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Advances in Solid Oxide Fuel Cells VII
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The 8th International Symposium on Solid Oxide Fuel Cells (SOFC): Materials, Science, and Technology was held during the 35th International Conference and Exposition on Advanced Ceramics and Composites in Daytona Beach, FL, January 23 to 28, 2011. This symposium provided an international forum for scientists, engineers, and technologists to discuss and exchange state-of-the-art ideas, information, and technology on various aspects of solid oxide fuel cells. A total of 85 papers were presented in the form of oral and poster presentations, including twelve invited lectures, indicating strong interest in the scientifically and technologically important field of solid oxide fuel cells. Authors from fifteen countries (China, Denmark, Germany, Greece, India, Iran, Italy, Japan, Russia, South Korea, Spain, Sweden, Switzerland, United Kingdom and U.S.A.) participated. The speakers represented universities, industries, and government research laboratories.

These proceedings contain contributions on various aspects of solid oxide fuel cells that were discussed at the symposium. Eighteen papers describing the current status of solid oxide fuel cells technology are included in this volume.

The editors wish to extend their gratitude and appreciation to all the authors for their contributions and cooperation, to all the participants and session chairs for their time and efforts, and to all the reviewers for their useful comments and suggestions. We hope that this volume will serve as a valuable reference for the engineers, scientists, researchers and others interested in the materials, science and technology of solid oxide fuel cells.

Narottam P. Bansal, NASA Glenn Research Center
Prabhadakar Singh, University of Connecticut
Introduction

This CESP issue represents papers that were submitted and approved for the proceedings of the 35th International Conference on Advanced Ceramics and Composites (ICACC), held January 23–28, 2011 in Daytona Beach, Florida. ICACC is the most prominent international meeting in the area of advanced structural, functional, and nanoscopic ceramics, composites, and other emerging ceramic materials and technologies. This prestigious conference has been organized by The American Ceramic Society's (ACerS) Engineering Ceramics Division (ECD) since 1977.

The conference was organized into the following symposia and focused sessions:

Symposium 1  Mechanical Behavior and Performance of Ceramics and Composites
Symposium 2  Advanced Ceramic Coatings for Structural, Environmental, and Functional Applications
Symposium 3  8th International Symposium on Solid Oxide Fuel Cells (SOFC): Materials, Science, and Technology
Symposium 4  Armor Ceramics
Symposium 5  Next Generation Bioceramics
Symposium 6  International Symposium on Ceramics for Electric Energy Generation, Storage, and Distribution
Symposium 7  5th International Symposium on Nanostructured Materials and Nanocomposites: Development and Applications
Symposium 8  5th International Symposium on Advanced Processing & Manufacturing Technologies (APMT) for Structural & Multifunctional Materials and Systems
Symposium 9  Porous Ceramics: Novel Developments and Applications
Symposium 10  Thermal Management Materials and Technologies
Symposium 11  Advanced Sensor Technology, Developments and Applications
Symposium 12  Materials for Extreme Environments: Ultra-high Temperature Ceramics (UHTCs) and Nanolaminated Ternary Carbides and Nitrides (MAX Phases)
Symposium 13  Advanced Ceramics and Composites for Nuclear and Fusion Applications
Symposium 14  Advanced Materials and Technologies for Rechargeable Batteries
Focused Session 1  Geopolymers and other Inorganic Polymers
Focused Session 2  Global Mineral Resources for Strategic and Emerging Technologies
Focused Session 3  Computational Design, Modeling, Simulation and Characterization of Ceramics and Composites
Special Session  Pacific Rim Engineering Ceramics Summit

The conference proceedings are published into 9 issues of the 2011 Ceramic Engineering & Science Proceedings (CESP); Volume 32, Issues 2-10, 2011 as outlined below:

- Mechanical Properties and Performance of Engineering Ceramics and Composites VI, CESP Volume 32, Issue 2 (includes papers from Symposium 1)
- Mechanical Properties and Performance of Engineering Ceramics and Composites VI, CESP Volume 32, Issue 2 (includes papers from Symposium 1)
- Advanced Ceramic Coatings and Materials for Extreme Environments, Volume 32, Issue 3 (includes papers from Symposia 2 and 12)
- Advances in Solid Oxide Fuel Cells VI, CESP Volume 32, Issue 4 (includes papers from Symposium 3)
- Advances in Ceramic Armor VII, CESP Volume 32, Issue 5 (includes papers from Symposium 4)
- Advances in Bioceramics and Porous Ceramics IV, CESP Volume 32, Issue 6 (includes papers from Symposia 5 and 9)
- Nanostructured Materials and Nanotechnology V, CESP Volume 32, Issue 7 (includes papers from Symposium 7)
- Advanced Processing and Manufacturing Technologies for Structural and Multifunctional Materials V, CESP Volume 32, Issue 8 (includes papers from Symposium 8)
- Ceramic Materials for Energy Applications, CESP Volume 32, Issue 9 (includes papers from Symposia 6, 13, and 14)
- Developments in Strategic Materials and Computational Design II, CESP Volume 32, Issue 10 (includes papers from Symposium 10 and 11 and from Focused Sessions 1, and 2)
The organization of the Daytona Beach meeting and the publication of these proceedings were possible thanks to the professional staff of ACerS and the tireless dedication of many ECD members. We would especially like to express our sincere thanks to the symposia organizers, session chairs, presenters and conference attendees, for their efforts and enthusiastic participation in the vibrant and cutting-edge conference.


Sujanto Widjaja and Dileep Singh
Volume Editors

June 2011
Cell/Stack Development
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ABSTRACT

We have developed a pinhole free anode support cell (120mm in diameter) with a scandia alumina doped zirconia (SASZ) electrolyte, a LaNi$_{0.4}$Fe$_{0.6}$O$_3$ (LNF) cathode and a Ni-SASZ anode. The LNF cathode and SASZ electrolyte were developed by NTT. SASZ is a phase transition free electrolyte whose conductivity is three times that of 8YSZ. LNF has several merits including high electrical conductivity, high thermal expansion compatibility with zirconia electrolyte and very high resistance to chromia poisoning. To improve the cathode performance, a composite active layer consisting of LNF and Ce$_{0.9}$Gd$_{0.1}$O$_2$ is placed between the electrolyte and the LNF current collection layer. This prevents the LNF from reacting with zirconia (La$_2$Zr$_2$O$_7$ forming reaction). The cell was tested at 800°C for 6000h and exhibited good voltage retention (-0.4%/1000h) at 0.4A/cm$^2$. We also fabricated a stack consisting of 40 cells and ferritic stainless steel interconnectors containing chromium. The stack operated stably for about 400h at 800°C with humidified CH$_4$ (S/C=3.0) fuel (U$_{fuel}$=60%) and air (U$_{air}$=30%). The maximum efficiency of the stack was 64% (DC, LHV) at U$_{fuel}$=85%.

INTRODUCTION

Nippon Telegraph and Telephone Corporation (NTT) is a telecommunications company that is a heavy user of electric power accounting for 1% of Japan's commercial electric power consumption. As shown in Fig. 1, the power consumption has been increasing with the increase in telecommunications traffic in Japan [1]. Most of the power is consumed by central offices and data centers, which are located in the centers of cities. The central offices of NTT have been using electric power for the - 48V DC power supply needed for metallic telephone subscriber lines. AC grid power is converted to DC power and supplied to servers in the data centers. Therefore, the solid oxide fuel cell (SOFC) system is a promising alternative way of meeting such electric power demands [2,3]. This is because SOFCs are clean, quiet and efficient DC power generating systems that emit less CO$_2$ than conventional thermal power generation systems [2,3]. A large amount of the electric power consumed by NTT is used for air conditioning the facilities. If an SOFC system with cogeneration is introduced, this energy demand can also be met. One of our development targets is a medium scale...
Recent Development of SOFC Cell and Stack at NTT

We have been investigating anode support planar cells, ferritic stainless steel interconnectors and stacks composed of them. One of the advantages of anode support cells is that it is possible to reduce the thickness of the electrolyte with a wet process such as screen printing [2,4-6]. A thin electrolyte enables the cells to operate at a high current density that leads to high power density generation [2,4-6]. Planar type cells have a simple structure and are suitable for cost reduction [2,6].

The cost of producing metallic interconnectors is potentially low, because of their very low material costs for high-volume production [2,7,8]. Therefore, SOFC systems using anode support planar cells with stainless steel interconnectors can achieve high performance power generation at a reduced cost.

This paper reports NTT’s development of SASZ electrolyte material, LNF cathode materials, planar cells using those materials, and stacks employing the cells and stainless steel manifolds.

**SASZ FOR ELECTROLYTE MATERIAL**

Rare-earth doped zirconia electrolytes are suitable for anode support cells, because their ionic transport number is very close to 1.0 [2,9]. This characteristic is essential for cells with a thin electrolyte, because the amount of electronic leak current density across the electrolyte is proportional to its thickness. Sc2O3 doped zirconia (SSZ) has the highest ionic conductivity among the doped zirconias [9], but it has a phase transition around 650°C. As shown in Fig. 2, the ionic conductivity changes by approximately two orders at this temperature. Moreover, the thermal expansion coefficient (TEC) changes abruptly at this transition, as shown in Fig. 3(a). We use Al2O3 dopant to suppress this phase transition. In Fig. 4, the phase transition temperature is plotted against the doping amount.

Figure 2. Temperature dependence of ionic conductivity for zirconias, (a) SASZ (doped with 10.5mol% Sc2O3 and 0.5mol% Al2O3), (b) SSZ (doped with 12mol% Sc2O3) and (c) 8YSZ (doped with 8mol% Y2O3).

Figure 3. Thermal expansion and thermal expansion coefficient for (a)SSZ(0.88ZrO2 - 0.12Sc2O3), (b)SASZ(0.88ZrO2-0.115Sc2O3-0.005Al2O3).

Figure 4.
Only a very small amount of Al₂O₃ is required to reduce the phase transition at room temperature (According to the XRD, the sample with X=0.005 was in the cubic phase). Because of this, the ionic conductivity of scandia alumina doped zirconia (SASZ) is almost the same as that of SSZ. The ionic conductivity of SASZ (0.89 ZrO₂-0.105 Sc₂O₃-0.005 Al₂O₃) at 800°C is 0.1S/cm, which is approximately three times that of conventional zirconia electrolyte (8mol% yttria doped zirconia). As shown in Fig. 3(b), the abrupt TEC change disappeared. These thermal expansion characteristics are very important for practical electrolytes, because the electrolyte layer must withstand thermal cycles caused by the starting and stopping of the operation.

LaNi(Fe)O₃ FOR CATHODE MATERIAL

We have been investigating LaNi(Fe)O₃ as a cathode material [10]. This perovskite type oxide has several advantages including high electronic conductivity, good TEC matching with zirconia, good cathodic performance and high durability against chromium poisoning [10-14].

LaNi(Fe)O₃ PROPERTIES

LaNiO₃ is known to exhibit high electronic conductivity [10]. But it is not stable at the high temperature needed for SOFC operation, and decomposes into NiO and La₂NiO₄[10]. LaNiO₃ forms a solid solution with LaFeO₃, which is a very stable oxide. This solid solution is stable at or above 800°C when X in LaNi₁₋ₓFeₓO₃ exceeds 0.3 [10]. In Fig. 5(b), the electrical conductivity at 800°C and the crystal structure at room temperature are plotted against the LaNi₁₋ₓFeₓO₃ composition. The electronic conductivity was measured in air by the DC four terminal method for well-sintered rod shaped samples. The crystal structures of the synthesized powder samples were analyzed with an X-ray diffractometer at room temperature. The samples were in the rhombohedral phase and the conductivity exhibited the highest value of 580S/cm at 800°C and X=0.4. This value is much higher than that of conventional cathode material (around 200S/cm for La₀.₈Sr₀.₂MnO₃) [2,10]. The thermal expansion coefficient (TEC) for LaNi₁₋ₓFeₓO₃ is plotted against X in Fig. 5(a). The figure shows the mean values between room temperature and 800°C or 1000°C, respectively. TEC decreased monotonically as X increased. We selected a composition where X=0.4, at which the thermal expansion is closer to the value of zirconia than La₀.₈Sr₀.₂MnO₃. This is also the composition for the

La(Sr)MnO₃ For Cathode Material (a) Thermal Expansion Coefficient and (b) Conductivity at 800°C and Crystal Structure of LaNi(Fe)O₃. In Fig. 5(b), R, T and O indicate rhombohedral, tetragonal, orthorhombic phases, respectively.
Recent Development of SOFC Cell and Stack at NTT

The highest electronic conductivity of LaNi$_{1-x}$Fe$_x$O$_3$. The cathodic overvoltage of LaNi$_{1-x}$Fe$_x$O$_3$ depends on the composition. We investigated the overvoltage of LaNi$_{1-x}$Fe$_x$O$_3$ cathodes at 800°C by the three terminal current interruption method, using an SASZ electrolyte supported single cell. The overvoltage exhibited its minimum value at $X=0.4$. This may be because higher electronic conduction is preferable for a cathodic electrochemical reaction [11]. Therefore, this composition is the best with respect to both cathodic overvoltage and electronic conductivity. This composition is also preferable in terms of the thermal expansion coefficient.

CHROMIUM POISONING DURABILITY OF LNF CATHODE

The use of a stainless steel interconnector containing Cr is an effective way to reduce cell stack production costs [15,16]. However, the conventional cathode material, La(Sr)Mn$_3$ (LSM), is easily poisoned by the deposition of chromium species at its triple phase boundary [17]. If the metallic interconnector surface is coated with an oxide layer, CrO$_3$ vaporization can be mitigated [18,19]. However, this leads to increased production costs. Therefore, the cathode material itself should be resistant to chromium poisoning. We tested the durability of LNF cathode material with respect to chromium poisoning. In Fig. 6, we plot the change in the cathode overvoltage with operating time. The measurements were performed with the three terminal current interruption method using an electrolyte supported single cell at 800°C. The IR factor was subtracted with this method. The LNF and LSM cathodes were screen-printed directly on the SASZ electrolyte sheet. An Inconel 600 mesh was placed near the cathodes, which were operated in air at 800°C. A conventional LSM cathode degraded rapidly with operating temperature even at low cathode overvoltage in the initial stage, but we observed no degradation of the LNF cathode at 0.2V cathode overvoltage. For comparison, results for experiments on LSM and LNF cathodes performed under almost the same conditions are also shown in Fig. 6 (a) and (b). But these cathodes were operated without the Inconel 600 mesh. The results demonstrated that an LNF cathode is much more durable than an LSM cathode as regards chromium poisoning.

![Figure 6. (a) Cathodic overvoltage IR corrected for cells using LSM cathode with/without Inconel 600 as a function of time. Triangle: LSM / YSZ / NiO-YSZ cell at 0.076A/cm$^2$, Diamond: LSM / SASZ / NiO-YSZ cell at 0.064A/cm$^2$, Circle: LSM/YSZ/NiO-YSZ cell without Inconel 600 at 0.6 A/cm$^2$.](image)

![Figure 6. (b) Cathodic overvoltage IR corrected for cells using LNF cathode as a function of time. Triangle: LNF / SASZ / NiO-YSZ cell with Inconel 600 at 0.7A/cm$^2$, Diamond: LNF/SASZ/NiO-YSZ cell without Inconel600 at 0.7A/cm$^2$, Circle: LNF / YSZ / NiO-YSZ cell with Inconel600 at 0.5A/cm$^2$.](image)
Recent Development of SOFC Cell and Stack at NTT

Those cathodes were observed with EPMA after the operation. Fig. 7(a) and (b) show the Cr atom distribution at a cross section of the cathodes. The brightness corresponds to the Cr concentration. As shown in Fig. 7(b), the Cr atoms were deposited particularly at the triple phase boundary of the LSM. The chromium species are attracted to the TPB of LSM and react with LSM to form manganese-spinel phases [12-14]. But no particular chromium deposition was observed at the TPB of LNF, as shown in Fig. 7(a). Only a small amount of chromium was distributed all over the LNF layer. This showed that LNF is very stable under the cathode operating conditions including in a chromia vapor atmosphere.

**Cr distribution**

![Cr distribution](image)

Figure 7. Chromium distribution determined by EPMA near interface of LNF cathode or LSM cathode and SASZ electrode of cells after power generation tests with Inconel 600 at 800°C for 150 h.

**ACTIVE LAYER IN LNF CATHODE**

If we are to apply LNF to cells of a practical size, the adhesion of the cathode layer should be sufficiently strong. The adhesion strength tends improve as the sintering temperature increases. This is because high temperature sintering promotes an interdiffusion between the cathode and the electrolyte interface. But the diffusion of La atoms from LNF into the zirconia electrolyte causes La2Zr2O7 to form at the interface [20]. This results in a large interface resistance on the cathode side. Fortunately, the interface resistance at the LNF cathode improves greatly after operation or current application at the cathode [20,21]. This interface resistance change is shown in Fig. 8. The AC impedance measurements were all conducted at OCV. The measurements for (b) and (c) were done one hour after switching off the current. The diameter of the semicircle of the impedance plots represents the interface resistance. The interface resistance was very high before the current loading, but it fell to one thirty of its initial value. Fig. 9 plots the temporal change in the LNF cathode potential. After applying the current loading, the cathode potential decreased with the...