DIRECT METHANE OXIDATION IN MICRO-TUBULAR SOFCs USING DOPED LaGaO₃ ELECTROLYTE

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ABSTRACT

A problem associated with the direct oxidation of hydrocarbon fuels such as methane in a solid oxide fuel cell (SOFC) has been the rapid deactivation of the anode as a result of carbon deposition. However, the use of doped-ceria in the SOFC anode can potentially overcome this problem. A micro-tubular SOFC using strontium- and magnesium doped lanthanum gallate (LSGM) of composition La₀.₈Sr₀.₂Ga₀.₈₅Mg₀.₁₅O₂.₈₂₅ as the electrolyte was developed and tested using a doped-ceria based anode and a cathode material of La₀.₆Sr₀.₄Co₀.₃. A power density of 307 mW/cm² was achieved for a methane/oxygen fuel corresponding to a current density of 614 mA/cm² at 900°C. The procedures involved in the extrusion of micro-tubular lanthanum gallate (LaGaO₃) electrolyte tubes are also discussed in this paper. This study shows that achieving a commercial SOFC which could be operated at intermediate temperatures (650-800°C) and that could avoid the direct use of hydrogen as the fuel, is not an impractical task in the near future.

INTRODUCTION

Micro-tubular solid oxide fuel cells (SOFCs) based on yttria-stabilized zirconia (YSZ) have several advantages over other SOFC designs (1-4). The use of YSZ as an electrolyte places a constraint on the operating temperature of SOFCs, which must be operated at around 900-1000°C, because of the relatively poor ionic properties of YSZ for SOFC applications at lower operating temperatures.

Developing high performance electrolyte and electrodes is necessary in order to realize a practical SOFC that operates at intermediate temperature (650-800°C). The operation at such temperatures would minimize material degradation and enable the use of lower cost components (5). The discovery of strontium- and magnesium-doped lanthanum gallate (LaGaO₃) electrolyte, La₁₋ₓSrₓGa₁₋ₓMgₓO₃₋₅ (LSGM), with excellent oxide-ion conductivity over a broad range of oxygen partial pressures and at intermediate temperatures (6,7), has given a considerable drive to this area of research. Several compositions of the LSGM electrolyte have been studied in recent years. Amongst them, La₀.₈Sr₀.₂Ga₀.₈₅Mg₀.₁₅O₂.₈₂₅ exhibiting an ionic conductivity of 0.14 S/cm at 800°C (8), a 500 µm thick La₀.₉Sr₀.₁Ga₀.₈Mg₀.₂O₃.₀ exhibiting a power density of 0.425 W/cm² at

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800°C (9), and a thin film (130 μm) La0.9Sr0.1Ga0.8Mg0.2O3.0 exhibiting a power density of 0.7 W/cm² at 800°C (10) are of particular interest.

Hydrogen is the preferred long-term fuel for SOFCs as the product of combustion is water. However, hydrogen’s high production cost and complex storage issues have made hydrocarbon fuels such as natural gas the ideal fuel for SOFCs. Currently, demonstration power plants and other fuel cell applications make use of an external reformer that converts hydrocarbon fuel into hydrogen. Direct oxidation of hydrocarbon fuels (e.g. methane) in SOFCs would eliminate the need for use of such external reformers and result in improved efficiency and reduction in the system’s volume and cost. The main problem associated with direct oxidation of hydrocarbons has been rapid deactivation of the anodic oxidation reaction, due to carbon deposition on the SOFC anodes (11,13). This has been the case when conventional Ni – YSZ is used as the anode material. However, based on recent work by Mogensen et al. (14), Murray et al. (15), Park et al. (16), and Kim et al. (17) it has been shown that the internal reformation of CH₄ within the cell leading to excellent performance can be achieved if a doped-ceria containing anode is used for the SOFC. A power density of 0.570 W/cm² at 1000°C with a CH₄ conversion of 23.1% was achieved for the La0.9Sr0.1Ga0.8Mg0.2O3.0 electrolyte based on the work of Ishihara et al. (18). Internal reformation of CH₄ within a SOFC, based on La0.9Sr0.2Ga0.8Mg0.15Co0.05O2.8 electrolyte, has been examined by Akikusa et al. (19) and about 93% of the cell output performance of the H₂ fuel was attained without any carbon deposition.

This paper follows the work of Du and Sammes (20) on the fabrication and performance of a LaGaO₃-based micro-tubular SOFC. These techniques are used to study the optimum composition of the LSGM electrolyte and the compatible anode material that would efficiently oxidize methane at an intermediate temperature.

**EXPERIMENTAL**

**Electrolyte Tube Fabrication**

The electrolyte tubes were fabricated using the basic process described by Du and Sammes (21). Commercially available La0.8Sr0.2Ga0.8Mg0.2O2.8 (LSGM) powder (Praxair Inc.) was mixed with lubricant PEG-40 (Union Carbide Co.), pH control agent AMP-95 (Angus Chemical), binder B1051/B1052 (Duramax), and distilled water, in a sigma blade mixer (Jaygo Incorporated) for 1 hour until the mix formed a dough. A vacuum (28 mm Hg) was then applied for 10 minutes to the mixing chamber to allow the dough to be degassed, while the mixer was running. Homogeneous dough was obtained after aging overnight. The degassed and homogeneous dough was then extruded into tubes using a 16-T ram extruder (Loomis Products Co.), under a ram pressure of 5.5 tons. The extrudates were dried at room temperature in air, in in-house designed tube holders, followed by sintering in an electrical furnace at 1500°C for 6 hours in air. The equipment used in the fabrication of the electrolyte tubes is shown in Fig. 1.

The dimensions of the tubes after sintering were 6 mm outside diameter, 0.55 mm wall thickness, and 100-200 mm length.
Cell Preparation

The anode was prepared by mixing NiO/8YSZ (50:50 vol%) with Ce$_{0.8}$Sm$_{0.2}$O$_{1.9}$ (SDC) in a 50:50 wt% ratio. NiO was reduced to elemental Ni in the anode-reducing atmosphere. High performance La$_{0.6}$Sr$_{0.4}$CoO$_3$ (LSC), (Praxair Inc.), was selected as the cathode material.

The anodes and cathodes were first made into slurries in order to apply onto the electrolyte support tubes. The ceramic powders were ball milled in ethanol with PVP/MEKET binders until the mean particle size was less than 1 μm. The anode slurry was dip coated inside the electrolyte tubes by sucking the slurry up into the tubes using a syringe-pipe configuration. The coating was fired at 1200°C for 2 hours and the fired anode coat was observed as being 15-20 μm thick. The cathode slurry was brush painted onto the electrolyte tubes and was fired at 1100°C for 2 hours.

The cathode current collector, 99.9% silver wire (Silver State Wire), was wound onto the outside of the tubes after the anode and cathode had been fired on. The anode current collector, nickel mesh (Alfa Aesar), was then prepared and inserted into the tubes to complete the single cells. The effective dimension of the cells prepared was OD 6 mm, wall thickness 0.55 mm, and active length 50 mm.

Fuel Cell Test Setup

The electrical performance of the fuel cells was tested using a furnace test station setup described in Fig. 2. Methane and methane/oxygen (ratio 3:1) was fed inside the tubular cell at 30 ml/min, and air was used as the oxidant gas. Dry hydrogen was also used as a
comparison. V-I data were collected using a potentiostat/galvanostat in the temperature range 600°C to 900°C with an interval of 50°C. Current density and power density were then calculated using the raw V-I data and the fuel cell active area. Repeatability was tested by measuring the cell performance on a number of different cells of the same configuration.

RESULTS AND DISCUSSION

Typical cell potential vs current-density and power-density vs current-density curves of the fuel cell running on different fuels measured in this study are shown in Figs. 3 and 4, respectively. These measurements were done at 900°C. The cell performance was observed to be constant over a 6-hour period. Dry methane gave a maximum power density of 282.5 mW/cm² at a current density of 565 mA/cm², while that of hydrogen was

![Figure 3. V-I curves for a LSGM-based micro-tubular SOFC with a NiO/SDC/YSZ anode running on different fuels at 900°C.](image-url)

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observed to be 308 mW/cm² corresponding to a current density of 616 mA/cm². The methane/oxygen (with a fuel/oxygen ratio of 3.0) gave comparable performance to that of hydrogen. This can be attributed to increased hydrogen availability due to partial oxidation. This work is in agreement with the earlier work performed by Kendall et al. (22) in a zirconia based micro-tubular SOFC, who has shown that for such a fuel cell configuration, there is no surface carbon formation, which was observed in a post reaction TPO.

CONCLUSIONS

Micro-tubular LSGM electrolyte tubes were successfully fabricated, and the performance of a single cell using a doped-ceria based anode was studied, running on different fuels. Methane with a fuel/oxygen ratio of 3.0 gave comparable performance to that of hydrogen.

These initial results are encouraging and show a way of utilizing readily available hydrocarbon fuels for intermediate temperature operation of SOFCs. The next step of this study would be to focus upon La₀.₈Sr₀.₂Ga₀.₈Mg₀.₁₅O₂.₈₂₅ and La₀.₉Sr₀.₁Ga₀.₈Mg₀.₂O₃₀ compositions of the electrolyte towards direct methane oxidation and to arrive at an optimum composition of the doped-ceria SOFC anode material.

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Figure 4. P-I curves for a LSGM-based micro-tubular SOFC with NiO/SDC/YSZ anode running on different fuels at 900°C.
REFERENCES

1. K. Kendall and M. Prica, in Proc. First European Solid Oxide Fuel Cell Forum, U. Bossel, Editor, Lucerne, Switzerland (1994).
2. I. P. Kilbride, J. Power Sources, 61, 167 (1996).
3. C. Hatchwell, N. M. Sammes, and I. W. M. Brown, Solid State Ionics, 126, 201 (1999).
4. C. Hatchwell, N. M. Sammes, and K. Kendall, J. Power Sources, 70, 85 (1998).
5. H. L. Tuller, in High temperature Electrochemistry: Ceramics and Metals,
6. F. W. Poulsen, N. Bonanos, S. Linderoth, M. Mogensen, and B. Zachau-Christiansen, Editors, p. 139, Risø National Laboratory, Roskilde, Denmark (1996).
7. T. Ishihara, H. Matsuda, and Y. Takita, J. Amer. Chem. Soc., 116, 3801 (1994).
8. M. Feng and J. B. Goodenough, Eur. J. Solid State Chem., 31, 663 (1994).
9. P. Huang and A. Petrie, J. Electrochem. Soc., 143, 1644 (1996).
10. R. Marie, S. Ohara, T. Fukui, H. Yoshida, M. Nishimura, T. Inagaki, and K. Miura, J. Electrochem. Soc., 146, 2006 (1999).
11. T. Fukui, S. Ohara, K. Murata, H. Yoshida, K. Miura, and T. Inagaki, J. Power Sources, 106, 142 (2002).
12. J. Sfeir, J. Van herle, and A. McEvoy, in Proc. Third European Solid Oxide Fuel Cell Forum, P. Stevens, Editor, p. 267, Nantes, France (1998).
13. E. Putna, J. Stubenrauch, J. Vohs, and R. Gorte, Langmuir, 11, 4832 (1995).
14. T. Aida, A. Abudala, M. Ihara, H. Komiyama, and K. Yamada, in Proc. Fourth Intl. Symp. On Solid Oxide Fuel Cells, M. Dokiya, O. Yamamoto, H. Tagawa, and S. C. Singhal, Editors, p. 801, Yokohama, Japan (1995).
15. M. Mogensen, N. M. Sammes, and G. A. Tompsett, Solid State Ionics, 129, 63 (2000).
16. E. P. Murray, T. Tsai, and S.A. Barnett, Nature, 400, 649 (1999).
17. S. Park, R. Craciun, J. M. Vohs, and R. J. Gorte, J. Electrochem. Soc., 146, 3603 (1999).
18. H. Kim, C. Lu, W. L. Worrell, J. M. Vohs, and R. J. Gorte, J. Electrochem. Soc., 149, A247 (2002).
19. T. Ishihara, H. Furutani, T. Yamada, and Y. Takita, in Proc. Fourth Euroconference on Solid State Ionics, Galway, Ireland (1997).
20. J. Akikusa, K. Adachi, K. Hoshino, T. Ishihara, and Y. Takita, J. Electrochem. Soc., 148, A1275 (2001).
21. Y. Du and N. M. Sammes, submitted to Ionics (2002).
22. Y. Du and N. M. Sammes, J. European Ceramic Soc., 21, 727 (2001).
23. K. Kendall, C. Finnerty, and J. Staniforth, in Proc. Fourth European Solid Oxide Fuel Cell Forum, A. J. McEvoy, Editor, Lucerne, Switzerland (2000).