MATERIAL AND PROCESS DEVELOPMENT LEADING TO ECONOMICAL HIGH-PERFORMANCE THIN-FILM SOLID OXIDE FUEL CELLS

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ABSTRACT

This document summarizes the technical progress from April to September 2003 for the program, Material and Process Development Leading to Economical High-Performance Thin-Film Solid Oxide Fuel Cells, contract number DE-AC26-00NT40711. Characteristics of doped lanthanum gallate (LSGMF) powder suitable for thin electrolyte fabrication have been defined. Bilayers with thin LSGMF electrolyte supported on an anode were fabricated and the fabrication process was improved. Preliminary performance was characterized. High performance cathode material $\text{Sr}_{0.5}\text{Sm}_{0.5}\text{CoO}_3$ has been down-selected and is being optimized by modifying materials characteristics and processing parameters. The selected cathode exhibited excellent performance with cathode polarization of $\sim 0.23 \text{ ohm-cm}^2$ at 600°C

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1 EXECUTIVE SUMMARY

This document summarizes the technical progress from April to September 2003 for the program, Material and Process Development Leading to Economical High-Performance Thin-Film Solid Oxide Fuel Cells, contract number DE-AC26-00NT40711.

The program goal is to advance materials and processes that can be used to produce economical, high-performance solid oxide fuel cells (SOFC). The overall objective is to demonstrate an SOFC cell that is capable of achieving high power densities at reduced temperatures. The materials and fabrication processes are economical, scalable, and amenable to high-volume manufacture of fuel cells.

An integrated approach has been applied to develop a high-performance, reduced-temperature SOFC. The approach is based on the development of materials and structures with superior electrolyte and electrode properties. The cell package consists of a high performance cathode and a thin-film electrolyte supported on an anode substrate.

Electrolyte materials are based on highly conductive lanthanum gallate. The ohmic losses from electrolyte have been further reduced with thin-film electrolyte configuration. Processes based on tape calendering have been developed to fabricate thin lanthanum gallate electrolyte. High performance cathode has been screened, down selected, and improved with engineered electrode structures for catalytic activity enhancement. The following lists the key technical highlights achieved during this reporting period:

- Anode-supported thin electrolyte based on lanthanum gallate has been developed using tape-calendering process. The raw materials characteristics have been found to be critical to the thin-electrolyte fabrication. With high surface areas lanthanum gallate materials, densification of electrolyte has achieved at sintering temperature of 1350°C.
- Interaction between Ni in anode and lanthanum gallate electrolyte has been observed during bilayer fabrication. The migration of Ni from anode to electrolyte has been reduced with decreasing the sintering temperature and increasing the thickness of ceria barrier layer.
- High performance cathode has been selected and engineered with materials and fabrication processes. Performance in temperature range of 600~800°C has been characterized. High performance cathode with polarization of $\sim 0.23 \text{ ohm-cm}^2$ has been achieved at 600°C.

2 INTRODUCTION

The ability to fabricate multilayer structures is an important element in the development of a fuel cell with high performance at lower temperatures. The tape-calendering process is well suited to the fabrication of multilayer composites discussed above and studies have shown tape calendering as a reliable and potentially the most economical among known processes for fabricating supported thin-film solid oxide electrolytes. As discussed in the previous reports [1, 2], fabrication of an anode-supported thin-LSGMF-electrolyte solid oxide fuel cell has been demonstrated. However, the initially fabricated thin electrolyte cell showed low OCV and the cell OCV gradually decayed with time. Less densification of electrolyte and possible Ni migration could have caused this issue based on analysis in the last report. In this reporting period, work has been focused on development of high performance cathode materials as well as improvement of dense and thin gallate electrolyte fabrication.

3 EXPERIMENTAL

3.1 CELL FABRICATION

The tape calendering process has been modified for fabricating $\text{La}_{0.8}\text{Sr}_{0.2}\text{Ga}_{0.8}\text{Mg}_{0.15}\text{Fe}_{0.05}\text{O}_3$ (LSGMF)-based cells. In this process, the electrolyte (LSGMF), interlayer (ceria) and support anode (NiO/ceria) materials are mixed with organic binders and plasticizer in a high-shear mixer, respectively. The heat generated by the mixing process softens the organics and forms a homogeneous plastic mass. Each plastic mass (electrolyte and electrode) is then rolled to produce a flexible sheet. To make self-supported electrolyte, LSGMF tape is then sized and fired. For anode-supported thin LSGMF electrolyte fabrication, the electrolyte and interlayer tape are laminated together to form a bilayer tape and subsequently rolled to reduce thickness of each layer. The anode layer was then attached to the interlayer side and rolled down to a thin tape. Another anode electrode tape is added to the resulted tape and again rolled to a thin tape. Such a process is repeated until the desired thickness of electrolyte is reached. At this point, the final tape (often denoted as bilayer tape) is cut to the desired shape and size and then fired at elevated temperatures to remove the organics and sinter the ceramics.

For self-supported LSGMF-based cells, $\text{Sr}_{0.5}\text{Sm}_{0.5}\text{CoO}_3$ and $\text{NiO/Ce}_{0.8}\text{Gd}_{0.2}\text{O}_2$ were applied on two electrolyte surfaces as cathode and anode, respectively, to form a complete fuel cell. The self-supported LSGM electrolyte can be used as substrate in evaluation of cathode materials when cathode materials were applied to both surfaces of the electrolyte. For anode-supported thin-LSGMF-electrolyte cells, cathode $\text{Sr}_{0.5}\text{Sm}_{0.5}\text{CoO}_3$ was applied on the electrolyte surface to produce a complete cell.

3.2 CELL AND MATERIALS ANALYSIS

Cell microstructure and composition were analyzed with Scanning Electron Microscopy (SEM) and Energy Dispersive X-ray Diffraction (EDX). Powder morphology was characterized with

SEM and BET surface analyzer. Powder composition and structure were characterized with X-ray diffractometry (XRD).

3.3 CELL ELECTROCHEMICAL EVALUATION

In cathode evaluation, a four-probe configuration as outlined in Figure 1 was used. The sample consisted of two electrodes (WE and CE) made of cathode materials and screen-printed on the self-supported thick gallate electrolyte. Reference electrodes (RE) were also screen-printed on the electrolyte surfaces. Cell impedance was analyzed with AC impedance analyzer, which separated electrode polarization and electrolyte contribution in the impedance spectra.

Figure 1 Schematic cell configuration for cathode evaluation

In fuel cell characterization, the cell was mounted to a ceramic tube. AC impedance and DC polarization with hydrogen as fuel and air as oxidant was used to characterize the whole cell and each cell component performance.

4 RESULT AND DISCUSSION

4.1 PROGRESS HIGHLIGHTS

During this reporting period, work has been focused on development of high cathode materials as well as fabrication of dense and thin gallate electrolyte supported on an anode. Key progresses have been made:

- Characteristics of LSGMF powder suitable for thin electrolyte fabrication have been defined. Bilayer with thin LSGMF electrolyte supported on an anode was fabricated. Preliminary performance was characterized.
- High performance cathode material $\text{Sr}_{0.5}\text{Sm}_{0.5}\text{CoO}_3$ has been down-selected. This material was selected based on screening of various cathode candidates (different compositions and sources) fabricated under various processing parameters. The selected cathode exhibited excellent performance with cathode polarization of $\sim 0.23 \text{ ohm-cm}^2$ at 600°C

4.2 GALLATE ELECTROLYTE ENGINEERING AND BILAYER FABRICATION

Figure 2 Schematic of the anode supported thin electrolyte configuration

The anode-supported thin electrolyte structure based on LSGMF is shown in Figure 2. The structure consists of a thin electrolyte (10-30 micron) made of LSGMF. Under the LSGMF electrolyte is a thin interlayer of ceria to prevent the possible reaction between electrolyte and Ni in the anode. The electrolyte and interlayer are supported by the anode consisting of a thin active anode and a thick support anode both made of Ni-ceria cermet. The difference in these two anode layers is thickness, microstructure, and porosity.

In the last reporting period, analysis on the cell microstructure revealed that the electrolyte layer made with previous LSGM powders ($d_{50} \sim 4 \mu\text{m}$, $SA \sim 0.58 \text{ m}^2/\text{g}$) contains large grain size and undesired porosity. A considerable amount of Ni was also found in the LSGM electrolyte even though a ceria interlayer was implemented between electrolyte and the Ni-ceria anode. The less densification of the electrolyte was due to low surface area of starting ceramic powders. Ni contamination in the electrolyte could be due to Ni migration occurred during sintering at 1450°C . These defects might have caused the poor performance observed in the initial thin-LSGM cell tests that showed low OCVs ($< 800 \text{ mV}$) once fuel was introduced to the anode.

To solve these issues, a couple of approaches were proposed and tried. First, characteristics of raw material properties desired for electrolyte densification were defined based on in-house activities and exploration with different vendors. LSGM powder with SA of $6.6 \text{ m}^2/\text{g}$ and d_{50} of $0.63 \mu\text{m}$ was found to be acceptable for bilayer fabrication improvement. Second, thickness of both LSGM electrolyte and ceria are being engineered to reduce the ohmic losses while to maintain gas tightness and reduce the Ni migration.

Figure 3 shows the cross section of as-sintered anode-supported LSGM structure. It can be seen that the LSGM electrolyte was dense and continuous. The supported anode shows the desirable porosity and more porosity will be generated once the NiO is reduced to Ni before fuel cell operation.

Figure 3 Micrographs of fabricated anode-supported structure with gallate electrolyte

Figure 4 compared the cross sections of bilayers made at 1400°C with fine LSGM powder to that made with coarse LSGM at 1450°C. As shown in the pictures, with fine LSGM powders dense LSGM electrolyte and ceria barrier layer were clearly defined and the quality is much better than that obtained with coarse powders. With the new powders, the electrolyte can be densified at lower temperature, 1400°C. The ceria barrier layer also appears to be dense and continuous.

Figure 4 Microstructure of anode supported thin-LSGM electrolyte structure: (a) and (b) fabricated with coarse powder at 1450°C, (c) and (d) fabricated with fine LSGM powder at 1400°C.

However, in a close examination of polished cross-sections of the fabricated bilayer, second phase is still noticeable in the electrolyte even though the ceria interlayer appeared to be dense and continuous (Figure 5). But the amount of second phase is much smaller. The second phase (dark gray) was believed to be Ni-containing phase, which was confirmed in the following analysis as indicated in Figure 6. It is interesting to notice that no Ni-containing phase was observable inside the ceria layer but more Ni-containing phase was observed at the interface between gallate electrolyte and ceria interlayer. It is believed that the Ni migration from anode might have caused this issue. Similar results were also reported in the literature [3].

Figure 5 Polished cross section of fabricated thin LSGM electrolyte at 1400°C with fine powders

1 and 2

3 and 4

5 and 6

Figure 6 Composition analysis of fabricated bilayers

4.3 CATHODE DEVELOPMENT:

The focus of this effort is to develop high performance cathode with cathode polarization less than $\sim 0.2 \text{ ohm-cm}^2$ at 600°C .

The cathode compositions were selected based on catalytic activity, conductivity, stability, and compatibility with electrolyte at both processing and operating temperatures. Based on the performance screening tests with samarium strontium cobaltite ($\text{Sm}_x\text{Sr}_{1-x}\text{CoO}_3$) and lanthanum strontium ferrite ($(\text{La-Sr-Co/Fe})\text{-O}_3$), the cathode composition has been focused on $\text{Sm}_{0.5}\text{Sr}_{0.5}\text{CoO}_3$ (SSC) to optimize the microstructure through materials characteristics modification and process engineering.

Preliminary evaluation of the SSC cathode revealed high cathode polarization which is attributable to:

- Significant densification of cathode
- Reaction between cathode and electrolyte with intermigration of Co.

As indicated in Figure 7, the SSC cathode processed at 1200°C was significantly densified and the interfacial properties between cathode and electrolyte need to be improved. Migration of Co through the interface into the electrolyte and formation of secondary phases are also evident from the results shown in Figures 8 and 9.

Figure 7 SEM micrograph of SSC cathode layer sintered at 1200°C for 1 hr

Figure 8 SEM micrograph of the SSC-LSGM showing the reaction at the interface

Figure 9 EDX analysis of the interesting spots in the SSC-LSGM cross section shown in Figure 8.

To improve the cathode performance, SSC cathode powder characteristics and processing parameters such as temperature, thickness, and ink solid loadings were being optimized. Shown in Figure 10 are cathode polarizations at various temperatures as a function of different processing temperatures. As evident in the figure, the polarization was minimized at processing temperature of 1100°C for SSC-2 cathode; however, the cathode polarization decreases with processing temperature for SSC-1 cathode.

The SSC-1 powder was down-selected and three sets of sintering temperatures were further tried at 900, 1000 and 1100°C. The plot of ASR vs. sintering temperature is shown in Fig 11. Cathodic polarizations were reduced to around 0.23 ohm-cm² at 600°C with processing temperature of 900 and 1000°C. There is no noticeable change in ASR up to sintering temperature of 1050°C. Shown in Figure 12 are the microstructures of cathodes processed at different temperatures. As indicated in Figure 11 and 12, it is concluded that temperature range of 900-1050°C is desired for the SSC-1 cathode processing.

Figure 10 Cathodic polarizations as a function of processing temperatures

Figure 11 Polarization at 600°C with SSC-1cathode processed at different temperatures

Figure12 SEM micrographs of SSC-1 cathodes processed at 900, 1000, and 1050°C

4.4 FUTURE PLAN

Future work will further improve the thin-LSGMF electrolyte fabrication. The improved bilayer and high performance cathode will be combined together to evaluate the performance characteristics and demonstrate high cell performance.

5 CONCLUSION

Characteristics of LSGMF powder suitable for thin electrolyte fabrication have been defined. Bilayer with thin and dense LSGMF electrolyte supported on an anode was fabricated and improved. Preliminary cell performance was characterized. High performance cathode material $\text{Sr}_{0.5}\text{Sm}_{0.5}\text{CoO}_3$ has been down-selected and is being optimized with modification of materials characteristics and processing parameters engineering. The selected material exhibited excellent performance with cathode polarization of $\sim 0.23 \text{ ohm-cm}^2$ at 600°C

6 REFERENCES

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