00(1)
U*100 (Å ²)	0.33(2)	0.27(3)	0.41(5)
χ^2	1.25	1.58	1.74
R_{wp} / R_{exp} (% / %)	4.88 / 4.37	2.42 / 1.96	2.65 / 2.01
R_{Bragg}	7.30	3.83	5.11
S.G. <i>Pnma</i>: 4c (<i>x</i> 1/4 <i>z</i>), 4b (0 0 1/2), 8d (<i>xyz</i>)			

Further characterization of the material obtained by microwave-assisted sol-gel synthesis (Method 3) at 1000 °C and microwave-assisted combustion synthesis at 900 °C (Method 2) was performed, with Table 2-2 giving the elemental analysis of the materials, obtained from the regions in the squares in FIG. 11. Table 2-2 shows the atomic percentage of each component in the catalysts. The second column of results corresponds to the microwave-assisted combustion synthesis (Method 2) and the third column corresponds to microwave-assisted sol-gel synthesis (Method 3). The atomic percentage observed by EDX is comparable to the theoretical values, based on the expected stoichiometry of $\text{La}_{0.3}\text{Ca}_{0.7}\text{Fe}_{0.7}\text{Cr}_{0.3}\text{O}_{3-\delta}$.

Table 2-2. EDX-determined composition (atomic %) of LCFCr powders, formed by microwave-assisted combustion (Method 2) and microwave-assisted sol-gel synthesis (Method 3) approaches

Atomic % composition of $\text{La}_{0.3}\text{Ca}_{0.7}\text{Fe}_{0.7}\text{Cr}_{0.3}\text{O}_{3-\delta}$			
	MW & comb	MW & sol-gel	Theoretical
La	16±0.5	16±0.5	15
Ca	35±0.5	34±0.5	35
Cr	15±0.5	15±0.5	15
Fe	34±0.5	36±0.5	35

Table 2-3

Specific surface areas of LCFCr powders, formed by regular combustion (Method 1) and microwave-assisted combustion (Method 2) approaches.

Sample	S_{BET} ($\text{m}^2 \text{g}^{-1}$)
Regular combustion (Method 1)	0.89
Microwave-assisted combustion (Method 2)	10.4

Transmission Electron Microscopy analysis was also performed on the LCFCr powder obtained using the different synthetic methods described above. The cation composition, measured semi-quantitatively by X-ray energy dispersive spectroscopy in

more than ten single crystals is in good agreement with the theoretical proportions in $\text{La}_{0.3}\text{Ca}_{0.7}\text{Cr}_{0.3}\text{Fe}_{0.7}\text{O}_{3-\delta}$, indicating the high purity of the powder.

In the HTREM images of the crystals prepared by microwave-assisted combustion synthesis (Method 2) (FIG. 12a) and assisted sol-gel synthesis (Method 3) (FIG. 12b), nanosized twinned domains are seen. The appearance of these domains can be associated with the pseudo-cubic nature of these materials. Furthermore, their presence avoids the formation of tetrahedral chains and therefore the formation of undesired brownmillerite-type defects (18). We have only detected the formation of defects in the sample prepared by sol-gel synthesis, Method 3 (FIG. 12b), showing a periodicity of 1.12 nm. This corresponds to the *c* axis of the $\text{A}_3\text{B}_3\text{O}_8$ type structure, which results from the intergrowth of a perovskite ABO_3 and a brownmillerite phase. HTREM images of the crystals prepared by the regular combustion method (Method 1) are shown in our parallel electrochemical study (17). It is worth noting that the microwave-assisted combustion synthesis (Method 2), as it involves very fast processes, favors disordered phases (perovskite in our case).

4. Conclusions

The mixed ion-electron conducting perovskite, $\text{La}_{0.3}\text{Ca}_{0.7}\text{Fe}_{0.7}\text{Cr}_{0.3}\text{O}_{3-\delta}$ (LCFCr), was prepared here by using several microwave-assisted methods, for ultimate use as a cathode in solid oxide fuel cells (SOFCs). The material was successfully prepared by microwave-assisted combustion (Method 2) and microwave-assisted sol-gel synthesis (Method 3). The desired product was obtained in crystalline form in only 7 hrs (vs. 13 hrs) and the synthesis temperature was roughly 300 °C lower than what is required for conventional solid-state combustion synthesis. This new approach has enhanced the rate of formation of the LCFCr powder by several orders of magnitude, and also increased the specific surface area from 0.89 to 10.4 m² g⁻¹. These results are very encouraging, as they suggest that microwave synthesis can be used in the preparation of the perovskite materials used in this work. Whether the microwave-synthesized materials will give superior electro- chemical performance is currently under investigation. It is suggested here that the partial substitution of Ca for Sr may promote oxygen-vacancy disordering and thus stabilize the perovskite phase vs. the brownmillerite phase. In our HRTEM work, the formation of brownmillerite-type defects was detected only in the sample prepared by sol-gel synthesis (Method 3). In addition, the calcination temperature for microwave-assisted combustion (Method 2) was 900 °C vs. 1000 °C for microwave-assisted sol-gel synthesis (Method 3). Based on the lower calcination temperature and

the absence of brownmillerite-type defects, microwave-assisted combustion (Method 2) would be the preferred method for the future synthesis of highly active SOFC cathodes composed of the $\text{La}_{0.3}\text{Ca}_{0.7}\text{Fe}_{0.7}\text{Cr}_{0.3}\text{O}_{3-\delta}$ material.

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Example 3: Sulfur Tolerance of $\text{La}_{0.3}\text{M}_{0.7}\text{Fe}_{0.7}\text{Cr}_{0.3}\text{O}_{3-\delta}$ (M = Sr, Ca) Solid Oxide Fuel Cell Anodes

1. Introduction

Solid oxide fuel cells (SOFCs) are highly efficient electrochemical devices that also demonstrate excellent fuel flexibility and function well on fuels such as H_2 , CO, and methane. Traditionally, SOFCs have been based on a Ni-YSZ (yttria stabilized zirconia) cermet anode, a YSZ electrolyte, and a lanthanum strontium manganite (LSM) cathode. Although Ni-YSZ cermets are excellent SOFC anodes, largely because of their excellent catalytic activity towards fuel oxidation, work in our group and by others has shown that Ni is susceptible to poisoning at low levels (1-100 ppm) of H_2S exposure at SOFC operating temperatures (700-1000 °C) (1-5). It has been suggested that H_2S inhibits the H_2 oxidation reaction (HOR) rates because it readily dissociates to form a surface adsorbed Ni-S layer (S_{ads}) on catalytic sites normally involved in H_2 dissociation and subsequent oxidation (4), thereby decreasing the performance of the SOFC. As a result, extensive research has been carried out to develop sulfur tolerant SOFC anode materials based on Ni-free conducting metal oxides, such as perovskites. For example, $\text{La}_{0.75}\text{Sr}_{0.25}\text{Cr}_{0.5}\text{Mn}_{0.5}\text{O}_3$ (LSCM) has been reported to exhibit a comparable electrochemical performance for hydrogen oxidation as seen at Ni-YSZ at 900 °C (6). However, LSCM has been shown to be less sulfur tolerant in fuels containing 10% H_2S (7). Studies by Mukundan et al (8) showed that $\text{La}_{0.4}\text{Sr}_{0.6}\text{TiO}_3$ (LST) is a sulfur tolerant SOFC anode, as it did not exhibit any form of degradation in a 5000 ppm H_2S + H_2 fuel. Studies by Haag et al (9) showed that $\text{LaSr}_2\text{Fe}_2\text{CrO}_{9-\delta}\text{-Gd}_{0.1}\text{Ce}_{0.9}\text{O}_{2-\delta}$ composite anodes, exposed to 22 ppm H_2S , exhibited only a slight decrease in performance relative to the response in H_2 . Also, $\text{La}_{0.3}\text{Sr}_{0.7}\text{Fe}_{0.7}\text{Cr}_{0.3}\text{O}_{3-\delta}$, (LSFCr), operated on wet-(50% H_2 + CO) containing 10 ppm H_2S , showed only a small drop in cell potential, indicating very good stability as an anode in sulfur-containing fuels (10).

However, other perovskites have been reported to show an enhancement in the rate of hydrogen oxidation in the presence of H_2S , including $\text{La}_{0.7}\text{Sr}_{0.3}\text{VO}_3$ (LSV) (11), $\text{Sm}_{0.95}\text{Ce}_{0.05}\text{Fe}_{0.97}\text{Ni}_{0.03}\text{O}_{3-\delta}$ (SCFN) (12), and $\text{Y}_{0.9}\text{Sr}_{0.1}\text{Cr}_{0.9}\text{Fe}_{0.1}\text{O}_{3-\delta}$ (YSCF) (13). For LSV, the observed enhancement was attributed to the formation of an active SrS phase, replacing an insulating phase ($\text{Sr}_3\text{V}_2\text{O}_8$) (11), while for SCFN and YSCF, it was suggested that the active phase that forms in the presence of H_2S is probably FeS (12,13).

Previous and current studies in our group have explored the substitution of the A-site (M) in the mixed conducting perovskite, $\text{La}_{0.3}\text{M}_{0.7}\text{Fe}_{0.7}\text{Cr}_{0.3}\text{O}_{3-\delta}$, with Sr and Ca to form $\text{La}_{0.3}\text{Sr}_{0.7}\text{Fe}_{0.7}\text{Cr}_{0.3}\text{O}_{3-\delta}$ (LSFCr) and $\text{La}_{0.3}\text{Ca}_{0.7}\text{Fe}_{0.7}\text{Cr}_{0.3}\text{O}_{3-\delta}$ (LCFCr) (10, 14, 15), respectively. These $\text{La}_{0.3}\text{M}_{0.7}\text{Fe}_{0.7}\text{Cr}_{0.3}\text{O}_{3-\delta}$ (M = Sr, Ca) perovskite oxides have been successfully employed as both fuel and O_2 electrodes for SOFC/SOEC applications. We have reported previously that symmetrical SOFCs, based on the LSFCr perovskite, showed tolerance to low ppm sulfur content in the fuel stream, also exhibited excellent electrochemical activity towards H_2 and CO oxidation, and was also an active oxygen reduction reaction (ORR) material (10). More recently, we have also demonstrated that LCFCr shows excellent catalytic properties for both the ORR and the oxygen evolution reaction (OER) (15).

However, the performance of LCFCr as a fuel electrode has not been studied as yet. Therefore, in this example, LCFCr is examined as a SOFC anode in H_2 and/or CO atmospheres, with or without H_2S , in comparison to the more well studied LSFCr. Electrochemical methods employing both ac and dc techniques were used in a symmetrical SOFC configuration in H_2 and/or CO fuels, with or without the addition of 9 ppm H_2S , all at 800 °C. It is shown that LCFCr is a very good anode catalyst in H_2 , CO, and H_2+CO fuels, and although an explanation is not yet available, this mixed conducting perovskite material demonstrates a fully reversible enhanced catalytic activity when ca. 10 ppm H_2S is added to the H_2 fuel stream.

Experimental

A glycine-nitrate combustion process was employed to prepare the $\text{La}_{0.3}\text{M}_{0.7}\text{Fe}_{0.7}\text{Cr}_{0.3}\text{O}_{3-\delta}$ (M = Sr, Ca) perovskite powders, using methods reported previously (10,14,15). The ash obtained from combustion was subsequently pulverized and pre-calcined at 1200 °C for 2 h in air (conditions under which single phases are generated). Powders were ballmilled (high energy planetary ball mill, Pulverisette 5, Fritsch, Germany) in an isopropanol medium at a rotation speed of 300 rpm for 2 h using zirconia balls. The $\text{La}_{0.3}\text{M}_{0.7}\text{Fe}_{0.7}\text{Cr}_{0.3}\text{O}_{3-\delta}$ (M = Sr, Ca) powders were then screen printed symmetrically onto both sides of a 275 μm dense YSZ electrolyte coated with a porous, ca. 10 micron thick SDC buffer layer (Fuel Cell Materials), followed by firing at 1100 °C for 2 h. Au paste (C 5729, Heraeus Inc. Germany) was painted on the $\text{La}_{0.3}\text{M}_{0.7}\text{Fe}_{0.7}\text{Cr}_{0.3}\text{O}_{3-\delta}$ (M = Sr, Ca) layers on both sides of the pellet to serve as the current collector and Pt wires were used as the electrical leads.

The cells were fixed in a FCSH-V3 cell holder (MaterialsMate, Italy) for the purpose of determining their electrochemical properties. A glass sealant (Type 613, Aremco Products, USA) was used to isolate the fuel and O₂ sides from each other. The total flow rates were 25 ml/min and 40 ml/min at the fuel and O₂ electrodes, respectively. The performance of the two electrode cells was evaluated using a four-probe method at 800 °C. Impedance spectra were collected under both open circuit and polarized conditions using a 50 mV perturbation in the frequency range of 0.01 Hz to 60 kHz using a Solartron 1287/1255 potentiostat/galvanostat/impedance analyzer.

2. Results and Discussion

2.1 Performance of La_{0.3}M_{0.7}Fe_{0.7}Cr_{0.3}O_{3-δ} (M = Sr, Ca) anodes in wet 30% H₂/N₂ at 800 °C

To carry out a first stage comparison of the performance of LCFCr and LSFCr, impedance (EIS) and potentiodynamic studies were carried out. It can be seen from the Nyquist plot in FIG. 13 that a polarization resistance of 1.06 and 1.5 Ω·cm² was obtained for LCFCr and LSFCr in 30% humidified H₂ at 800 °C, respectively. The performance of LCFCr is slightly better than LSFCr. This is consistent with preliminary electronic conductivity analysis in H₂ at 800 °C for LCFCr which gave a value of 0.6 S/cm, which is a little higher than the 0.2 S/cm value obtained for LSFCr (10). Despite this, the EIS response is quite similar for the two materials, with two time constants (R/CPE) seen for both LSFCr and LCFCr. From the Bode plot shown in the inset of FIG. 13, the dominant summit frequencies are seen to be ca. 100 Hz and ca. 1 Hz.

To determine which of the processes arises from the air (cathode) vs. fuel (anode) electrode, the cathode in the LCFCr cell was fed with either air or pure oxygen. From FIG. 14A, it is clear that the high frequency (100 Hz) arc can be attributed to the cathode, since in pure O₂, the high frequency resistance (R_{HF}) decreased from 0.37 to 0.28 Ω·cm², while the low frequency resistance (R_{LF}) remained unchanged, as shown in Table 3-1. The resistance values were obtained by fitting the Nyquist plot in FIG. 14A to the R_s (R_{HF}/CPE_{HF})(R_{LF}/CPE_{LF}) equivalent circuit model (FIG. 14B). R_s is the series resistance, R_p is the polarization resistance (the sum of all of the parallel resistances), and (R_{HF}/CPE_{HF}) and (R_{LF}/CPE_{LF}) are the time constants at high (100 Hz) and low (0.5 Hz) frequencies, respectively. Therefore, the low frequency arc (R_{LF}/CPE_{LF}) is predominantly due to contributions from the fuel electrode (anode) while the high frequency arc (R_{HF}/CPE_{HF}) arises from the air electrode (cathode), consistent with what

has been reported in the literature for other mixed conducting perovskite systems, including LSFCr (10).

Table 3-1

Circuit element values* obtained by fitting the results in Figure 2** to the $R_s(R_{HF}CPE_{HF})(R_{LF}CPE_{LF})$ equivalent circuit model

Cathode gas	$R_s (\Omega \cdot \text{cm}^{-2})$	$R_{HF} (\Omega \cdot \text{cm}^{-2})$	$R_{LF} (\Omega \cdot \text{cm}^{-2})$	$R_p^{\#} (\Omega \cdot \text{cm}^{-2})$
Air	1.07	0.37	0.68	1.05
O ₂	1.06	0.28	0.63	0.91

* R_{HF} and R_{LF} obtained from the high (ca. 100 Hz) and low (ca. 1 Hz) frequency arcs, respectively.

** Symmetrical fuel cell based on LCFCr electrodes, operated at 800 °C in wet 30% H₂/N₂ gas mixtures at the fuel electrode and with air or O₂ exposure at the O₂ electrode.

$\# R_p = R_{HF} + R_{LF}$

DC experiments were also carried out to evaluate the performance of

$\text{La}_{0.3}\text{M}_{0.7}\text{Fe}_{0.7}\text{Cr}_{0.3}\text{O}_{3-\delta}$ (M = Sr, Ca). FIG. 15 shows the performance plots of LCFCr and LSFCr cells operated on 30% humidified H₂ at 800 °C. LCFCr shows a maximum current and power density of 270 mA/cm² and 142 mW/cm², respectively, while the analogous values for LSFCr are 255 mA/cm² and 134 mW/cm², consistent with the EIS data in FIG. 13. The performance of our $\text{La}_{0.3}\text{M}_{0.7}\text{Fe}_{0.7}\text{Cr}_{0.3}\text{O}_{3-\delta}$ (M = Sr, Ca) based cells is comparable to that of other symmetrical cells (based on perovskite electrodes) reported in the literature, such as $\text{La}_{0.8}\text{Sr}_{0.2}\text{Ti}_{1-x}\text{Fe}_x\text{O}_{3-\delta}$ (LSTF), which showed power densities of 90-100 mW/cm² at 950 °C in humidified H₂ (16).

2.2 Performance of LCFCr in other fuel mixtures at 800 °C

The performance of the LCFCr electrode was also examined in CO and syngas (H₂+CO) atmospheres. FIG. 16 shows that the polarization resistance of the cell is 0.95 $\Omega \cdot \text{cm}^2$ in H₂, which is slightly smaller than both the R_p values obtained in CO (1.11 $\Omega \cdot \text{cm}^2$) and CO+H₂ (1.00 $\Omega \cdot \text{cm}^2$) atmospheres. This indicates that the material is only a somewhat better catalyst for H₂ oxidation than CO oxidation. This shows that LCFCr is a very promising SOFC anode material that can be employed in a range of fuels, giving a very good performance in all case. Also, from the Nyquist plot, it is seen that it is the low frequency arc (R_{LF}/CPE_{LF}) that is changing with changing fuel environments, again confirming that the low frequency arc is associated primarily with the anode, as suggested earlier on. The performance plot of the cell in these three gases is shown in FIG. 17. The OCP in the three gases is seen to be ca. 1.06 V, which is very close to the theoretical value, indicating that the anode and cathode compartments are well sealed and that there is no gas leakage. As stated earlier, there is not much difference in the activity of the LCFCr material in H₂, CO and H₂+CO atmospheres, and this is supported here by the dc measurements. The maximum power density obtained is between 140 to

150 mW/cm² in all of the environments, while the maximum current density is in the range of 250-270 mA/cm², all at 800 °C.

2-4 Effect of low ppm H₂S on performance of LCFCr in 30% H₂ (bal wet N₂) at 800 °C

FIG. 18A shows that, when 9 ppm H₂S is added to 30% H₂ under OCP conditions, the polarization resistance decreased slightly, from 1.00 to 0.96 Ω·cm², translating to a ca. 4 % decrease in R_p in the presence of H₂S. No poisoning/deactivation of the LCFCr at 800 °C is seen. This was also seen for LSFCr, although only the results for LCFCr are shown here. In comparison, most of the sulfur-induced performance enhancement behavior reported for other types of perovskites has usually been observed at much higher concentrations of H₂S (1-5%). To better understand these results, the effect of ac polarization on the cell was investigated.

FIGs. 18B and 18C show the polarized EIS results for the LCFCr-based cell in H₂, with or without the addition of 9 ppm H₂S at 800 °C. When the cell was polarized at -100 mV vs. the full cell open circuit voltage, i.e., at a cell voltage of ca. 0.95 V, (Figure 18B), R_p decreased from 0.97 Ω·cm² in H₂ to 0.90 Ω·cm² in the presence of H₂S, while when the anode was polarized at -300 mV (ca. 0.75 V cell voltage), R_p decreased from 0.80 to 0.72 Ω·cm² (Figure 18C). The plot in the inset of Figure 18D shows the % R_p change vs. the applied voltage, calculated based on the R_p data in FIG. 18D (%R_p change = [(R_pH₂-R_pH₂S)] x 100/ (R_pH₂)). It can be seen that R_p decreased by 4 % at the cell OCP and by 7 % and 11 % in the presence of H₂S when the cell was polarized at -100 and -300 mV vs. the full cell open circuit voltage, respectively. This indicates that the enhancement of the performance of LCFCr in H₂ in the presence of H₂S improves with polarization at 800 °C.

As stated earlier, some ferrite-based perovskites, such as Sm_{0.95}Ce_{0.05}Fe_{0.97}Ni_{0.03}O_{3-δ} (12) and Y_{0.9}Sr_{0.1}Cr_{0.9}Fe_{0.1}O_{3-δ} (13), have been reported to show enhanced H₂ oxidation activity or electrochemical oxidation of H₂S only in high concentrations of H₂S (1-5%), due to the formation of sulfide species (e.g., FeS) at 600 - 800 °C. On the other hand, probably under our testing conditions, some type of adsorbed surface sulfide species (possibly FeS) is being formed even when H₂S is present at ppm levels at 800 °C. However, detailed surface characterization studies are required to confirm the presence of FeS in our experiments.

To further study the performance of the LCFCr electrode towards H₂ oxidation in the presence or absence of 9 ppm H₂S, potentiostatic studies were also carried out at

the -100 and -300 mV vs. OCP cell polarization, respectively. Figure 19A shows the results of polarization at -100 mV vs. the full cell voltage at open circuit for 9 h with and without H₂S. As can be seen, upon the addition of 9 ppm H₂S to the H₂ fuel, the current density increased from about 95 mA/cm² to 98 mA/cm², giving a 2.1 % improvement in performance. After 4 h of removal of H₂S, the current density decreased to about 95 mA/cm², similar to the value observed before H₂S exposure. This shows that the enhancement is only observed in the presence of H₂S and that the cell fully recovers in the absence of H₂S, suggesting that no bulk sulfide phase forms but rather only a surface species is generated. This behaviour is also seen at -300 mV vs. the full cell voltage at open circuit (FIG. 19B), where the cell improved by 4.3 % in the presence of H₂S and fully recovered when the H₂S was removed. Although the present work is in a preliminary stage, a range of surface characterization methods, such as XPS and AES, are currently being employed to determine what surface species are being formed, as well as to establish the effect of temperature on these materials in the presence of H₂S.

3. Conclusions

This application has focused on the development of mixed conducting perovskite oxides for use at both electrodes in reversible solid oxide fuel cells (RSOFCs). In this example, the performance of LCFCr, in comparison with LSFCr, has been investigated in a range of fuel environments, with and without ppm levels of H₂S, all at 800 °C. The symmetrical full cells were constructed by screen-printing La_{0.3}M_{0.7}Fe_{0.7}Cr_{0.3}O_{3-δ} (M = Sr, Ca) on a Ytria-stabilized zirconia (YSZ) electrolyte covered by a thin Samaria-doped ceria (SDC) buffer layer, and then tested using both impedance and potentiostatic techniques. It was found that the LCFCr is an equally good fuel electrode (anode) and O₂ electrode (cathode) as LSFCr, exhibiting very good electrochemical performance in H₂, CO and syngas (H₂+CO) atmospheres, giving polarization resistance of 0.95 Ω·cm² in wet 30% H₂ and 1.00 Ω·cm² and 1.11 Ω·cm² in wet 15% H₂:15% CO and 30 % CO atmospheres, respectively. The maximum power density obtained using these gases were between 140 to 150 mW/cm², while the maximum current density was in the range of 250-270 mA/cm². The LCFCr and LSFCr anodes were also evaluated in the presence of 9 ppm H₂S, showing a small, but reproducible and reversible, decrease in polarization resistance (R_p). Chronoamperometric studies at cell polarizations of -100 and -300 mV vs. the full cell voltage at open circuit showed a ca. 2-4 % increase in

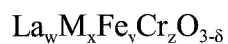
current density in the presence of 9 ppm H₂S + 30 % H₂, with the cell recovering fully when H₂S was removed. This is very promising and may indicate that some type of adsorbed surface sulfide species (possibly FeS) is being formed in the presence of low ppm H₂S at 800 °C, leading to the observe enhancement in hydrogen oxidation activity.

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We Claim:

1. An electrode material having the formula:



where:

M is Ca or a mixture of Ca and Sr where the molar ratio of Ca to Sr ranges from 1:1 to 100:1;

w is 0.2 to 0.4;

x is 0.6 to 0.8;

y is 0.6 to 0.8;

z is 0.2 to 0.4; and

δ represents oxygen deficiency.

2. The electrode material of claim 1 wherein:

w is 0.27 to 0.33;

x is 0.67 to 0.73;

y is 0.67 to 0.73; and

z is 0.27 to 0.33.

3. The electrode material of claim 1 wherein:

w is 0.29 to 0.31;

x is 0.69 to 0.71;

y is 0.69 to 0.71; and

z is 0.29 to 0.31.

4. The electrode material of claim 1 wherein w is 0.3; x is 0.7; y is 0.7; and z is 0.3.

5. The electrode material of any one of claims 1-4 wherein M is the mixture of Ca and Sr.

6. The electrode material of claim 5 wherein the molar ratio of Ca to Sr is 1:1.

7. The electrode material of claim 5 wherein the molar ratio of Ca to Sr is 10:1.
8. The electrode material of any one of claims 1-3 wherein M is Ca.
9. The electrode material of claim 1 which is $\text{La}_{0.3}\text{Ca}_{0.7}\text{Fe}_{0.7}\text{Cr}_{0.3}\text{O}_{3-\delta}$.
10. An electrode for a solid oxide fuel cell which comprises the electrode material of any one of claims 1-9.
11. A fuel electrode for a solid oxide fuel cell or a reversible solid oxide fuel cell which comprises the electrode material of any one of claims 1-9.
12. An air or oxygen electrode for use in a solid oxide fuel cell which comprises the electrode material of any one of claims 1-9.
13. A solid oxide fuel cell having an electrode which comprises the electrode material of any one of claims 1-9.
14. A solid oxide fuel cell having an electrode which comprises the electrode material of claim 9.
15. A reversible solid oxide fuel cell having an electrode which comprises the electrode material of any one of claims 1-9.
16. A reversible solid oxide fuel cell having two electrodes wherein both electrodes comprise the electrode material of any one of claims 1-9.
17. The reversible solid oxide fuel cell of claim 15 or 16 wherein the electrode material is of claim 9.

18. The reversible solid oxide fuel cell of any one of claims 15-17 further comprising a solid electrolyte.
19. The reversible solid oxide fuel cell of claim 18 wherein the solid electrolyte is gadolinium doped ceria or yttria stabilized zirconia.
20. A method for generating electricity which comprises operating the solid oxide fuel cell of claim 13.
21. A method for generating electricity or employing electricity to generate a fuel which comprises selectively operating (1) a solid oxide fuel cell or (2) a reversible solid oxide fuel cell to generate the electricity or to generate the fuel, wherein each fuel cell has at least one electrode comprising the electrode material of any one of claims 1-9.
22. The method of claim 21 wherein the solid oxide fuel cell or the reversible solid oxide fuel cell is operated in the presence of a fuel containing hydrogen sulfide.
23. The method of any one of claims 21-22 wherein the solid oxide fuel cell or the reversible solid oxide fuel cell is operated at a temperature in the range of 600-800°C.
24. The electrode material of any one of claims 1-9 which is prepared by microwave-assisted combustion, microwave-assisted co-precipitation or a microwave-assisted sol-gel method.

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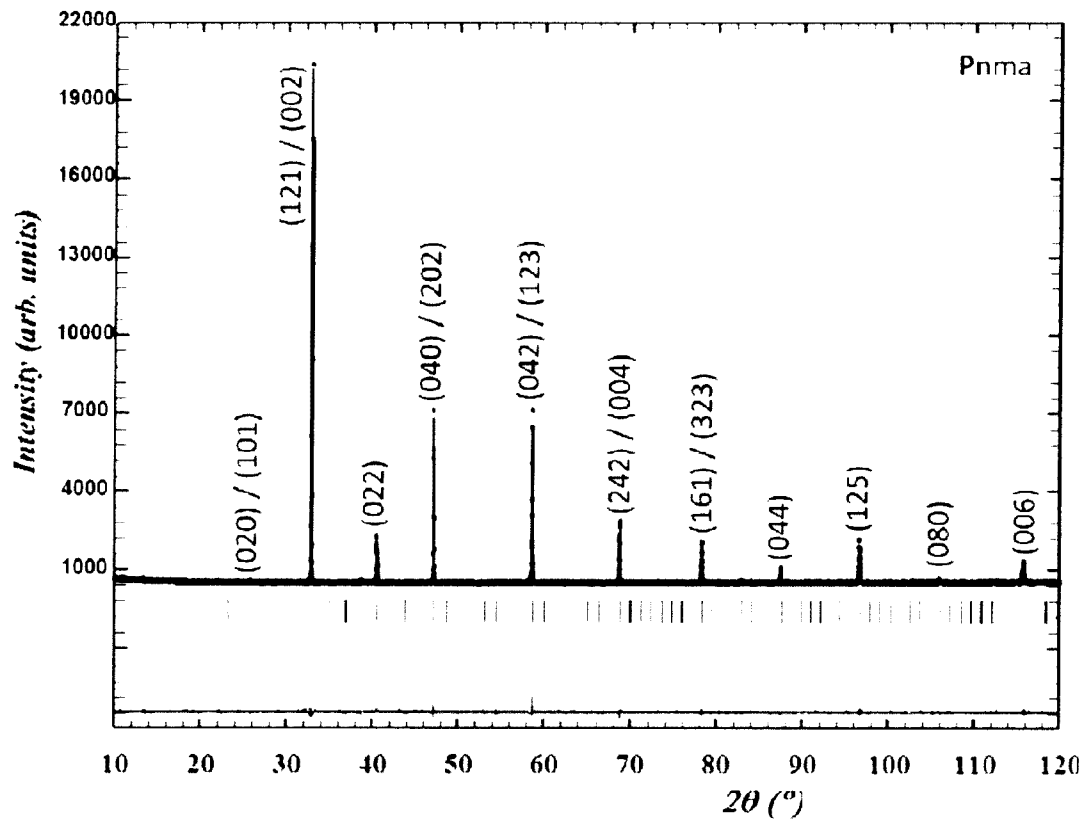


FIG. 1

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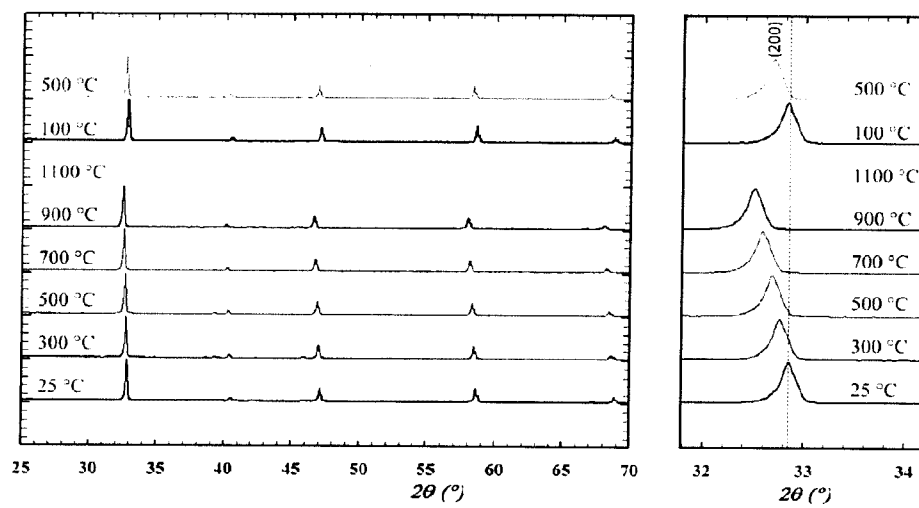


FIG. 2A

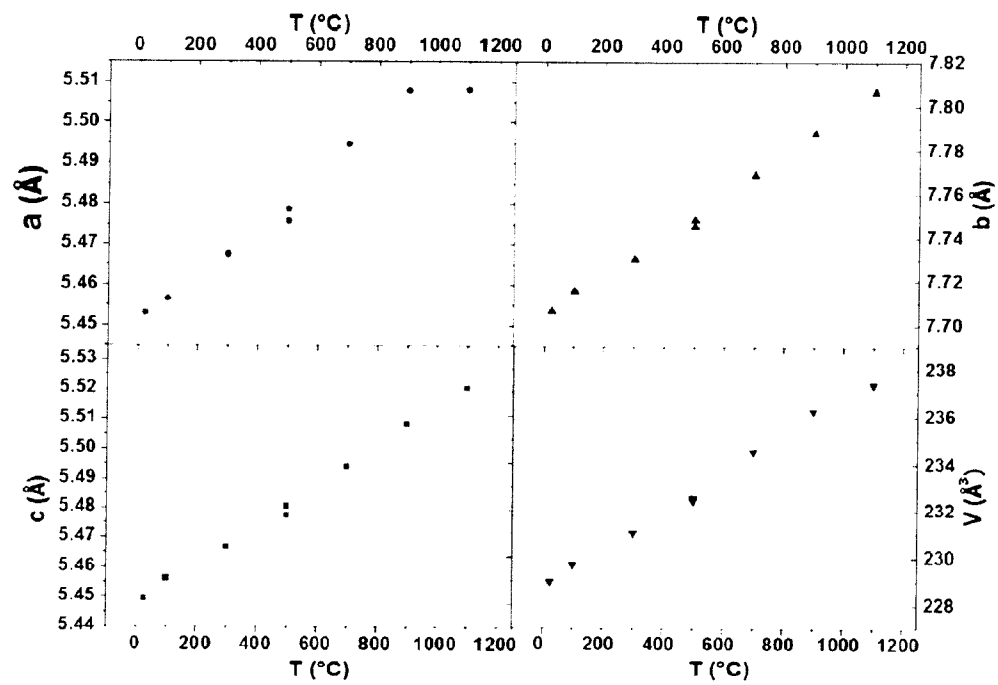


FIG. 2B

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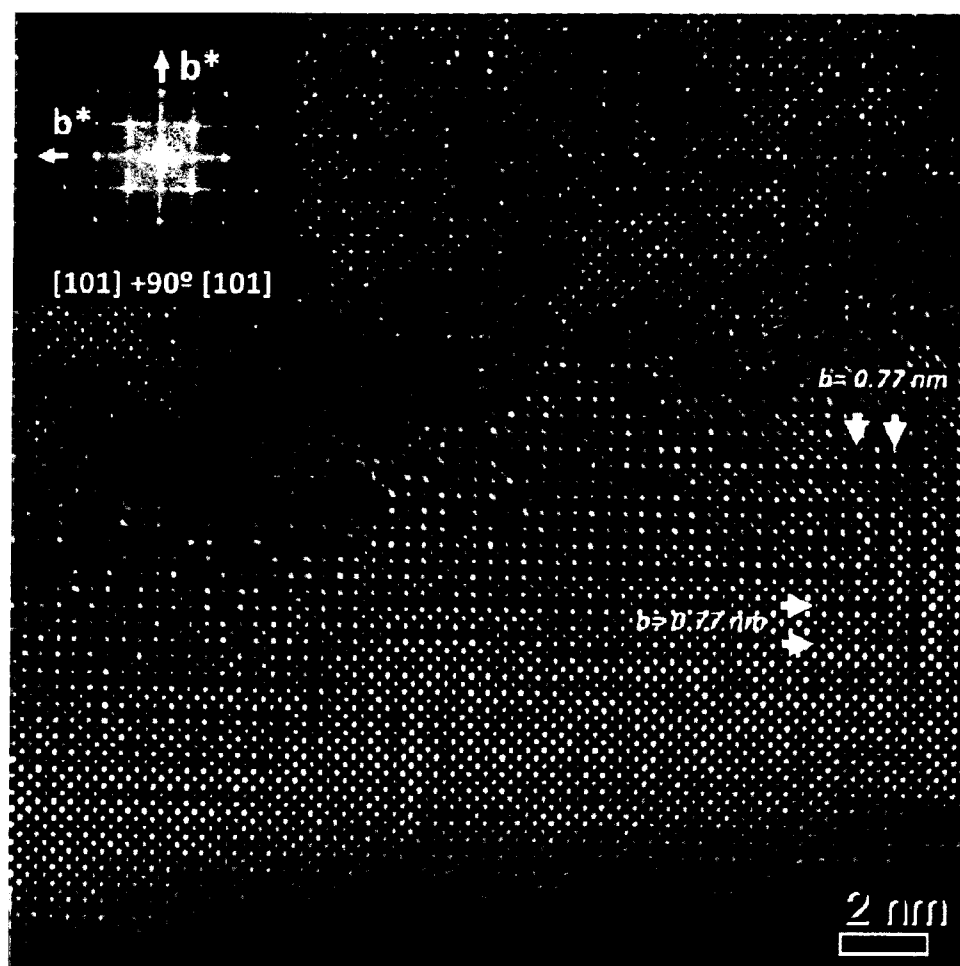


FIG. 3

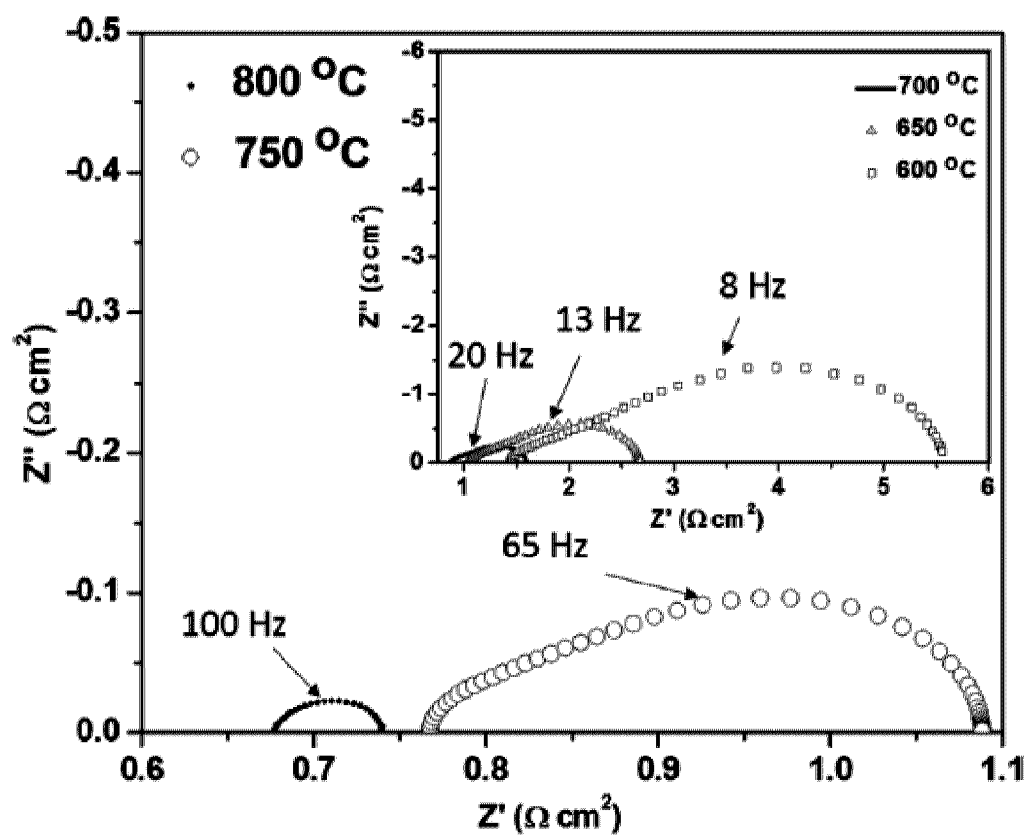


FIG. 4A

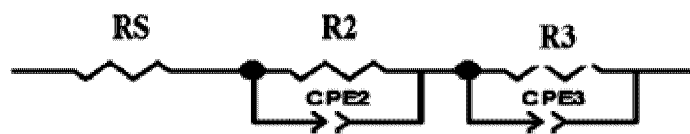


FIG. 4B

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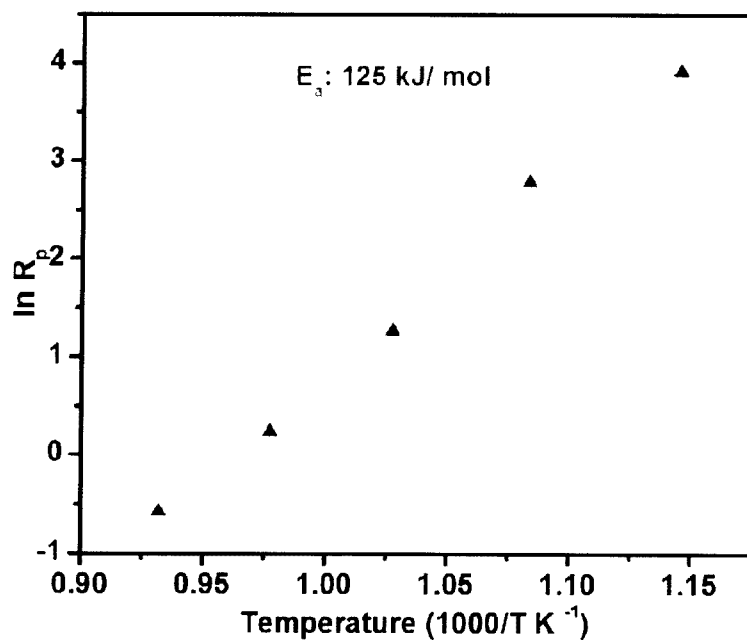


Fig. 5

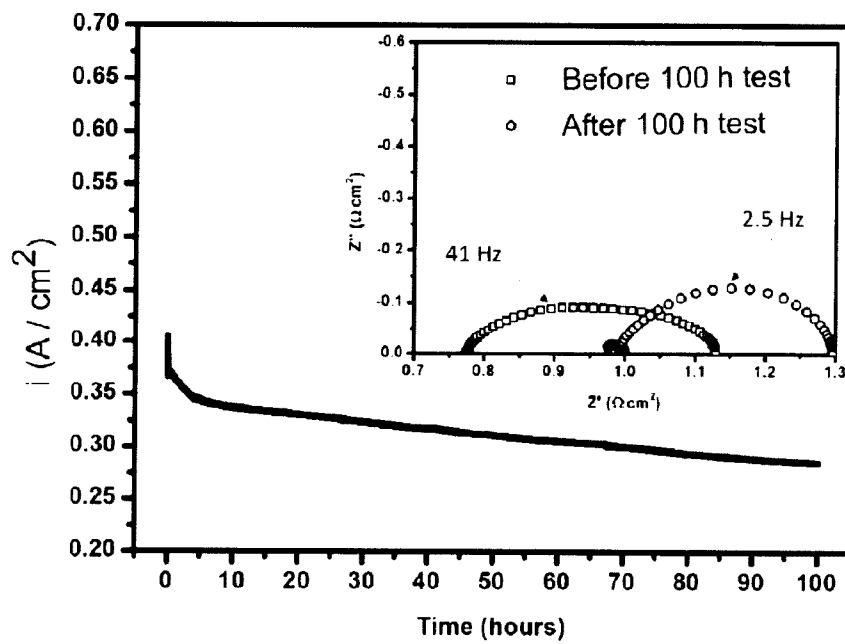


FIG. 6

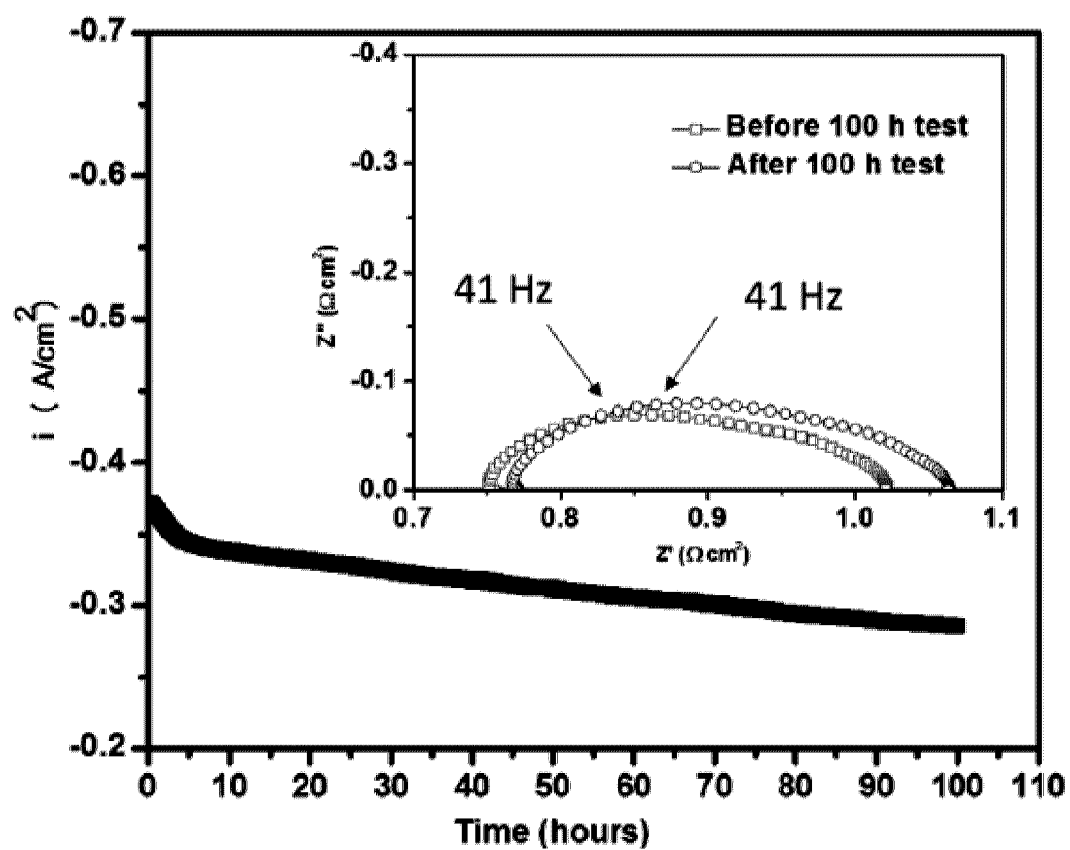


FIG. 7

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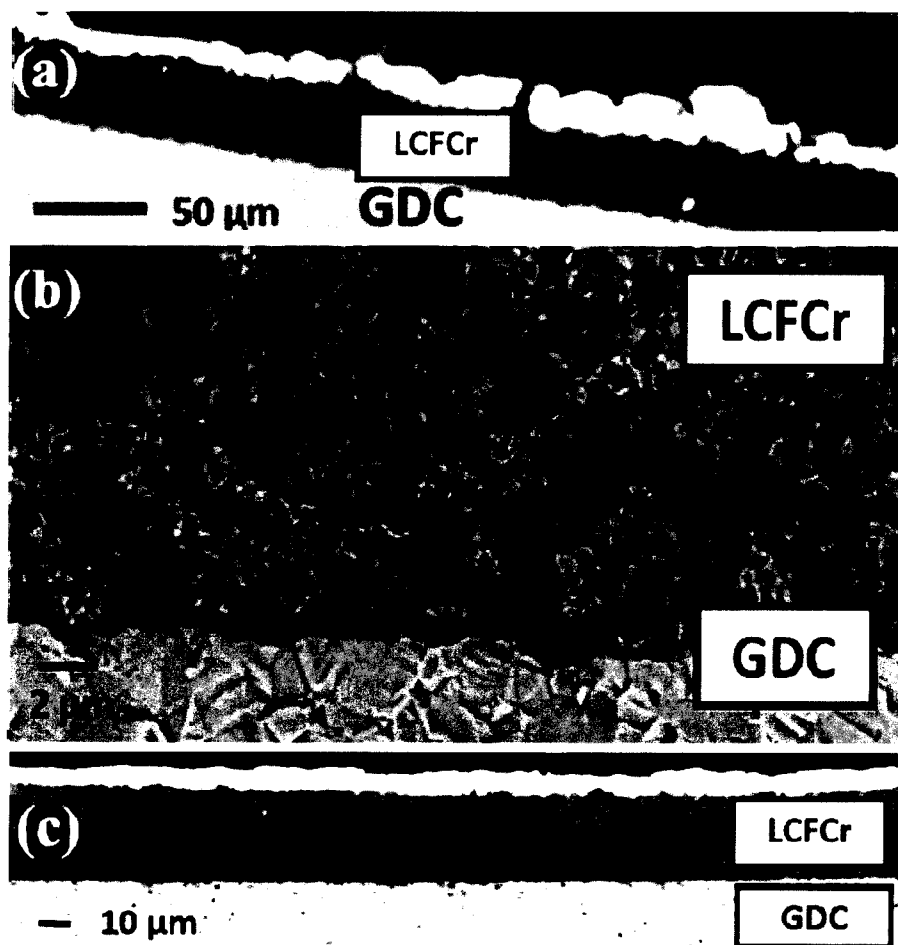


FIG. 8

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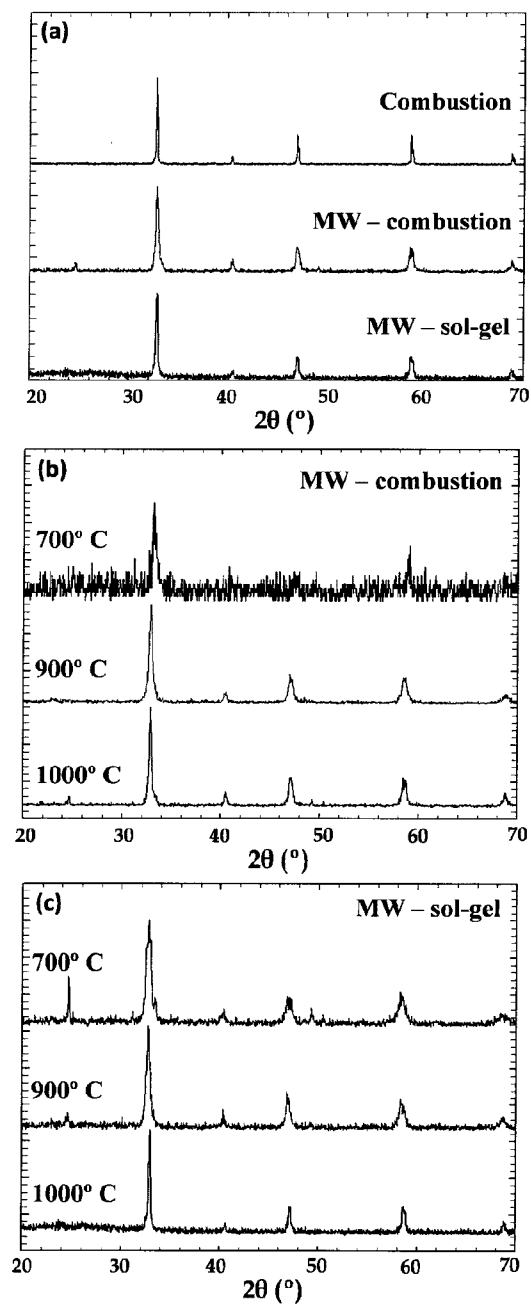


FIG. 9

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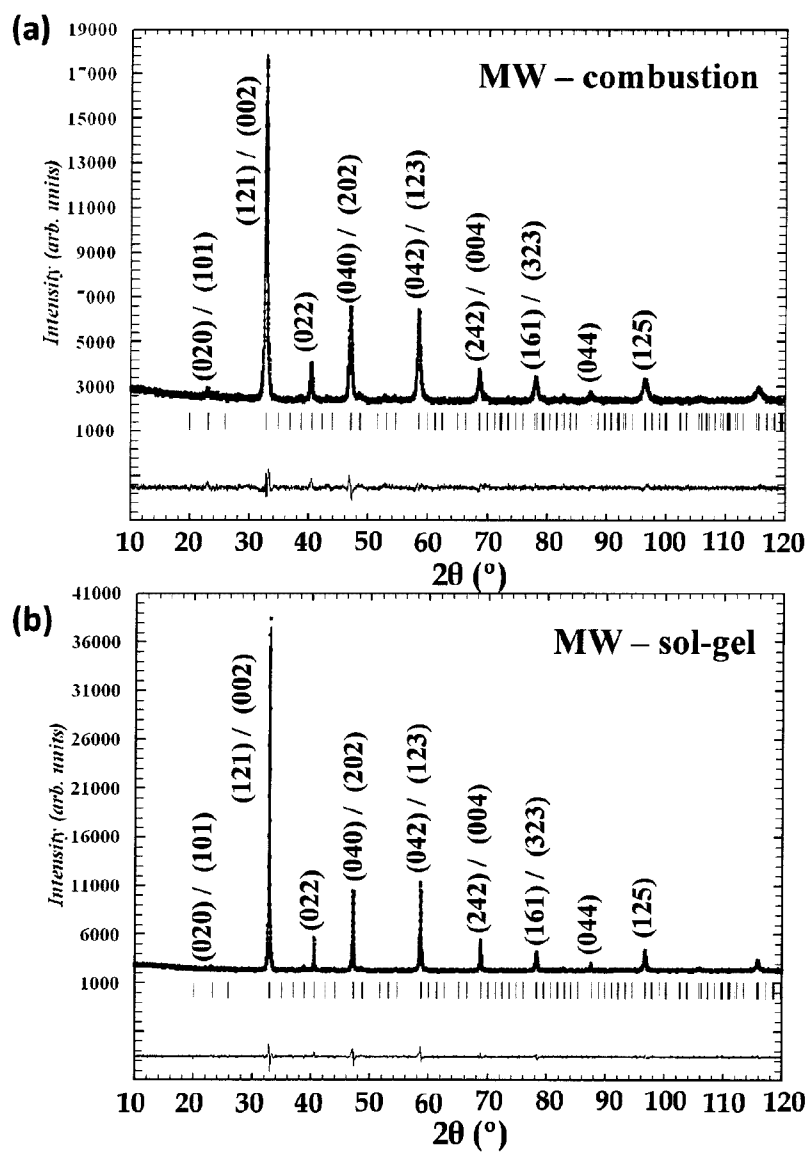


FIG. 10

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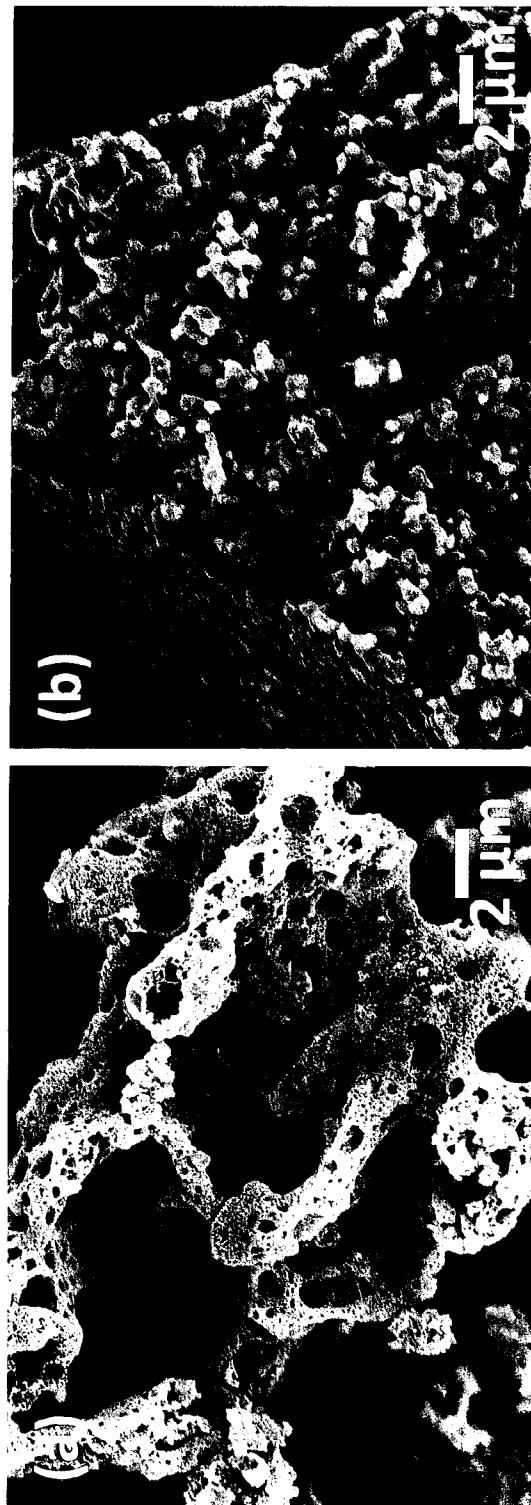


FIG. 11

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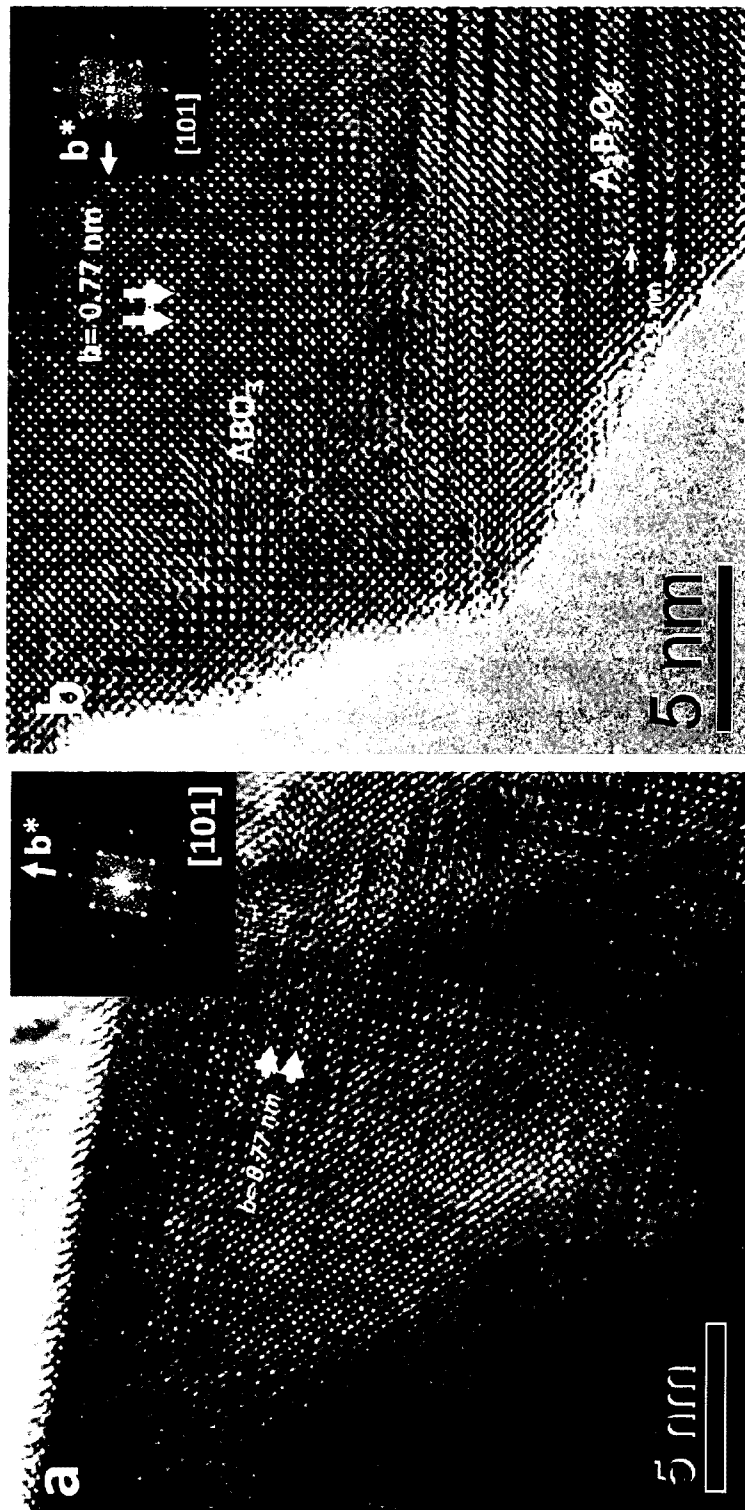


FIG. 12

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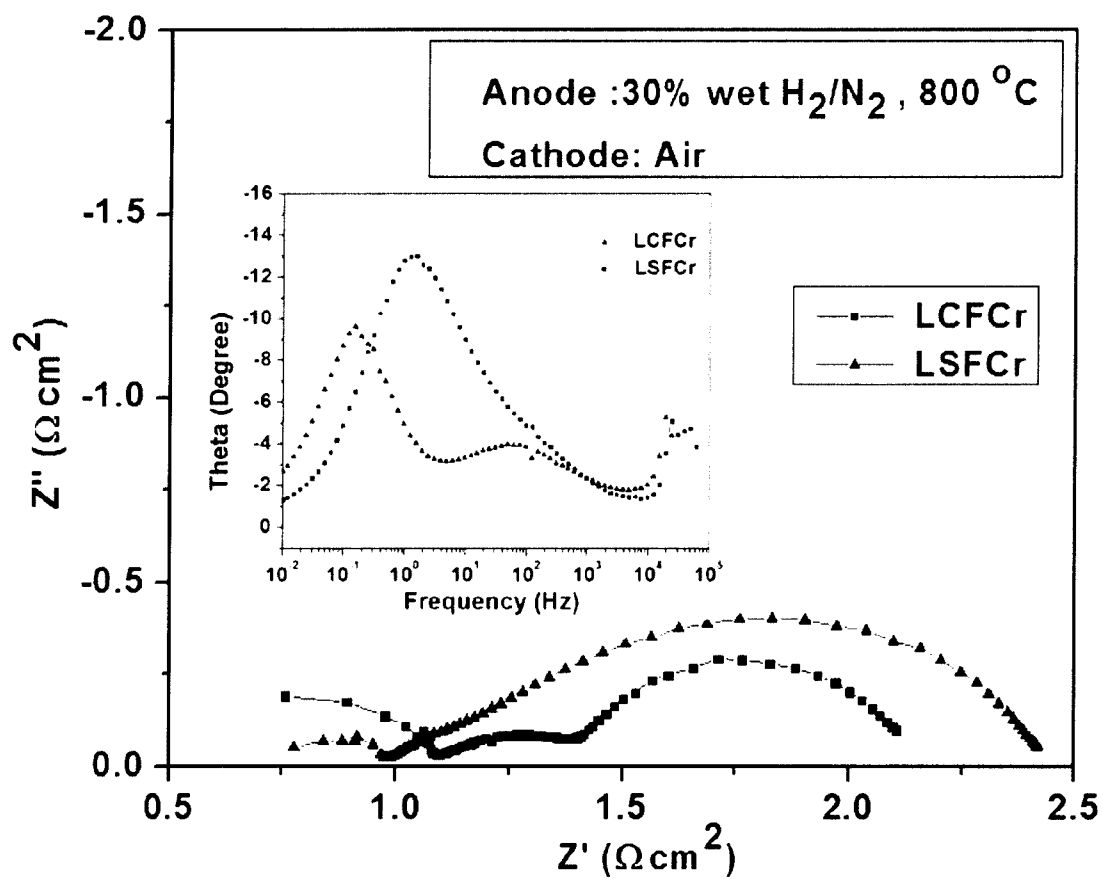


FIG. 13

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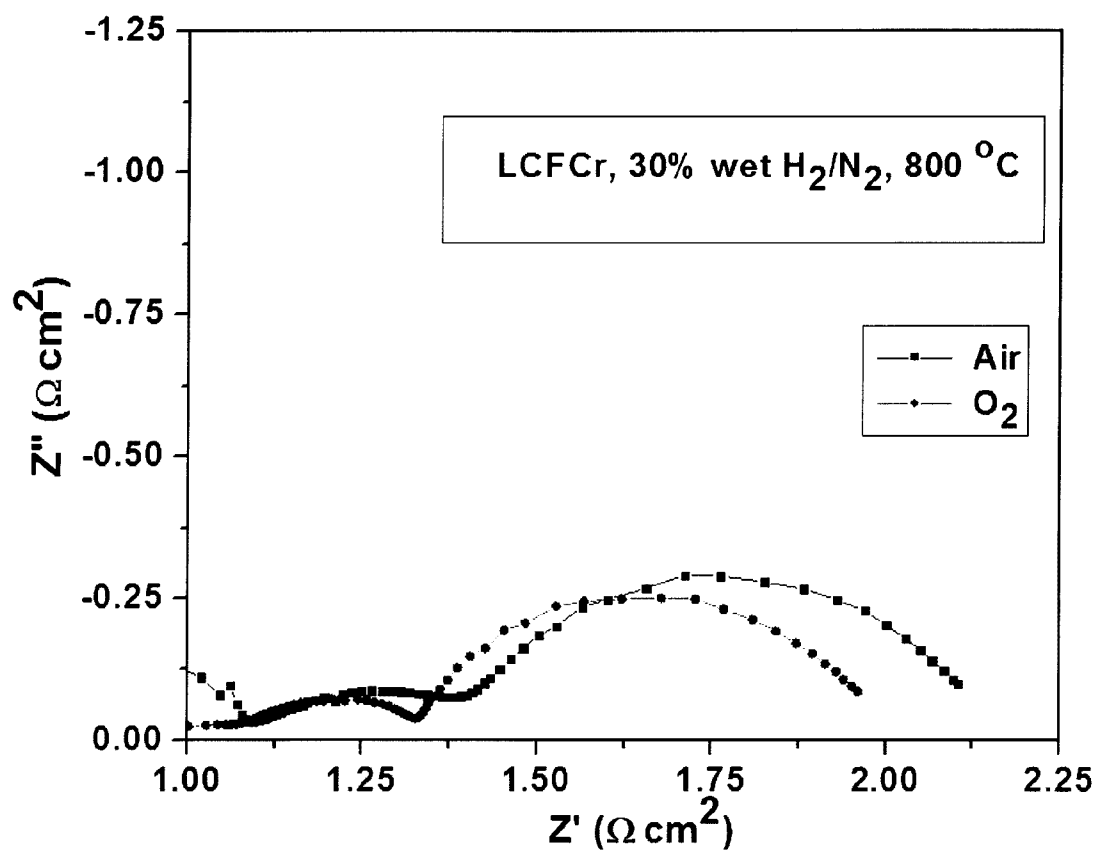


FIG. 14

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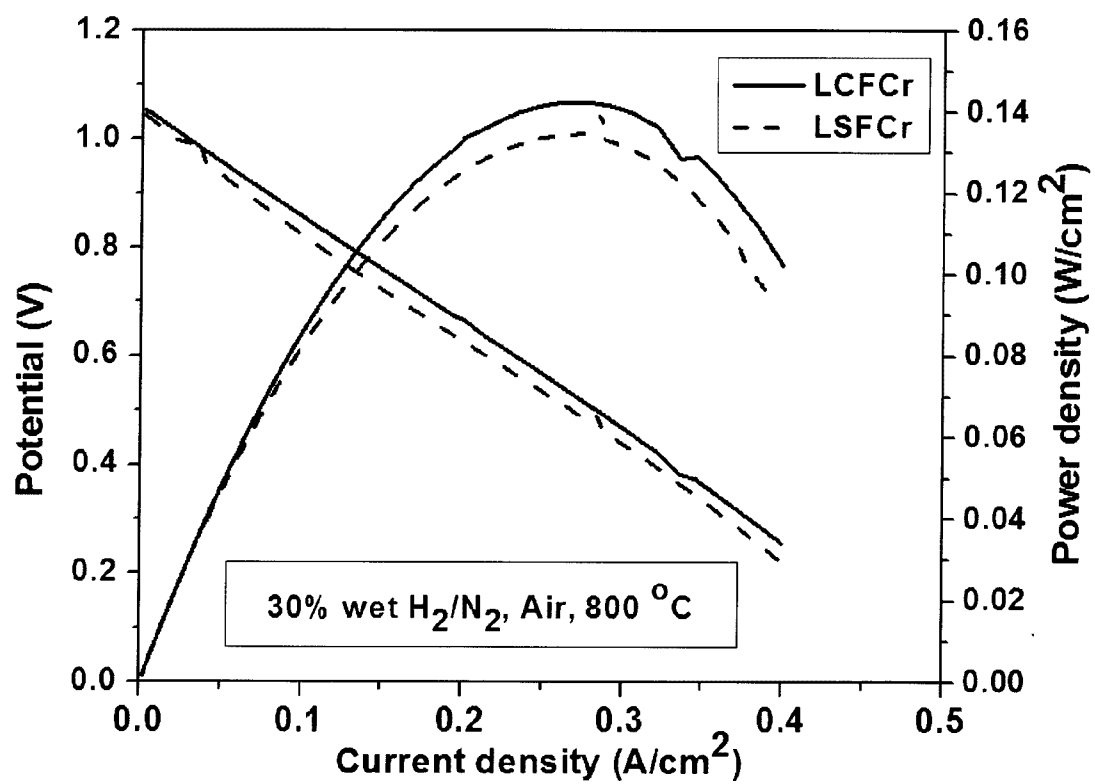


FIG. 15

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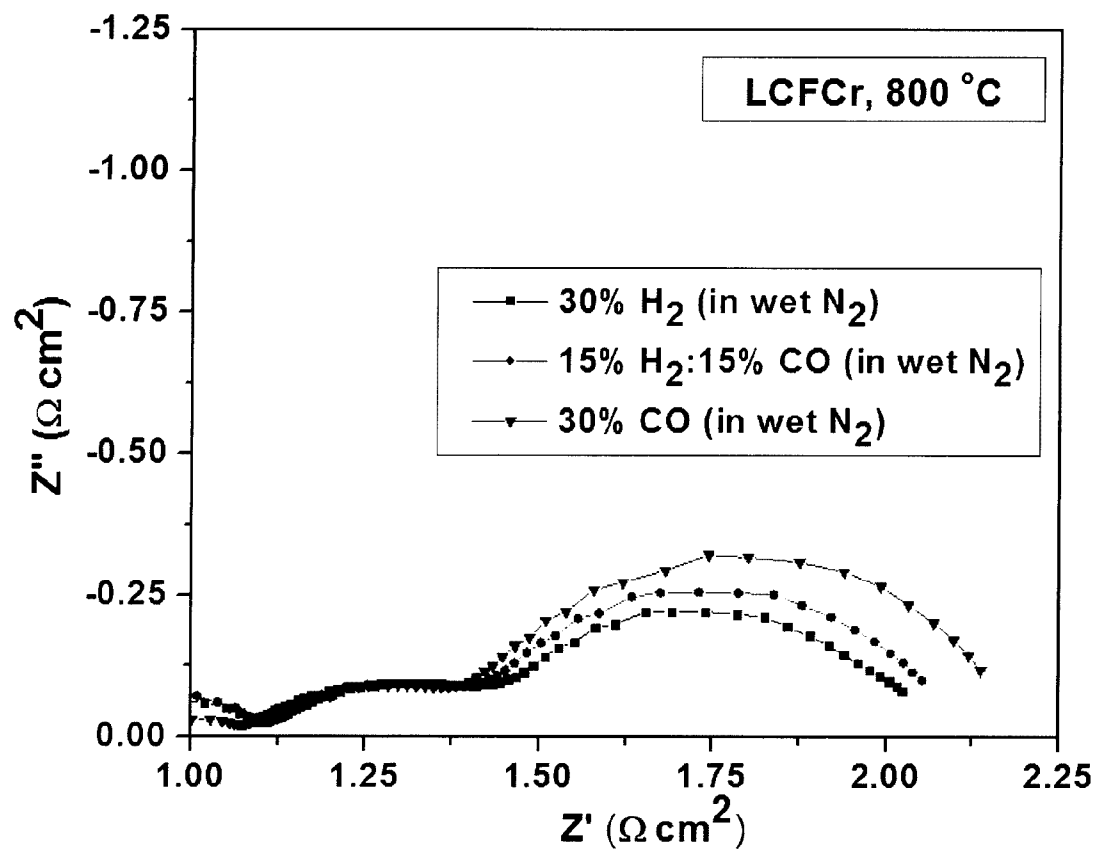


Fig. 16

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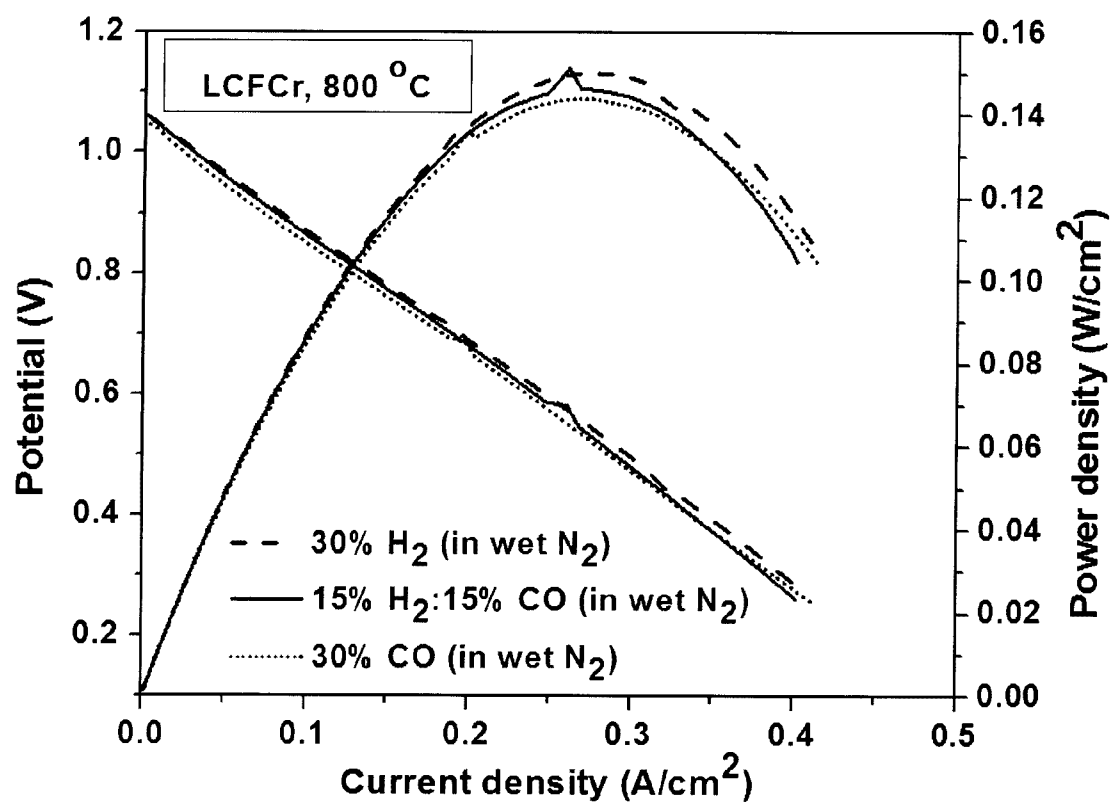


FIG. 17

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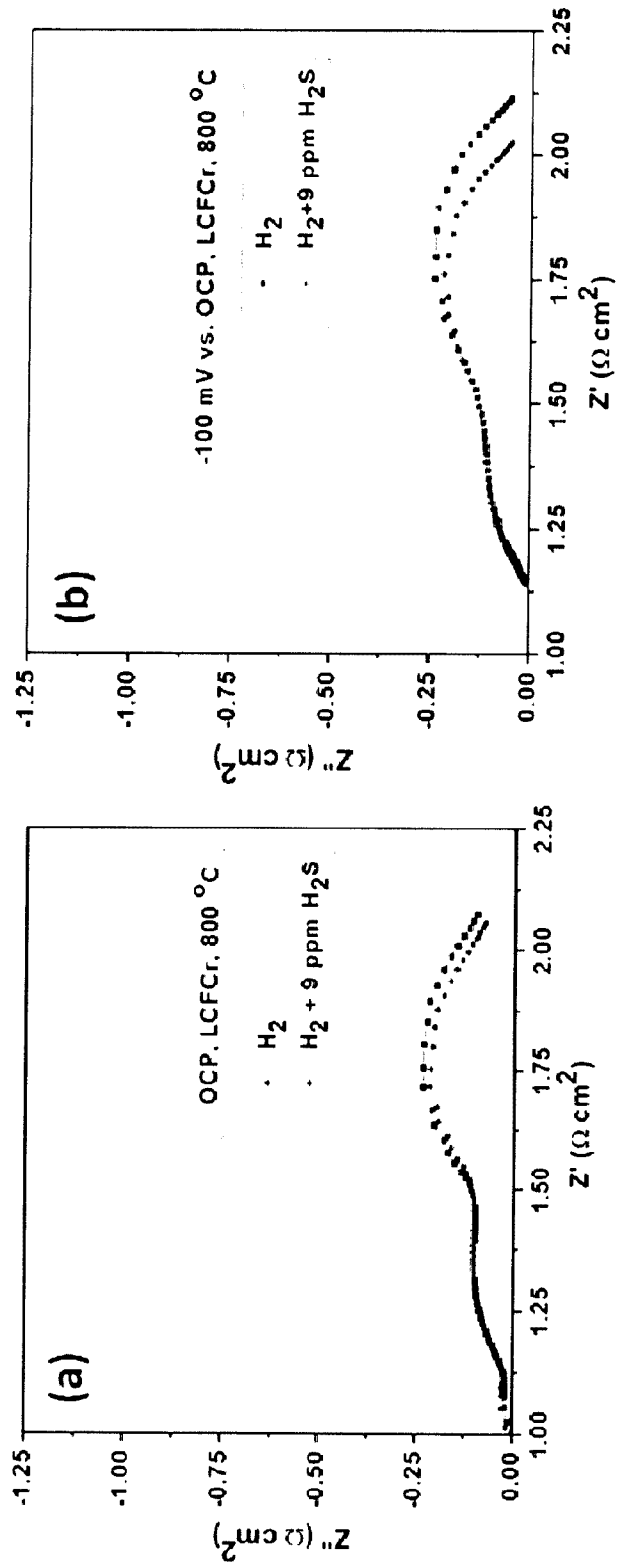


FIG. 18A

FIG. 18B

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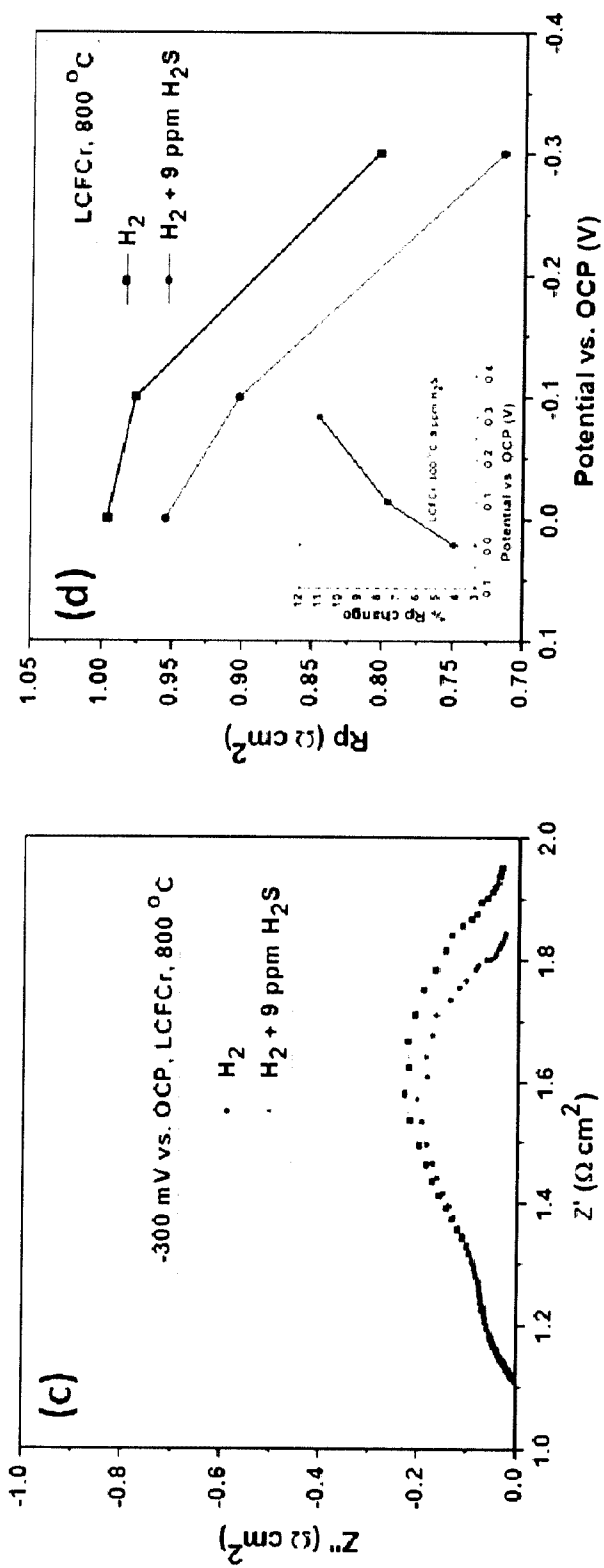


FIG. 18D

FIG. 18C

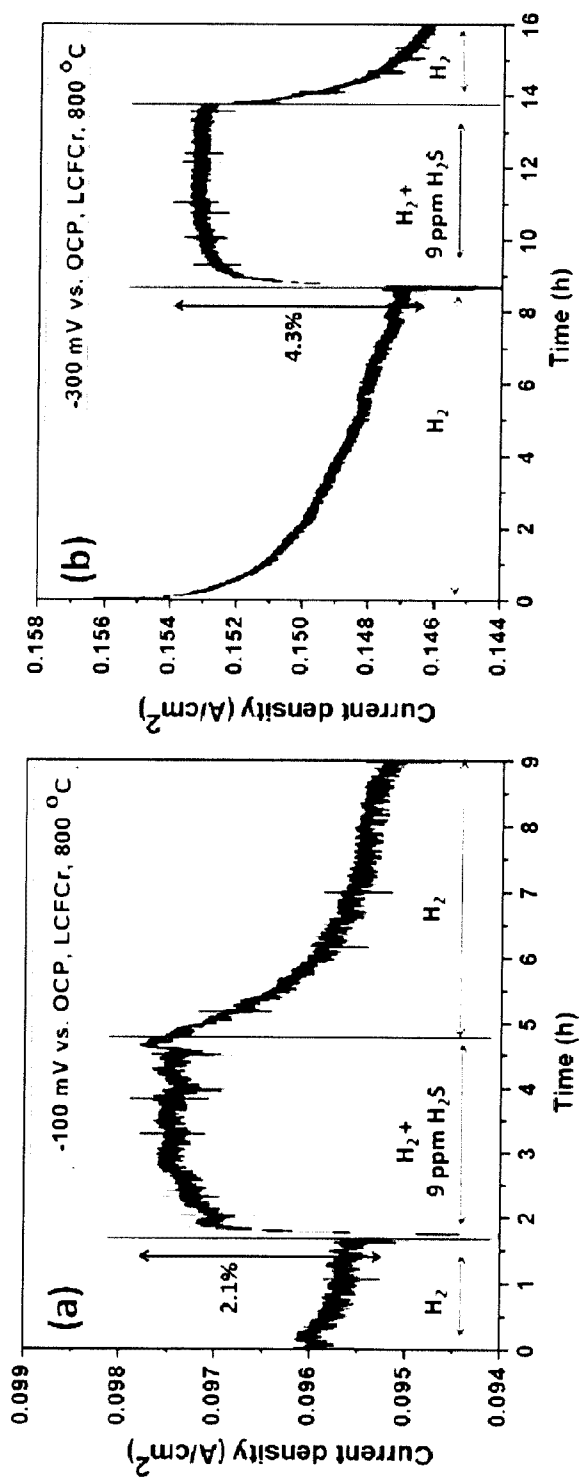


FIG. 19A

FIG. 19B