Technical Overview

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.

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

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].

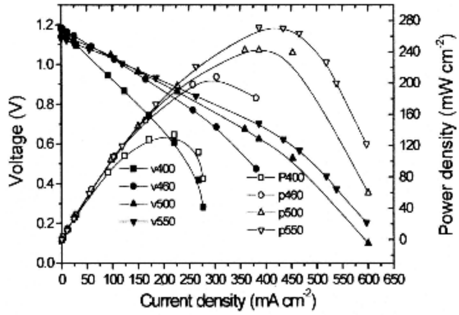

Fig. 1 V-I and P-I curves of a cell consisted of Ni-GDC anode, GDC-LiCl-$SrCl_2$ electrolyte (0.40mm thick), and $LiNiO_2$ cathode [4,5]

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 ($La_{0.8}Sr_{0.2}Ga_{0.8}Mg_{0.2}O_{3-\delta}$), 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].

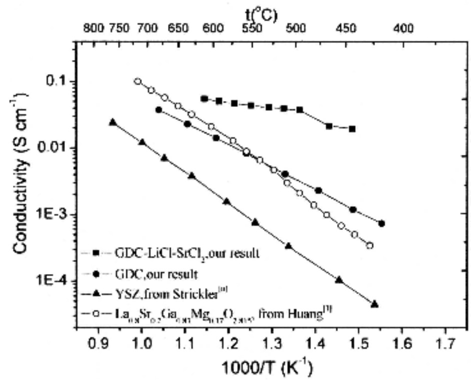

Fig.2 The conductivity of the composite electrolyte

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.

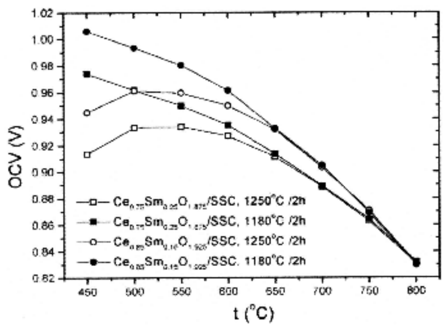

Fig. 3 OCVs of the cells with SDC electrolyte: the effect of interface microstructure on OCVs (electrode sintering condition) [13]

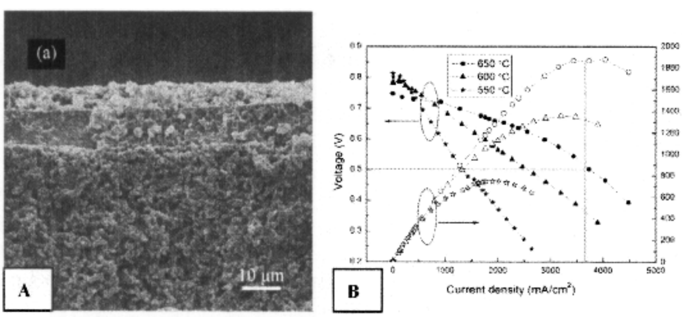

Fig. 4 The microstructure(A) and performance(B) of a cell made by co-pressing and co-firing Ni–SDC anode and BSCF cathode with SDC electrolyte the powders made by polymer assisted combustion method [20]

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-SD C	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)

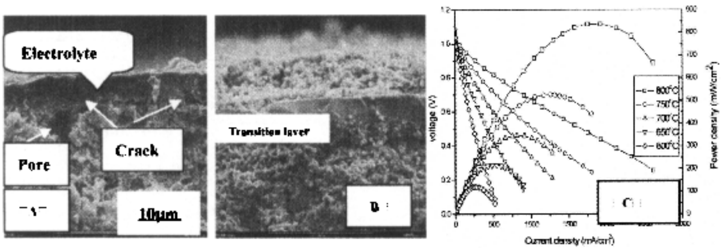

Fig.5 The microstructures and performance of the cells made by suspension spray process[26]

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.

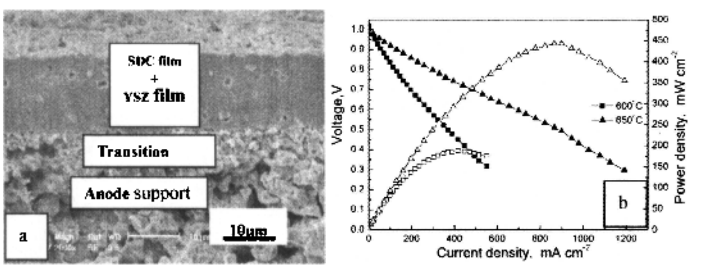

Fig 6 (a) Section view of the cell with anode transition layer and active cathode SDC layer, and (b) V-I, P-I curves of the cell in Fig.6-a

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].

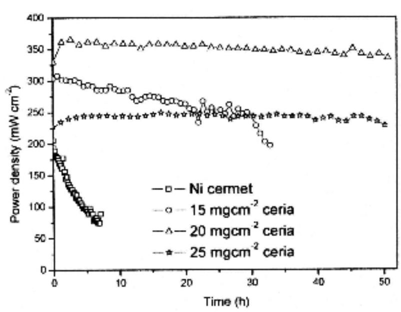

Fig.7 The longer term performance of SOFC cells with various SDC coating on Ni-SDC anode for CH_4 as fuel, operated at 0.5V and 600°C

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 °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.

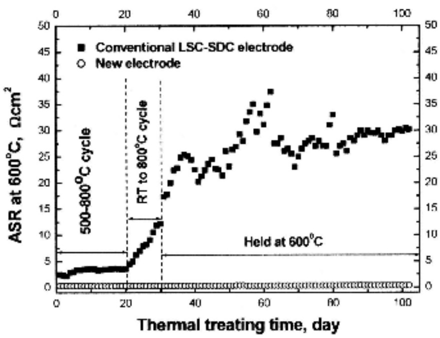

Fig.8 A comparison in ASR of the new designed cathode with conventional SDC-LSC composite cathode during thermal cycling in longer term

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.

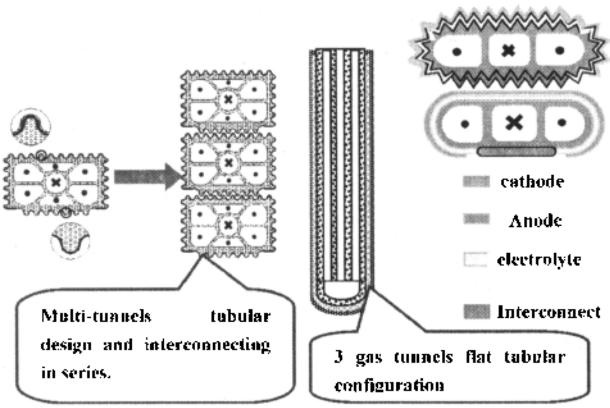

Fig.9 _China patent ZL02113198.8

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/cm^2 at 850°C and gradually decreased to 270 mW/cm^2 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.

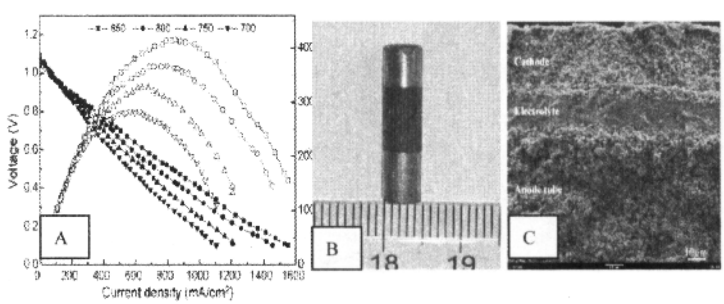

Fig 10 the cell performance and microstructure of a tubular cell made by cost effective process [40, 41]

(A) V-I, P-I curves of a tubular Cell fueled with H_2

(B) Picture of the cell made by dip-coating, and

(C) Section view of the cell, showing the very well coherent electrode interfaces.

For planner 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, hinter its applications, especially for cost effective fabrication of H-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 $La_{0.7}Ca_{0.3}CrO_3$ (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 $Gd_{0.7}Ca_{0.3}CrO_3$ (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/cm at 900°C for $La_{0.75}Sr_{0.25}Cr_{0.5}Mn_{0.5}O_3$ 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]

SDC content (weight%)	Relative density (%)	TEC at 1000°C (10^{-6} K^{-1})	The oxygen permeation flux (mol S·cm^{-2})	Electrical conductivity σ at 800°C (Scm^{-1}) in air
0	97.4	11.12	6.51×10^{-10}	17.77
2	97.6	11.33	9.76×10^{-10}	180.25
4	97.7	11.65	2.33×10^{-9}	341.76
5	97.9	11.93	4.68×10^{-9}	687.81
6	98.1	12.22	5.23×10^{-9}	127.72
8	98.4	12.24	6.31×10^{-9}	129.09
10	98.7	12.46	7.88×10^{-9}	96.18

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 H_2 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 9×10^{6} kJm^{-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 $BaCeO_3$ based proton electrolytes due to the CO_2 existence, because of no carbon species in anode apartment and in case of CMFC-H cases the H_2O formed at cathode-electrolyte interface would hinder the diffusion of CO_2 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 NH_3 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:

$$2NH_3 + 5O^{2-} = 2NO + 3H_2O + 10e^{-}$$

Our first work was based on a full ceramic cell of anode supported thin proton electrolyte($BaCe_{0.8}Gd_{0.2}O_{2.9}$, 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/cm^2 [52]. The subsequent research works were trying to answer the interested problems, such as NH_3 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 bellow:

(1) As theoretically expected, the Ni based anode was the effective catalysis for NH_3 thermal decomposition, and conversion of NH_3 into H_2 and N_2 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]

(2) It is proved by from the experimental OCV data of the cells that it is the H_2 instead of NH_3 itself responsible for anode process in both CMFC-H and CMFC-O [52-57].

(3) For CMFC-O fueled by NH_3, there was no NOx detected and it was consistent to the theoretical prediction that on anode it is O^{2-} ions from cathode, which exhibit much less oxidative reactivity than oxygen molecules or atoms [54].

(4) For CMFCs with a thicker electrolyte membrane thus have lower cell power density(maximum 200-800 mW/cm^2), direct liquid NH_3 fueled cells may provide power density quite close to the H_2 fueled cell[52-56], that means higher than the expected 75% power density of H_2 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 NH_3 and H_2 as fuel, respectively [57].

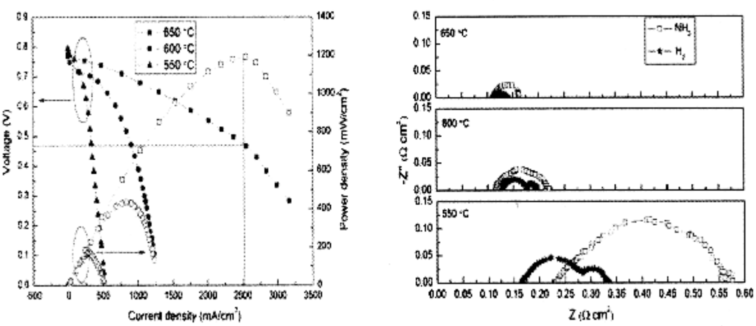

Fig.11 (a) Cell performance with NH_3 fuel at various temperatures, and (b) Impedance spectra of the cell with H_2 and NH_3 under open-circuit conditions.

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/cm^2 at 650°C, which is only 63.8% of the value for H_2 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 NH_3 gas in the anode compartment as well as the mass transfer behavior much different from the H_2 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 $BaCeO_3$ 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 $BaCeO_3$ 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 $BaCeO_3$ are preferred.

(2) CMFCs with thin membrane electrolyte (YSZ, SDC or doped $BaCeO_3$) 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) NH_3 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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