LANTHANUM GALLATE ELECTROLYTE
FOR INTERMEDIATE TEMPERATURE OPERATION

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ABSTRACT

Achieving the cost threshold required for fuel cell commercialization necessitates a significant reduction in the operating temperature of solid oxide fuel cells. A reduction in system cost and an improvement in long term performance stability are expected at the lower operating temperature. Even with demonstrated high power density operation using thin film zirconia at 800°C, additional reduction in operating temperature may necessitate the use of an alternate electrolyte material. Lanthanum gallate, with its high conductivity and material stability has shown the potential for 600 – 700°C operation. Chemical reactions at the electrode-electrolyte interface are considered to be the source of performance degradation in gallate electrolyte system. A modified anode composition has been shown to be substantially non-reactive, within the detection limits of X-ray diffraction. The single cell performance with the new electrode was verified in an electrolyte-supported cell configuration. Processing techniques are under evaluation to fabricate and characterize the gallate in an electrode-supported thin film configuration.

INTRODUCTION

It has long been recognized that lowering the operating temperature would provide a more expeditious route to commercialization of solid oxide fuel cell (SOFC) based power systems. The intermediate operating temperature (600 to 800°C) allows the use of lower cost materials in both the stack and the balance of plant, and additionally significantly slows down potential deleterious materials interaction, thus extending the useful stack life. When the operating temperature is in the range of 600 to 700°C, it is also possible to reform hydrocarbon fuels within the stack. The endothermic nature of this reaction provides a significant cooling effect, thereby reducing the parasitic losses associated with excess air requirements for stack cooling.

The operating temperature of the fuel cell system is largely governed by the electrolyte material. Electrolyte materials such as doped bismuth oxide or doped ceria exhibit superior ionic conductivity at lower temperatures. However, the chemical instability of bismuth oxide and the mixed conduction of ceria under fuel gas conditions are difficult to overcome. Sr and Mg doped LaGaO₃ (LSGM) has been shown to have an ionic conductivity at 800°C equivalent to that of YSZ at 1000°C. Unlike other materials possessing a high oxygen ion conductivity, lanthanum gallate not only possesses high
conductivity relative to zirconia, it is stable in both fuel and air. Ishihara et al., reported a power density of > 0.5 W/cm² at 800°C in relatively thick single cells (1). Huang et al., (2,3) have reported extensive materials characterization information.

The relative performance degradation of LSGM based cells has limited the wide use of this material by SOFC developers. Investigations by Huang and Goodenough (3) suggested that the likely formation of an insulating phase, LaNiO₃, at the anode – electrolyte interface may be the source of degradation. In addition to long-term stability, the reaction between the anode and electrolyte limits the cell fabrication options. For example, anode-supported thin electrolyte approach that has been successfully demonstrated in zirconia based cells cannot be readily employed with the gallate electrolyte. The gallate electrolyte based cells presently have been fabricated only as electrolyte-supported cells. A zirconia matrix supported thin gallate electrolyte has been reported (4). Again, the reactivity with zirconia to form lanthanum zirconate insulating phase at the interface is of concern and is expected to affect the performance potential of thin gallate electrolyte.

EXPERIMENTAL

The primary approach of our investigation is to understand the fabrication process boundaries of the anode–electrolyte reaction and modify the anode material to mitigate such reactions. It was determined, using powder mixtures of LSGM and NiO that not only the severity of the reaction but also the nature of the second phase depends on the reaction temperature. At 1250°C the reaction phase formed was La₃NiO₈, while the predominant phase at 1350°C was LaNiO₃. A chemical modification to the anode was evaluated in order to reduce the reaction (5). Powder mixtures of LSGM and modified NiO were calcined at 1250°C and 1350°C. The calcined powders were evaluated using powder x-ray diffraction technique to identify the phase content. The modified anode composition is also shown to perform equivalent to standard NiO based anode. The performance of an electrolyte supported LSGM cell, using the modified anode is shown in Figure 1. Using an electrolyte thickness of 350 microns, the area specific resistance (ASR) at 800°C was 0.4 ohm.cm². At 850°C, an ASR value of 0.3 ohm.cm² was obtained.

Although the modified anode shows a lower propensity for reaction with electrolyte, it is essential that the gallate material possess two critical characteristics that are necessary for sintering anode-electrolyte bi-layers. First, the material must be phase-pure in order to achieve high conductivity values. This was achieved by careful control of powder synthesis and process conditions using the Pechini process. The phase purity was verified using x-ray diffraction technique. The second requirement for successful bi-layer fabrication is to lower the sintering temperature. This was achieved by controlling the powder characteristics using standard ceramic processing techniques. Pressed pellets of LSGM are routinely sintered at 1350 – 1400°C to greater than 97% theoretical density.

BI-LAYER FABRICATION

Recent focus has been to evaluate sintering of anode-electrolyte bi-layers. In an initial trial the bi-layers were sintered at 1350-1400°C to provide a 10-micron thick LSGM electrolyte supported on the anode. Some nickel diffusion was seen in the electrolyte region. The diffused nickel appears to destabilize the LSGM phase. Upon reduction of

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the anode, regions of the electrolyte that showed high nickel content developed porosity. Micrographs of as-fired and reduced bi-layers are shown in Figure 2. Subsequently bi-layer samples were sintered using a modified anode. The micrographs of the bi-layers with improved anode are shown in Figure 3. Considerable reduction in Ni diffusion was observed and the electrolyte was chemically stable during anode reduction. Further characterization and process modification trials are underway to evaluate the bi-layers.

SUMMARY

The key technical issue with the gallate system is the chemical interaction of the gallate with the nickel in the anode resulting in low conductivity second phases. The focus of the research effort at Ceramatec was to identify and verify a nickel-based anode, with appropriate modifications, to reduce the nickel reactivity. Such an anode has been successfully demonstrated using powder reaction studies. In addition to providing long-term stability, the new anode material is expected to allow fabrication of thin gallate electrolyte using the anode-supported approach. This approach provides flexibility in the selection of stack operating temperatures based on system requirements and not electrolyte stability conditions. Initial trials provided encouraging results and electrochemical tests are planned to evaluate the cell performance.

ACKNOWLEDGMENT

This work was supported by the U.S. Department of Energy under a Small Business Innovation Research Phase II Grant Number DE-F2-03-01ER83212.

REFERENCES

1. T. Ishihara, M. Honda, T. Shibayama, H. Minami, H. Nishiguchi and Y. Takita, J. Electrochem. Soc., 145, 3177 (1998).
2. K. Huang, M. Feng and J.B. Goodenough, J. American Ceramic Soc., 79, 4, (1996).
3. K. Huang and J. Goodenough, Final Report to EPRI, Report No. TR-108742, October 1997.
4. J. W. Yan, Z. G. Lu, Y. Jiang, Y. L. Dong, C. Y. Yu, and W. Z. Li, J. Electrochem. Soc., 149(9), A1132 (2002).
5. S. Balagopal, I. Bay and S. Elangovan, in Proc. Fifth European SOFC Forum, Lucerne, Switzerland, p. 233 (2002).
Figure 1. Single Cell Performance.

Figure 2. LSGM – Anode Bi-layer.
(Excessive Ni diffusion tends to destabilize LSGM Phase – upon reduction the second phase shows Ni metal precipitation)
Figure 3. LSGM-Anode bi-layer.
(Minor amount of Ni diffusion does not destabilize LSGM phase)