Advances in Solid Oxide Fuel Cells IV

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A Collection of Papers Presented at the 32nd International Conference on Advanced Ceramics and Composites January 27–February 1, 2008 Daytona Beach, Florida

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Preface

The Fifth International Symposium on Solid Oxide Fuel Cells (SOFC): Materials, Science, and Technology was held during the 32nd International Conference and Exposition on Advanced Ceramics and Composites in Daytona Beach, FL, January 27 to February 1, 2008. 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 120 papers were presented in the form of oral and poster presentations indicating strong interest in the scientifically and technologically important field of solid oxide fuel cells. Authors from 17 countries (Australia, Austria, Brazil, Canada, China, Denmark, Germany, India, Italy, Japan, Netherlands, South Korea, Switzerland, Taiwan, Ukraine, 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. Twenty five papers describing the current status of solid oxide fuel cells technology and the latest developments in the areas of fabrication, characterization, testing, performance, long term stability, anodes, cathodes, electrolytes, interconnects, seals, cell and stack design, proton conductors, electrolyzer, etc. are included in this volume. Each manuscript was peer-reviewed using The American Ceramic Society review process.

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. Financial support from the American Ceramic Society is gratefully acknowledged. Thanks are due to the staff of the meetings and publications departments of The American Ceramic Society for their invaluable assistance. Advice, help and cooperation of the members of the symposium's international organizing committee (Tatsumi Ishihara, Tatsuya Kawada, Nguyen Minh, Mogens Mogensen, Nigel Sammes, Robert Steinberger-Wilkens, Jeffry Stevenson, and Eric Wachsman) at various stages were instrumental in making this symposium a great success.

It is our earnest 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.

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Introduction

Organized by the Engineering Ceramics Division (ECD) in conjunction with the Basic Science Division (BSD) of The American Ceramic Society (ACerS), the 32nd International Conference on Advanced Ceramics and Composites (ICACC) was held on January 27 to February 1, 2008, in Daytona Beach, Florida. 2008 was the second year that the meeting venue changed from Cocoa Beach, where ICACC was originated in January 1977 and was fostered to establish a meeting that is today the most preeminent international conference on advanced ceramics and composites

The 32nd ICACC hosted 1,247 attendees from 40 countries and 724 presentations on topics ranging from ceramic nanomaterials to structural reliability of ceramic components, demonstrating the linkage between materials science developments at the atomic level and macro level structural applications. The conference was organized into the following symposia and focused sessions:

Symposium 1	Mechanical Behavior and Structural Design of Monolithic and Composite Ceramics
Symposium 2	Advanced Ceramic Coatings for Structural, Environmental, and Functional Applications
Symposium 3	5th International Symposium on Solid Oxide Fuel Cells (SOFC): Materials, Science, and Technology
Symposium 4	Ceramic Armor
Symposium 5	Next Generation Bioceramics
Symposium 6	2nd International Symposium on Thermoelectric Materials for Power Conversion Applications
Symposium 7	2nd International Symposium on Nanostructured Materials and Nanotechnology: Development and Applications
Symposium 8	Advanced Processing & Manufacturing Technologies for Structural & Multifunctional Materials and Systems (APMT): An International Symposium in Honor of Prof. Yoshinari Miyamoto
Symposium 9	Porous Ceramics: Novel Developments and Applications

Symposium 10	Basic Science of Multifunctional Ceramics
Symposium 11	Science of Ceramic Interfaces: An International Symposium Memorializing Dr. Rowland M. Cannon
Focused Session 1	Geopolymers
Focused Session 2	Materials for Solid State Lighting

Peer reviewed papers were divided into nine issues of the 2008 Ceramic Engineering & Science Proceedings (CESP); Volume 29, Issues 2-10, as outlined below:

- Mechanical Properties and Processing of Ceramic Binary, Ternary and Composite Systems, Vol. 29, Is 2 (includes papers from symposium 1)
- Corrosion, Wear, Fatigue, and Reliability of Ceramics, Vol. 29, Is 3 (includes papers from symposium 1)
- Advanced Ceramic Coatings and Interfaces III, Vol. 29, Is 4 (includes papers from symposium 2)
- Advances in Solid Oxide Fuel Cells IV, Vol. 29, Is 5 (includes papers from symposium 3)
- Advances in Ceramic Armor IV, Vol. 29, Is 6 (includes papers from symposium 4)
- Advances in Bioceramics and Porous Ceramics, Vol. 29, Is 7 (includes papers from symposia 5 and 9)
- Nanostructured Materials and Nanotechnology II, Vol. 29, Is 8 (includes papers from symposium 7)
- Advanced Processing and Manufacturing Technologies for Structural and Multifunctional Materials II, Vol. 29, Is 9 (includes papers from symposium 8)
- Developments in Strategic Materials, Vol. 29, Is 10 (includes papers from symposia 6, 10, and 11, and 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 and BSD 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.

ACerS and the ECD invite you to attend the 33rd International Conference on Advanced Ceramics and Composites (http://www.ceramics.org/daytona2009) January 18–23, 2009 in Daytona Beach, Florida.

TATSUKI OHJI and ANDREW A. WERESZCZAK, Volume Editors
July 2008

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Technical Overview

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RESEARCH ACTIVITIES AND PROGRESS ON SOLID OXIDE FUEL CELLS AT USTC

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ABSTRACT

This article briefly introduces the research activities and progress on Solid Oxide Fuel Cells (SOFC) at USTC. Lab. directed by one of the present author, prof. Meng, in recent ten years. The content includes the following topics:

(1) Searching new electrolyte materials for SOFCs
(2) Development of preparation techniques for thin electrolyte membranes on porous anode support
(3) Modification of both cathode and anode by nano-techniques
(4) Tubular CMFCs : low cost fabrication and ceramic interconnect materials
(5) Ammonia fueled CMFCs with proton and oxide ion electrolytes

INTRODUCTION

Solid Oxide Fuel Cells (SOFCs) have attracted worldwide interest for their high energy conversion efficiency, structure integrity, easy operation, and less compact to environment as well as the high tolerance to fuels.

The research on SOFCs was started relatively late in China, and in late 1980's, there were only a few research groups dealing with materials related to SOFCs. The major event for R & D of SOFCs in China was the 97th Xiangshan Scientific Conference, topic of which was 'New Solid Fuel Cells', held in June 14th – 17th, 1998, Xiangshan Hotel, Beijing. The conference established developing the intermediate temperature SOFCs (IT-SOFCs) as the main target in R & D of SOFCs, and the routes of searching high performance key materials, developing techniques to prepare thin electrolyte membranes on porous electrode supports as well as preparing active electrodes with nano-microstructures were proposed in order to realize IT- SOFCs [1]. Since then, laboratory for solid state chemistry and inorganic membranes at USTC as one of the major units dealing with SOFCs has joined in the main research projects on SOFCs granted by NSFC and MSTC in the 10th five year program in China. In recently years, our work emphasis has been put on the R and D of tubular ceramic membrane fuel cells (CMFCs) from viewpoint of practical applications and following a research route based on 'counter-main stream consideration'. This article would introduce briefly the results in these research activities in the following sections.

1. Searching and investigation of new electrolytes rather than yttrium stabilized zirconia (YSZ)

In order to pursue IT-SOFCs, early research work was first focused on searching new electrolyte materials to substitute YSZ for its rather low conductivity particularly at temperature below 800°C. In a work trying to utilize high proton conductive Li_2SO_4 in the dual phase of Li_2SO_4␣Al_2O_3␣+ Ag as a hydrogen permeation reactor, we noticed the H_2S formation in H_2 which was further confirmed in a

H_2/O_2 cell with Li_2SO_4-Al_2O_3 as electrolyte[2] due to the following reaction occurred,

$$Li_2SO_4 \quad 4H_2 \rightarrow H_2S\uparrow \quad 2LiOH \quad 2H_2O$$

This work reminded researchers the importance to consider the thermodynamic stability of the electrolyte materials that had not been paid sufficient attention. Knowing chloride exhibiting high chemical stability Dr. S.W. Tao who was a Ph.D. student of mine then made an attempt to use doped NaCl (adding 70% Al_2O_3 to enhance the strength) as electrolyte to assembly H_2 and O_2 concentration cells and found the remarkable O^{2-}/ H^+ conduction in 650-750°C with oxide ion transference number of 0.98 at 700°C [3]. Further investigation found that a composite of LiCl-$SrCl_2$ with doped ceria exhibited even higher conductivity at the temperature above the eutectic point (485°C for 53mol% LiCl – 47mol% $SrCl_2$. As can be seen from the V-I and P-I curves of a cell consisted of Ni-GDC anode, LiCl-$SrCl_2$–GDC (Gd doped CeO_2) electrolyte (0.40mm thick) and $LiNiO_2$ cathode, shown in Fig.1, the open circuit voltages of the cell (OCV) are close to 1.2V indicating the pure ionic conductivity of the electrolyte material and the peak power densities of the cell are in the range of 120 – 270 mW/cm^2 in 460-550°C [4]. And another cell showed the even better performance with a peak power density of 500 mW/cm^2 at 625°C [5]. The data were remarkably higher than the best record at that time, 140 mW/cm^2 at 500°C by Doshi et. al., with the cell based on GDC electrolyte about 30 μm in thickness [7].

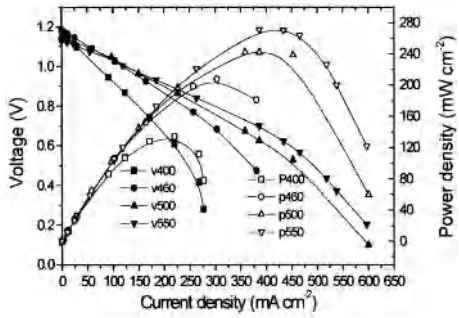

Fig. 1 V-I and P-I curves of a cell consisted of Ni-GDC anode, GDC-LiCl-$SrCl_2$ electrolyte (0.40mm thick), and $LiNiO_2$ cathode [4,5]

The electrolyte conductivity versus temperature were roughly obtained from the slope of the cell V-I curves and shown in Fig. 2[6]. It can be seen that the conductivity of the composite electrolyte is about 2~10 times higher than that of pure GDC or LSGM ($La_{0.6}Sr_{0.2}Ga_{0.8}Mg_{0.2}O_{3-\delta}$), and 1~2 orders of magnitude higher than that of YSZ in the temperature range of 400~600°C. And the most interesting characteristics was that the conductivity was not only high but also the activation energy of the conduction was quite low and less sensitive to the temperature, compared with all the well known oxide ion electrolytes. This was most attractive for the development of IT-SOFCs. To interpret the high conductivity with no record before, a model for the electric conduction mechanisms was proposed [8]. The model supposed that there were four possible paths for the electric charge carriers to go through: (1) continuous molten chloride salt, (2) continuous ceria particles, (3) continuous ceria- molten salt and (4) disconnected ceria particle- molten salt ambient. Possibly, the Path (2) is the most conductive path because the molten salt exhibits much higher ionic mobility and the path of GDC-Chlorides interface is

also the easy way to go for ions. In the case of continuous solid GDC particles, the cell OCV may lower than 0.9V due to the partial electronic conduction of GDC. But the cell could have higher power density because of more efficient parallel ionic paths that was proved to be true [6,8,9].

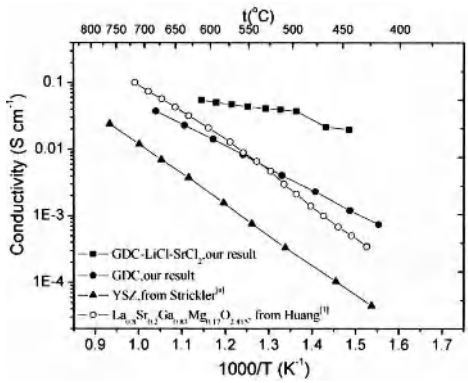

Fig.2 The conductivity of the composite electrolyte

The conductive salt-oxide composites demonstrated surely an attractive new route to search more efficient electrolyte systems with unique characteristics for reduced temperature fuel cells. After further investigation, however, we discovered that the cells with these composite electrolytes could not keep long duration due to the volatility of the salt component, particularly in the gas flow systems. The study on such material systems was stopped for many years, but we do think this kind of electrolyte systems may find their proper usages in future.

As to the well known alternative oxide conductors, including doped $LaGaO_3$ and doped CeO_2 (GDC or SDC), our investigation was mainly put on developing so called 'soft chemical synthesis' routes to prepare high reactivity powders and optimizing the properties by composition refinement[10-19]. For the $La_{0.9}Sr_{0.1}Ga_{0.8}Mg_{0.2}O_3$(LSGM) the powder prepared by citrate method reached a 97% relative density at 1450°C [10], while the densification temperature was usually around 1600°C for the powders by conventional solid phase reaction. With $La_{0.6}Sr_{0.4}Ga_{0.8}Ni_{0.2}O_{3-\delta}$ as a compatible anode, the cell with LSGM electrolyte of 0.5mm provide a power density of 270 mW/cm^2 at 750°C, predicting the even much higher performance for the cells with thinner electrolyte [11]. Owing to the less Ga source and lack of compatible electrode materials we turned the research efforts onto GDC and SDC for IT-SOFCs [12-19]. Our investigation showed that Sm doped CeO_2, $Ce_{0.8}Sm_{0.2}O_{2-\delta}$ or $Ce_{0.85}Sm_{0.15}O_{2-\delta}$, exhibited better properties than GDC which got more reports in the literature. As shown in Fig. 3, the OCV value of the cell with SDC can be above than 0.9 V when operates at a temperature lower than 700°C [13]. The SDC powder prepared by a polyvinyl alcohol-induced low temperature synthesis had a particle size of 20-30 nm and could be densified into 98% relative density at 1300°C and got a conductivity of 0.033S/cm at700°C that was a quite good value.[14]. And based on the nano-particle powders prepared by such a polymer assisted process, a method so called triple layer co-pressing and co firing was developed in our laboratory to make disc fuel cells with very thin electrolyte membrane which has been the powerful route to investigate materials and cell performance

[19]. Fig. 4 is the result from such a cell with thin membrane electrolyte [20]. We may see that the SDC membrane is only about 12 μm and the power density reaches 1872 mW/cm^2 at 650°C and 748 mW cm^{-2}at 550°C, which are surely in the highest range in literature. The co-pressing and firing process, however, is only suitable for laboratory but not for scaling up and for the later it will be described in the nest section.

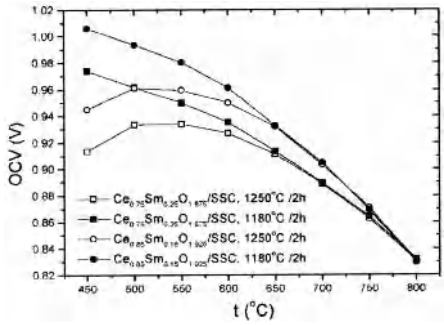

Fig. 3 OCVs of the cells with SDC electrolyte: the effect of interface microstructure on OCVs (electrode sintering condition) [13]

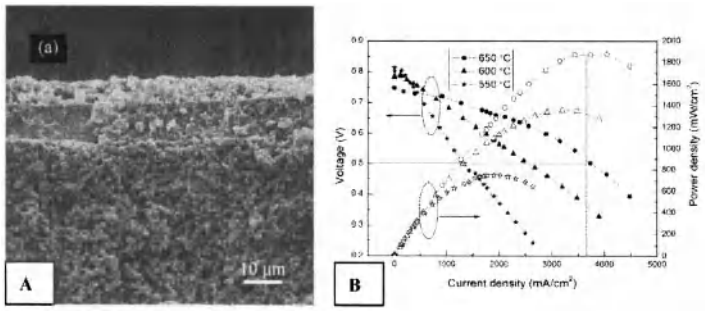

Fig. 4 The microstructure(A) and performance(B) of a cell made by co-pressing and co-firing Ni+SDC anode and BSCF cathode with SDC electrolyte the powders made by polymer assisted combustion method [20]

2. Fabrication techniques for thin PEN membranes on porous anode supports

It is of essential significance to develop proper techniques to fabricate thin electrolyte membrane on porous anode support for reducing operation temperature and enhancing performance of SOFCs with ether YSZ electrolyte and other high conductive electrolytes. And it has been commonly recognized that the advanced ceramic processing and co-firing of multi-layers would be the right route as low cost fabrication techniques for SOFCs. A number of techniques, usually the polymer assisted ceramic processing was developed to make dense thin layer of electrolyte on porous anode of YSZ + NiO or DCO + NiO and then deposit a porous cathode. As the results from the cells summarized in Table 1, the

techniques were all successful to make a thin and dense electrolyte as thin as 10 to 50 μm in our attempts [21-26].The tape casting technique was readily employed to make both support and the top electrolyte layer, by which the bi-layers fabricated were good at co-firing, but the cell performance was not so satisfied [21]. The silk screen printing was the first process for us to successfully prepare thin $Ce_{0.8}Y_{0.2}O_{1.9}$ electrolyte of 15μm and got a pretty high cell power density of 360 mW/cm^2 at 650°C [22]. Multi-Spin-coating technique could provide very thin electrolyte and got a fairly high cell performance even with YSZ electrolyte [23], but is not suitable to calling up and also not cost effective. The modified dip-coating and powder spray process are of cost effective and suitable to scaling up for both planner and tubular SOFCs [24-26].

Table 1 Various techniques for thin electrolyte membranes and the cell performance, developed at USTC Lab. of SSC & IM.

Technique for thin membranes	Electrolyte material	Sintering temperature (°C)	Thickness (μm)	Power density (mW/cm^2)	Reference
Tape casting	SDC/NiO -SDC	1400	50	260 (700°C)	[21]
Screen printing	$Ce_{0.8}Y_{0.2}O_{1.9}$	1350	15	360 (650°C)	[22]
Spin-coating	YSZ/Ni-SDC	1300	12	535 (750°C)	[23]
Dip- coating	YSZ	1400	30	190 (800°C)	[24]
Electrostatic spray	YSZ	1400	15	315 (800°C)	[25]
Suspension spray	YSZ	1400	10	837 (800°C)	[26]

Suspension spray technique is not only the right technique to fabricate electrolyte membranes on porous anode or cathode support as thin as around 10μm, but also the right process to make active or transition layers to modify the electrode interfaces[24-26]. Fig. 5 shows the result of a fuel cell made by suspension spray technique on porous disk anode [26]. The YSZ electrolyte membrane was around 10μm and the maximum powder density was only 400 mW/cm^2 at 800°C probably due to the cracks and pores on the YSZ - anode interface as seen in Fig.5(a). After making a modification layer on the rough surface of the anode by the same process (see Fig. 5-b), the power density of the cell increased to 837 mW/cm^2 at 800°C, but still 214 mW/cm^2 at 650°C (Fig.5-c).

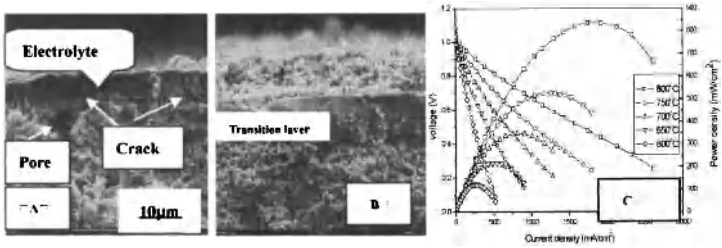

Fig.5 The microstructures and performance of the cells made by suspension spray process[26]

As seen from Fig.5 (b), the interface of YSZ and cathode is still poor, and thus there is obvious electrode polarization on the V-I curves of the cell (Fig.5-c). A recent result shows that after adding a SDC active layer by the suspension spray process on YSZ surface before coating cathode, cell power density reaches 443 mW/cm^2 at 650°C and 187 mW/cm^2 at 600°C, as seen from the Fig.6 [27]. This means that YSZ could also be used as electrolyte material for IT-SOFCs as long as the proper fabrication technique developed.

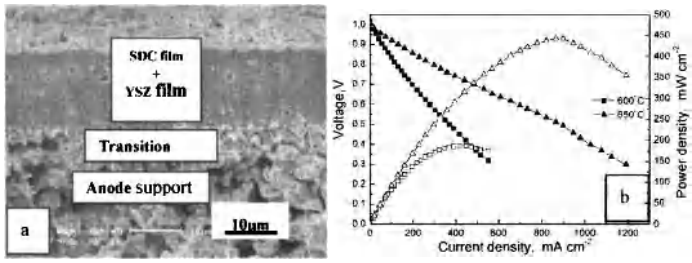

Fig 6 (a) Section view of the cell with anode transition layer and active cathode SDC layer, and (b) V-I, P-I curves of the cell in Fig.6-a

3. Modification of both cathode and anode by nano-techniques

It has been recognized that the composition and microstructure of the electrodes are the major factors to affect both performance and life duration of a cell. In recent years, our research work on electrodes has included following topics:

- New material systems[28-30]
- Interface modification of anode or cathode by chemical routes[25-27,31-33]
- New designs of electrode structure and preparation for the long term stability[34-36]

As mentioned above that modification of the interfaces by spraying nano-particles made by wet chemical routes could provide a significant enhancement to the cell performance because of the increase of triple phase boundaries and the improvement of interface coherency [25-27,31-33]. Both anode and cathode still have their own problems, such as the carbon deposit on Ni based anode when hydrocarbon fuels are used and the contradiction of catalysis activity of cathode materials and their thermal expansion consistence with electrolyte. Our lab. firstly investigated the performance of SOFCs with

natural gas and biomass gas and got a peak power density of over 300mW/cm^2 at 600°C for the cell of Ni SDC/SDC/SSC with biomass fuel[34]. In order to create a high performance anode with against carbon-deposit, proper catalytic activity, structure stability as well as higher ionic conductivity a new anode structure with branch-like-microstructure was designed recently [35]. The anode consisted of porous Ni-SDC and micron size SDC to form a continuous branch like structure coated with nano-particle SDC. It gives a number of advantages:

1 Against coking on anode because of the nano-SDC coatings on Ni-SDC surface
2 High electrochemical activity comes from nano-size SDC particles which exhibit high oxidation reactivity.
3 High conductivity from Ni based Ni-SDC anode
4 Ni-SDC based anode is compatible to SDC electrolyte thermo- mechanically, thus thermodynamic stable
5 Easy to fabricate, the simple dip-coating process can be employed to coat nano-SDC on Ni - SDC anode

As presented in Fig. 7, the cells with new structure anode coated with various amount of nano-SDC particles display a great improvement in their cell performance against carbon-deposit with methane as fuel. The cell with 25 mg/cm^2 SDC coating was operated in CH_4 at 600°C for 50 hrs without obvious decrease in power output or structure change. While the power density of the cell without SDC coating on anode decreased by 60% after only 10hrs operation [34].

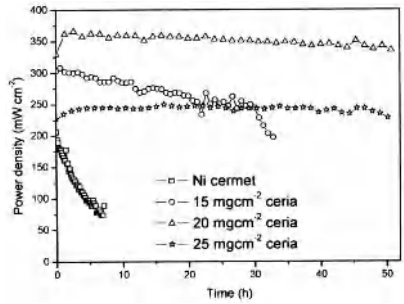

Fig.7 The longer term performance of SOFC cells with various SDC coating on Ni-SDC anode for CH_4 as fuel, operated at 0.5V and 600°C

Similar to the anode structure described above, the cathode side can be improved by the same idea. With nano-LSC ($La_{1-x}Sr_xCoO_3$) coating on porous and branch like cathode the cell illustrated very high performance stability in longer term and multi-thermal cycles as shown in Fig. 8[35]. As can be seen that the area specific resistance(ASR) (measured by ac impedance spectroscopy technique in situ)of a cell with a conventional SDC-LSC cathode made by silk screen printing increased obviously, from the

original value of 2.4Ωcm^2 to 3.5Ωcm^2 during the thermal cycles between 500-800°C for 20 times in 20 days and further increased to 12.5 Ωcm^2 during thermal cycles of 10 times from room temperature to 800 ^{O}C in 10 days, and then remained changeless at 600°C for more than 60 days. While the ASR of the cell with new cathode coated by nano-size LSC has a very low value (0.30 Ωcm^2) and kept stable during the testing for more than 100 days. The results demonstrate solidly that the novel design of the electrodes has remarkably improved the performance of SOFCs that is certainly promising for the commercialization of this new energy source.

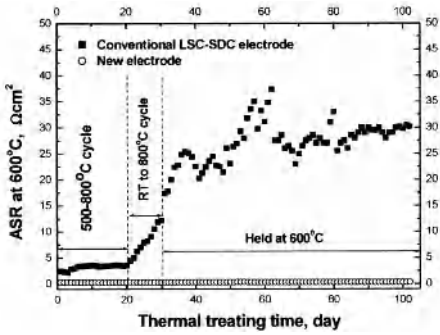

Fig.8 A comparison in ASR of the new designed cathode with conventional SDC-LSC composite cathode during thermal cycling in longer term

4. Tubular CMFCs: design, fabrication [37-41] and interconnect ceramics [42-50]

The first attempt according to 'counter-main stream consideration route' was turned on the development of tubular SOFCs. A new tubular design of anode supported with multi-gas tunnels shown in Fig. 9 was proposed and patented [36]. This configuration exhibits 3 major characteristics:

(1) The fuel (e.g. CH_4 + 3% H_2O) inlets through the central tunnel and flies out through the other tunnels, thus it can easily perform internal reforming.

(2) The cathode surface is designed in wave or tentacle form so that the effective electrode area will be increased by 40-50% compared with flat surface.

(3) It can be easily fabricated by cost effective ceramic processing techniques which are developed in the lab. , including extrusion, gel-casting[37], silk screen printing[22], dip-coating[24] and suspension spray[25,26] etc.