Performance of planar single cell lanthanum gallate based solid oxide fuel cells

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Abstract

A novel synthesis of high purity, single phase strontium–magnesium doped lanthanum gallate through a nitrate route is described. The prepared powder is formed into planar monolithic elements by uniaxial pressing followed by isostatic pressing and sintering. XRD analysis of the sintered elements reveal no detectable secondary phases. The performance of the electrolyte in solid oxide fuel cells (SOFC) with three different anode/cathode combinations tested at 700°C with respect to the J–V and power density is reported. The data show that the characteristics of this SOFC are strongly dependent on the particular anode/cathode system chosen. © 1998 Minister of Natural Resources, Canada. Published by Elsevier Science S.A. All rights reserved.

1. Introduction

The increasing concern over greenhouse gas emissions worldwide has forced countries to focus their efforts on reduction of these pollutants. Consequently, fuel cells are receiving significant attention as viable alternatives in transportation and stationary power generation. Fuel cells convert chemical energy directly into electrical energy and their thermodynamic efficiencies are not limited by the Carnot cycle [1–3]. ZrO_2-based solid oxide fuel cells (SOFC) have received considerable attention in the past because of the high oxygen ion conductivity of the zirconia electrolyte system. But the high operating temperatures ($> 1000°C$) required for the zirconia reduce the reliability and operating life of these cells through materials problems.

A ceria-based electrolyte is an alternative to ZrO_2 because of its high oxygen conductivity at 700°C [4]. This electrolyte, however, shows considerable electronic conductivity also, which is detrimental to fuel cell operation. In addition, it is unstable under the hydrogen environment of the anode [5]. Recently, an oxygen ion conductor, based on a modification of the perovskite, lanthanum gallate, has been shown to be another potential candidate for lower temperature SOFC [6,7]. Synthesis of this material in a pure state, however, reportedly has been difficult, because of the presence of small amounts of impurity phases [6]. The purpose of this work is to report a novel, simple synthesis route for doped lanthanum gallate which eliminates the undesirable secondary phase from the product. The performance of the phase-pure material in a planar type SOFC with three different anode/cathode systems, is also presented in this paper.

2. Experimental

The strontium–magnesium doped lanthanum gallate, $La_{0.9}Sr_{0.1}Ga_{0.8}Mg_{0.2}O_{2.85}$ (LSGM) electrolyte was prepared by starting with high purity oxides and carbonates through a chemically modified process. The materials, lanthanum oxide (La_2O_3), strontium carbonate ($SrCO_3$), magnesium oxide (MgO) and gallium oxide (Ga_2O_3) were all 99.99% pure. Stoichiometric amounts of these ingredients were separately weighed out. In a 400 ml beaker, the MgO was first dissolved in a minimum amount of a 1:1 dilute aqueous nitric acid solution, with constant stirring. To the clear solution thus obtained was added the strontium carbonate, when effervescence started. More of the dilute nitric acid was added to this mixture in drops, with stirring, until the effervescence stopped, and the solution

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became clear again. Next the La_2O_3 powder was added to the solution and a sufficient amount of dilute nitric acid solution was again added to the mixture to dissolve the lanthanum oxide, and to get a clear solution. The magnesium, strontium and lanthanum compounds have all been converted into the nitrate in solution, by this procedure. The Ga_2O_3 powder was then added to the solution and stirred well until all the oxide powder had dispersed, resulting in a slurry with a milky white consistency. The slurry was evaporated on a hot plate while being simultaneously stirred, and further dried in a drying oven (120°C) overnight. The dried powder was ground in an agate mortar and calcined at 1300°C in air for 12 h, in a covered platinum crucible. The powder was removed from the crucible, reground, and subsequently recalcined at the same temperature for 12 h, for powder conditioning (grain growth).

Samples 3.175 cm in diameter and 1–2 mm nominal thickness were prepared by mixing the calcined powder with a 15% PVA solution and uniaxially pressing it at 69 MPa, resulting in a green density of greater than 50%. The samples were then isostatically pressed at 275 MPa, which increased the green density to 60–65%. The pellets were sintered at 1500°C for 12 h in air with a heating and cooling rate of 5°C/min. The sintered density of all the samples was greater than 95% of the expected theoretical value.

Phase content of the powders and sintered elements were investigated with a Rigaku MINIFLEX XRD system using Cu K_α radiation. Thermogravimetric studies to determine the stability of the lanthanum gallate in a hydrogen atmosphere were conducted in a Shimadzu TGA-50 Thermogravimetric Analyzer. Calcined powder samples weighing 15 mg were used for these experiments. Runs were made in platinum pans at a heating rate of 5°C/min to 1000°C in a 40 cm^3/min gas purge of 4% H_2 balance N_2 gas mixture.

Conductivity of the LSGM electrolyte was determined by impedance measurements made with an HP4192A LF impedance analyzer. Engelhard platinum paste A-3380 was applied to both sides of the LSGM discs which were then fired at 1000°C for 1 h in air. The frequency range investigated was 0.1–100 kHz, with an oscillator level of 50 mV. The conductivity data were collected under a compressed air flow of 50 cm^3/min.

Planar single cells in three configurations were fabricated for fuel cell evaluation; one structure utilized Engelhard platinum ink A-4338 for both the anode and cathode. The electrodes were air dried and then fired at 1000°C for 1 h in air, with heating and cooling rates of 10°C/min. The second configuration studied used NiO–CeO_2 for the anode and $La_{0.6}Ca_{0.4}Fe_{0.8}Co_{0.2}O_{3-\delta}$ (LCFC) pervoskite for the cathode. The preparation of this perovskite cathode has been previously described [8,9]. The calcined oxide powder was ground and mixed with a polyvinyl butyral binder, ethanol, and a polyethylene glycol plasticizer, as described in Ref. [8]. The slurry was brushed onto the LSGM substrate and sintered at 1150°C for 6 h with heating and cooling rates of 5°C/min. The third fuel cell configuration utilized the same NiO–CeO_2 anode electrode but incorporated lanthanum strontium cobaltite, $La_{0.6}Sr_{0.4}CoO_{3-\delta}$, (LSC), as the cathode. The LSC powder was also synthesized through a nitrate route—by dissolving $SrCO_3$ in 1:1 dilute nitric acid solution and combining with La_2O_3 and cobalt oxide (Co_2O_3)—a procedure similar to the one used to produce LSGM. After dissolving the strontium carbonate in nitric acid, La_2O_3 was added to the solution followed by the Co_2O_3; distilled water was added and stirred until the powders got dispersed. The dried slurry was calcined at 1200°C for 6 h with heating and cooling rates of 5°C/min. The cathode material thus prepared was ground and mixed with a 15% PVA solution and slurry-coated onto the LSGM electrolyte. The coated disc was fired at 1150°C for 6 h, with a heating and cooling rate of 5°C/min. During fuel cell operation, a 4% H_2/96% Ar gas mixture at a flow of 50 cm^3/min was supplied at the anode while a flow of compressed air at 50 cm^3/min was maintained at the cathode. The gas flow to the anode was introduced at 300°C to ensure that the NiO got reduced to Ni metal by the time the cell operating temperature of 700°C was reached. Platinum mesh was placed on top of the anode and cathode to act as current collectors.

3. Results and discussion

Previous synthesis routes for LSGM involved mixing and heating together, either high purity oxides [6,7,10,11] or a combination of oxides and carbonate reactants [12–14]. The sintered samples made by this procedure invariably contained minor impurity phases; powders synthesized by the carbonate route, not only contained impurity phase, but often had not decomposed even after 24 h of calcination [14]. The powders had to be repeatedly recalcined until all the reactants had decomposed and the correct phase had formed [14]. An alternative synthesis route based on a glycine–nitrate combustion technique has also been reported for the synthesis of phase-pure LSGM [15]. This technique, however, was more complex than the method reported here, and was critically dependent on the amount of fuel used in the combustion step. The synthesis route described in this paper is simple and does not require prolonged periods of calcination. Fig. 1 shows an XRD pattern for a LSGM sample sintered at 1500°C for 12 h. All the detected peaks matched those given in the JCPDS card 24-1102, no secondary phases were detected. Fig. 2 presents the TG data for the LSGM precursor powder prepared by the nitrate route, prior to calcination, and shows that all the nitrates are completely converted to the oxide below 1000°C.
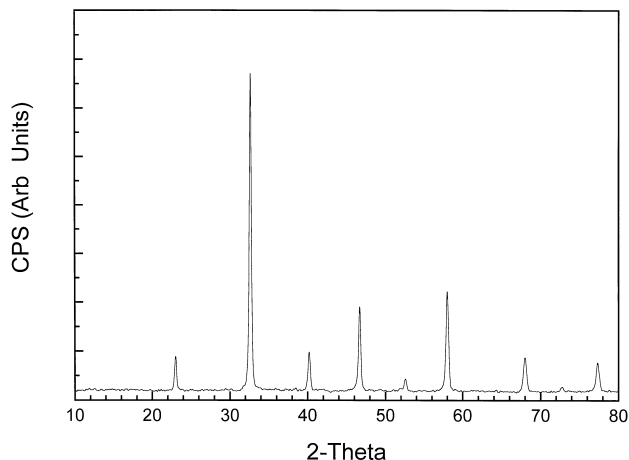
Fig. 1. XRD pattern for single phase LSGM synthesized by the nitrate route and sintered at 1500°C.

Fig. 3. Conductivity (σT) vs. reciprocal temperature for LSGM electrolyte with platinum electrodes.

Impedance spectroscopy was used to determine the total conductivity of the LSGM electrolyte. The total conductivity (σT) vs. reciprocal temperature is given in Fig. 3. The data exhibited an Arrhenius type behaviour of the form:

$$\sigma T = \sigma_0 \exp(E/kT)$$

where E is activation energy, k Boltzmann's constant and T absolute temperature. The overall activation energy, determined by a NLLSF of the data in Fig. 3, was 1.00 eV. However, closer examination of the data revealed the presence of two different slopes, one for high temperature conduction, $T > 600°C$, and one for the low temperature conductivity, $T < 600°C$. A similar observation has been made on the conductivity of LSGM powders synthesized by the glycine–nitrate route [15]. The activation energy for the high temperature and low temperature regimes were 1.09 eV and 0.75 eV, respectively. These values compare favourably to the values reported by Stevenson et al. [15] of 1.08 and 0.74 eV, respectively.
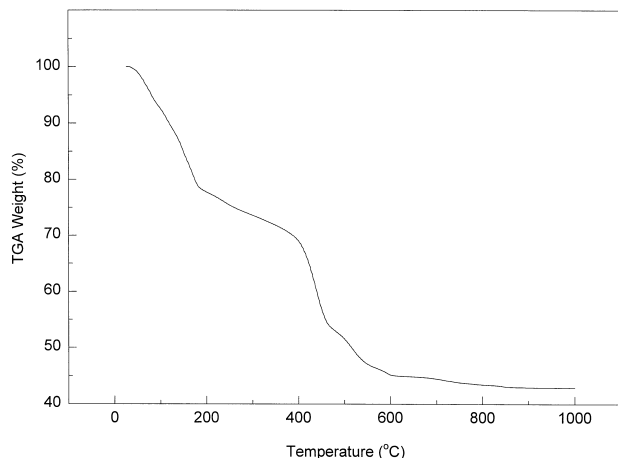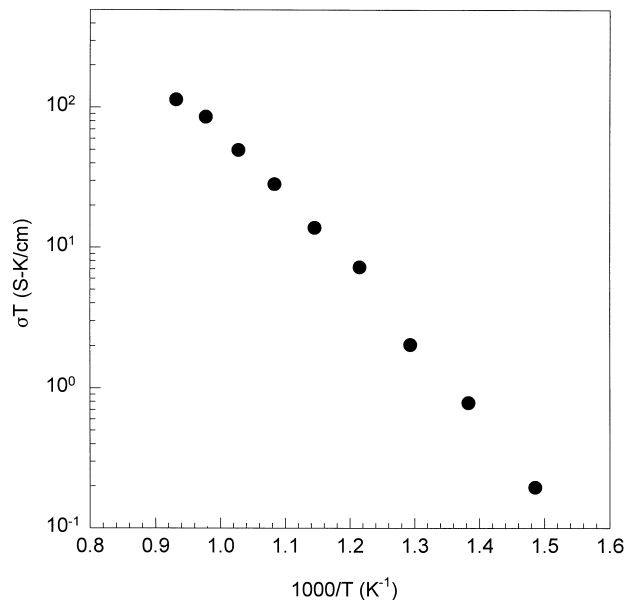
A major concern with ceria-based electrolytes is their stability under the reducing hydrogen environment present at the anode. LSGM, on the other hand, does not get reduced in a hydrogen ambient. This is evidenced by TG studies done in 4% H_2–N_2 gas mixture to 1000°C performed in this study, wherein no significant weight change was observed.

The J–V characteristics of a planar SOFC incorporating a single 0.86 mm thick LSGM disc with porous platinum electrodes are shown in Fig. 4. The cell was operated continuously for 24 h. The non-linear J–V data indicate the presence of significant polarization at the

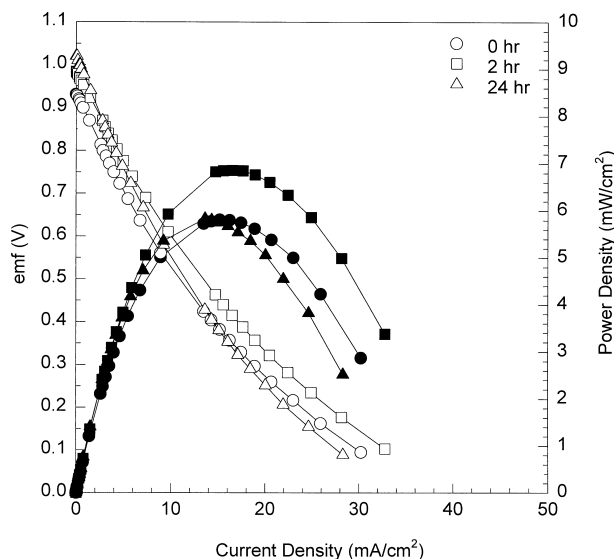Fig. 2. TG data for LSGM nitrate precursor powder in air to 1000°C, at a heating rate of 5°C/min.

Fig. 4. J–V (open symbols) and power density (closed symbols) data for a single planar fuel cell with the Pt/LSGM/Pt configuration.

electrode/electrolyte interface. The power density for the same fuel cell is also shown in Fig. 4. The relatively low values for current and power densities indicate that the Pt electrodes are less than ideal for LSGM. A similar finding has been previously reported [7]. The deterioration in performance of the cell can be ascribed to the spalling of the Pt electrode observed at the cathode side of the device. The same cell was thermally cycled several times (each time with new cathode coating) and exhibited similar deterioration in performance.

The oxidizing conditions present at the cathode tend to affect the platinum electrode detrimentally, after long periods of fuel cell operation in this system. In addition, the high cost of platinum is a disadvantage for its use in commercial fuel cells. LCFC is an inexpensive alternative for the cathode and like LSGM, possesses a perovskite structure. This material has been shown to have good surface exchange coefficients and exchange current densities [16]. LCFC has been used as a cathode material in ceria-based fuel cells but has not been tested with LSGM. The $J–V$ characteristics for a planar type fuel cell with the NiO–CeO$_2$/LSGM/perovskite configuration is shown in Fig. 5, along with the corresponding power density data. The linear $J–V$ behaviour suggests little, if any, polarization of the electrodes. Although, the current density levels of this configuration are similar to the Pt/LSGM/Pt cell, its overall performance is superior. Even after 24 h of operation the power density of this cell continued to increase. Clearly, the LCFC/LSGM electrolyte interface performed better than the Pt/LSGM counterpart. These data suggest that the LCFC electrode is a viable cathode material for SOFC based on LSGM. The cell was thermally cycled several times without any deterioration.
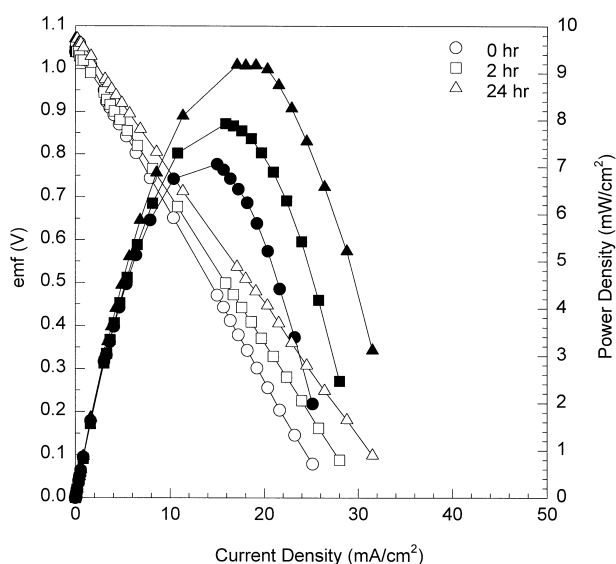

Fig. 6. $J–V$ (open symbols) and power density (closed symbols) data for a single planar fuel cell with the NiO–CeO$_2$/LSGM/LSC cell configuration.

The most frequently used cathode material for LSGM is LSC [6,7,10–13], and like LCFC has high electronic conductivity and oxygen activity [17]. The $J–V$ data for NiO–CeO$_2$/LSGM/LSC cell are given in Fig. 6, and the accompanying power density data are also given. The linear behaviour of the $J–V$ data suggests very little polarization of the fuel cell structure. The current density and power density for this cell were the highest of the three configurations studied. The data suggest that LSC is the most appropriate cathode material for LSGM, as reported previously [7].

4. Summary

A novel, simple synthesis route for LSGM electrolyte has been reported. The new process yields material that is phase pure without the need of any complicated or elaborate processing and can easily be scaled up. The performance of three single element fuel cells with different anode/cathode combinations was tested at 700°C. The $J–V$ data indicated that porous Pt was the least desirable material for both the anode and cathode. A NiO–CeO$_2$ anode performed well with both LCFC and LSC cathodes. The LCFC performance was slightly inferior to the LSC cathode; nevertheless, it performed well and can be considered a viable cathode material for LSGM based fuel cells.

Acknowledgements

Fig. 5. $J–V$ (open symbols) and power density (closed symbols) data for a single planar fuel cell with a NiO–CeO$_2$/LSGM/LCFC anode/electrolyte/cathode configuration.
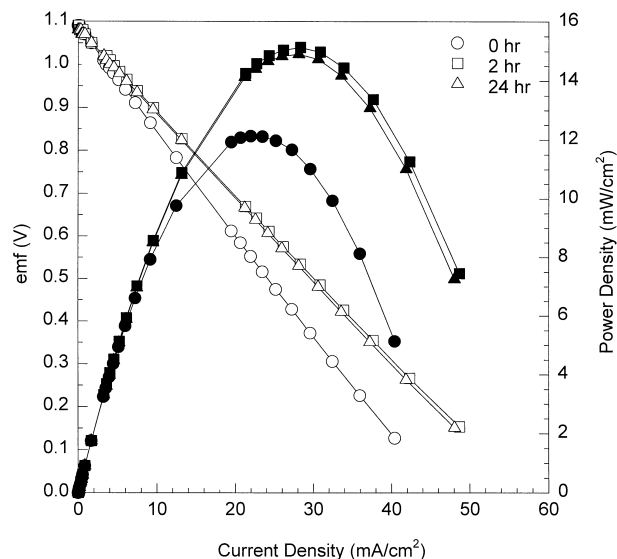
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