SOFC Research and Development at NIMTE

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Abstract

Ningbo Institute of Material Technology and Engineering (NIMTE), Chinese Academy of Sciences, has currently run the biggest activities in Solid Oxide Fuel Cell research and development program in mainland China. A Division named Fuel Cell and Energy Technology (FCET) has been established for Solid Oxide Fuel Cell (SOFC) research and develoment and its relevant energy technology since end of 2006. The FCET currently has 30 full time staffs and they are vertically integrated in specializing in Materials Engineering, Applied Chemistry, Mechanics, Thermal Engineering, Electric and Electronic Engineering. The activities cover from powder, cell, stack to system development. A pilot production capable of producing 5000 planar cells per year has been commissioned by the end of November, 2007. Single cells in size of ranging from 10×10 cm^2 to 30×30 cm^2 are routinely produced. Conventional materials such as Y_2O_3 stablised ZrO_2 (YSZ), NiO and $(La,Sr)MnO_3$ (LSM) are currently used to fabricate cells with a configuration of (NiO+YSZ)/YSZ/(LSM+YSZ). The total cell thickness is between 400 to 450 µm with 10 µm YSZ electrolyte. The anode support made by tape casting and sintering has a flexural strength around 200MPa. Relationships between NiO/YSZ composition, bulk density, open porosity, electronic conductivity as well as flexural strength are investigated for the (NiO+YSZ) anode support. Cathode materials of mixed conductors $(La,Sr)(Co,Fe)O_3$ (LSCF) and $(La,Sr)CoO_3$ (LSC) are investigated for the cell application being operated at low temperature. Cell and stack testing facilities are established with equipped of six 100W single cell testing stands, one 500W and four 1kW stack testing stands. Planar cells with active area of 4×4 cm^2 are measured in terms of current and voltage under different conditions of temperature, moisture, and gas compositions. 90% successful rate has been achieved in single cell testing with a criterion of more than 1 volt in open circuit voltage obtained. This indicates dense YSZ electrolyte and satisfied sealing technique for the single cell testing. Power density of 0.6 W/cm^2 is achieved at 750 ℃. Cell degradation is investigated under constant current conditions. Impedance spectra are used to determine the cell resistance. A technique under limit current mode with 2 voltage leads at the cell anode and cathode, respectively and 2 current leads at the whole testing house is used to distinguish the resistance contribution from cell, the current leads and current collect, as well as contact at different interfaces. Internal manifold stack design is used with gas channels made by laser cutting to achieve a high volumetric power density. Stack repeating unit has been investigated under mutliple thermal cycle experiement with the stack experienced of more than 40 cycles and 700 hours. Stacks with 1kW power are under development. Heat and power co-generation system in kW range is designed and is currently under manufacturing.

Introduction

Ningbo Institute of Material Technology and Engineering (NIMTE), Chinese Academy of Sciences (CAS), was established officially in March, 2006. It was jointly invested by CAS, Zhejiang provincial government and Ningbo municipal government. The mission of NIMTE is to bridge the gap between scientific research and commercialization. The core value of NIMTE is “facilitating the application of the results from scientific research, not only of our own, but also of any others around the world, our goal is to deliver innovative solutions for industry, society and the environment”. NIMTE is aiming to become a unique world-class research institute in materials science, technology and engineering. NIMTE has set up six divisions on Polymers and Composites, Magnetic Materials and Equipment, Functional Materials and Nano-devices, Surface Engineering, Fuel Cell and Energy Technology, and High Performance Fibres.

Fuel Cell and Energy Technology Division (FCET) for SOFC R&D was established in the end of 2006, our goal is through collaboration with other research institutes and industry partners, to develop state-of-art Solid Oxide Fuel Cell (SOFC) technology, to demonstrate feasibility of the technology, to attract venture capitals, and to accelerate the commercialisation. FCET is consisting of four research groups and one production group. The four research groups are Powder and Cell Development, Cell Testing, Stack Development, and System Development. The production group is running a single cell production in our pilot production facility. Currently FCET has 30 full time staffs. They are vertically integrated with specialties of chemical engineering, materials science, mechanical engineering, thermal engineering, electric and electronic engineering. FCET is fabricating anode supported planar SOFCs, manufacturing stacks, and then integrating stacks into fuel cell systems.

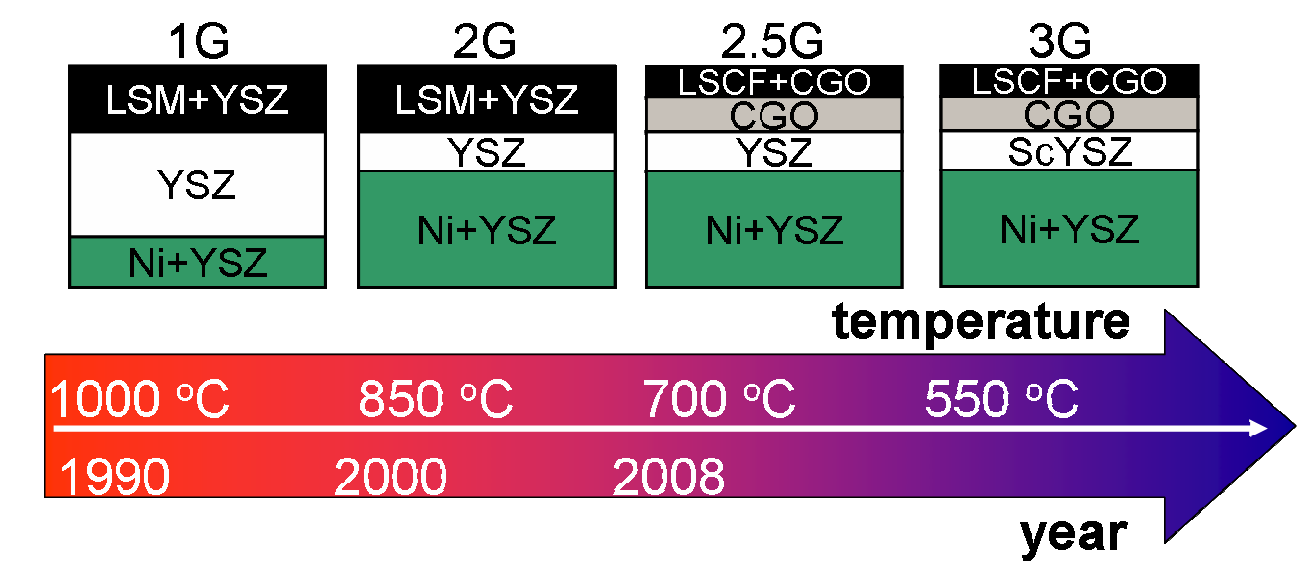

Figure 1 Cell development trend for anode supported planar SOFC

Powder and Cell Development

Powder and Cell Development Group is doing cell development for SOFC. Figure 1 shows the cell development trend as we have understood. Cell configuration changed from electrolyte supported cell to anode supported cell for dramatically reducing the resistive contribution from electrolyte. Such change allows the cell operation temperature reduced from 950℃ to 800℃ in the middle of 90s. However, there are groups still using electrolyte supported cell configuration due to good mechanical strength of thick YSZ electrolyte and fair redox stability of thin Ni+YSZ anode. This is the consideration from mechanical property side. In terms of electrical property, for further reducing operation temperature, mixed conductor (La,Sr)(Co,Fe)O_3 (LSCF) and (La,Sr)CoO_3 (LSC) are needed to replace the electronic conductor (La,Sr)MnO_3. But, the LSCF and LSC are suffering stability issues though they have better catalytic property in comparison of LSM. They are not yet the first option of the cathode for the cells to build a stack. On the other hand, in the electrolyte side, Gd doped CeO_2 (CGO) and Sc doped ZrO_2 (ScZO) are widely studied to replace YSZ due to their high conductivity at middle and low temperature range. Because CGO has an electronic conduction in a reduced atmosphere and relative high temperature, the cells made of CGO electrolyte will generate a lot of heat when the operation temperature is above 600℃. SZO is a better choose because it is YSZ like, though it is expensive. From the considerations illustrated, we are currently running several projects that towards a cell with the characteristics of strong mechanical strength, less internal stresses, and low polarization resistances in the middle temperature range from 650 to 750℃. They are projects: (1) optimising electronic conductor (La,Sr)MnO_3 (LSM) as the cathode component in the composite cathode of LSM+YSZ, (2) development mixed conductor cathodes such as LSCF and LSC to replace LSM for low temperature operation, (3) develop Sc doped ZrO_2 to replace YSZ for increasing conductivity of the electrolyte, (4) enhancing strength of anode support, (5) decreasing thermal expansion coefficient of anode support by doping.

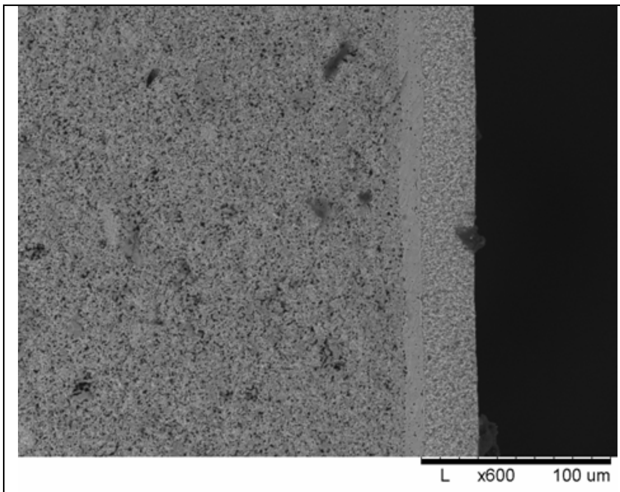

Figure 2 SEM picture of a typical cell transverse cross section.

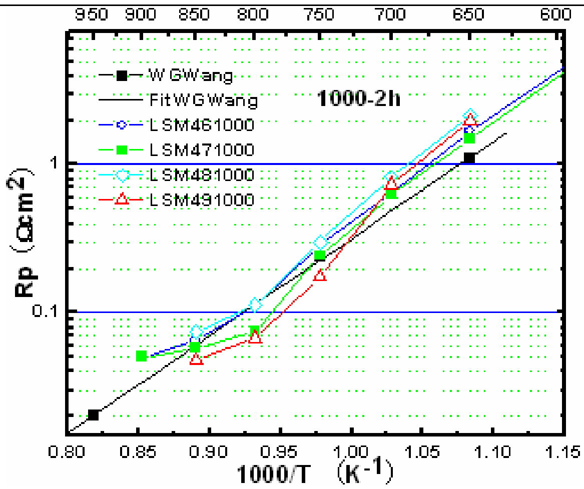

Figure 3 R_p versus temperature shown in Arrhenius plot of the symmetric cells.

Figure 2 shows the typical microstructure of a cell, the cell consists of anode support made of NiO+3mol% Y_2O_3 stabilised ZrO_2 (3YSZ), active anode made of NiO+8mol% Y_2O_3 stabilised ZrO_2 (8YSZ), electrolyte made of 8YSZ, and cathode made of LSM+8YSZ. One of the efforts has been made is to further optimising LSM+YSZ composite cathode based on Wang's work [1]. By carefully adjusting $(La_{0.75}Sr_{0.25})_{0.95}MnO_3$ content in the composites, we have found that the R_p versus T^{-1} having a nonlinearity in the Arrhenius plot when the LSM content deviated from 50 wt%. We have achieved a performance with R_p of 0.07 Ωcm^2 at 800℃ and less than 0.2 Ωcm^2 at 750℃ in symmetric cells with the configuration of (LSM+YSZ)/YSZ/(LSM+YSZ). The reasons for improved performance are still under investigation. It can be postulated that the conductivity of LSM and YSZ network, the microstructure of three dimensional network of LSM, YSZ and pores are playing important roles. The highlights of this work are the potential for further improvement of cell performance using conventional materials such as LSM where LSM is the only cathode material with proved stability in long term cell operation.

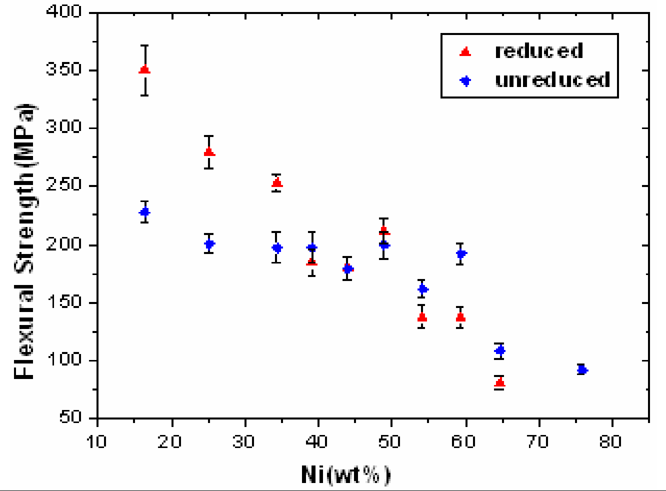

Figure 4 Flexural Strength as a function of Ni content in anode support.

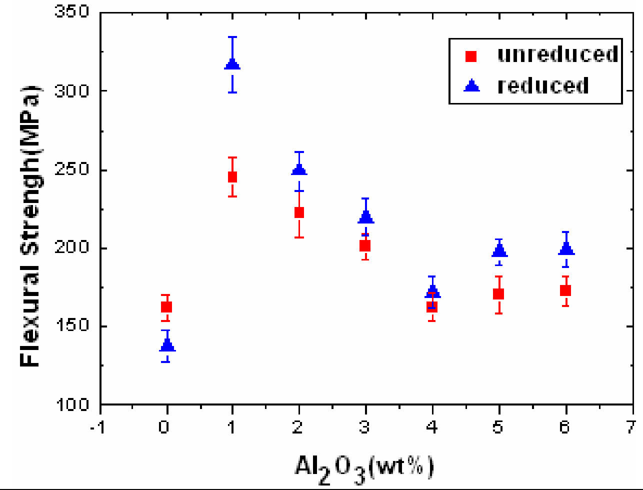

Figure 5 Flexural Strength as a function of Al_2O_3 content in anode support.

Increasing mechanical strength of the Ni+YSZ anode support is another important topic. When we consider building a large stack with high power, the cell has to been scaled up to large size. From this point of view, several issues for the anode support are considered to be more crucial for the cells to build large stacks in comparison of the one to build small stacks. The mechanical strength, thermal expansion coefficient (TEC), and sinkage of anode support during sintering are important factors to influence the manufacturing ability of stack building. The TEC and sintering sinkage of the different layer for a half cell (Anode support/NiO+YSZ/YSZ) are important to the internal stresses of a half cell when it is cooled down to room temperature. Figure 4 shows the flexural strength change as a function of Ni content. It is found that the strength decreased when the Ni content increased. However, it has to be analysed that the strength of anode support is in larger values after reduction in comparison of unreduced one when the Ni content is less than 50 wt%. The relative density of the samples is not identical because all the samples are made by tape casting and sintering. Effort in increasing strength by Al_2O_3 doping is made which is shown in Figure 5. Here the composite composition is fixed in which the Ni content is 50 wt%. By 1 wt% Al_2O_3 doping, the flexural strength is significant increased. This work is presented in details by Changrong He in this proceeding [2].

Single Cell Pilot Production

Here in NIMTE, a pilot production for fabricating anode supported single cells has been established which is capable of producing 5000 cells per year. The processes to produce a cell include tape casting to make anode support, air spraying to make active anode and electrolyte, and then co-sintering half cells. Cathode is air sprayed and sintered to finalise the full cell production. Figure 6 shows the 10 meter long tape casting machine and the anode support green tapes. Figure 7 shows a picture of full cells with size of 10×10 cm^2. Conventional materials YSZ, NiO and LSM are currently used to fabricate cells with a configuration of (NiO+YSZ)/YSZ/(LSM+YSZ). The total thickness of the cell is between 400 to 450 µm with 10 µm YSZ electrolyte. The cell has a flexural strength around 200MPa. The power density of our cells reached 0.6W/ cm^2 at 750℃ when we measured the I-V curves in an active cell with the size of 4×4 cm^2. We have a wide tape casting machine with the doctor blade width of 50 cm. By using this tape casting machine we can produce 30×30 cm^2 large cells aiming for large power stack building.

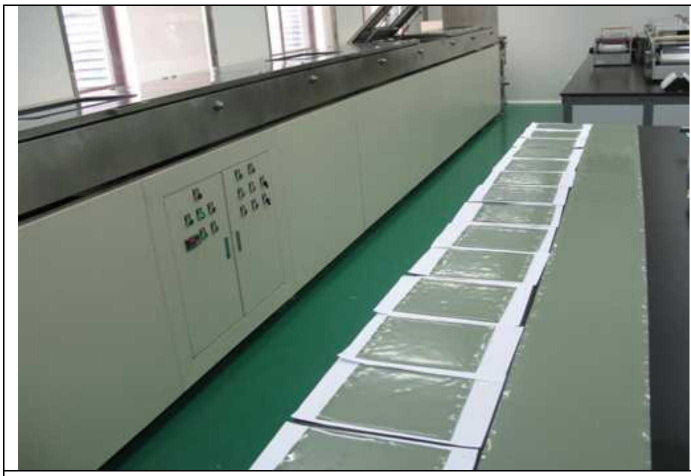

Figure 6 Tape casting machine and anode support green tapes.

Figure 7 Full cells with size of 10×10 cm^2 fabricated from our pilot production.

Single Cell Testing

NIMTE is trying to build a comprehensive cell testing platform in evaluating the performance of planar SOFC singlecells. Currently 6 100W testing strands are in operation. Cells are investigated under different currents, voltages, moistures, and gas compositions. A typical set up is shown in Figure 8. A ceramic testing house is designed which is made of Al_2O_3 for capable of repeating and long term measurements. A composite sealing configuration with a high temperature ceramic glass is designed. The testing set up has been developed to be appropriate to the temperature ranging from 600 to 900℃ for testing of single cell with an active area of 4×4cm^2. A single cell was discharged at 850℃ using the set up shown in Figure 9. The voltage probes are placed on the surface of anode support and cathode. When the current is drawn, the cell voltage can be obtained without the influence of the contribution from current leads and contacts between cell and current collector. Figure 9 shows two discharge I-V curves. The slope of solid points represents the inner resistance of the single cell R_C, and the slope of open points represents the resistance of the total resistance R_H including resistances from single cell, electrical current leads and contacts. By these measurements, it can be calculated that the R_C and the R_H. The sum of the resistance from contacts and current leads is $R_H - R_C$. This part of work is presented in details by Wan Bing Guan in this proceeding [3].

Figure 8 A set-up of cell testing for planar SOFCs

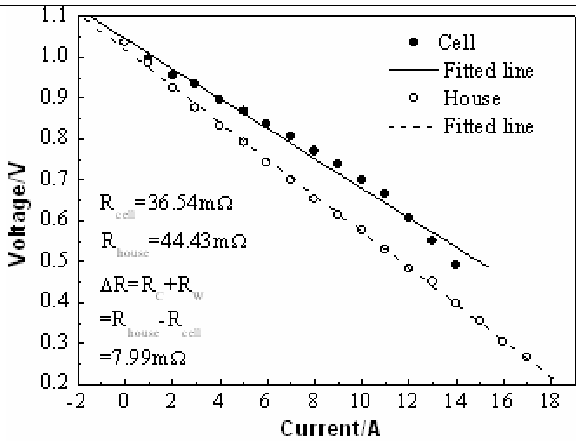

Figure 9 I-V curves are measured where the voltage probes are placed at cell and house.

Stack Development

Stack development is one of the most important activities in FCET. For the components processing, we established a laser cutting machine and plasma spraying equipment. Internal manifolding compact design is used. The holes of gas tunnel in cells and steel interconnects are made by laser cutting process. LSM coating is made on interconnect stainless steel by plasma spraying to lessen oxidation of the steel exposed at high temperature. Different steel types including APU22 are examined in oxidation scales, cycling properties, and electrical resistances. Figure 10 shows a three cell short stack after testing. Short stacks are developed to study stack component properties, leakage problems, and electrical contacts between various components. A thermal cycle experiment has been conducted when the stack repeating unit has been run at constant current of 2A and 750℃, and then cooled down and heated up. Figure 11 shows the degradation behaviour when the unit was first run by a stable operation for more than 100 hours, and then the furnace has been turned on and off everyday. The temperature was not reached to room temperature in many cycles because the furnace was kept relatively warm after cooling. The temperature at the low end is ranging from room temperature to 200℃ depending on the weather and the timing when the operator turns on the furnace. The stack repeating unit containing top and bottom plate, interconnects, sealant, and one cell. The degradation is less than 1% per thermal cycle. After first stage of 16 cycles, we increased the gas flow, and then the voltage was increased after 520 hours. Second stage of cycling experiment contains 15 cycles and 350 hours. The experiment is still running and it demonstrates the feasibility of our stack technology.

Figure 10 A three cell short stack after testing.

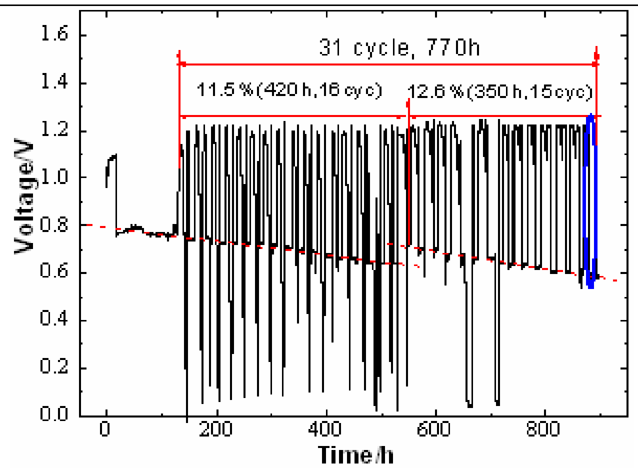

Figure 11 Thermal cycle experiment of a stack repeating unit.

Fuel Cell System Development

Fuel Cell System Group was established in the summer of 2007. We have started to design a test stand to examine the system design concept. Figure 12 shows the design flow chart for a heat and power cogeneration system with start up burner, steam generator, partial reforming unit, heat exchanger, fuel cell stack, exhaust burner, and so on. According to this design, a testing system is in development. Figure 13 shows a partially built testing stand for examining our design concept. A compacted system for real commercial product is in design phase. We expect the kW system demonstration will be realised in the end of 2009.

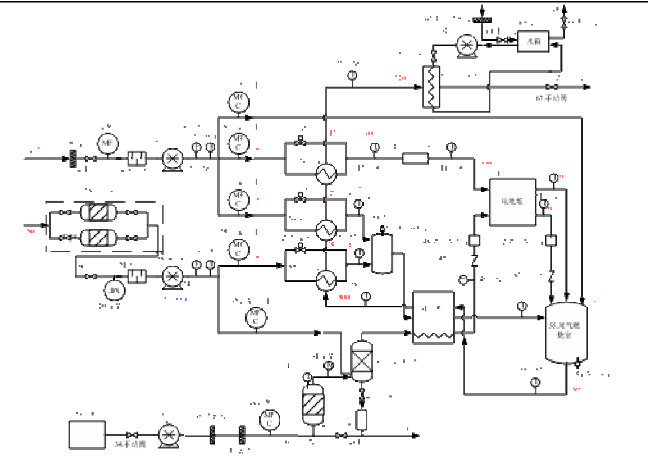

Figure 12 A flow diagram of a heat and power cogeneration system design.

Figure 13 A fuel cell testing system with all the functions to be examined.

Acknowledgement

This work is partly supported by the National High Technology Research and Development Program of China (863 Program, Grant No. 2007AA05Z140) and the Chinese Academy of Sciences.

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