Advances in Solid Oxide Fuel Cells IV

A Collection of Papers Presented at the 32nd International Conference on Advanced Ceramics and Composites
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Contents

Preface ix

Introduction xi

TECHNICAL OVERVIEW

Research Activities and Progress on Solid Oxide Fuel Cells at USTC 3
Guangyao Meng, Ranran Peng, Changrong Xia, and Xingqin Liu

CELL AND STACK DEVELOPMENT AND PERFORMANCE

Development of Micro Tubular SOFCs and Stacks for Low Temperature Operation under 550°C 21
Toshio Suzuki, Toshiaki Yamaguchi, Yoshinobu Fujishiro, Masanobu Awano, and Yoshihiro Funahashi

The Properties and Performance of Micro-Tubular (Less than 1mm OD) Anode Supported Solid Oxide Fuel Cells 29

Performance of the Gen 3.1 Liquid Tin Anode SOFC on Direct JP-8 Fuel 41
M.T. Koslowske, W.A. McPhee, L.S. Bateman, M.J. Slaney, J. Bentley and T.T. Tao

Effect of Interconnect Creep on Long-Term Performance of SOFC of One Cell Stacks 53
W.N. Liu, X. Sun, and M.A. Khaleel
Effects of Compositions and Microstructures of Thin Anode Layer on the Performance of Honeycomb SOFCs Accumulated with Multi Micro Channel Cells
Toshiaki Yamaguchi, Sota Shimizu, Toshio Suzuki, Yoshinobu Fujishiro, and Masanobu Awano

FABRICATION

Formation of Gas Sealing and Current Collecting Layers for Honeycomb-Type SOFCs
Sota Shimizu, Toshiaki Yamaguchi, Yoshinobu Fujishiro, and Masanobu Awano

CHARACTERIZATION AND TESTING

Evaluating Redox Stability of Ni-YSZ Supported SOFCs Based on Simple Layer Models
Trine Klemensø and Bent F. Sørensen

Degradation Phenomena in SOFCs with Metallic Interconnects
Norbert H. Menzler, Frank Tietz, Martin Bram, Izaak C. Vinke, and L.G.J. (Bert) de Haart

Pressure and Gas Concentration Effects on Voltage vs. Current Characteristics of a Solid Oxide Fuel Cell and Electrolyzer
V. Hugo Schmidt and Laura M. Lediaev

In-Situ Temperature-Dependent X-Ray Diffraction Study of Ba(Zr_{0.8-x}Ce_xY_{0.2})O_{3-δ} Ceramics

Evaluation of the Residual Stress Profiles of Practical Size Lanthanum Gallate-Based Cells in Radial Direction
Hiroyuki Yoshida, Mitsunobu Kawano, Koji Hashino, Toru Inagaki, Hiroshi Deguchi, Yoshiyuki Kubota, and Kei Hosoi

ELECTRODES

Effect of Spray Parameters on the Microstructure of La_{1-x}Sr_xMnO_3 Cathode Prepared by Spray Pyrolysis
Hoda Amani Hamedani, Klaus-Hermann Dahmen, Dongsheng Li, and Hamid Garmestani

Examination of Chromium’s Effects on a LSM/YSZ Solid Oxide Fuel Cell Cathode
T.A. Cruse, M. Krumpelt, B.J. Ingram, S. Wang, and P.A. Salvador
<table>
<thead>
<tr>
<th>Title</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>Evolution of Ni-YSZ Microstructure and Its Relation to Steam</td>
<td>159</td>
</tr>
<tr>
<td>Reforming Activity and YSZ Phase Stability</td>
<td></td>
</tr>
<tr>
<td>D. L. King, J.J. Strohm, P. Singh</td>
<td></td>
</tr>
<tr>
<td>Synthesis and Characterization of Ni Impregnated Porous YSZ Anodes</td>
<td>173</td>
</tr>
<tr>
<td>for SOFCs</td>
<td></td>
</tr>
<tr>
<td>C. Anand Singh and Venkatesan V. Krishnan</td>
<td></td>
</tr>
<tr>
<td>The Reduction of NiO-YSZ Anode Precursor and Its Effect on the</td>
<td>181</td>
</tr>
<tr>
<td>Microstructure and Elastic Properties at Ambient and Elevated</td>
<td></td>
</tr>
<tr>
<td>Temperatures</td>
<td></td>
</tr>
<tr>
<td>Thangamani Nithyanantham, Saraswathi Nambiappan Thangavel,</td>
<td></td>
</tr>
<tr>
<td>Somnath Biswas, and Sukumar Bandopadhyay</td>
<td></td>
</tr>
<tr>
<td>Microstructure Analysis on Network-Structure Formation of SOFC Anode</td>
<td>193</td>
</tr>
<tr>
<td>from NiO-SDC Composite Particles Prepared by Spray Pyrolysis</td>
<td></td>
</tr>
<tr>
<td>Technique</td>
<td></td>
</tr>
<tr>
<td>Hiroyuki Yoshida, Mitsunobu Kawano, Koji Hashino, Toru Inagaki,</td>
<td></td>
</tr>
<tr>
<td>Seiichi Suda, Koichi Kawahara, Hiroshi Ijichi, and Hideyuki Nagahara</td>
<td></td>
</tr>
<tr>
<td>Functionally Graded Composite Electrodes for Advanced Anode-Supported</td>
<td>203</td>
</tr>
<tr>
<td>Intermediate-Temperature SOFC</td>
<td></td>
</tr>
<tr>
<td>Juan L. Sepulveda, Raouf O. Loutfy, Sekyung Chang, Peiwen Li, and</td>
<td></td>
</tr>
<tr>
<td>Ananth Kotwal</td>
<td></td>
</tr>
<tr>
<td>ELECTROLYTES</td>
<td></td>
</tr>
<tr>
<td>High Efficiency Lanthanide Doped Ceria-Zirconia Layered Electrolyte</td>
<td>217</td>
</tr>
<tr>
<td>for SOFC</td>
<td></td>
</tr>
<tr>
<td>Juan L. Sepulveda, Sekyung Chang, and Raouf O. Loutfy</td>
<td></td>
</tr>
<tr>
<td>Oxygen Ion Conductance in Epitaxially Grown Thin Film Electrolytes</td>
<td>229</td>
</tr>
<tr>
<td>S. Thevuthasan, Z. Yu, S. Kuchibhatla, L.V. Saraf, O. A. Marina,</td>
<td></td>
</tr>
<tr>
<td>V. Shuttthanandan, P. Nachimuthu, and C. M. Wang</td>
<td></td>
</tr>
<tr>
<td>INTERCONNECTS</td>
<td></td>
</tr>
<tr>
<td>Development of New Type Current Collector for Solid Oxide Fuel Cell</td>
<td>243</td>
</tr>
<tr>
<td>Tsuneji Kameda, Kentaro Matsunaga, Masato Yoshino, Takayuki Fukasawa,</td>
<td></td>
</tr>
<tr>
<td>Norikazu Osada, Masahiko Yamada, and Yoshiyasu Itoh</td>
<td></td>
</tr>
<tr>
<td>Electrical Conductivity and Oxidation Studies of Ceramic-Intermetallic</td>
<td>249</td>
</tr>
<tr>
<td>Materials for SOFC Interconnect Application</td>
<td></td>
</tr>
<tr>
<td>Yukun Pang, Hua Xie, and Rasit Koc</td>
<td></td>
</tr>
</tbody>
</table>
SEALS

Improvement in Interface Resistance of Conductive Gas-Tight Sealing Materials for Stacking Micro-SOFC
Seiichi Suda, Koichi Kawahara, Kaori Jono, and Masahiko Matsumiya

ELECTROLYZER

Carbon Dioxide Electrolysis for Production of Synthesis Gas in Solid Oxide Electrolysis Cells
Sune Dalgaard Ebbesen and Mogens Mogensen

Author Index
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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Narottam P. Bansal  
*NASA Glenn Research Center*
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
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.


Tatsuki Ohji and Andrew A. Wereszczak, Volume Editors
July 2008

xii  Advances in Solid Oxide Fuel Cells IV
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 (SOFCs) 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 Li2SO4 in the dual phase of Li2SO4-Al2O3-Ag as a hydrogen permeation reactor, we noticed the H2S formation in H2 which was further confirmed in a
Research Activities and Progress on Solid Oxide Fuel Cells at USTC

H₂/O₂ cell with Li₂SO₄∥Al₂O₃∥ as electrolyte[2] due to the following reaction occurred,

\[ \text{LiSO}_4 + 3 \text{H}_2 \rightarrow \text{H}_2\text{SO}_4 + 3 \text{H}_2\text{O} \]

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% Al₂O₃ to enhance the strength) as electrolyte to assemble H₂ and O₂ concentration cells and found the remarkable O²⁻/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∥SrCl₂ with doped ceria exhibited even higher conductivity at the temperature above the eutectic point at 485°C for 53mol.% LiCl∥47mol.% SrCl₂. As can be seen from the V-I and P-I curves of a cell consisted of Ni-GDC anode, LiCl-SrCl₂-GDC (Gd doped CeO₂) electrolyte (0.40mm thick) and LiNiO₂ 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/cm² in 460-550°C [4]. And another cell showed the even better performance with a peak power density of 500 mW/cm² at 625°C [5]. The data were remarkably higher than the best record at that time, 140 mW/cm² at 500°C by Doshi et. al., with the cell based on GDC electrolyte about 30 μm in thickness [7].

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 (La₀.₆Sr₀.₄Ga₉₀₅₋ₓMgₓO₃₋ₓ), 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].

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 LaGaO3 and doped CeO2 (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 La0.8Sr0.2Ga0.8Mg0.2O3 (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 La0.8Sr0.2Ga0.8Ni0.2O3 as a compatible anode, the cell with LSGM electrolyte of 0.5mm provide a power density of 270 mW/cm2 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 CeO2, Ce0.8Sm0.2O2.5 or Ce0.85Sm0.15O2.6, 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.

Fig.2 The conductivity of the composite electrolyte

![Fig.2 The conductivity of the composite electrolyte](image-url)
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/cm² 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 next 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 either 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 Ce₀.₈Y₂O₁₉ electrolyte of 15μm and got a pretty high cell power density of 360 mW/cm² 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 planer and tubular SOFCs [24-26].

<table>
<thead>
<tr>
<th>Technique for thin membranes</th>
<th>Electrolyte material</th>
<th>Sintering temperature (°C)</th>
<th>Thickness (μm)</th>
<th>Power density (mW/cm²)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tape casting</td>
<td>SDC/NiO-SDC</td>
<td>1400</td>
<td>50</td>
<td>260 (700°C)</td>
<td>[21]</td>
</tr>
<tr>
<td>Screen printing</td>
<td>Ce₀.₈Y₂O₁₉</td>
<td>1350</td>
<td>15</td>
<td>360 (650°C)</td>
<td>[22]</td>
</tr>
<tr>
<td>Spin-coating</td>
<td>YSZ/Ni-SDC</td>
<td>1300</td>
<td>12</td>
<td>535 (750°C)</td>
<td>[23]</td>
</tr>
<tr>
<td>Dip-coating</td>
<td>YSZ</td>
<td>1400</td>
<td>30</td>
<td>190 (800°C)</td>
<td>[24]</td>
</tr>
<tr>
<td>Electrostatic spray</td>
<td>YSZ</td>
<td>1400</td>
<td>15</td>
<td>315 (800°C)</td>
<td>[25]</td>
</tr>
<tr>
<td>Suspension spray</td>
<td>YSZ</td>
<td>1400</td>
<td>10</td>
<td>837 (800°C)</td>
<td>[26]</td>
</tr>
</tbody>
</table>

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/cm² 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/cm² at 800°C, but still 214 mW/cm² 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/cm² at 650°C and 187 mW/cm² 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.
natural gas and biomass gas and got a peak power density of over 300mW/cm² 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/cm² SDC coating was operated in CH₄ 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 CH₄ as fuel, operated at 0.5V and 600°C](image)

Similar to the anode structure described above, the cathode side can be improved by the same idea. With nano-LSC (La₀.₆Sr₀.₄Co₃O₇) 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 $2.4 \Omega \text{cm}^2$ to $3.5 \Omega \text{cm}^2$ during the thermal cycles between 500-800°C for 20 times in 20 days and further increased to $12.5 \Omega \text{cm}^2$ during thermal cycles of 10 times from room temperature to 800°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 ($0.30 \Omega \text{cm}^2$) 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.

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$_2$O) 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.
The tubular anode (Ni-YSZ) supports has been fabricated by extrusion, gel-casting [37] and the techniques described above have been employed to make single PEN cells on the tubular anode support [24-26]. Fig. 10 shows the morphology of a small round tubular single cell and its performance [40]. The cell power density was improved very much, when the interface modification was made on anode and cathode [38]. As we can see that the peak power density (Fig.10-A) of the cell with YSZ electrolyte membrane in 20μm is over 400 mW/cm² at 850°C and gradually decreased to 270 mW/cm² at 700°C, indicating the smaller ASR contribution to the total cell resistance [41]. The SEM picture of the cell section (Fig.10-B) shows very intimately electrode interfaces that display the better cell performance.

![Fig 9](image.png)

Fig 9 - China patent ZL02113198.8

![Fig 10](image.png)

Fig 10 the cell performance and microstructure of a tubular cell made by cost effective process [40, 41]

A) V-I, P-I curves of a tubular Cell fueled with H₂
B) Picture of the cell made by dip-coating, and
C) Section view of the cell, showing the very well coherent electrode interfaces.
For planned SOFCs, the metal based materials could be chosen to make interconnect. But for the stacks of tubular cells, the interconnect layer must be ceramic and directly prepared on the tubes. Doped chromates, typically La$_{0.7}$Ca$_{0.3}$Cr$_3$ (LCC) and La$_{0.7}$Sr$_{0.3}$CrO$_3$ (LSC), exhibit excellent properties, particular high stability in both oxidant and reducing ambient. But two major shortcomings: lower electric conductivity and too high temperature for densification, hinder its applications, especially for cost effective fabrication of IT-SOFCs. To realize the tubular cell stacks we have done much effort to search new material systems and obtained progress [42-50]:

1) Full or partial substitution of La in La$_{0.7}$Ca$_{0.3}$Cr$_3$O$_7$ -LCC-, the best interconnect ceramics, by other rare earth element (Gd, Pr, Nd, Tb) much increased the conductivity of the materials. For instance, the conductivity of Gd$_{0.7}$Ca$_{0.3}$Cr$_3$O$_7$ -GCC- at 700°C in air was 24 S/cm -30% higher than LCC 18.5 S/cm and 130% higher than LSC 10.4 S/cm. The more important is that its conductivities in H$_2$ are 8.4 S/cm at 900°C and 6 S/cm at 500°C, which are much higher than that reported in literature, e.g. 1.5 S/cm at 900°C for La$_{0.7}$Sr$_{0.3}$CrO$_3$ reported by Tao et al.[51].

2) It was found that doping DCO (GDC, SDC, YDC) into LCC created a new structure or form a composite, which displayed extremely high conductivity [43-47]. As listed in Table 2, the conductivity values for samples of LCC doped with 2-10 % SDC were 5-38 time higher than LCC and the oxygen permeation and thermal expansion coefficient remain changeless compared with LCC. Another interesting point was that the samples showed a relative density of 97-98%, indicating that the sintering ability of the materials was also much improved. This was probably related to the nano-size particle prepared by the soft chemistry method [42].

3) More recently, the sintering temperature for densification has been further lowered by putting sintering adds [48,49] and controlling B site deficiency [50]. The results showed that Zn doped LCC sintered at 1250 1400°C for 5hrs could obtain 96-98 relative density and its conductivity reached 45.7 S cm$^{-1}$ at 800°C and 34.5 S cm$^{-1}$ at 500°C in air, and 2.06-6.1 S cm$^{-1}$in H$_2$, respectively.

These results illustrated that the new material systems have resolved the two major problems of the conventional LCC or LSC, and can well meet the requirements for tubular SOFC stacks. Particularly, the ceramic interconnect can be fabricated by utilizing low cost ceramic processing and co-firing at 1350 1400°C.

Table 2. Properties of LCC with adding SDC as new interconnect ceramics [45]

<table>
<thead>
<tr>
<th>SDC content (weight %)</th>
<th>Relative density (%)</th>
<th>TEC at 1000°C (10$^{-6}$ K$^{-1}$)</th>
<th>The oxygen permeation flux (mol/3 cm$^2$)</th>
<th>Electrical conductivity at 800°C (S/cm$^{-1}$) in air</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>97.4</td>
<td>11.32</td>
<td>6.51×10$^{-10}$</td>
<td>17.27</td>
</tr>
<tr>
<td>2</td>
<td>97.5</td>
<td>11.33</td>
<td>6.76×10$^{-10}$</td>
<td>180.25</td>
</tr>
<tr>
<td>4</td>
<td>97.7</td>
<td>11.65</td>
<td>2.33×10$^{-9}$</td>
<td>341.76</td>
</tr>
<tr>
<td>5</td>
<td>97.9</td>
<td>11.93</td>
<td>4.60×10$^{-9}$</td>
<td>667.81</td>
</tr>
<tr>
<td>6</td>
<td>98.1</td>
<td>12.22</td>
<td>5.23×10$^{-9}$</td>
<td>127.72</td>
</tr>
<tr>
<td>8</td>
<td>98.4</td>
<td>12.24</td>
<td>6.31×10$^{-9}$</td>
<td>129.09</td>
</tr>
<tr>
<td>10</td>
<td>98.7</td>
<td>12.46</td>
<td>7.88×10$^{-9}$</td>
<td>96.18</td>
</tr>
</tbody>
</table>
5. Ammonia fueled CMFCs with proton or oxide ion electrolytes

Industrial Liquid ammonia directly fueled CMFCs has been one of the research activities recent years at USTC Lab. [52-57], initiated by “counter main-stream consideration in R & D of SOFCs”, noticing that great efforts have been made to search ways to prepare pure H₂ for PEMFC and to resolve the anode coking problem for SOFCs. Nowadays exploring proper fuels seems to be crucial for the commercialization of SOFCs since there are significant difficulties for pure hydrogen and hydrocarbons, the now-extensively used fuels for SOFCs. Pure hydrogen is both expensive and hard to store or transport; hydrocarbons will cause a severe coking for traditional Ni anode of SOFCs, and little progress has been made to find replacements for Ni. Ammonia is a good hydrogen carrier and a less concerned feedstock for SOFCs, and will be a nice substitute for hydrogen and hydrocarbons in fuel cells for the following reasons:

- High energy density. It contains 75 mol % H and the volumetric energy density of liquid ammonia is about 9 x 10⁶ kJ m⁻³, higher than that of liquid hydrogen.
- Relative safe. Ammonia is less flammable compared with other fuels and the leakage of ammonia can be easily detected by the human nose under 1 ppm.
- Great suitability to CMFCs-O or CMFCs-H [55]. There are no concerns about anode coking and un-stability of BaCeO₃ based proton electrolytes due to the CO₂ existence, because of no carbon species in anode apartment and in case of CMFC-H cases the H₂O formed at cathode-electrolyte interface would hinder the diffusion of CO₂ possibly existed in air as oxidant to electrolyte.
- The right candidate of liquid fuel for distributed and portable SOFC/CMFCs devices, at least at the present stage when the coking problem of hydrocarbon fuels is not yet resolved.
- Low price and good competition for CMFC marketing. The price of ammonia is as competitive as hydrocarbons, 30-40 % of LPG and petroleum.

Attempt to use NH₃ as fuel for YSZ based SOFC was first made by Wojcika et al. [58], but was paid little attention, probably because of the lower cell performance (about 50 mW cm⁻² at 800°C due to the thick YSZ electrolyte supported cell with Pt as electrode) and the worry that the toxic NOₓ may be produced:

\[ 2\text{NH}_3 + 5\text{O}^2^- = 2\text{NO} + 3\text{H}_2\text{O} + 10\text{e}^- \]

Our first work was based on a full ceramic cell of anode supported thin proton electrolyte (BaCe₀₉Gd₀₂O₁₉, 50µm thick) and achieved a maximum power density of 355 mW cm⁻² at 700°C, which was in the range accepted for applications. For comparison, cells were also tested at 700°C with hydrogen as fuel, where the power density was about 371mW/cm² [52]. The subsequent research works were trying to answer the interested problems, such as NH₃ usage efficiency, the possible NOₓ formation in case of oxide ion electrolyte cell (CMFC-O) as well as the performance with different electrolytes in various thickness [53-57]. The results have been fairly positive and attractive, which are summarized below:
As theoretically expected, the Ni based anode was the effective catalysis for NH3 thermal decomposition, and conversion of NH3 into H2 and N2 was experimentally determined to be completed (> 99%) above 500°C, depending on the gas flow rate. The smaller the gas flow rate, the more completely the ammonia decomposes. [53]

It is proved by from the experimental OCV data of the cells that it is the H2 instead of NH3 itself responsible for anode process in both CMFC-H and CMFC-O [52-57].

For CMFC-O fueled by NH3, there was no NOx detected and it was consistent to the theoretical prediction that on anode it is O2' ions from cathode, which exhibit much less oxidative reactivity than oxygen molecules or atoms [54].

For CMFCs with a thicker electrolyte membrane thus have lower cell power density (maximum 200-800 mW/cm²), direct liquid NH3 fueled cells may provide power density quite close to the H2 fueled cell [52-56], that means higher than the expected 75% power density of H2 cells. While for the cells with very thin electrolyte the cell performance could very close to the theoretical ratio, 0.75:1.0 for a cell with NH3 and H2 as fuel, respectively [57].

![Fig. 11](image_url) (a) Cell performance with NH3 fuel at various temperatures, and (b) Impedance spectra of the cell with H2 and NH3 under open-circuit conditions.

Shown in Fig. 11 is the result of a cell with SDC electrolyte (10µm thick). We may see that the maximum power density is 1190 mW/cm² at 650°C, which is only 63.8% of the value for H2 fueled cell (see Fig.4) and an obvious concentration polarization behavior is observed. At lower operation temperatures (600–550°C), the V–I curves of the cell are rather strange in that they fall down rapidly at quite small current densities resulting in the peak power densities much lower than the expected. This phenomenon may be attributed to the incomplete decomposition of NH3 gas in the anode compartment as well as the mass transfer behavior much different from the H2 cell, because that the cell resistances measured in situ by impedance spectroscopy did not have much difference, as presented in Fig.11(B) [57].
Compared with CMFC-O, CMFCs with doped BaCeO₃ proton electrolytes showed some unique characteristics:

- The cell OCV values are around 1.0V in temperature range of 500-750°C, which are quite close to theoretical EMF value, indicating less electronic conduction of these proton conductors than SDC or GDC.
- There is almost no activation polarization on V-I curves, implying the quick charge transfer on the electrode interfaces.
- The conductivity activation energies obtained from the slopes of V-I curves were similar to SDC cells and even lower in lower temperature range.

These properties should be certainly related to the structure and the carrier transfer nature in the CMFC-H systems that are worth to study further [56].

6. Conclusion Remarks
The article has recalled the research activities and the progresses on SOFC/CMFCs at USTC and the following remarks are made:

1. Solid electrolyte materials as the core material of SOFCs have been extensively studied, including salt-oxide composites, doped ceria and doped BaCeO₃ proton conductors. Among them proton conductive materials including chloride -ceria composite and doped barium cerates have some excellent characteristics worth to investigate further. For commercialization of SOFCs/CMFCs, YSZ, SDC as well as the newly developed doped BaCeO₃ are preferred.

2. CMFCs with thin membrane electrolyte (YSZ, SDC or doped BaCeO₃) in thickness of around 10µm have been routinely fabricated by cost effective ceramic processing and showed fairly good performance in intermediate temperature range (600-850°C).

3. The interesting results based on new electrode materials, unique electrode structure designs and nano-technique processing have extensively improved the cell performance and studies are on going.

4. An advanced tubular CMFC design was proposed, and the cost effective fabrication process as well as the interconnect ceramics with high performance have been developed in order to promote the CMFC commercialization.

5. NH₃ fueled SOFCs/CMFCs with ether oxide ion or proton electrolytes have demonstrated satisfied performance and would be great of promise to perform the distributed CMFC devices without the need to concern the problems such like coking on Ni-based anode and the degradation for doped Barium cerate based CMFCs.

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