RECENT DEVELOPMENT OF SOLID OXIDE FUEL CELLS IN JAPAN

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ABSTRACT

The R&D activities on solid oxide fuel cells in Japan are summarized with emphases on the national projects, industrial efforts and university activities. The important feature of fabrication technology in Japan is the success in utilizing wet processes by three major groups of developers. TOTO, Kyushu Electric Co. and Nippon Steel have succeeded in testing 1 kW module of tubular SOFCs. Mitsubishi Heavy Industries and Chubu Electric Co. have completed a test of 5 kW module of planar SOFCs with a high power density and high efficiency. Mitsubishi Heavy Industries and Electric Power Development Co. have tested 1 kW module of tubular SOFCs made with a new interconnect material by a wet process, in addition to testing a pressurized 10 kW module made by plasma spray. These successes make it technologically and economically feasible to fabricate SOFCs by wet processes on a mass production scale. Activities on development of alternative materials/processing/design have been also active. Electrotechnical Laboratory has proposed the tubular SOFC on metallic substrates. National Institute of Materials and Chemical Research has proposed small non-reforming SOFCs for methane with high efficiency and the utilization of electrophoretic deposition technique for small tubular cells. Toho Gas has proposed a honeycomb type design. Emphases should be placed also on the development of LaGaO3-based electrolyte, one-chamber fuel cells, and membrane reactors for producing CO+H2 gas from methane.

INTRODUCTION

The research and development of solid oxide fuel cells actually started in late 1980s in Japan. By that time, Westinghouse had already proposed the basic materials, materials processing based on the electrochemical vapor deposition (EVD) technique, and the non-sealing-type tubular design. The R&D efforts in Japan have been therefore focused on other aspects than those which Westinghouse tubular stacks had already succeeded. These can be summarized as:

1. Increase the power density by adopting planar design.

2. Fabricate SOFC stacks by wet processes or by another cost-effective way.
First, research on SOFC was initiated at national laboratories. National Chemical Laboratory for Industry (which has now been reorganized into National Institute of Materials and Chemical Research, NIMC) made efforts mainly in confirming the technological feasibility of applying wet processes to planar cells. Electrotechnical Laboratory (ETL) had also made efforts in investigating tubular SOFCs since 1974. On the basis of these activities by national laboratories, Japanese national project on solid oxide fuel cells started to develop the technology for fabricating SOFCs in 1989. This is the Moon Light / New Sun Shine project (1-3). Since then, many private companies, national laboratories and universities have gotten involved in R&D on SOFCs. In addition to national projects, electric and gas utilities have contributed to support stack development and also to promote the research on materials, processing and cell design. Recent advances in stack development are:

1. Wet processes have been successfully applied to both tubular and planar stacks.
2. Development of planar stacks has progressed in fabrication technology and improvement of design.

In this paper, these activities are briefly reviewed together with the recent progress on alternative materials, processing, and cell design.

MOON LIGHT/NEW SUNSHINE PROJECT

National Laboratories Activities

In the initial stage of SOFC R&D in Japan, national laboratories made the major contributions to the fundamental investigations on the SOFC technology.

National Institute of Materials and Chemical Research (NIMC) has focused on the application of wet process, particularly to planar cells, and has confirmed the technological feasibility of wet processes on the laboratory scale as follows:

1. Although chemical reactions during sintering are the main issue when wet-sintering processes are applied to the SOFC fabrication, it has been found that the chemical reactivity between the lanthanum manganese and YSZ can be avoided by adopting the A-site deficient lanthanum manganese;

2. Although poor sinterability of lanthanum chromite-based interconnect was a shortcoming of wet-sintering processes, it has been found that lanthanum calcium chromite can be sintered in air when a composition of chromium deficit is adopted;

3. Ni/YSZ cermet suitable for wet process can be prepared by adopting high temperature pre-annealing of NiO and YSZ powders and high temperature treatment for preparing the interface with YSZ.

These advances provided the physicochemical basis of applying wet processes without lowering cell characteristics (4).

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11
Electrotechnical Laboratory (ETL), on the other hand, has focused on the application of a dry process such as plasma spray technique to tubular cells. This posed a challenge in adopting metallic components in their tubular cell.

First Term (1989-1991)

On the basis of above investigations by the national laboratories, the SOFC project in the MOON LIGHT / NEW SUNSHINE PROJECT stepped up to a larger scale. That is, NEDO (New Energy and Industrial Technology Development Organization) started in 1989 the first term of the development of solid oxide fuel cells as one part of the Moon Light projects.

In the first stage, module development had focused on the planar SOFCs with metal interconnect (SANYO) or with oxide interconnect (FUJI Electric Corp.). In addition, several different technologies have been investigated in the NEDO project. For example, co-firing technology was investigated by Murata Mfg. Co., and planar cells with interconnects made with magnesium spinel and lanthanum chromite was made by Mitsui Engineering & Shipbuilding Co.

Outside the NEDO project also, there have been many activities on R&D. Electric companies supported the development of the planar and the tubular stacks of Mitsubishi Heavy Industries. Gas utilities companies made extensive efforts by themselves in developing the stack technology; for example, Osaka Gas built a 1 kW tubular module by adopting the electrochemical vapor deposition of YSZ, deposition of lanthanum strontium chromite by laser ablation, and the Ru based anode by EVD and showed an excellent performance. On the other hand, Tokyo Gas has focused mainly on planar SOFCs. Petroleum companies were also interested in developing the planar stacks (TONEN) or in investigating those anodes which can be tolerant to hydrocarbons.

Two important features can be seen in the development of the SOFC technology in Japan. These are:

1. Interest in metal interconnect was much stronger than first thought, although this tendency is common to U.S., Europe and Australia. In the early stages, we thought that metal interconnect should be investigated because the technology associated with metal interconnect has not been established yet; many characteristic features of alloys as interconnect were still unknown. In other words, it was, we thought, too early to use alloys as interconnect without basic research.

2. Some, but only a small number, of groups have strong interest in fabricating tubular SOFCs by wet processes. These are TOTO supported by Kyushu Electric Power Co., Totsu supported by Saibu Gas Co. and Yuasa Batteries. Note that this interest was evident only in Japan. This can be ascribed to the appropriate knowledge on the applicability of ceramic technology to fabrication of complicated devices and also on the costs on mass production level.
Second Term (1992-1997)

In 1992, NEDO started the second 6-year-term SOFC project in the Moon Light project which was reorganized as the New Sunshine Project (NSS) in 1993. The target of the initial four years was to test several kW modules and that of the final two years was to test several 10 kW modules. In 1995, the intermediate term evaluation was made and the start of the development of several 10 kW modules was postponed. This is because the planar stack development encountered severe problems of gas sealing and durability for thermal cycles. In 1997, another intermediate term evaluation was made on the SOFC project.

Table 1. Targets of NSS Project for Module Development

| 1. Stack Target (1997) | 2-3 kW model cell stack | 2-3 kW model cell stack |
|-----------------------|------------------------|------------------------|
|                       | Natural gas reformate as fuel | Natural gas reformate as fuel |
|                       | 0.18 W/cm² at 1 atm | 0.18 W/cm² at 1 atm |
|                       | U_f 70% | U_f 70% |

| 2. Stack Target (2001) | 1) 2-3 kW model cell stack | 2) Degradation rate (Voltage lowering) |
|------------------------|------------------------|---------------------------------|
|                       | Natural gas reformate as fuel | 1%/1000 h |
|                       | 0.18 W/cm² at 1 atm | (including the effect due to thermal cycles) |
|                       | U_f 70% | |

At that time, two companies (both SANYO and FUJI) had been developing planar module with metal interconnect. In Japanese projects, it was common to set the milestone’s target for the short term. These are shown in Table 1. In the NEDO project, the module development of SOFCs had been focused on planar stacks. However, no specification was given for the use of interconnect materials. Thus, FUJI Electric Corp. had changed the interconnect material from an oxide to a metal. When the appropriateness of the metal interconnect is considered, we have to recognize that the fabrication of interconnect is the most crucial point in the development of SOFC stacks. The major strategy of developing SOFC stacks depends largely on what materials are chosen as interconnect. Therefore, change in interconnect materials represents an important change in strategy. One of the reasons to select metal interconnect seems to be that establishment of the fabrication technology associated with oxide interconnect largely depends on the R&D abilities. There are many material problems to be surmounted; air sinterability, thermal expansion matching with YSZ, small volume change on reduction, etc. To develop appropriate oxide interconnect materials requires long-term extensive and intensive investigations. In view of this nature of the interconnect technology, it was not a good way to set the target without specification of the important technological aspects.
When the 1997 intermediate term evaluation was made, the module development had been made on two planar stacks with metal interconnects. Although the gas sealing technology had been improved, the metal interconnect for planar stacks was not able to show the reliability for thermal cycle and long term stability. On the other hand, the research and development of the oxide interconnect has been made by Murata Mfg. Co. in the NEDO project with great success. Outside the NEDO project, the oxide interconnect has been successfully utilized by Mitsubishi Heavy Industries and Tokyo Gas. In view of these achievements on the oxide interconnect, the NEDO evaluation committee suggested to confirm the technological feasibility of planar SOFCs and also to include tubular SOFCs, for which the wet process has been applied by TOTO.

Second Term Extension (1998-2000)

After the 1997 evaluation, the SOFC project was extended for another three years up to 2001. The new target, as shown in Table 1, is about the same as before in the module size, fuel to be used, power density and fuel utilization. However, there are significant differences in some aspects:

1. New target for degradation is added.
2. Tubular SOFC is also included for the module to be developed.
3. It is expected that the new target should be achieved by those technologies that will be utilized in commercialization of SOFCs.

The NEDO project from 1998-2000 will be conducted as follows:

1. Module development
   - Tubular cell by wet process
     TOTO, Kyushu EPC, Nippon Steel Corp.

2. Development of Materials and Fundamental Technology
   i. Reliability Test on Cell Module (Thermal Cycle Characteristics)
     Chubu Electric Power Company; Planar cells by MHI Kobe
   ii. Reliability Test on Cell Module (Cell performance, Stress analysis)
     Tokyo Gas; Interconnect Materials by Murata
   iii. Cost Reduction of Cell Materials (Chemical properties)
     Central Research Institute of Electric Power Industry (CRIEPI)
     (Ln,A)MnO₃, (Ln,A)CrO₃
   iv. Cost Reduction of Cell Materials (Mechanical and Thermophysical Property)
     Japan Fine Ceramic Center (JFCC)
     (Ln,A)MnO₃

3. System Analysis: Application field of small stacks & Optimization
   Nippon Steel Corp.

The main contractor for module development is a team of TOTO, Kyushu Electric Power Company and Nippon Steel Corp. The module development is based on the technology of fabricating tubular SOFC stacks by wet processes; the wet processes have been widely recognized in Japan as the most promising for fabricating SOFCs on mass
production level. Recently, it has also been recognized that the cost reduction by adopting
the wet process is possible not only in the commercialization stage but also in the
development and demonstration stage.

In addition to the module development, reliability tests will be made on planar cells by
Chubu Electric Power Co. and by Tokyo Gas Co., respectively. Chubu Electric Power Co.
is making reliability tests (starting up test, load-following test, thermal-cycle test) using
MOLB cells manufactured by Mitsubishi Heavy Industries (MHI) with good results so far.
Tokyo Gas is investigating reliability of planar SOFCs by combining experimental test and
simulation technique on the mechanical stability due to thermal stresses in the planar cells.
They have also started extensive compilation of the electrical properties, oxygen
permeability, diffusion coefficients, and physicochemical properties by making their own
experiments on LaCrO₃-based interconnects manufactured by themselves, by Murata and
by MHI as well as collecting from the literature.

Materials optimization should be made by including consideration of the cost
reduction due to change in cell materials. For the tubular stack, the air electrode made of
the lanthanum strontium manganite is the major contribution to the materials cost, whereas
the lanthanum chromite-based interconnect is the major cost for the planar stacks. CRIEPI
and JFCC will jointly investigate the physicochemical, mechanical, and thermophysical
properties of rare-earth doped perovskite materials.

A system analysis will be made by Nippon Steel Corp. This is to focus on plausible
markets for the smaller SOFC applications as earliest market entry in Japan. The power
generation plants are thought to be the largest market for SOFCs in the future. It is,
however, expected to take a longer time for SOFCs to be introduced in such applications
in view of the well-developed power grid system in Japan; this is based mainly on nuclear
power plants and natural gas fueled combined cycles. A survey will be made to clarify the
potential of small SOFCs ranging several 10 to several 100 kW as low-emissive, high-
efficient and low-cost power plants for supplying electricity and heat.

The evaluation on the SOFC project will be made in 1999 and the future program from
2001 onward will be planned after this evaluation.

RECENT TOPICS OF SOFC STACK DEVELOPMENT

The major developments in SOFC stacks in Japan can be summarized as follows:

1. TOTO/Kyushu Electric Power Co. has fabricated tubular 1 kW stacks by wet process.

2. Mitsubishi Heavy Industries (MHI) Nagasaki/Electric Power Development Co. has
developed tubular stacks by spray coating technique and has tested a pressurized
10 kW class module.

3. MHI Nagasaki has also succeeded in fabricating 1 kW tubular stacks by co-sintering
method.
4. MHI Kobe/Chubu Electric Power Co. has developed planar MOLB stacks by wet process in the 5 kW size and plans to scale up to 25 kW module.

5. Osaka Gas/Murata Mfg. Co. has developed the cell-connection type planar SOFC in the 1 kW size. This design has been adopted to make easy mass production of planar cells.

6. Tokyo Gas has developed 1 kW planar stacks and tested with natural gas.

7. Toho Gas has fabricated honeycomb-type small cells by wet process.

Cost Reduction in Tubular Stacks

The cost reduction can be achieved by several means:

1. Change in materials: lanthanum oxide in air electrode is the biggest contribution to the cost of raw materials.

2. Change in processing: wet process combined with sintering process is the main target.

3. Improvement in cell performance: when the power density is improved, the fabrication cost per unit power decreases.

4. Change in cell design.

5. Improvement in system design.

In Japan, the main progress has been made in adopting the wet process in the fabrication of SOFC stacks as follows.

1. TOTO

They have developed technologies to fire SOFC materials in gas furnaces. They use successfully the calcium doped lanthanum chromite in tubular cells, although the same materials cannot be used in planar cells because of large volume expansion on reduction. This is a good example that the materials development depends strongly on processing and cell design. They plan to use their own tunnel furnace in commercialization. The cost reduction in mass production can be expected even at a small scale such as 1 MW/year. This will make the early market entry of the smaller size SOFC systems feasible.

2. MHI Nagasaki

Adoption of wet process in MHI stack has been achieved by development of TiO2-based interconnect. Detailed information on this new material has not been published yet except for patent documents. It seems that the TiO2-based interconnect shows good sinterability but slightly low electrical conductivity. It should be emphasized that without having the interconnect material which can be easily sintered in air, wet process cannot be
utilized. This is also a good example to understand that the materials development is highly correlated with development of the materials processing and the cell design.

Within the NEDO project, the cost reduction has been investigated by use of the lanthanum concentrate. It will therefore be expected that changes in cell performance, cell design and system design might occur.

**Planar SOFC**

In the early stage of the national project, it was expected that the planar SOFCs can be compatible with the Siemens Westinghouse type tubular cells in the sense that the cost effective fabrication process can be applied and also that the higher power density can be obtained. At present, the adoption of the wet process has been achieved even for the tubular stacks so that the power density becomes one of the important features to examine the technological appropriateness of the planar stacks against the tubular stacks. In this sense, recent achievement of the higher power density (0.34 W/cm²) at the current density of 0.49 A/cm² and fuel (hydrogen) utilization of 77% in MOLB stacks can be regarded as highly significant. In addition, the oxide interconnect in MOLB has no rib and this makes it easy to fabricate and makes it possible to avoid the stress concentration in the interconnect.

Murata Mfg. Co. made extensive analysis of the degradation in terms of the individual contributions from the resistivity increase in the electrolyte plate, the overpotential increase in the cathode or in the anode. This provides the experimental evidence for the wet process that the stacks fabricated by wet process have also the greater long-term stability. In addition, the cell-connection type planar cells developed by Osaka Gas and Murata are interesting in the sense that quality control is planned to be made on respective assemblies of cathode/electrolyte/anode layers and interconnect. For this purpose, they made the electrolyte layer and the interconnect into firmly bonded planar cells. To make these assemblies strong enough against thermal cycles, they have to have the match in thermal expansion behaviors of the electrolyte and the interconnect.

**ALTERNATIVE MATERIALS / PROCESSING / DESIGN**

**Metallic Cells**

Tubular SOFCs on metallic substrates have been fabricated and tested by Electro-technical Laboratory (ETL). Although the use of metal interconnect in planar stacks has encountered severe problems, ETL has shown that the situation in tubular cells is not as severe as in planar cells. In particular, in their tubular design, the electrical path does not necessarily pass through the surface oxide scale on the metal interconnect. This difference gives some hope for the metal interconnect to be used.

**New Electrolyte and its Utilization in SOFCs**

The fundamental properties of lanthanum strontium gallium magnesium oxides (LSGM) have been investigated. The vaporization of the gallium component from LSGM
(LSGM) have been investigated. The vaporization of the gallium component from LSGM presents some limitation in its use in the reducing atmosphere at high temperatures. Even so, the high ionic conductivity of this material makes it attractive to use in many applications (membrane for partial oxidation of methane, electrolyte for low temperature SOFC, electrolyte for one chamber SOFC etc.).

**Electrophoretic Deposition Technique**

Several years ago, Ishihara et al first applied the electrophoretic deposition technique to the fabrication of YSZ electrolyte thin film. Recently, the National Institute of Materials and Chemical Research has started the investigation of adopting this technique to fabricate the tubular cells; lanthanum manganite tube with one closed end was deposited on graphite rod and sintered at high temperature. Attempts have also been made to fabricate a lanthanum manganite/YSZ/Ni-YSZ multilayer by co-deposition and co-sintering technique.

**New Cell Designs**

Toho Gas has proposed to adopt the honeycomb type stacks on the basis of extrusion technique. A new SOFC design with high power density generation has been proposed by NGK. This is a kind of mixture of planar and tubular cells.

**Efforts for High Power Densities Based on Anode Substrates**

Mitsui Engineering & Shipbuilding Co. has focused on development of anode support-type planar cells. Similar efforts have also been made by Tokyo Gas.

**Application to Transportation**

The NEDO international cooperation team with Professor Mizusaki at Tohoku University as its head, is conducting research on the application of SOFCs to automobiles. Similar attempts are also made by ETL, Yokohama National University and Kansai Research Institute.

**REFERENCES**

1. H. Sasaki and K. Takasu, in *Solid Oxide Fuel Cells V*, U. Stimming, S. C. Singhal, H. Tagawa, W. Lehnert, Editors, PV 94-40, p. 12, The Electrochemical Society Proceedings Series, Pennington, NJ (1997).
2. M. Nishikawa, in *Solid Oxide Fuel Cells IV*, M. Dokiya, O. Yamamoto, H. Tagawa, and S. C. Singhal, Editors, PV 95-1, p. 3, The Electrochemical Society Proceedings Series, Pennington, NJ (1995).
3. H. Iwahara, in *Solid Oxide Fuel Cells III*, S. C. Singhal, H. Iwahara, Editors, PV 93-4, p. 6, The Electrochemical Society Proceedings Series, Pennington, NJ (1993).
4. H. Yokokawa, T. Horita, N. Sakai, M. Dokiya, and T. Kawada, in *Ceramic Interfaces: Properties and Applications*, R. C. Smart and J. Nowotny, Editors, pp. 171-201, IOM Communication, Ltd. London (1998).