Ceramic membrane fuel cells based on solid proton electrolytes

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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 BaCe0.8Gd0.2O2.9 (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, La0.9Sr0.1Ga0.8Mg0.2O3−α (LSGM), is a pure proton conductor in H2 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. © 2007 Elsevier B.V. All rights reserved.

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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.
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/cm². 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 BaCeO₃ and La(Ca,Nb)O₅, 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 BaCe₀.₈Gd₀.₂O₂.₉ (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 BaCe₀.₈Gd₀.₂O₂.₉ 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 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–BaCe₀.₈Gd₀.₂O₂.₉ (BCGO)/BCGO (50 μm)/La₀.₅Sr₀.₅CoO₃−δ (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 NH₃. 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 CO₂ free air. The power density of the cell with CO₂ 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 NH₃ and pure H₂ at 700 °C. The OCV value of the cell with pure H₂ is quite close to that using NH₃, the peak power density is 371 mW cm⁻², only 4.5% higher than the NH₃ fuel, though NH₃ only contains 75%

![Fig. 1. Cell voltage (solid) and power density (hollow) as a function of current density for the O₂||LSCO-BGCO/BGCO/Ni-BGCO||NH₃ cells, with pure ammonia as fuel and pure oxygen as oxidant at different temperatures.](image1)

![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/O₂||LSCO-BGCO/BGCO/Ni-BGCO||NH₃ cells, at the temperature of 700 °C, with pure ammonia as fuel.](image2)

![Fig. 3. Comparison of cell voltage (solid) and power density (hollow) as a function of current density between pure ammonia and pure hydrogen-fuelled O₂||LSCO-BGCO/BGCO/Ni-BGCO||NH₃/H₂ cells, at the temperature of 700 °C, with pure oxygen as oxidant.](image3)
H₂. The better data were even 1.04 V for OCV and 420 mW/cm² 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.

\[ \text{N}_2 + \text{O}_2 \rightarrow 2\text{NO}, \frac{1}{2}\text{N}_2 + \text{O}_2 \rightarrow \text{NO}_2 \]

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 H₂O in much larger affinity than that for forming NOx with N₂. 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 ºC, 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 (H₂) from anode apartment does not contain H₂O, 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 H₂ of H₂ + N₂) 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 H₂O into hydrocarbons externally or internally to reform them into H₂ + CO. A thermodynamic analysis on CMFC-H indicated that with mixture of CH₄ and 2.6 mol of H₂O 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,

\[ \text{CH}_4 + 2\text{H}_2\text{O} \rightarrow 3\text{H}_2 + \text{CO} + \text{H}_2\text{O} \rightarrow \text{H}_2 + \text{CO}_2 \]

extracted into cathode side

(1)

The electrochemically permeation of H₂ across proton-conductive membrane electrolyte to cathode side reacts with oxygen to accelerate the reaction of CO₂ 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 CH₄ and CH₃OH for the cells: Ni–BaCe₀.₈Gd₀.₂O₂.₉ (BCGO)/BCGO (50 μm)/La₀.₅Sr₀.₅CoO₃–δ (LSCO)-BCGO. The preliminary result indicated that noticeable carbon deposit at temperature of 700 ºC was not observed with mixture of CH₄ or CH₃OH and 50% H₂O as fuels, but carbon deposit occurred in case of C₂H₅OH+H₂O as fuel. Obviously this can be attributed to take the place of the parallel reaction of process (1):

\[ \text{C}_2\text{H}_5\text{OH} \rightarrow 2\text{C} \downarrow + 2\text{H}_2 + \text{H}_2\text{O} \]

and removal of H₂ 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 H₂ through proton-conduction membrane in CMFC-H may act as the membrane catalyst 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 CO₂ due to the BaCO₃ formation at the temperature below 800 ºC, 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$_x$O$_3$). Norwick et al. [7] reported that Ba$_2$Ca$_{1-x}$Nb$_x$O$_{2.5}$ (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$_{0.2}$O$_3$-δ, 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$_3$-δ and BaCe$_{0.9}$Y$_{0.1}$O$_3$-δ. 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 super oxide ion conductor, doped LaGaO$_3$ — the mixed H$^\text{+}$/O$^{2\text{-}}$ 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$_2$Zr$_2$O$_7$, Sr$_2$Ti$_4$O$_9$, Ba$_3$SnY$_3$O$_{12.5}$, LnSrCeO$_3$ (Ln = La, Nd, Sm, Gd) and non-stoichiometric mixed perovskite-type Ba$_3$Ca$_{1-x}$Nb$_x$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$_x$Ce$_{0.90-x}$Y$_{0.10+x}$O$_{3-\alpha}$ (0 ≤ $x$ ≤ 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 $t = (r_{\text{La}} + r_\alpha)/\sqrt{2(r_{\text{Ga}} + r_\alpha)}$, where $r_{\text{La}}$, $r_{\text{Ga}}$ and $r_\alpha$ 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 super 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 $E_{\text{obs}}$ is close to the theoretical $E_{\text{cal}}$. The ionic transport number, $t_\alpha$, determined from $E_{\text{obs}}/E_{\text{cal}}(=t_\alpha)$, 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
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 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. But, they also show oxide-ion conduction in pure proton atmosphere 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. 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
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 CMFCs 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-acylene combustion AACVD” [38]. These techniques have been used to prepare key materials thin films for SOFCs, such as CeO₂ [29], SrCeO₃ [30], Pd–Ni [31], YSZ [28,36,39], YDC [32], GDC [35,37,38], SDC [40], LaMnO₃ [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

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 BaCe₀.₈Y₀.₂O₂.₉ (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].
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/cm² 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 CO₂. Thus, CMFCs-H has a bright future.

(4) It has been found that the well known super oxide ion conductor, La₀.₃Sr₀.₇Ca₀.₇Mg₀.₃O₃⁻δ (LSGM), is a pure proton conductor in H₂ 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⁺/O₂⁻ 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.

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