R&D FOR LOW TEMPERATURE (300 TO 600°C) SOFCs

Bin Zhu\textsuperscript{a,b}, Juncai Sun\textsuperscript{c}, Zifeng Ma\textsuperscript{d}, Qizhao Lin\textsuperscript{e}, Zhigang Zhu\textsuperscript{f}, Zongqiang Mao\textsuperscript{b}

\textsuperscript{a}Department of Chemical Engineering & Technology
Royal Institute of Technology (KTH), S-100 44 Stockholm, Sweden

\textsuperscript{b}China Association for Hydrogen Energy
Qinghua University, Beijing, P. R. China

\textsuperscript{c}Institute of Materials and Technology
Dalian Maritime University, Dalian 116026, P. R. China

\textsuperscript{d}Department of Chemical Engineering & Technology
Shanghai Jiaotong University, Shanghai, P. R. China

\textsuperscript{e}Department of Thermal Science and Energy Engineering
University of Science and Technology of China, 20026, Hefei, Anhui, P. R. China

\textsuperscript{f}Göta Technology Developer International
S-171 60, Solna, Sweden

ABSTRACT

A Swedish-Chinese research framework has been established targeting for low temperature solid oxide fuel cells (LTSOFCs, 300-650°C) based on ceria-based composites. The ceria-based composite electrolytes have excellent ionic conductivity of 0.01 to 1 S\textsuperscript{-1} cm\textsuperscript{-1} at temperatures 300 to 650°C. For these electrolytes, new compatible electrode materials have been investigated, especially nickel and copper-based compounds. These electrolytes and electrodes were used to construct LTSOFCs which demonstrated a performance from 100 to 1000 mW\textsuperscript{-1} cm\textsuperscript{2} at temperatures between 400 and 650°C. This paper reports recent progress on LTSOFC R&D.

INTRODUCTION

There is a strong interest in fuel cell R&D to develop low temperature (300-650°C) solid oxide fuel cells (LTSOFCs). These fuel cells are expected to present a strong competition to other fuel cell technologies for automobile and stationary applications. In order to
develop cost-competitive SOFCs, many studies have been oriented toward reducing SOFC's operation temperature, either by using thin film technology to minimise the resistance of the yttria-stabilized zirconia (YSZ) electrolyte (1-4) or by using alternative electrolyte materials, such as doped ceria, etc. (5-12). All these efforts have, however, limitations due to the deficiency of technology and instability of the materials. For developing new generation SOFC technology for automobile or various portable applications, a fuel cell operation temperature below 500°C is preferable. In order to realise such low temperature SOFCs, new materials are the key. Although there are activities, by using thin film technology, to develop ITSOFCs based on YSZ or doped ceria etc. electrolyte materials, these efforts do not offer a solution for developing high performance LTSOFCs for operation below 600°C.

Our approach is to develop new hybrid and nanocomposite materials based on rare earth oxides both for electrolytes and the compatible electrodes. Low temperature, say 300 to 600°C, operation for SOFCs is realized based on these materials. The materials were prepared usually by mixing different cationic doped ceria, e.g., gadolinium doped ceria (GDC), yttrium doped ceria (YDC) and samaria-doped ceria (SDC) with various salts, e.g., chlorides, fluorides, hydroxides and carbonates based on ceria. The materials contain at least two phases, e.g., the ceria phase and the salt phase. Studies were carried out on the GDC-NaCl (13), GDC-LiCl-SrCl₂ (14), GDC-NaOH (14), and carbonate (e.g., MC₀₃, M=Ca, Ba, Sr) composites, demonstrating promising results for LTSOFC applications (14, 15). These materials have combined oxygen ion and proton conductivity, varying from 0.01 to 1 Scm⁻¹ between 300 and 600°C. With these materials, LTSOFCs were constructed. The single cell performance of 0.1 to 1 Wcm⁻² was obtained in the temperature region of 300 to 600°C. The cell could even function at as low a temperature as 200°C. These results have demonstrated a new generation SOFC technology. Based on this, following engineering and system work has been carried out in our Swedish-Chinese bilateral cooperation framework involving a number of Swedish and Chinese universities/institutes:

i. Materials R&D: functional ceria-salt composites for both electrolyte and electrodes;
ii. LTSOFC technologies: involving material shaping, fabrication of LTSOFC components and construction of devices;
iii. Theoretical simulation and modelling;
iv. Stack engineering and development.

EXPERIMENTAL

Preparation and Characterization of Materials

Electrolyte materials of the type SDC-M₂CO₃, (M= Li, Na, K) were prepared using following two steps.
Step 1. Doped ceria, e.g., samaria-doped ceria (SDC) was prepared through wet chemical route, i.e., co-precipitation approach. Raw chemicals used were as follows: cerium nitrate hexahydrate and samarium(III) nitrate hexahydrate (supplied by Sigma-Aldrich). These chemicals were prepared as 1 M solutions. Then the samarium(III) nitrate hexahydrate solution was mixed with the cerium nitrate hexahydrate solution according to the desired molar ratios, e.g., 20 mol% Sm in ceria. An appropriate amount of oxalate acid solution (2M) was added to prepare the SDC precursor in the oxalate state. The precipitate was rinsed several times in deionized water, followed by ethanol washing for several times in order to remove water from the particle surfaces. The obtained precipitates were dried in an oven at 100°C overnight and then ground in a mortar. The resulting powder was sintered at various temperatures between 300 and 600°C for 1 hour. The sintered powders were ground for use.

Step 2. SDC and M2CO3 (M = Li, Na, K) powders were prepared by mixing SDC and carbonates according to the weight ratio of 80 wt% SDC: 20 wt% binary carbonates, e.g., Li-Na, Li-K, or Na-K carbonates with a typical composition like 67 mol% Li2CO3 to 33 mol% Na2CO3. The mixtures of SDC and binary carbonates were ground, then sintered at 650°C for 0.5-1.0 hours. The sintered sample was ground again for various electrical and fuel cell measurements.

The crystal structure and microstructures, the morphology and the composition, of the samples were analyzed by X-ray diffractometer (XRD), scanning electron microscopy (SEM), scanning probe microscopy (SPM) and energy dispersion spectroscopy (EDS). The electrical properties were studied using a.c. impedance analysis, and were also directly characterised by fuel cell measurements.

Various techniques were developed to fabricate fuel cell components via wet chemical and physical routes in parallel. The wet chemical routes involved screen printing, tape-casting and sol-gel. The physical preparations included sputter deposition, plasma spray and explosion spray. In addition, a hot-pressing technique was also used to directly construct the fuel cell PEN assemblies by loading a mold with the powders of anode followed successively by the electrolyte and the cathode, all being pressed in one step to form a complete fuel cell assembly for measurements.

The LTSOFC stack was constructed based on the common planar type SOFC stack technology. Stainless steel was employed for the bipolar plates and stack materials. The cathode chamber (air side) of the bipolar plate/stack was covered by a silver thin film to prevent the oxidation of stainless steel in air and high temperature operation. The fuel cells were tested between 200 to 650°C. Hydrogen was used as the fuel in the most cases, air as the oxidant. The gas (fuel and air) flows were controlled between 100-200 mL/min under 1 atm pressure.
RESULTS AND DISCUSSION

Material Phase and Microstructures

Pure SDC has a fluorite structure, which can be crystallized from the SDC oxalate precursor above 350°C. A temperature of 400°C is sufficient to make SDC crystalline. Figure 1 shows the structure of the SDC sample heat-treated at various temperatures showing changes from the amorphous/gel state; see Fig. 1 (a), in the precursor state, to the crystalline state at 400°C, (b) and then remaining in crystalline state at higher temperatures, see (d) for 560°C. The particle size grows with increasing sintering temperature, resulting in sharper and narrower XRD peaks. In Fig. 1 the sharpest XRD peaks are observed for 560°C. From this narrowing effect of the XRD peaks we can calculate the corresponding crystalline particle sizes growing from 20 nm (350°C), to 50 nm (400°C) and then to 90 nm (560°C), respectively.

Figure 1. XRD patterns for SDC and SDC-20NLCO at various temperatures; (a) SDC precursor; (b) SDC at 400°C; (c) SDC-20NLCO at 400°C; (d) SDC at 560°C.

For the SDC composites, the introduction of the carbonates does not change the SDC phase structure. For example, in the SDC-carbonates composites, a typical composition: 80 wt% SDC: 20 wt% (67 mol% Li₂CO₃ : 33 mol% Na₂CO₃) written as SDC-20NLCO, only one set of SDC XRD pattern is observed, which is the same as (b). In this case, the NLCO may be assumed to exist as an amorphous phase co-existing with SDC, highly likely as cover on SDC particles because during the heat-treatment the NLCO can melt and be coated on SDC particles. On the other hand, there are no new XRD patterns observed for the SDC-20NLCO, which means there is neither a chemical reaction nor any intermediate compound between SDC and the NLCO materials/phases. The microstructure of the SDC-20NLCO was further studied by SEM. Significant changes in particle topography can be seen from the SEM analysis as shown in Figure 2. In the SEM analysis the nanograin size cannot be clearly and directly observed because the particles are always formed in an aggregate during the preparation and a heat-treatment process.
For low temperatures, e.g. at 400°C, heat-treatment, see Fig. 2 (a), a clear separated interface and individual particles can be identified. However, a homogenous composite bulk was formed without clear interfaces for the sample heated at 500°C, see Fig. 2 (b). The particle (aggregate) morphologies are quite different at different heat-treatment temperatures. For the 500°C heat-treatment, the surface morphology of the SDC-20NLCO composite particles (aggregate) appears to form a homogeneous bulk which may be caused by the molten NLCO covering homogeneously the SDC particle surfaces, thus the particles form as a composite on a SDC core; while for temperature below the NLCO melting point, e.g. 400°C, the particles (aggregate) look finer with clear interfaces, see Fig. 2 (a). These studies on the phases and microstructures help us to better understand the ion-conduction and fuel cell processes and performances for the SDC-carbonate composite materials.

**New Compatible Electrodes Development**

Corresponding to SDC-carbonate or other ceria-salt composite electrolytes, various new compatible electrode materials were developed. Most interesting materials are nickel-based or nickel-free copper-based metal oxides/composites. Typical examples are NiO-CuOₓ, CuOₓ-FeOₓ, CeO₂-CuOₓ etc. These electrode materials can act as fuel cell anodes in reducing atmosphere, while in the oxidised state the same materials can be used as fuel cell cathodes. LTSOFCs using these electrode materials for the anode and the cathode reached a power density between 100 and 1000 mWcm⁻² in the temperature region 300 to 600°C. Typical results are presented below. The new electrodes can be manufactured inexpensively and the copper-based electrodes are anticipated to be beneficial for direct hydrocarbon fuel operation in order to avoid carbon deposition problem.

**Fabrication Techniques for LTSOFCs**

When the sputtered ion or atom or atomic cluster deposits on a substrate, the cooling rate substantially determines the film structure. The cooling rate of atoms and/or atomic clusters in the sputtering process is fast enough to hamper atoms from moving. If the
substrate temperature is higher, the structure can change from amorphous to nanocrystalline and finally to polycrystalline. The nanocrystalline structure is, in fact, the transitional state between amorphous and crystalline compound, which may also be obtained from heating the amorphous material at a specific temperature, depending on particular electrolyte material. As a LTSOFC composite electrolyte, the nanocrystalline structure may provide the electrolyte with high ion conductivity. It may be stable at the ITSOFC operation temperature due to co-existence of the second composite salt or other nanooxide phase material. In this case, one nanophase, e.g., crystalline ceria, will precipitate first from the amorphous parent as a lattice skeleton in the second phase material, to form a homogenous composite material. This is an interesting concept to develop nanocomposite thin film electrolyte materials.

When the electrolyte is deposited by plasma spray, the surface morphology is coarser compared to that of sputtered film. However, the surface morphology of the plasma spray films can be improved by optimisation of the material, apparatus and operation parameters, such as proper sizes of the powder particle, spray power and powder flowing rate as well as distance of the specimen from the spray nozzle.

The explosive spray was also used to fabricate the electrolyte film on the anode-support substrates. In this study, we found the thin film preparation via spray techniques, e.g., explosion spray or plasma spray, has much to do with the sample particle size. It requires often a particle coarsening technique. The anode substrate was fabricated by using the explosion spray on a Ni-foam, the anode was made afterwards by tape-casting followed the plasma deposited electrolyte layer, and the cathode fabricated on the electrolyte surface.

These three methods are applicable to the fabrication of the electrolyte film in different film thicknesses. The ion beam sputter deposition makes the best quality thin film in structure and density than plasma spray and explosive spray. It is suitable for fabricating thin film because of its low deposition rate and growing film rate. The plasma spray and explosive spray have a much higher growing film rate than that the sputtering technique, and are suitable for fabricating thick films. These three methods can be very useful for fabricating functional ITSOFC components with high performances.

In parallel, the tape-casting technique was developed to prepare the components for the ceria-salt composite electrolyte and electrodes with an acrylic latex binder in a water based system. The fuel cell components for the anode support (about 1.0 mm thick) with a 0.2 mm thick ceria-composite electrolyte were prepared. The size for these tape-casting components can be scaled-up currently to an area of 100 x 100 mm. The actual functional components measured for fuel cells had a diameter of 50 mm. However, at present the fuel cell performance, e.g., power density, obtained by using 50 mm diameter components, is far below than that of smaller size fuel cells, e.g., 13 and 20 mm in diameter, made by the hot-pressing. There are some technical problems associated with
the scale-up process. Major problem at present is to obtain high density electrolyte. It is very likely the tape-casting technique alone is difficult to prepare pore-free, gas-tight and dense electrolyte layer on the porous electrode support (> 30% porosity). In order to solve this problem, the sol-gel process was used to modify further the tape-cast electrolyte surface. It was found that the power density of fuel cells with the sol-gel modification of electrolyte was significantly improved compared to that of without modification. In addition, using the sol-gel process, we have successfully developed various functional ceria and doped ceria-composite thin films with a nanostructure and a thickness in the μm level. Typical thin films prepared by the sol-gel process are CeO2-Al2O3, CeO2-SiO2, doped ceria (e.g., GDC)-alumina, etc. with promising application for LT-SOFCs. These ceria-composite thin films showed significant conductivity enhancement compared to their bulk materials with identical chemical compositions. Screen-printing was usually used to fabricate the electrode layers/films combined with the tape-cast electrolyte to complete PEN assembly fabrication.

**LT-SOFC Performance**

Higher temperature (above 400 to 600°C) performance for the SDC-20 NLCO fuel cells are reported elsewhere (14). Low temperature (below 400°C) studies for the SDC-20NLCO fuel cells are discussed here. The SDC-20NLCO composites have sufficient conductivities at low temperatures, e.g., greater than $10^{-2}$ S cm$^{-1}$ for temperatures above 300°C (14). In order to develop high performance LT-SOFCs at lower temperatures, e.g., below 400°C, we have to use the compatible catalytic electrodes. Our goal is to develop catalytic and functional electrode materials without noble elements. In recent work, we have successfully obtained such high performance electrodes through a novel microwave-synthesis procedure. Figure 3 shows some typical I-V and I-P characteristics for a cell using the SDC-20NLCO as the electrolyte between 200 and 400°C. The cell power output reached 250 mW cm$^{-2}$ (the peak value) at 400°C, and 155 mW cm$^{-2}$ at 320°C. The cell could even function as a fuel cell at as low a temperature as 200°C.

![Figure 3. The SDC-20NLCO LT-SOFC performance at temperatures below 400°C. Fuel H$_2$, oxidant: air, gas flow: 80 to 120 ml/min, gas pressure: 1 atm.](image-url)
Nanotechnology for preparation of ceria-based composites is of high value, especially to control the microstructure. The host oxide structure-dependent properties of these ceria-based composites prepared by the nanotechnology are significantly different from those of the conventional bulk materials in many cases (16,17). High defect concentration existing in the nanostructured host oxide phase can provide a large number of active sites for ion conduction as well as gas-solid catalysis. In addition, high diffusivity through nanometer-sized inter-phase boundaries promotes fast kinetics of catalyst activation and ion transport. On the other hand, the ceria-salt-composites have a hybrid conduction of oxygen ion (from ceria) and proton conduction (from the salt). The addition of proton conduction has dual effects. On one hand, it enhances the conductivity; and on the other hand, it may promote the electrode reaction and the kinetics between the electrolyte and electrode interfaces, consequently enhancing the current exchange rate resulting in the high current outputs. In fact the electrode-electrolyte interfaces are keys to determine the fuel cell performance.

A two-cell stack was constructed using these new materials based on the common planar type SOFC stack technology, and tested. The tested single cell size was 20 mm in diameter, and two single cells were connected in series. Figure 4 shows this stack performance, see curve (b), in contrast to the single cell, curve (a). As expected this two-cell stack reached almost double the power output than that of the single cell.

LTSOFCs based on these ceria-composite electrolytes and compatible electrodes have also demonstrated wide fuel flexibility for direct operation on many fuels, such as natural gas, biomass gas, coal gas, alcohol and ammonia etc. (18). In addition, these new materials are extremely cost-effective.

Figure 4. Cell performance for a two-cell stack at 600°C H₂/air operation.

992 Electrochemical Society Proceedings Volume 2003-07
CONCLUSIONS

Material R&D focusing on LT-SOFCs has concentrated on various ceria-based composite electrolytes and compatible electrode materials. These new materials have been developed based on nanotechnology, ceramic composite, and hybrid conducting material technologies. The electrolytes have conductivities in the region of 0.01 - 1.0 S cm\(^{-1}\) in the low temperature region.

Being different from the conventional YSZ and ceria materials used in the conventional SOFCs, the new ceria-based composite materials are two-phase composite ceramics with both oxygen ion and proton conduction. In the ceria-salt composites, one phase, e.g., doped ceria, has high oxygen ion conductivity, while the other phase, the salt, has significant proton conductivity. Certain amount of proton conduction promotes the electrode reaction and the kinetics between the electrolyte and electrode interfaces, consequently enhancing the current exchange rate resulting in high current outputs.

Advanced ceria-composite electrolytes combined with the high performance and compatible electrodes have made excellent LT-SOFCs, the cells functioning at as low a temperature as 200°C.

ACKNOWLEDGEMENTS

One of the authors would like to sincerely thank Prof. B.-E. Mellander, Dr. I. Albinsson and Mr. Roshan Bokalawela, Physics and Engineering Physics, Chalmers University of Technology, Sweden, for supporting conductivity measurements for electrode materials through a research cooperation under the Swedish-Chinese bilateral co-operation framework.

This work is supported by the Swedish Research Council (VR), the Swedish National Energy Administration (STEM), the Swedish Agency for Innovation Systems (VINNOVA) and Carl Tryggers Stiftelse for Vetenskap Forskning (CTS). Further financial support is received from a joint venture between Goeta and Fucellco Inc., USA.

REFERENCES

1. T. Tsai, E. Perry, S. Barnet, J. Electrochem. Soc. 144, L130 (1997).
2. E. P. Murray, T. Tsai, S. A. Barnett, Nature, 400, 649 (1999).
3. P. Charpentier, P. Fragnaud, D. M. Schleich, C. Lunot, Ionics, 2, 312 (1996).
4. S. de Souza, S. J. Visco, L. C. DeJonghe, Solid State Ionics, 98, 57 (1997).
5. B. C. H. Steele, Solid State Ionics, 92, 86 (1996).
6. W. Bakker, C. Milliken, J. Hartvigsen, S. Elangovan, A. Khandkar, in SOFC-V, U. Stimming, S. C. Singhal, H. Tagawa, W. Lehnert, Editors, PV 97, p. 254, The Electrochemical Society Proceedings Series, Pennington, NJ, (1997).

7. C. Milliken, S. Guruswamy, A. Khandkar, J. Electrochem. Soc. 146, 872 (1999).

8. N. Maffei, A. K. Kuriakose, J. Power Sources, 75, 162 (1998).

9. R. Maric, S. Ohara, T. Fukui, H. Yoshida, M. Nishimura, T. Inagaki, K., Miura. J. Electrochem. Soc., 146, 2006 (1999).

10. K. Eguchi, H. Mitsuyasu, Y. Mishima, M. Ohtaki, H. Arai, in SOFC-V, U. Stimming, S. C. Singhal, H. Tagawa, W. Lehnert, Editors, PV 97, p. 138, The Electrochemical Society Proceedings Series, Pennington, NJ, (1997).

11. R. Doshi, Von L Richards, J. D. Carter, X. P. Wang, M. Krumpelt, J. Electrochem. Soc., 146, 1273 (1999).

12. K. Huang M. Feng, J. B. Goodenough, J. Electrochem. Soc., 144, 3620 (1997).

13. B. Zhu, B.-E. Mellander, in SOFC-V, U. Stimming, S. C. Singhal, H. Tagawa, W. Lehnert, Editors, PV 97, p. 244, The Electrochemical Society Proceedings Series, Pennington, NJ, (1997).

14. B. Zhu, Functional ceria-salt-composite materials for advanced ITSOFC applications, J. Power Sources, (2002), in press.

15. B. Zhu, X.R. Liu, P. Zhou, X.T. Yang, Z.G. Zhu and W. Zhu, Electrochemistry Communication, 3, 566 (2001).

16. B. Zhu, J. Mater. Sci. Letts., 17, 1287 (1998).

17. B. Zhu, C. R. Xia, X. G. Luo and G. Niklasson, Thin Solid Films, 385, 209 (2001).

18. B. Zhu, J. New Mater. Electrochem Sys., 4, 239 (2001).