Ceramic membrane fuel cells based on solid proton electrolytes

Guangyao Meng [a,*], Guilin Ma [b], Qianli Ma [a], Ranran Peng [a], Xingqin Liu [a]

[a] *USTC Lab. for Solid State Chemistry and Inorganic Membranes, Department of Materials Science and Engineering, University of Science and Technology of China, Hefei 230026, China*
[b] *School of Chemistry and Chemical Engineering, Suzhou University, Suzhou 215123, China*

Abstract

The development of solid oxide fuel cells (SOFCs) has reached its new stage characterized with thin electrolytes on porous electrode support, and the most important fabrication techniques developed in which almost all are concerned with inorganic membranes, and so can be named as ceramic membrane fuel cells (CMFCs). CMFCs based on proton electrolytes (CMFC-H) may exhibit more advantages than CMFCs based on oxygen-ion electrolytes (CMFC-O) in many respects, such as energy efficiency and avoiding carbon deposit. Ammonia fuelled CMFC with proton-conducting $BaCe_{0.8}Gd_{0.2}O_{2.9}$ (BCGO) electrolyte (50 µm in thickness) is reported in this works, which showed the open current voltage (OCV) values close to theoretical ones and rather high power density. And also, we have found that the well known super oxide ion conductor, $La_{0.9}Sr_{0.1}Ga_{0.8}Mg_{0.2}O_{3-\alpha}$ (LSGM), is a pure proton conductor in H_2 and mixed proton and oxide ion conductor in wet air, while it is a pure oxide ion conductor in oxygen or dry air. To demonstrate the CMFC-H concept to get high performance fuel cells the techniques for thin membranes, chemical vapor deposition (CVD), particularly novel CVD techniques, should be given more attention because of their many advantages.
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Keywords: SOFC; Proton conduction; Ammonia; CVD

1. Introduction

Fuel cells, because of their high energy conversion, simple operation and less pollution to environment, are commonly considered as an excellent green energy source in the future. Among all categories of the fuel cells, solid oxide fuel cells (SOFCs) and proton exchange membrane fuel cells (PEMFC) provide the outstanding advantages, particularly for their module integrity, which enable them to be both suitable to larger and to dispersive power stations, transportation driving force as well as portable power supply devices.

From the viewpoint of effectively utilizing fossil fuels and biomass energy in the future, SOFCs, which operate at higher temperatures promoting cell reaction kinetically and also accompanying with high quality heat to enable higher energy conversion efficiency as well do not have problems such as CO poison to electrode and the water management etc., are superior to PEMFCs. PEMFC operates at a temperature lower than 100 °C and starts up fast, therefore is mainly developed to serve as driving force in future automobiles. But the pure hydrogen preparation from the current hydrocarbon fuels has been the most difficult problem.

SOFCs may employ either oxygen-ionic or proton conductors as electrolytes. SOFCs based on oxygen-ion conductors (SOFC-O) such as YSZ and doped ceria (DCO) have been attracting extensive studies in recent decades. The major progresses can be summarized as the following:

(1) The electrode supported single cell design enables to reduce the electrolyte thickness and hence much decrease in the cell internal resistance.
(2) Materials development and modifications, particularly the active layers between electrolyte and electrodes dramatically minimize the interfacial resistance and improve the cell performance.
(3) Fabrication techniques are mature enough for thin membranes of both dense electrolyte and nano-porous

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* Corresponding author.
E-mail address: mgym@ustc.edu.cn (G. Meng).

active transition layers as well as porous electrodes with desired microstructures.

With the above developments the peak power densities of single cells have commonly reached to over 1000 mW/cm^2. The total power output of a stack has been 1–25 kW even at a reduced temperature (typically 600–800 °C). The current development status of SOFCs can be actually called as ceramic membrane fuel cells (CMFCs) because they are naturally the high temperature ceramic membrane reactors characterized with the configurations of thin functional layers and employed the fabrication techniques commonly developed for ceramic separation membranes.

Nowadays, more and more research institutions and companies have devoted to research and development or the commercialization of SOFCs. Compared with SOFCs-O the SOFCs based on proton electrolytes (SOFC-H, or CMFC-H), such as doped BaCeO$_3$ and La(CaNb)O$_5$, are less studied and developed under much lower level. However, CMFC-H exhibit intrinsic characteristics that make them more promising for the applications in the future, as Prof. Iwahara has made an overview on that recently [1]. It is expected that introducing the knowledge and techniques obtained from CMFC-O into research and development of CMFC-H in new materials investigation and the development of fabrication techniques may promote the progress and further reveals the advantages of CMFC-H systems. This article would take the performance of liquid ammonia fuelled CMFC with BaCe$_{0.8}$Gd$_{0.2}$O$_{2.9}$ (BCGO) electrolyte as an example to discuss the relevant aspects about the further research and development work for CMFCs-H.

2. Liquid ammonia fuelled CMFC with BaCe$_{0.8}$Gd$_{0.2}$O$_{2.9}$ electrolyte

CMFCs with liquid fuels are currently of great commercial interests as a kind of distributed power supply. The carbon deposition on the nickel based anodes employs the liquid hydrocarbon fuels, such as alcohols and liquefied petroleum gas (LPG) etc. Liquid ammonia has been considered the good liquid
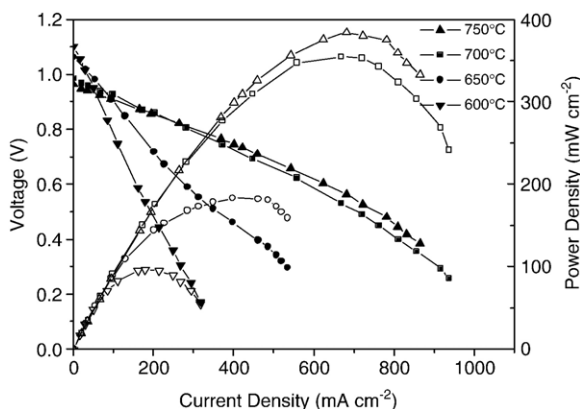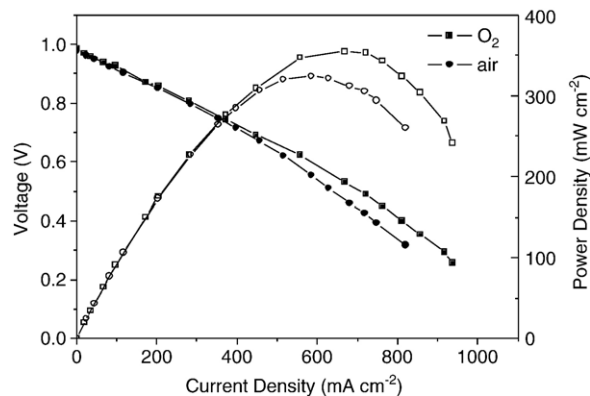
Fig. 2. Comparison of cell voltage (solid) and power density (hollow) as a function of current density for the cell between pure oxygen and air-oxidized air/ O$_2$‖LSCO-BGCO/BGCO/Ni-BGCO‖NH$_3$ cells, at the temperature of 700 °C, with pure ammonia as fuel.

fuel which possesses a number of advantages including no harmful elements to anode and mass production with lower cost. Recently the author's group made a cell consisting of Ni–BaCe$_{0.8}$Gd$_{0.2}$O$_{2.9}$ (BCGO)/BCGO (50 μm)/La$_{0.5}$Sr$_{0.5}$CoO$_{3-\delta}$ (LSCO)-BCGO, and directly fuelled with industrial liquid ammonia. Performance of the single cell was tested in the temperature range of 600–750 °C [2]. The results showed the OCV values of the cells with pure oxygen as oxidant was fairly consistent to the ones theoretically calculated from the complete decomposition of ammonia. Fig. 1 shows the performance of the cell directly fuelled with NH$_3$. The maximum power density reaches 355 mW cm^{-2} at 700 °C and 384 mW cm^{-2} at 750 °C. Fig. 2 shows the comparison of performance for the cell fuelled by oxygen and CO$_2$ free air. The power density of the cell with CO$_2$ free air as oxidant at 700 °C was 324 mW cm^{-2}, very similar to that of fuelled by oxygen. Fig. 3 shows the performance of the cell fuelled with NH$_3$ and pure H$_2$ at 700 °C. The OCV value of the cell with pure H$_2$ is quite close to that using NH$_3$, the peak power density is 371 mW cm^{-2}, only 4.5% higher than the NH$_3$ fuel, though NH$_3$ only contains 75%

Fig. 1. Cell voltage (solid) and power density (hollow) as a function of current density for the O$_2$‖LSCO-BGCO/BGCO/Ni-BGCO‖NH$_3$ cells, with pure ammonia as fuel and pure oxygen as oxidant at different temperatures.
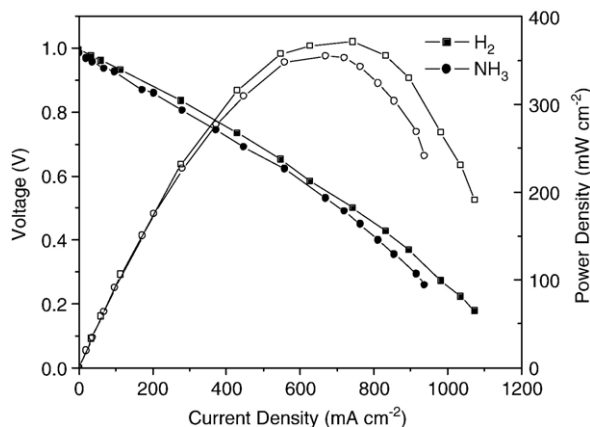
Fig. 3. Comparison of cell voltage (solid) and power density (hollow) as a function of current density between pure ammonia and pure hydrogen-fuelled O$_2$‖LSCO-BGCO/BGCO/Ni-BGCO‖NH$_3$/H$_2$ cells, at the temperature of 700 °C, with pure oxygen as oxidant.

H_2. The better data were even 1.04 V for OCV and 420 mW/cm^2 for peak power density at 700 °C (Fig. 4). This value is more than ten times higher than that reported by Maffei et al. [3], mainly because the thickness (50 μm) of electrolyte, BCGO in this work was much smaller than the latter (0.5 mm) as well as the compatible cathode. The output power density would be even much higher when the thickness of electrolyte is reduced to 10 μm as commonly obtained by currently developed techniques for thin layer electrolyte in SOFC-O. The fairly good performance of the cells tested under various conditions implied that ammonia might be a good substitute fuel for SOFC. This demonstrates the promise of practical utilization of liquid fuel SOFC-H.

In the case of CMFC (O), however, at anode side the following reactions would occur [3], and may lead to NOx pollution.

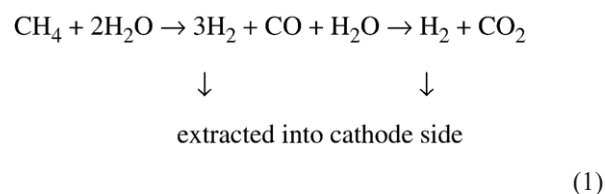$$N_2 + O_2 \rightarrow 2NO, \ 1/2N_2 + O_2 \rightarrow NO_2$$
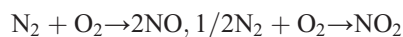
But detection by gas chromatograph did not prove the existence of NOx in the anode-off gas at current density of 1000 mA. This result is believable to note that the oxygen ions transferred from cathode through electrolyte membrane to the anode/electrolyte interface pose rather low concentration and also exhibit much lower reaction activity compared with oxygen atmosphere, that react with hydrogen to form H_2O in much larger affinity than that for forming NOx with N_2. However, it does not mean that the CMFC-H has no advantages to the CMFC-O. Fig. 4 shows a performance comparison of a cell with BCGO electrolyte and a cell with SDC electrolyte in the same thickness (50 μm). We can see that the CMFC-H does not only provide much higher power output density but also shows an OCV value about 20 mv higher than that of SDC cell. This is because BCGO is a pure ionic conductor below 750 °C, while SDC exhibits obvious electronic conduction that lost power more than 50% through internal short circuit.

Not only ammonia but also hydrogen fuelled CMFCs provide more advantages than CMFCs-O or PEMFCs [1]. In CMFC-H the exhaust fuel (H_2) from anode apartment does not
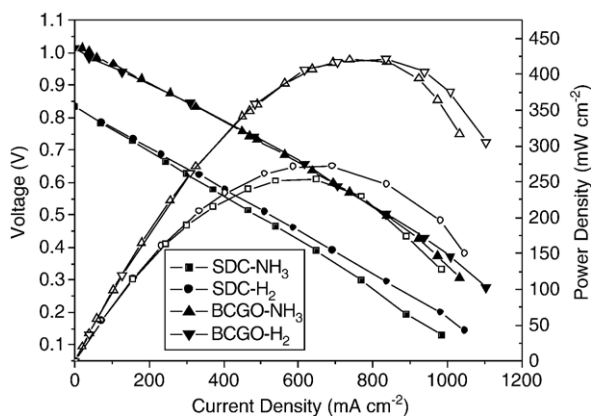

Fig. 4. Comparison of cell voltage (solid) and power density (hollow) as a function of current density between ammonia and hydrogen-fuelled cells with BCGO and SDC as the electrolyte, respectively, at the temperature of 700 °C.

contain H_2O, which is the reaction product on anode in SOFC-O and the necessary additive in PEMFCs, and can be easily recycled to be used completely. Besides, the simplified anode ambient (only H_2 of H_2+N_2) in the case of hydrogen fuelled CMFC-H may avoid the concentration polarization that is possibly occurring in anode support. This is of great interest in the future of hydrogen energy economy where CMFCs-H can act as high efficiency power generation devices from hydrogen produced or stored by other energy conversion such as solar cells, wind energy and water electrolysis to use excess net-power at night time.

One of the major problems for SOFC/CMFC is the carbon deposit on anode when hydrocarbons are used as fuels due to the too high catalysis capacity of Ni containing anode. Temporally, a suitable solution is to add H_2O into hydrocarbons externally or internally to reform them into H_2+CO. A thermodynamic analysis on CMFC-H indicated that with mixture of CH_4 and 2.6 mol of H_2O as fuels the cell may achieve a power efficiency even 15% higher than CMFC(O) [4]. This can be understood from the following reaction process in the case,

$$CH_4 + 2H_2O \rightarrow 3H_2 + CO + H_2O \rightarrow H_2 + CO_2$$
$$\downarrow \qquad\qquad \downarrow$$
$$\text{extracted into cathode side}$$

$$(1)$$

The electrochemically permeation of H_2 across proton-conductive membrane electrolyte to cathode side reacts with oxygen to accelerate the reaction of CO_2 formation on anode apartment and shifts the process forward to completeness. Recently we have experimentally checked the above conclusion by trying various hydrocarbon fuels, such CH_4 and CH_3OH for the cells: Ni–BaCe$_{0.8}$Gd$_{0.2}$O$_{2.9}$ (BCGO)/BCGO (50 μm)/La$_{0.5}$Sr$_{0.5}$CoO$_{3-\delta}$ (LSCO)-BCGO. The preliminary result indicated that noticeable carbon deposit at temperature of 700 °C was not observed with mixture of CH_4 or CH_3OH and 50% H_2O as fuels, but carbon deposit occurred in case of $C_2H_5OH+H_2O$ as fuel. Obviously this can be attributed to take the place of the parallel reaction of process (1):

$$C_2H_5OH \rightarrow 2C\downarrow + 2H_2 + H_2O \qquad (2)$$

and removal of H_2 from anode apartment also accelerates the reaction. Recently more and more works are devoted to search new anode materials with less catalytic capacity in order to avoid the carbon deposit [5,6]. However, the power density of the cell output was also somewhat depressed due to the insufficient catalysis activity of the newly used anode. The electrochemical extraction of H_2 through proton-conduction membrane in CMFC-H may act as the membrane catalyzer to promote the cell reaction. Thus they may provide more opportunity for searching new anode systems.

The major difficulty in SOFC/CMFC-H known so far is the instability of Barium cerate in CO_2 due to the BaCO$_3$ formation at the temperature below 800 °C, but at temperature above

800 °C the obvious electronic conduction would lower the cell performance. To overcome the problems there have been two approaches. One is to search new proton-conductive electrolytes. A good example was the $Ba(Ca_{1-x}Nb_xO_3)$. Norwick et al. [7] reported that $Ba_3Ca_{1.18}Nb_{1.82}O_{9-\delta}$(BCN18) showed a proton conductivity of 10^{-2} S/cm at 600 °C and the cell with BCN18 electrolyte was not degraded after operation in CO/CO_2 for 100 h. Recently Tao and Irvine reported [8] that Zn substituted for Y in doped Barium cerate, $BaCe_{0.5}Zr_{0.3}Y_{0.16}Zn_{0.04}O_{3-\delta}$, has a fairly high conductivity, 10^{-2} S/cm at 600 °C, and no CO_2 adsorption or carbonate formation in pure CO_2 when cycling from room temperature to 1200 °C that indicated its thermodynamic stability in CO_2 improving much the mother materials, $BaCe_{0.5}Zr_{0.3}Y_{0.2}O_{3-\delta}$ and $BaCe_{0.8}Y_{0.2}O_{3-\delta}$. These results demonstrated that there are wide rooms to search for new proton conductors with improved properties to meet the requirements of CMFCs, that will be further discussed in next section.

3. Proton conduction in the supper oxide ion conductor, doped $LaGaO_3$ — the mixed H^+/O^{2-} ionic conduction will govern the CMFCs

3.1. The perovskite ceramic proton conductors

The most important key material for CMFC-H is the proton-conductive ceramic electrolyte. Since the discovery of high temperature proton conduction in doped perovskite-type $SrCeO_3$ [9], a number of materials such as doped $BaCeO_3$, $AZrO_3$ (A = Ca, Sr and Ba), $KTaO_3$, $Ln_2Zr_2O_7$, Sr_2TiO_4, $Ba_2SnYO_{5.5}$, $LnScO_3$ (Ln = La, Nd, Sm, Gd) and non-stoichiometric mixed perovskite-type $Ba_3Ca_{1+x}Nb_{2-x}O_9$ have been found to exhibit appreciable proton conduction under hydrogen-containing atmosphere at elevated temperatures. Though the essential factors affecting the proton-conduction property in these materials are still not completely clear, some knowledge gives empirical rules in searching good proton conductors in ABO_3 perovskite family. First of all, the existence of high content oxygen vacancies is most necessary. The relative opening structure of perovskite oxides and plenty of ways to introduce compensative oxygen vacancies by aliovalent ionic substitution provide very wide opportunities to find good proton conductors. As reported by Ma et al. [10], the crystallographic free volume and the tolerance factor t of $Ba_{1-x}La_xCe_{0.90-x}Y_{0.10+x}O_{3-\alpha}$ ($0 \le x \le 0.40$) distinctly influence the proton and/or oxide-ion conductivities. The tolerance factor ($t=0.94$) of $BaCeO_3$ calculated using ionic radii is higher than that ($t=0.88$) of $SrCeO_3$, coinciding with the fact that doped $BaCeO_3$ has usually higher proton and/or oxide-ion conductivities than doped $SrCeO_3$. $LaGaO_3$ has a larger tolerance factor t ($t=0.97$) calculated from the equation $t = (r_{La} + r_O)/\sqrt{2}(r_{Ga} + r_O)$, where r_{La}, r_{Ga} and r_O are ionic radii of La-site ion, Ga-site ion and oxide ion, respectively, than those of $SrCeO_3$ and $BaCeO_3$. Therefore, there would be a possibility to illustrate excellent proton conduction in $LaGaO_3$-based perovskite-type oxides. $LaGaO_3$ doped with Sr and Mg, typically $La_{0.9}Sr_{0.1}Ga_{0.8}Mg_{0.2}O_{3-\alpha}$ is a well known supper oxide ion conductor over a wide range from 1 to 10^{-20} atm.

3.2. Proton conduction in the supper oxide ion conductor, doped $LaGaO_3$

According to the above consideration we have first investigated the proton conduction in $La_{0.9}Sr_{0.1}Ga_{0.8}Mg_{0.2}O_{3-\alpha}$ (LSGM) recently [11]. Fig. 5 shows the Arrhenius plots of the electrical conductivities for the LSGM specimen in hydrogen, oxygen, air, argon and wet argon atmosphere. It is clear that there is no obvious difference in the electrical conductivities under different atmospheres. The electrical conductivities were around 1.4×10^{-2} S cm^{-1} at 600 °C and 1.4×10^{-1} S cm^{-1} at 1000 °C, with activation energy of 60.5 kJ mol^{-1}. The further study indicated that the conductivity was almost independent of P_{O_2} over the range of oxygen partial pressures from 1–10^{-20} atm, which is analogous to the result reported by Ishihara et al. [12]. This confirms the nature of pure ionic conduction in LSGM but no further information about its conduction species and mechanism. Feng and Goodenough [13] reported that the conductivities of $La_{0.9}Sr_{0.1}Ga_{0.8}Mg_{0.2}O_{3-\alpha}$ measured from 350 °C to 800 °C in dry air, ambient air and water-saturated (at room temperature) air were the same but did not demonstrate the existence of proton conduction. In order to examine the proton conduction a hydrogen concentration cell was constructed by using LSGM pellet as an electrolyte: H_2 (1 atm), $Pt|La_{0.9}Sr_{0.1}Ga_{0.8}Mg_{0.2}O_{3-\alpha}|Pt$, H_2–Ar, Fig. 6 shows the EMF of the cell for various hydrogen pressures and the dash lines are the data calculated theoretically. It is clear, that each E_{obs} is close to the theoretical E_{cal}. The ionic transport number, t_i, determined from $E_{obs}/E_{cal}(=t_i)$, is almost united with the negligible electronic one at temperatures from 600–1000 °C. That indicates that the conductivity in hydrogen atmosphere shown in Fig. 5 is pure ionic.

To verify the proton conduction in the specimen the electrochemical hydrogen permeation (hydrogen pumping) is a more direct way. Discharge curve of the hydrogen concentration cell: H_2, $Pt|La_{0.9}Sr_{0.1}Ga_{0.8}Mg_{0.2}O_{3-\alpha}|Pt$, H_2–Ar at 900 °C was measured. A steady and stable current could be drawn from the cell, that confirmed proton as its charge carrier in H_2 gas. The
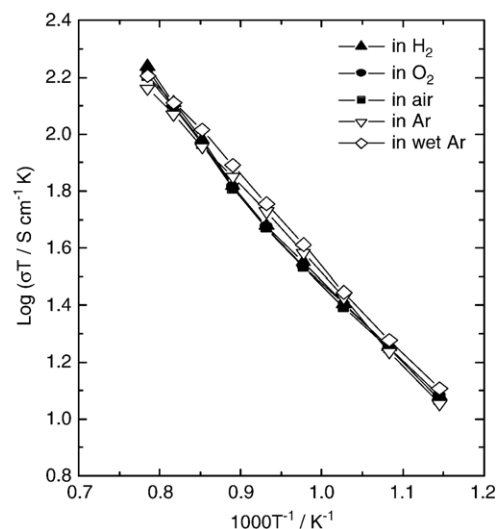

Fig. 5. Temperature dependence of the electrical conductivity for LSGM in H_2, O_2, air, Ar and wet Ar.

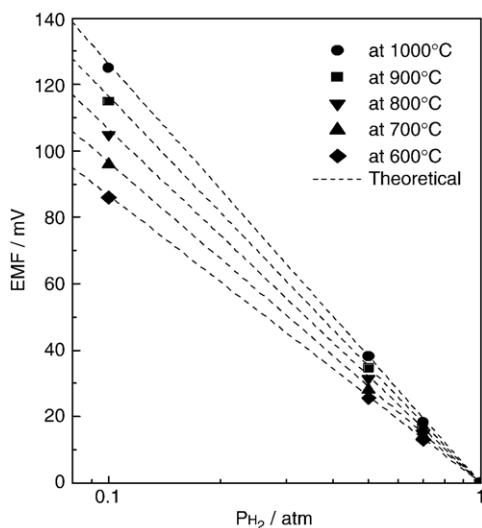Fig. 6. EMFs of the cell: H_2, Pt|LSGM$_\alpha$|Pt, H_2–Ar. Dotted lines: theoretical values. Thickness of the electrolyte is 1 mm.

hydrogen evolution rate in the cell as a function of current density at 900 °C is shown in Fig. 7. We can see that the dependence of hydrogen evolution rate on electrolytic current obeyed the Faraday's law (dashed line) when the current density was lower than 10 mA cm^{-2}, indicating that the charge carriers in this specimen are protons in hydrogen atmosphere. As the current density rose higher, the hydrogen evolution rate began to deviate from the theoretical value. The origin of this deviation is not clear yet. It may be related to the electrode polarization and a limiting protonic current due to low hydrogen concentration at the interface between electrode material (Pt) and electrolyte [14].

3.3. Will the mixed (H$^+$ and O^{2-}) ionic conductors govern the future development of CMFCs?

The mixed proton and oxide ion (H$^+$ and O^{2-}) conduction has been commonly found in a number of perovskite oxide
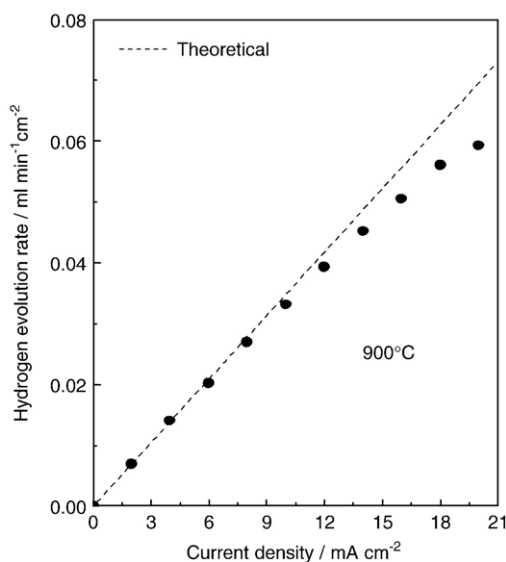

Fig. 7. Electrochemical hydrogen pumping using LSGM as solid electrolyte.

ceramics. Fujii et al. discovered the protonic conduction in oxide ceramics based on LnScO$_3$ (Ln = La, Nd, Sm or Gd) at high temperature [14]. At the same time, Lybye and Bonanos [15] investigated the proton and oxide ion conductivity of La$_{0.9}$Sr$_{0.1}$Sc$_{0.9}$Mg$_{0.1}$O$_{3-\alpha}$. According to the rules formulated by earlier researchers, doped LaScO$_3$ should be a better oxide ion conductor than the gallate, but it was found to be a proton conductor. Doped BaCeO$_3$ based oxides and complex perovskite Ba$_3$Ca$_{1.18}$Nb$_{1.82}$O$_{9-\delta}$ are thought to be superior proton conductors due to their higher proton conductivity and proton transport number in hydrogen-containing atmosphere. But, they also show oxide-ion conduction in oxygen-containing atmosphere [16–18]. The results described in last section clearly demonstrate that La$_{0.9}$Sr$_{0.1}$Ga$_{0.8}$Mg$_{0.2}$O$_{3-\alpha}$ is a superior proton conductor in hydrogen atmosphere, and a mixed proton and oxide-ion conductor in water vapor containing air atmosphere, comparable to BaCeO$_3$ based oxides and Ba$_3$Ca$_{1.18}$Nb$_{1.82}$O$_{9-\delta}$. The most distinct feature for LSGM is that it shows a pure ionic conduction until 1000 °C, but most of other distinct features start to display somewhat electronic conduction at a temperature below 1000 °C. This gives much benefit when it is employed as electrolyte for ceramic membrane fuel cells and electrolyzer in which the electronic conduction of the electrolyte would remarkably decrease the electrochemical efficiency due to the internal short circuit

Fig. 8 presents the temperature dependence of the conductivities of the well known proton conductors and oxide ion conductors with perovskite or fluorite structure. Among these oxides the proton conductors of perovskite-type ceramics possess the higher conductivity and their activation energy of conduction is remarkably smaller than the oxide ionic conductors with fluorite structure. The lower activation energy of LSGM (60 kJ/mol) may be related to its proton conduction. Compared with YSZ which is of pure oxide ion conductor the much higher conductivity and lower activation energy of the doped ceria, such as SDC and GDC, may also be related to its partial proton conduction that was proved by some researchers.

From the viewpoint of practical applications as electrolytes for CMFCs this mixed conduction certainly may play a positive and governing role in the electrochemical process. Unfortunately, the
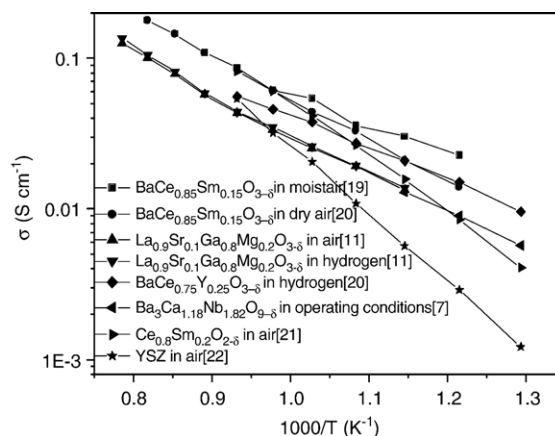

Fig. 8. Temperature dependence of the conductivities of some proton conductors and oxide ion conductors.

Table 1
Ceramic processing techniques for anode supported thin electrolytes and the performance of the cells

Preparation technique	Cell PEN configuration	Electrolyte thickness (μm)	Peak power density (mW/cm^2)/ temperature	Ref. literature
Tape-casting	SSC/SDC/ Ni-SDC	50	180/700 °C	2005 [20]
Screen printing	SSC/YDC/ YDC-Ni	20	290/650 °C	2002 [21]
Slurry coating	LSM/YSZ/ Ni-YSZ	30	190/800 °C	2004 [22]
Spin-coating	Ag-YSB/ YSZ/SDC-Ni	10	535/750 °C	2004 [23]
Powder spray	Ag/YSZ/ Ni-YSZ	5–15	469/800 °C	2005 [24]

research works on the proton-conductive ceramics are mostly limited to their bulk (thickness is larger 0.5 mm) materials. And CMFCs based on thin membrane electrolyte of proton conductors always showed surprising result. The ammonia fuelled CMFC with BCGO electrolyte reported in this work is also an example. Let's imagine a ceramic fuel cell with mixed ionic conductive ceramic membrane in a few microns as electrolyte. The almost pure proton conductor on anode side and oxygen-ionic conductor on cathode side, what will happen in performing the cell reaction? No doubt, the charge transfer and reaction process in such ultra-thin membranes would be of great significance to the study and the result will lead to even breakthrough progress in R and D of CMFCs.

4. Novel chemical vapor deposition (CVD) techniques and their potential applications for performing CMFCs-H

Techniques for fabrication of thin membranes, including dense electrolyte and nano-porous active electrode layers, are essential to perform the concept of ceramic membrane fuel cells of both SOFC-O and SOFC-H. There have been two categories of techniques: advanced ceramic processing and vapor phase deposition. The techniques of ceramic processing for thin electrolyte membranes developed at our laboratory so far include tape-casting [19], screen-printing [20], slurry coating [21], spin-coating [22], and electrostatic powder spray [23]. As summarized in Table 1 the thickness of anode supported thin

electrolytes was commonly in the range of 5–50 μm and the cell power density only reached a value around 500 mW cm^{-2} at below 800 °C due to poor cathode assembly.

Vapor phase depositions including physical and chemical ones are of atomic and molecular level process which can make complicated forms and the membranes as thin as a few microns or even sub-microns, while the traditional ceramic process can only make layers with a thickness larger than 5 μm. The very high power density (0.9 W cm^{-2} at 400 °C and 1.4 W cm^{-2}, at 600 °C).of a cell with ultra-thin BaCe$_{0.8}$Y$_{0.2}$O$_{2.9}$ (BCYO) electrolyte layer (0.7 μm) made by laser ablation [24] is a good sample. It is well known, however, that chemical vapor deposition (CVD), compared with physical vapor deposition (PVD) like laser ablation, exhibit more advantages including low cost and easily to scaling up [25]. High performance SOFCs fabricated by chemical vapor deposition (CVD) and electrochemical vapor deposition (EVD) were developed by Westinghouse in 1980s [26]. The attempt to search new CVD process to overcome the problems associated with conventional CVD/EVD techniques has been done by some research groups including the author's laboratory [27–41]. Various novel CVD techniques characterized with unique precursor supply and mass transport process, and much lower deposition temperatures etc. were developed for SOFC related material thin films. They include "Single mixed source MOCVD" [29–31], "Aerosol assisted metal-organic CVD (AA-MOCVD)" [32–37], and "Oxy-acetylene combustion AACVD" [38]. These techniques have been used to prepare key materials thin films for SOFCs, such as CeO$_2$ [29], SrCeO$_3$ [30], Pd–Ni [31], YSZ [28,36,39], YDC [32], GDC [35,37,38], SDC [40], LaMnO$_3$ [33,34] and doped LaCrO3 [41] etc. Fig. 9 shows the SEM micrographs of the cell structures respectively with YSZ, YDC, and GDC thin film electrolyte deposited on NiO-electrolyte substrates by AA-MOCVD. It can be seen that the thickness of electrolyte films is in the range of 0.5–5 μm. It's regretted that these single SOFCs showed OCV lower than 0.8 V and the maximal power density lower than 60 mW cm^{-2} at 750 °C. It is far away from the expectation due to some problems mainly associated with the rough anode support. In principle, however, these problems will be finally settled and illustrate the intrinsic capacity of these novel CVD processes, just like the CVD process in IC industry where we could say there would be no advanced development of the technology if there were no CVD techniques. And we should expect that these novel CVD techniques will play their key role in preparation of ultra-thin
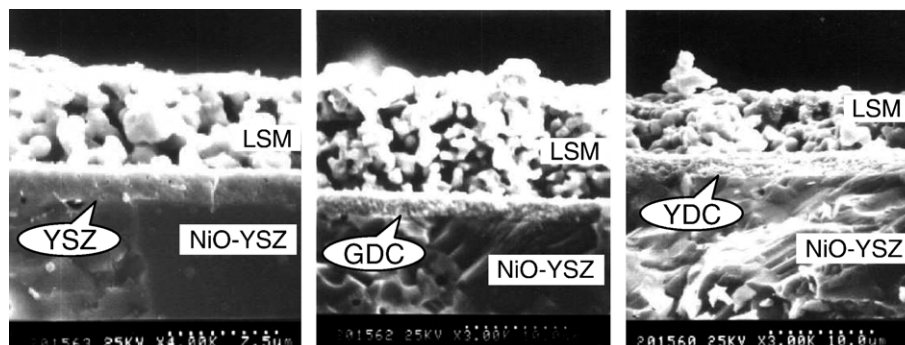

Fig. 9. Ultra thin electrolyte films deposited on NiO-YSZ anode by Aoresol assisted CVD.

membranes and make great contribution to the research and development of CMFC-O and CMFC-H.

5. Summary and conclusion remarks

On the discussions of the last sections the summarized conclusions are as follows:

(1) The research and development of SOFCs have reached its new stage characterized with thin electrolytes on porous electrode support and the fabrication techniques commonly developed for inorganic membranes, which can be named as ceramic membrane fuel cells (CMFCs) and CMFC-H is worthy of further research and development.

(2) Ammonia fuelled CMFC with BCGO electrolyte (50 μm) showed the OCV values close to theoretical ones and power density of 350–420 mW/cm^2 at 700 °C, which has still the potential to be further improved for thinner electrolyte, that demonstrated the promising future of the ammonia as the practical fuel for CMFCs.

(3) CMFC-H maybe superior to CMFC-O in energy efficiency and in avoiding carbon deposit. There is more opportunity to search new proton conductors which are stable in CO_2. Thus, CMFCs-H has a bright future.

(4) It has been found that the well known super oxide ion conductor, $La_{0.9}Sr_{0.1}Ga_{0.8}Mg_{0.2}O_{3-\alpha}$ (LSGM), is a pure proton conductor in H_2 and mixed proton and oxide ion conductor in wet air, while it is a pure oxide ion conductor in oxygen or dry air. This discovery provides a new route to search new proton or H^+/O^{2-} mixed conductors and gains insight into the electrochemical process in SOFCs with LSGM or similar electrolytes.

(5) To perform the CMFC-H concept to get high performance fuel cells, the techniques for thin membranes, chemical vapor deposition (CVD), particularly novel CVD techniques, should be given more attention because of their many advantages.

Acknowledgment

References

[1] Hiroyasu Iwahara, Proton conducting ceramic membranes and hydrogen devices, in: R. Bredeson, H. Raeder (Eds.), Proceedings of the 9th International Conference on Inorganic Membranes, Lillehammer, Norway, June 25–29 2006.

[2] Qianli Ma, Ranran Peng, Yongjing Lin, Jianfeng Gao, Guangyao Meng, A High-Performance ammonia-fuelled Solid Oxide Fuel Cell, J. Power Source, accepted for publication.

[3] N. Maffei, L. Pelletier, J.P. Charland, A. McFarlan, Journal of Power Sources 140 (2005) 264.

[4] A.K. Demin, P.E. Tsiakaras, V.A. Sobyyanin, S.Yu. Hramova, Solid State Ionics 152–153 (2002) 555.

[5] Shanwen Tao, John T.S. Irine, Journal of the Electrochemical Society 151 (2004) 252.

[6] Zongping Shao, Sossina M. Haile, Nature 143 (2004) 170.

[7] Yang Du, A.S. Nowick, Solid State Ionics 91 (1996) 85.

[8] Shanwen Tao, John T.S. Irine, Advanced Materials 18 (2006) 1581.

[9] H. Iwahara, T. Esaka, H. Uchida, N. Maeda, Solid State Ionics 3/4 (1981) 359.

[10] G. Ma, T. Shimura, H. Iwahara, Solid State Ionics 120 (1999) 51.

[11] Guilin Ma, Feng Zhang, Jianli Zhu, Protonic conduction in $LaGaO_3$-based ceramics, submitted for publication.

[12] T. Ishihara, H. Matsuda, Y. Takita, Journal of the American Chemical Society 116 (1994) 3801.

[13] M. Feng, J.B. Goodenough, European Journal of Solid State and Inorganic Chemistry 31 (1994) 663.

[14] H. Fujii, Y. Katayama, T. Shimura, H. Iwahara, Journal of Elecroceramics 2:2 (1998) 119.

[15] D. Lybye, N. Bonanos, Solid State Ionics 125 (1999) 339.

[16] T. Shimura, M. Komori, H. Iwahara, Solid State Ionics 86–88 (1996) 685.

[17] P. Murugaraj, K.D. Kreuer, T. He, T. Schober, J. Maier, Solid State Ionics 97 (1997) 1.

[18] G. Ma, T. Shimura, H. Iwahara, Solid State Ionics 110 (1998) 103.

[19] H.B. Li, C.R. Xia, X.H. Fang, X. He, X.L. Wei, G.Y. Meng, Key Engineering Materials 280–283 (2005) 779.

[20] R.R. Peng, C.R. Xia, X.Q. Liu, D.K. Peng, G.Y. Meng, Solid State Ionics 152–153 (2002) 561.

[21] Y.Z. Zhang, J.F. Gao, D.K. Peng, G.Y. Meng, X.Q. Liu, Journal of Applied Electrochemistry 34 (2004) 637.

[22] Xingyan Xu, Changrong Xia, Shouguo Huang, Dingkun Peng, Ceramic International 31 (2005) 1061.

[23] W.T. Bao, W. Zhu, G.Y. Zhu, J.F. Gao, G.Y. Meng, Solid State Ionics 176 (2005) 669.

[24] Naoki Ito, Masahiko Lijinma, Kenji Kimura, Satosh Iguchi, Journal of Power Sources 152 (2005) 200.

[25] G.Y. Meng, Chemical Vapor Deposition and New Inorganic Materials, Science Publishing House, Beijing, April 1984 (In Chinese).

[26] U. Pal, S.C. Singhal, Journal of the Electrochemical Society 137 (1990) 2937.

[27] D.K. Peng, Q. Fang, K.A. Xu, G.Y. Meng, Proceedings of Int. Symp. on Plasma Chemistry (ISPC), vol. 8, 1987, p. 1142, Tokyo.

[28] G.Y. Meng, C.B. Cao, W.J. Yu, D.K. Peng, K. de Vries, A.J. Burggraaf, Key Engineering Materials 61–62 (1991) 11.

[29] M. Pan, G.Y. Meng, H.W. Xin, C.S. Chen, D.K. Peng, Y.S. Lin, Thin Solid Films 324 (1998) 89.

[30] M. Pan, G.Y. Meng, C.S. Chen, D.K. Peng, Y.S. Lin, Materials Letters 36 (1998) 44.

[31] G.Y. Meng, L. Huang, M. Pan, C.S. Chen, D.K. Peng, Materials Research Bulletin 32 (1997) 385.

[32] H.B. Wang, H.Z. Song, C.R. Xia, D.K. Peng, G.Y. Meng, Materials Research Bulletin 35 (2000) 2363.

[33] H.B. Wang, G.Y. Meng, D.K. Peng, Thin Solid Films 368 (2000) 275.

[34] H.B. Wang, J.F. Gao, D.K. Peng, G.Y. Meng, Materials Chemistry and Physics 72 (2001) 297.

[35] G.Y. Meng, H.Z. Song, H.B. Wang, C.R. Xia, D.K. Peng, Thin Solid Films 409 (2002) 105.

[36] H.Z. Song, H.B. Wang, S.W. Zha, D.K. Peng, G.Y. Meng, Solid State Ionics 156 (2003) 249.

[37] H.Z. Song, C.R. Xia, Y.Z. Jiang, G.Y. Meng, D.K. Peng, Materials Letters 57 (2003) 3833.

[38] H.Z. Song, C.R. Xia, G.Y. Meng, D.K. Peng, Thin Solid Films 434 (2003) 244.

[39] Yinzhu Jiang, Haizheng Song, Jianfeng Gao, Guangyao Meng, Journal of the Electrochemical Society 157 (2005) 7.

[40] Yinzhu Jiang, Qianli Ma, Haizheng Song, Guangyao Meng, Thin Solid Films 510 (2006) 88.

[41] Yinzhu Jiang, Jianfeng Gao, Mingfei Liu, Yanyan Wang, Guangyao Meng, Materials Letters (accepted for publication).