NRC Publications Archive Archives des publications du CNRC

Stability and reactivity of LSGM electrolytes with nickel-based ceramic cathodes

Munnings, C. N.; Skinner, S. J.; Amow, Gisele; Whitfield, Pamela; Davidson, Isobel

This publication could be one of several versions: author's original, accepted manuscript or the publisher's version. / La version de cette publication peut être l'une des suivantes : la version prépublication de l'auteur, la version acceptée du manuscrit ou la version de l'éditeur.

For the publisher's version, please access the DOI link below. / Pour consulter la version de l'éditeur, utilisez le lien DOI ci-dessous.

Publisher's version / Version de l'éditeur:

<https://doi.org/10.1115/1.1842780>

Journal of Fuel Cell Science and Technology, 2, February 1, pp. 34-37, 2005

NRC Publications Record / Notice d'Archives des publications de CNRC:

<https://nrc-publications.canada.ca/eng/view/object/?id=37ec0ac1-6edd-4046-bc83-8e9ffca1c10b>

<https://publications-cnrc.canada.ca/fra/voir/objet/?id=37ec0ac1-6edd-4046-bc83-8e9ffca1c10b>

Access and use of this website and the material on it are subject to the Terms and Conditions set forth at

<https://nrc-publications.canada.ca/eng/copyright>

READ THESE TERMS AND CONDITIONS CAREFULLY BEFORE USING THIS WEBSITE.

L'accès à ce site Web et l'utilisation de son contenu sont assujettis aux conditions présentées dans le site

<https://publications-cnrc.canada.ca/fra/droits>

LISEZ CES CONDITIONS ATTENTIVEMENT AVANT D'UTILISER CE SITE WEB.

Questions? Contact the NRC Publications Archive team at

PublicationsArchive-ArchivesPublications@nrc-cnrc.gc.ca. If you wish to email the authors directly, please see the first page of the publication for their contact information.

Vous avez des questions? Nous pouvons vous aider. Pour communiquer directement avec un auteur, consultez la première page de la revue dans laquelle son article a été publié afin de trouver ses coordonnées. Si vous n'arrivez pas à les repérer, communiquez avec nous à PublicationsArchive-ArchivesPublications@nrc-cnrc.gc.ca.

C. N. Munnings

S. J. Skinner*

Department of Materials, Imperial College
London, Prince Consort Road, London, SW7
2BP, United Kingdom
e-mail: s.skinner@imperial.ac.uk

G. Amow

P. S. Whitfield

I. J. Davidson

ICPET, NRC Canada, 1200 Montreal Road,
Ottawa, K1A 0R6, Canada

Stability and Reactivity of LSGM Electrolytes With Nickel-Based Ceramic Cathodes

The surface of $\text{La}_{0.9}\text{Sr}_{0.1}\text{Ga}_{0.8}\text{Mg}_{0.2}\text{O}_{3-\delta}$ (LSGM 9182) has been examined through the use of secondary-ion mass spectrometry before and after surface modification by mechanical polishing. It was found that the cation stoichiometry varied at the surface in both cases. The effect of this change on the performance of the cathode material $\text{La}_2\text{NiO}_{4+\delta}$ was assessed through ac impedance spectroscopy of symmetrical cells prepared by depositing $\text{La}_2\text{NiO}_{4+\delta}$ on the surface of pellets of $\text{La}_{0.9}\text{Sr}_{0.1}\text{Ga}_{0.8}\text{Mg}_{0.2}\text{O}_{3-\delta}$. An improvement in the cathode performance of these cells at temperatures above 500°C was found on electrolytes with elevated levels of strontium and magnesium at the surface. [DOI: 10.1115/1.1842780]

Introduction

After the discovery of fast oxide ion conduction in LaGaO_3 -based materials [1–4], there has been increasing interest in the production of intermediate-temperature solid oxide fuel cells (IT-SOFC) based on the doped gallates, particularly the $\text{La}_{0.9}\text{Sr}_{0.1}\text{Ga}_{0.8}\text{Mg}_{0.2}\text{O}_{3-\delta}$ (LSGM 9182) composition [1]. This interest is due to the reported fast oxide ion conductivity of this material at temperatures below 800°C which shows a considerable performance improvement when compared to yttria-stabilized zirconia electrolytes [4]. If this material is to be used for the construction of a commercial product, then the long-term stability and the interaction of this material with other cell components must be fully understood. Studies of the interaction of this material with various electrode configurations have shown LSGM to perform well under oxidizing conditions with little interdiffusion of cation species [5–7]. Despite the slow interdiffusion of cation species in these materials, there is evidence to suggest that the gallium may be volatile at elevated temperatures ($\geq 1200^\circ\text{C}$) [8–10], and it should also be noted that LSGM has been reported to react with nickel-containing cermets at elevated temperatures ($\geq 1250^\circ\text{C}$) [11,12]. This is of relevance when considering the processing of the complete fuel cell rather than its operation.

Materials of the K_2NiF_4 -type structure, namely, $\text{La}_2\text{NiO}_{4+\delta}$ have been shown to possess fast oxide ion conduction ($D^* \sim 10^{-8} - 10^{-6} \text{ cm}^2 \text{ s}^{-1}$) [13] and electrical conductivity of up to about 100 S cm^{-1} [14] at temperatures between 600 and 800°C . These properties, combined with a thermal expansion coefficient of $13.7 \times 10^{-6} \text{ K}^{-1}$ [15], make this a promising potential cathode material for use in IT-SOFCs. It has been shown that $\text{La}_2\text{NiO}_{4+\delta}$ displays a considerable performance enhancement when tested as a cathode on LSGM when compared with other electrolyte materials (e.g., gadolinia-doped cerium oxide) [15], and from this it was concluded that the improvement in performance was most likely due to the interface, microstructure, or sintering characteristics. The purpose of the current investigation is to examine the surface of LSGM 9182 and the effect that this surface has on the performance of the cathode material $\text{La}_2\text{NiO}_{4+\delta}$.

Experiment

$\text{La}_2\text{NiO}_{4+\delta}$ was prepared via the standard citrate gel route and the phase purity of the materials was investigated with x-ray powder diffraction [14]. Electrolytes were prepared by pressing pellets (10 mm diam and ~ 3 mm thick) of LSGM 9182, supplied by Praxair, Inc., Danbury, CN, USA with a uniaxial press. These pellets were then sintered at 1500°C for 2 h to ensure fully dense electrolytes were produced. Phase purity of the dense electrolytes was confirmed with x-ray diffraction on a Philips PW1700 series diffractometer, with Cu K_α radiation and a graphite single-crystal secondary monochromator.

Once dense, three different electrolyte surfaces were prepared. For two of the surfaces the top layer of material was removed with 1200 grit SiC paper. Once the surface was removed, separate samples were heated to 1000°C for 24 and 48 h, respectively. The third surface was the untreated original sintered surface. For samples that were to be used in symmetrical cell testing, both surfaces were treated in an identical manner.

Surface Analysis. The surface analysis of the materials was carried out on an Atomika 6500 secondary-ion mass spectrometry (SIMS) microprobe with a 1.25 keV oxygen primary ion beam. Depth profiles were carried out perpendicular to the surface of the material. A raster scan was performed over an area of 5.76 mm^2 to ensure that a representative value for the bulk response of the surface was obtained. The secondary ions Sr^{2+} , Mg^{2+} , Ga^{3+} , and La^{3+} were monitored as a function of sputter time. A standard sample was prepared by the pressing of a 10-mm-diam pellet that was left unsintered; this pellet was used to determine the response of the bulk material.

Cathode Performance. Having produced single-phase cathode materials and dense electrolytes, the cathodes were deposited on both surfaces of the electrolyte. An ink was prepared from the cathode composition and terpinol, which was then painted onto the pre-treated LSGM electrolyte, dried, and sintered in argon at 1000°C for 2 h. Ac impedance spectroscopy measurements were carried out on a Solartron 1260 Frequency Response Analyzer over the frequency range 10 MHz to 0.01 Hz and a temperature range of $430 - 820^\circ\text{C}$. This data was then normalized to give an area-specific resistance (ASR) for each cell.

Results and Discussion

Surface Analysis. The surface of the material was examined through the use a reactive O_2^- ion beam to give the best response for the positive cations examined. A positive-ion mass spectrum of

*Author to whom all correspondence should be addressed; Tel: +44 (0)20 7594 6782; Fax: +44 (0)20 7584 3194

Manuscript received: April 7, 2004; revision received July 27, 2004
Review conducted by: N. M. Sammes.

Fig. 1 Comparison of the SIMS responses of the surfaces of differently treated samples: (a) standard, (b) ground surface, and (c) untreated sintered surface

the surface from mass 6 to 135 confirmed the presence of only La, Sr, Ga, and Mg ions, with minor peaks corresponding to SrO^+ and MgO^+ also present. The use of a low-energy beam (1.25 keV), a large sputter area, and a relatively short sputter time (>1 h) in all cases ensured that no more than the top 100 nm of material was examined. Attempts to quantify the sputter depth were not possible due to the fact that the surface roughness of each sample was considerably greater than the expected sputter depth ($\text{rms} = 0.335 \mu\text{m}$).

Results of the surface analysis can be seen in Fig. 1. The sputter yield will vary for each of the four elements examined in this material, so that the absolute intensity values do not relate directly to the cation stoichiometry. For this reason, a standard unsintered sample was used to determine the bulk response of this material (Fig. 1(a)). The variation during the first 200 s of the standard sample can be largely discounted due to the considerable surface roughness of the sample. After this time, the response of each element becomes constant. This response is taken to be the bulk response of the LSGM 9182 phase. It can clearly be seen that the response of the elements separate into four distinct lines, the most intense being for gallium, followed by magnesium, strontium, and finally lanthanum. The response of the sample which has had its

Fig. 2 SIMS response of sample heated to 1000°C for 24 h

surface removed after sintering (Fig. 1(b)), can be seen to be very similar to that of the standard sample with the four different elements separating into four distinct lines of similar relative intensities. This suggests that the stoichiometry of the surface of the ground sample (not unexpectedly) is similar to that of the bulk of the material. The initial curvature of this response is considered to be an effect of the instrument as it can be seen in all four of the elements examined and is not uncommon when examining samples with high surface roughness.

The response of the surface of the sintered sample, (Fig. 1(c)) is considerably different to that of the standard and of the ground sample. It can be seen that at the very near surface, the order of the response of the gallium, magnesium, and strontium is reversed, with the strontium giving the most intense response, followed by the magnesium and the gallium. The response of these three elements then converges to give lines of similar intensity that do not appear to diverge. This relates to either an increase in the concentration of magnesium and strontium at the surface and near surface, or to a depletion of gallium from the surface. Depletion of gallium at the near surface of the material would be consistent with previous studies examining this material [8–10], and is most likely. The outcome of either of these processes will lead to the same surface stoichiometry. The response of the lanthanum is not considered to vary greatly enough to comment on its relative concentration to the other three elements in this sample.

Samples annealed at 1000°C for 24 h showed behavior similar to that of the untreated sintered surface (Fig. 2), although the layer formed was very much reduced, with the strontium, magnesium, and gallium responses falling rapidly back to the expected bulk response. It is unclear at this time if this layer will increase in thickness with time or whether it will self-passivate and remain unchanged. However, it should be noted that the surface produced on heating for 48 h gave an almost identical SIMS response to that observed for the material annealed for 24 h. All that is clear is that there is a variation of cation stoichiometry at the very near surface of this electrolyte material after heating at relatively low temperatures.

Cathode Performance. The performance of the cathode was assessed through the use of ac impedance spectroscopy on symmetrical cells. Each cell was prepared from the same batch of ink, and all cells were sintered in the same furnace to ensure that the results were not affected by variations in the sintering temperature of the individual cells. Measurements were recorded on the same apparatus over the same temperature range and for identical time periods, and the ASR values calculated. From the ASR data (Fig. 3), it is evident that there is a considerable variation in performance between the two electrolyte surfaces considered: surface 3 and surface 4 (see Table 1). It can quite clearly be seen that, especially at elevated temperatures ($\sim 800^\circ\text{C}$), the performance of

Fig. 3 Comparison of the ASR of the untreated sintered surface (diamonds) and the ground surface (squares)

the untreated sintered sample (surface 4) is superior to the sample that had the surface removed (surface 3), with a difference of an order of magnitude seen in the ASR (Fig. 3). The reason for this difference in performance is still unclear, although it seems to be related to the variation in the cation stoichiometry at the surface, with the samples with a high concentration of both strontium and magnesium at the surface producing the best cathode response. The ac impedance response given by the untreated sintered sample and the ground sample are shown in Fig. 4. The untreated surface gives a single arc, whereas for the ground surface there is a definite change in behavior, with two merged arcs being seen in the response. The response of the surface annealed at 1000°C for 24 h (surface 1) is very similar to that of the ground surface (surface 3), with the additional heat treatment appearing to have little or no effect (Fig. 5). There was no notable difference in performance between the electrolyte surfaces annealed for 24 or 48 h at 1000°C prior to the deposition of the cathode (surfaces 1 and 2, respectively).

While it is interesting to note these differences in the cathode behavior, it is, as yet, unclear as to the origins of these differences. Several features of this cathode behavior require further investigation, notably the cathode/electrolyte interface, to elucidate both the composition and structure of this region. The possibility that a new electrochemically interface when $\text{La}_2\text{NiO}_{4+\delta}$ is sintered at 1000°C on to an LSGM electrolyte previously sintered at 1500°C, is potentially exciting. With further optimization of the

electrode deposition and microstructure, the use of the interstitial oxygen-containing cathodes on LSGM electrolytes now looks attractive.

Conclusion

It has been shown that the surface of LSGM 9182 appears to be chemically active with respect to $\text{La}_2\text{NiO}_{4+\delta}$ -type cathodes, after the cathode has been sintered, at 1000°C, onto the electrolyte previously sintered at 1500°C. It was found that thermal treatment of the electrolyte, at 1000°C, both with and without prior mechanical grinding, had an effect on the surface stoichiometry

Table 1 Summary of surface preparation. Samples 1–4 were sintered at 1500°C for 4 h prior to surface preparation

Sample	Thermal treatment
Standard	No thermal treatment, pressed pellet, unsintered
Surface 1	Surface removed with 1200 grit paper Sample annealed at 1000°C for 24 h
Surface 2	Surface removed with 1200 grit paper Sample annealed at 1000°C for 48 h
Surface 3	Surface removed with 1200 grit paper
Surface 4	Untreated sintered surface

Fig. 4 Comparison of the normalized ac impedance response for the untreated sintered sample (open squares) and the ground sample (open triangles) at ~680°C

Fig. 5 Comparison of the ASR of the ground surface (diamonds) and the sample with surface annealed at 1000°C for 24 h (triangles)

and that this stoichiometry change adversely affected the cathode performance. The best performance of the $\text{La}_2\text{NiO}_{4+\delta}$ cathode was observed on surfaces with elevated levels of strontium and magnesium that had no mechanical or thermal treatment, other than initial densification at 1500°C, prior to cathode deposition.

References

- [1] Huang, K., and Goodenough, J. B., 2000, "A Solid Oxide Fuel Cell Based on Sr- and Mg-doped LaGaO_3 Electrolyte: The Role of a Rare-Earth Oxide Buffer," *J. Alloys Compd.*, **303–304**, pp. 454–464.
- [2] Feng, M., and Goodenough, J. B., 1994, "A Superior Oxide-Ion Electrolyte," *Eur. J. Solid State Inorg. Chem.*, **31**, Nos. 8–9, pp. 663–672.
- [3] Huang, K. Q., Tichy, R. S., and Goodenough, J. B., 1998, "Superior Perovskite Oxide-Ion Conductor; Strontium- and Magnesium-Doped LaGaO_3 : I, Phase Relationships and Electrical Properties," *J. Am. Chem. Soc.*, **81**, No. 10, pp. 2565–2575.
- [4] Ishihara, T., Mitsudo H., and Takita Y., 1994, *J. Am. Chem. Soc.*, **116**, pp. 3801–3803.
- [5] Horita, T., Yamaji, K., Sakai, N., Yokokawa, H., Weber, A., and Ivers-Tiffée, E., 2000, "Stability at $\text{La}_{0.6}\text{Sr}_{0.4}\text{CoO}_{3-\delta}$ Cathode/ $\text{La}_{0.8}\text{Sr}_{0.2}\text{Ga}_{0.8}\text{Mg}_{0.2}\text{O}_{2.8}$ Electrolyte Interface Under Current Flow for Solid Oxide Fuel Cells," *Solid State Ionics*, **133**, Nos. 3–4, pp. 143–152.
- [6] Yamaji, K., Horita, T., Ishikawa, M., Sakai, N., and Yokokawa, H., 1998, "Compatibility of $\text{La}_{0.9}\text{Sr}_{0.1}\text{Ga}_{0.8}\text{Mg}_{0.2}\text{O}_{2.85}$ as the Electrolyte for SOFCs," *Solid State Ionics*, **108**, Nos. 1–4, pp. 415–421.
- [7] Schulz, O., and Martin, M., 2000, "Preparation and Characterisation of $\text{La}_{1-x}\text{Sr}_x\text{Ga}_{1-y}\text{Mg}_y\text{O}_{3-(x+y)/2}$ for the Investigation of Cation Diffusion Processes," *Solid State Ionics*, **135**, Nos. 1–4, pp. 549–555.
- [8] Matraszek, A., Miller, M., Singheiser, L., and Hilpert, K., 2003, "Phase Composition and Vapourization Study of $\text{LaGa}_{1-x}\text{Al}_x\text{O}_3$, $0 < x < 1$, and $\text{La}_{0.9}\text{Sr}_{0.1}\text{Ga}_{0.8-x}\text{Al}_x\text{Mg}_{0.2}\text{O}_{2.85}$, $x=0.1, 0.2, 0.3$," *J. Am. Chem. Soc.*, **86**, No. 11, pp. 1911–1917.
- [9] Kunczewicz-Kupczyk, W., Kobertz, D., Miller, M., Singheiser, L., and Hilpert, K., 2001, "Vapourization of Sr- and Mg-Doped Lanthanum Gallate and Implications for Solid Oxide Fuel Cells," *J. Electrochem. Soc.*, **148**, No. 6, pp. E276–E281.
- [10] Kunczewicz-Kupczyk, W., Kobertz, D., Miller, M., Chatillon, C., Singheiser, L., and Hilpert, K., 2002, "Vapourization Studies of the La_2O_3 - Ga_2O_3 System," *J. Am. Chem. Soc.*, **85**, No. 9, pp. 2299–2305.
- [11] Zhang, X., Ohara, S., Maric, R., Mukai, K., Fukui, T., Yoshida, H., Nishimura, M., Inagaki, T., and Miura, K., 1999, "Ni-SDC Cermet Anode for Medium-Temperature Solid Oxide Fuel Cell with Lanthanum Gallate Electrolyte," *J. Power Sources*, **83**, Nos. 1–2, pp. 170–177.
- [12] Maffei, N., and de Silveira, G., 2003, "Interfacial Layers in Tape Cast Anode-Supported Doped Lanthanum Gallate SOFC Elements," *Solid State Ionics*, **159**, Nos. 3–4, pp. 209–216.
- [13] Skinner, S. J., and Kilner, J. A., 2000, "Oxygen Diffusion and Surface Exchange in $\text{La}_{2-x}\text{Sr}_x\text{NiO}_{4+\delta}$," *Solid State Ionics*, **135**, pp. 709–712.
- [14] Amow, G., Whitfield, P., Davidson, I., Hammond, R. P., Munnings, C., and Skinner, S., 2003, "Structural and Physical Property-Trends of the Hyperstoichiometric series $\text{La}_2\text{Ni}_{1-x}\text{Co}_x\text{O}_{4+\delta}$," *Mater. Res. Soc. Symp. Proc.*, **755**, pp. 347–352.
- [15] Skinner, S. J., Munnings, C. N., Amow, G., Whitfield, P., and Davidson, I., 2003, "Evaluation of $\text{La}_2\text{Ni}_{1-x}\text{Co}_x\text{O}_{4+\delta}$ as a SOFC cathode material," in *SOFC VIII*, S. C. Singhal and M. Dokiya eds., *Electrochem. Soc. Series*, vol. 2003, No. 7, p. 552–560.