

# Functional ceria–salt-composite materials for advanced ITSOFC applications

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## Abstract

This paper reports our current material research and development for advanced intermediate temperature (IT, 400–700 °C) solid oxide fuel cells (SOFCs). The materials reported in this work are based on ceria–salt-composites, which have super function, e.g. displaying ionic conductivity of 0.01–1 S cm<sup>-1</sup> in the IT region. They are functional ceramic materials for advanced ITSOFC applications. When these new composites are used as ITSOFC electrolytes, a performance of 300–800 mW cm<sup>-2</sup> between 400 and 650 °C has been demonstrated.

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## 1. Introduction

The fuel cell (FC) R&D and commercialization are now experiencing the third historical hot period pushed strongly by the environmental concerns and by the automobile industry. It is expected that the coming 5 years constitute a critical period to determine the market success of FC technology, which needs aggressive cost reduction (one-tenth) and fuelling infrastructure for commercialization. From a technical point of view, the material challenge is still a critical issue for all the present FC systems; while from the market and economic points of view, it is indispensable to make the FC price affordable and to meet the existing fuel infrastructure, e.g. gasoline, fossil fuel, natural gas, liquefied petroleum gas (LPG) and other hydrocarbon containing fuels, especially, methanol and ethanol. All these existing fuels would provide FC economic solution to enter the market before the hydrogen time coming (in about 20 years). None of the existing FC systems provides a universal solution to solve the current problems for power generation and environmental protection. Each FC system has its own respective advantages and disadvantages. The challenges and future opportunities must be carefully weighed. Our strategy is therefore to develop an advanced FC system

based on new materials to combine advantages from present FC systems to create a new competitive vis-à-vis FC technology. To realize this strategy the material R&D plays a key role.

Solid oxide fuel cells (SOFCs), especially intermediate temperature (IT, 400–700 °C) ITSOFCs are among the most important FC technologies. The SOFC is being developed extensively and the commercialization will be accelerated in the next few years. However, the high operating temperature (HT, ~1000 °C) of the conventional SOFC technology puts very high demands on the materials and technology, which is the reason why the material R&D still poses a major challenge for further development of the SOFC technology into the market. In order to develop the market cost-competitive SOFCs, many studies have been oriented to reduced temperature (below 800 °C) and ITSOFCs, either by using thin film technology to reduce the operating temperature of the yttrium stabilized zirconia (YSZ) electrolyte thus lowering the SOFC operational temperatures [1–4] or by using alternative electrolyte materials, such as various ionic-doped ceria, etc. [5–11] that can make the SOFCs function at lower temperatures. All these efforts have, however, limitations due to the deficiency of technology and the stability of the material.

We have conducted research on new materials and technology for ITSOFCs and the related ceramic FCs [12–15] with more than 13 years of incessant efforts. A recent

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research breakthrough in IT materials has been achieved for ITSOFCs using ceria–salt ceramic composites (CSCs) as electrolytes. These new CSC materials have demonstrated a super high ionic conductivity ( $10^{-2}$  to  $1.0 \text{ S cm}^{-1}$ ) and FC operating performance,  $300\text{--}1000 \text{ mW cm}^{-2}$  (under  $400\text{--}2000 \text{ mA cm}^{-2}$ ), in the IT region. It may open the door for industrial and market-competitive SOFC technologies.

Conventional ion-coping ceria electrolytes, e.g. gadolinium-doped ceria (GDC) can cause a certain electronic conduction in the reduced fuel environment, e.g. in a FC device because of the instability of ceria in reduced atmospheres [16–19]. Based on this finding, we have developed CSC materials in two ways to improve the electrical property and chemical stability of the GDC, etc. ceria electrolytes. One way is to prepare various nano-structured thin film ionic-doped ceria, and composite  $\text{CeO}_2$  (or GDC)– $\text{SiO}_2$  and  $\text{CeO}_2$  (or GDC)– $\text{Al}_2\text{O}_3$  [20–23]. These thin films were found to enhance the ionic conductivity and chemical stability significantly compared with their bulk/powder types with great potential for being used in both electrolyte and electrode materials. The other way is to prepare the ceria-composites with various salts. The earlier work was contributed to prepare ceria–chloride composites, such as GDC–NaCl, etc. By studying their FC applications, we found the ceria–NaCl composites could effectively suppress the electronic conduction, thus enhancing the material stability in the fuel environment [24]. Although the above ceria-oxide thin films and GDC–NaCl composites improved the material stability in the fuel environment, the conductivity of such composite materials was not sufficient for advanced ITSOFC applications. In order to develop functional CSC electrolytes for practical applications, various ceria and salt composites were investigated in this work.

## 2. Sample preparation and characterization

Ionic conducting CSCs were prepared by mixing different cationic-doped ceria, e.g. GDC, yttrium-doped ceria (YDC) and samaria-doped ceria (SDC) with various salts, e.g. chlorides, fluorides, hydroxides and carbonates in different weight ratios. The mixtures were heat-treated at  $600\text{--}800 \text{ }^\circ\text{C}$  for 1–2 h depending on the use of various oxides and salts. The resulting materials were ground thoroughly for use. The samples with the fluoride components were heated and treated for the second time in the same procedure as used for the first time. In some cases an insulating oxide, like alumina or silica, was also added in the CSCs to improve their electrical and mechanical properties.

Electrical properties were measured using both ac impedance analysis and FC  $I\text{--}V$  characterization, i.e. the current density versus voltage. Although the ac impedance measurements are a common way to acquire the material conductivity, the FCs were suggested as a useful tool to characterize the electrolyte materials in situ. Through direct measurements for the FC  $I\text{--}V$  characteristics, the

conductivity of the FC electrolyte can also be determined after subtraction of the influence of the electrodes and electrolyte–electrode interfaces as described early. In some respect the conductivity obtained from the FC study may more correctly depict the electrical property of the materials, especially when considering the material stability in in situ environment. It is worth comparing the results from both measurements.

The ac impedance analysis was conducted using a computerized Hewlett-Packard HP4274A LCR-meter. The measured frequency range covers from 0.1 Hz to 100 kHz with an applied signal of 20 mV. The temperature of the sample holder was controlled by a Eutherm temperature controller and the sample temperature was measured using a platinum thermocouple attached at the position of the sample. In most cases, the measurements were carried out between 400 and  $700 \text{ }^\circ\text{C}$ .

FCs were constructed using various CSCs as the electrolytes in the following procedures. (i) *Hot-pressing procedure*: The hot-pressing was used as a standard method to fabricate the CSC electrolyte FC assemblies. It was performed with the help of a Swedish NIKE hot-presser, whose maximum heating temperature can reach up to  $600 \text{ }^\circ\text{C}$  and the pressing force ranges from 0 to 35 t corresponding to a pressure of  $0\text{--}490 \text{ kg cm}^{-2}$ . The hot-pressing technique involves loading a mold with the powders of anode followed successively by the electrolyte and finally the cathode, all being pressed in one step to form a complete FC assemble for measurements. The pressed FC cell size was 13–20 mm in diameter (two molded sizes) and 1.5–2.0 mm in thickness, which consisted of an approximate 0.5 mm thick electrolyte, 0.5–1.0 mm thick electrodes, anode and cathode, respectively. The anode was based on NiO mixed with the CSC and the cathode based on lithiated NiO with the CSC. (ii) *Tape-casting incorporated with screen-printing and sol-gel processes*: The tape-casting is a common processing technique used by the ceramic industry. This process involves dispersing the ceramic powder in a solvent [25], which contains dissolved binders (usually an organic compound), plasticizers, and additives to yield the proper slip rheology. The slip is cast over a moving smooth substrate, and the desired thickness is established with a doctor blade device. After drying the slip, the organic binder of the “green” structure is removed by thermal decomposition to form a ceramic FC component usually containing the anode support and electrolyte. The other electrode, cathode, was then applied on the tape-casting electrolyte surface by the screen-printing technique to perform an entire FC assembly fabrication. The screen-printing slurry was prepared almost the same as that of the tape-casting. The cathode film was prepared by the slurry through a screen-printer. Before screen-printing the cathode, it can often be combined with a sol-gel process to prepare a thin CSC electrolyte layer (several  $\mu\text{m}$  thick) on the tape-casting electrolyte surface, followed by a heating step at  $500 \text{ }^\circ\text{C}$  to solidify the thin film together with the tape-casting assembly. This sol-gel film aims at modifying the

tape-casting electrolyte surface and maintaining dense and gas-tight function of the electrolyte. In fact the sol-gel process is generally used to prepare nano-structured materials and thin film membranes (1–10  $\mu\text{m}$ ). This technique is suitable to modify the microstructure of the device components to obtain desired properties.

The tape-casting incorporated with screen-printing and sol-gel processes is amenable to scale-up, and thin FC components, e.g. an electrolyte structures (0.1–0.2 mm) can be produced with an area size up to 100 mm  $\times$  100 mm in our experiments.

In the FC measurements hydrogen was normally used as the fuel. In some cases, alcohol and ammonia were also tested. Air was used as the oxidant for the FC tests. The gas, fuel (hydrogen or vapors of alcohol and ammonia) and air flows were controlled at around 50–150 ml  $\text{min}^{-1}$  under 1 atm pressure. For comparison with dry hydrogen, 5% water vapor in hydrogen was used in some cases.

### 3. Results and discussion

Fig. 1 shows the impedance spectrum of the cell using the GDC–CSC electrolyte in air at 550  $^{\circ}\text{C}$ . The spectrum of the cell in the air shows two arcs. The first high frequency (HF) arc is obtained only partially due to the limitation of the measured frequency only up to 100 kHz. An intersection of 0.9  $\Omega$  for this arc on  $X$ -axis reflects the bulk resistance of the FC. The second arc at low frequencies (LFs) is caused by the electrolyte–electrode interfaces with an intersection of about 5.8  $\Omega$  on  $X$ -axis. The LF arc is usually much larger than the HF arc because of the barrier between the ionic (in the electrolyte) and electronic (in the electrode) conduction, and because the reaction kinetics in the electrode and the interfacial regions always play key roles in determining the electrochemical cell performance. In a hydrogen/air FC there is a reduction process for the NiO-based CSC anode. The cell displays a deformed impedance spectrum with some blocking electrode behavior, as shown in Fig. 2 once the hydrogen and air were supplied. When the FC reached a stabilized open circuit voltage (OCV), the related impedance response (the LF arc) becomes a small and completed loop with an intersection of only 0.62  $\Omega$  on  $X$ -axis, compared with 5.8  $\Omega$  in the air, the bulk (cell) resistance reflected by the HF arc being also reduced with an intersection of 0.38  $\Omega$  on  $X$ -axis (0.9  $\Omega$  in the air). The complete LF loop indicates a well non-blocking electrode process. In replacement of  $\text{H}_2$  by Ar and later the air, the impedance spectrum in  $\text{H}_2/\text{air}$  FC was changed back to that in the air, suggesting a reversible process associated with the electrolyte–electrode process.

In situ process under the FC discharging were further studied. Fig. 3 shows  $I$ – $V$  characteristics during the OCV set-up and discharging processes. In the FC (OCV) set-up process, accompanying with the NiO-based electrode reduction, the FC gradually reached the normal cell OCV. The polarization caused by the electrode reaction and kinetics

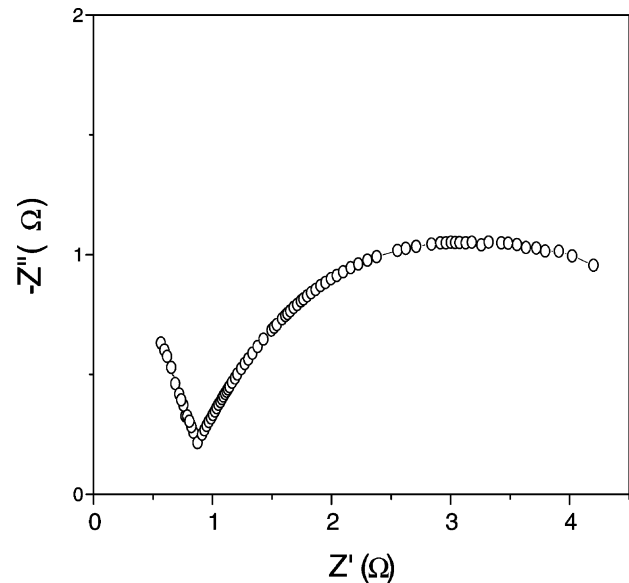


Fig. 1. Impedance spectra for FC with the GDC–CSC electrolyte in air (550  $^{\circ}\text{C}$ ).

results in a non-linearity of the  $I$ – $V$  characteristic in the initial step. It was reduced significantly during the continued OCV set-up process, thus the cell resistance was decreased from 2.2 to 1.1  $\Omega$  within the first 0.5 h. The discharge associated with the charge transfer between the electrolyte and the electrode more effectively improves the cell interfaces and removes the polarization effects. After discharge for 3 and 9 h, the cell resistance was dramatically decreased from 1.1 to 0.36  $\Omega$ . The polarization effects in the  $I$ – $V$  characteristics disappear partially and completely corresponding to the 3 and 9 h discharge. Thus, a good linearity

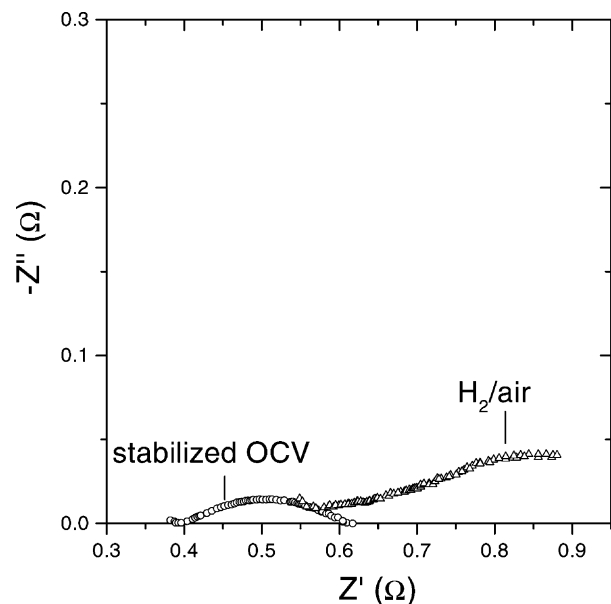


Fig. 2. In situ impedance spectra for a  $\text{H}_2/\text{air}$  FC with the GDC–CSC electrolyte in a  $\text{H}_2/\text{air}$  FC set-up process and in a stabilized OCV state, respectively (550  $^{\circ}\text{C}$ ).

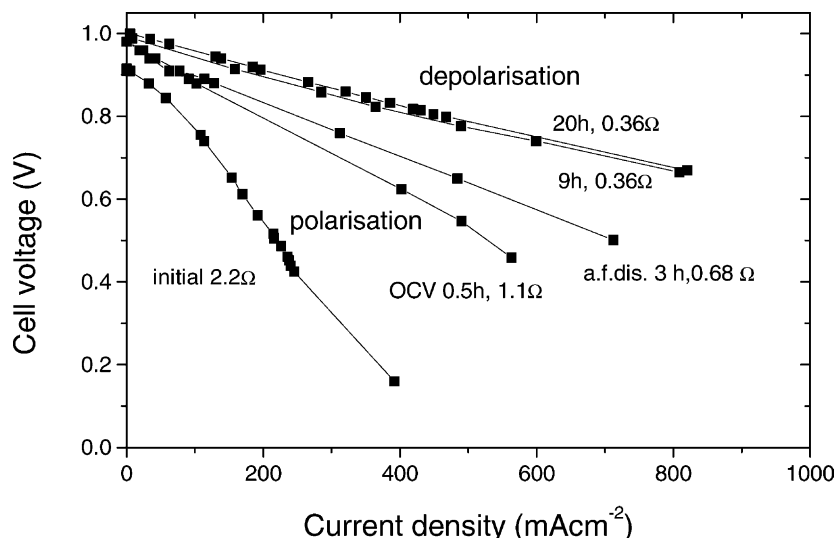


Fig. 3. In situ  $I$ - $V$  characteristics during a FC OCV set-up and discharging processes ( $550\text{ }^{\circ}\text{C}$ ).

of the  $I$ - $V$  characteristic is finally observed in Fig. 3. Continued discharge for 20 h does not change the linearity, displaying a depolarization process. In parallel to these studies, the impedance spectra were measured and the cell resistances were found to shift continuously to low resistances and finally maintain unchanged.

The CSC electrolyte FCs fabricated by the hot-pressing technique usually reached a voltage above 1.0–1.2 V in the IT region, which can be compared to around 0.8–0.9 V obtained for the non-composite ceria, e.g. GDC, YDC and SDC, as the electrolytes under the same FC fabrication conditions. The low voltages for the GDC, etc. electrolyte FCs result from the reduction and electronic conduction of the ceria electrolytes without composing in the fuel environment [16–19]. This situation is changed by using the CSC electrolytes. Fig. 4 shows  $I$ - $V$  and  $I$ - $P$  (power density) characteristics for various

GDC–CSC ITSOFCs at  $600\text{ }^{\circ}\text{C}$ . Figs. 5–7 show the  $I$ - $V$  (also  $I$ - $P$  in some cases) characteristics for the ITSOFCs using the GDC-, YDC- and SDC–CSC electrolytes operated at various temperatures, respectively. These ITSOFCs reach the power densities,  $300$ – $800\text{ mW cm}^{-2}$  with the current densities,  $400$ – $2000\text{ mA cm}^{-2}$ , in the IT region.

Further, by adding 5% water vapor in  $\text{H}_2$  as the fuel, the ITSOFCs showed rather similar performances with slightly lower (20–50 mV lower) cell voltage. Other fuels, like alcohol and ammonia were operated for the ceria–salt-composite electrolyte ITSOFCs. Initial results obtained are promising. When using alcohol (1–2 M) solution as the fuel it could reach a power density of about  $300$ – $350\text{ mW cm}^{-2}$  at  $600\text{ }^{\circ}\text{C}$ , and using ammonia (37% liquid) as the fuel, operation resulted in a power density output near  $600\text{ mW cm}^{-2}$  at  $620\text{ }^{\circ}\text{C}$ .

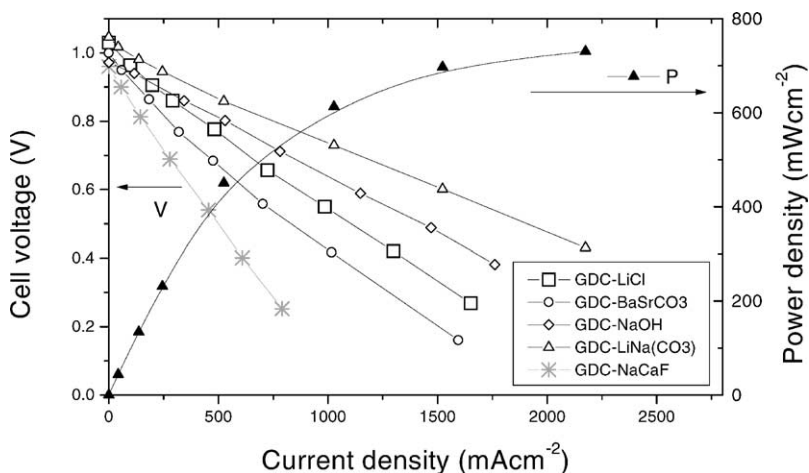


Fig. 4. Typical  $I$ - $V$  characteristics for various GDC–CSC electrolyte FCs at  $600\text{ }^{\circ}\text{C}$ , where GDC–LiCl means 80 wt.% GDC:20 wt.% LiCl; GDC–BaSrCO<sub>3</sub> is for 60 wt.% GDC:40 wt.% (50 mol BaCO<sub>3</sub>:50 mol SrCO<sub>3</sub>); GDC–NaOH for 80 wt.% GDC:20 wt.% NaOH; GDC–LiNa(CO<sub>3</sub>) for 80 wt.% GDC:20 wt.% (34 mol Na<sub>2</sub>CO<sub>3</sub>:66 mol Li<sub>2</sub>CO<sub>3</sub>); GDC–NaCaF for 80 wt.% GDC:20 wt.% (40 mol NaF:60 mol CaF<sub>2</sub>).

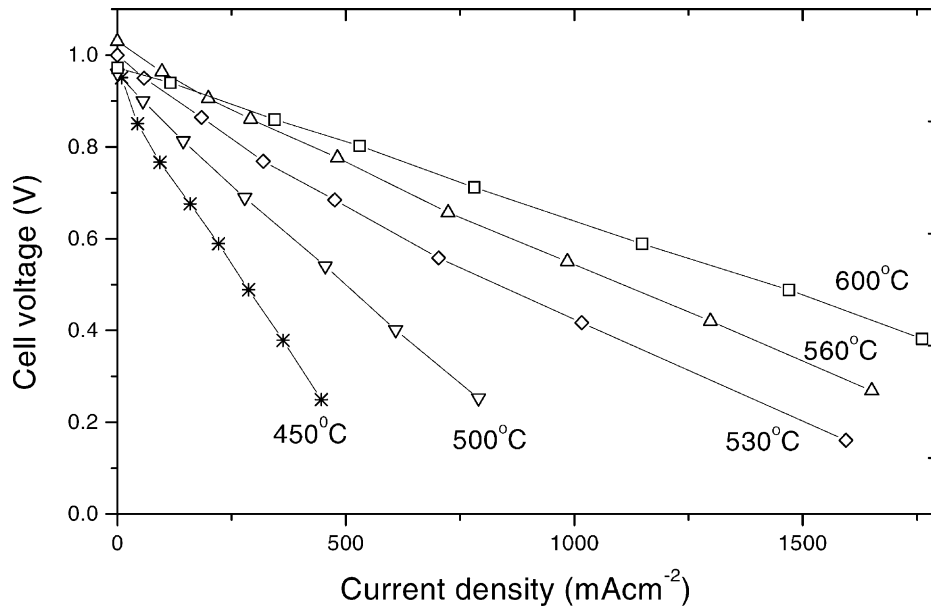


Fig. 5. Typical  $I$ - $V$  characteristics for GDC-CSC (containing 22 wt.% chlorite:1 LiCl:1 SrCl<sub>2</sub> in molar ratio) electrolyte SOFCs at various temperatures.

On the other hand, the tape-casting technique was developed to prepare the CSC electrolytes and electrodes with an acrylic latex binder in a water-based system. The FC components for the anode support (about 1.0 mm thick) with a 0.2 mm thick ceria-composite electrolyte were prepared through the tape-casting technique. The size for these tape-casting components can be scaled-up currently to an area of 100 mm × 100 mm. The actually functional components were measured for FCs with a diameter of 50 mm. However, at present, the FC results, e.g. unit-area power, obtained by using the larger area components, 50 mm in diameter, are far below than that made by the hot-pressing technique in a small size FC, e.g. 13 and 20 mm in diameter. There are some technical problems associated with the scale-up process. The major problem at present is to obtain

the high density of the electrolyte. It is very likely that the tape-casting technique alone is difficult to prepare pore-free, gas-tight and dense electrolyte on the porous electrode support (>30% porosity). In order to solve this problem, the sol-gel process was thus used to further modify the tape-casting electrolyte surface. It was found that the FC components with the sol-gel modification used for testing the FC power density was enhanced by 40% compared with that without the modification. The sol-gel combined with the tape-casting technique was thus able to make a FC power density reaching 100 mW cm<sup>-2</sup>. In addition, using the sol-gel process we have successfully developed various functional ceria and dope ceria-composite thin films with a nano-structure and a thickness in the μm level. Typical thin films prepared by the sol-gel process are CeO<sub>2</sub>-AlO<sub>2</sub>,

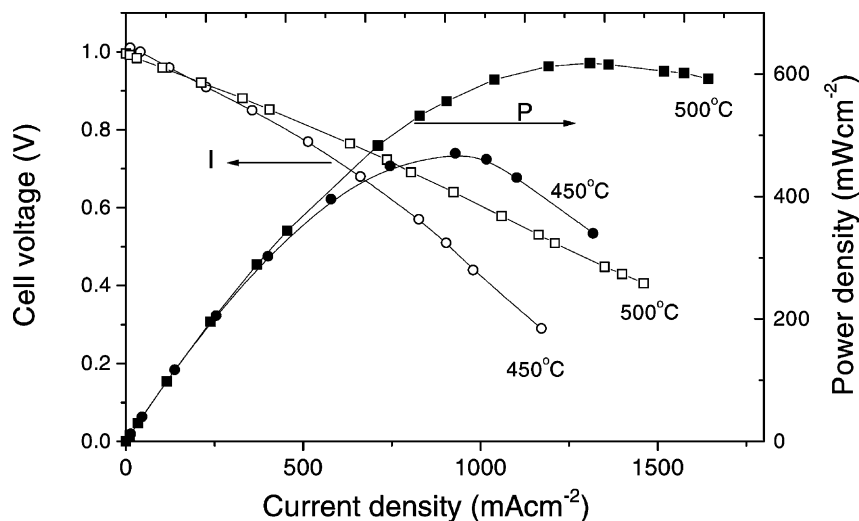


Fig. 6. Typical  $I$ - $V$  characteristics for YDC-CSC (containing 15 wt.% NaOH) electrolyte SOFCs at various temperatures.

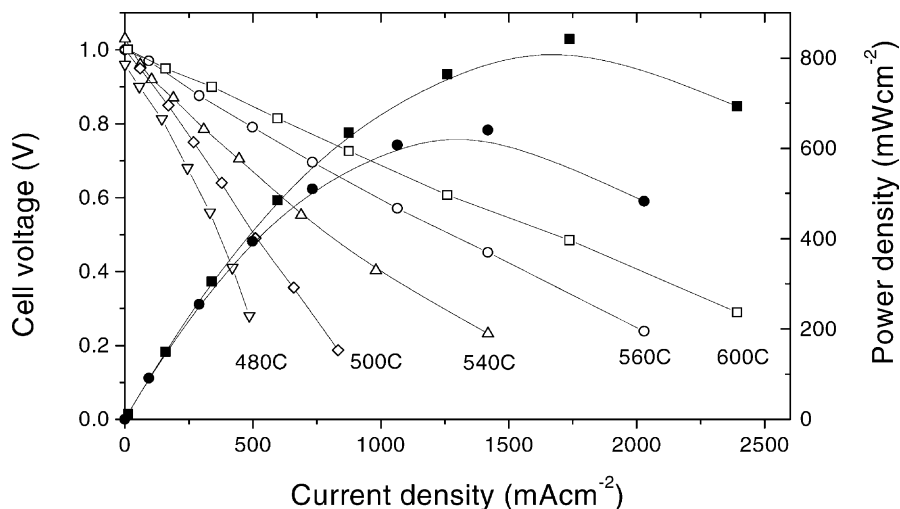


Fig. 7. Typical  $I$ - $V$  characteristics for SDC-CSC (containing 22 wt.% carbonate:2  $\text{Li}_2\text{CO}_3$ :1  $\text{Na}_2\text{CO}_3$  in molar ratio) electrolyte SOFCs at various temperatures.

$\text{CeO}_2$ - $\text{SiO}_2$ , doped ceria (e.g. GDC)-alumina and silica, etc. with promising application for ITSOFCs. These ceria-composite thin films showed significantly conductivity enhancement compared to their bulk materials with the identically chemical compositions. Fig. 8 shows temperature dependence of conductivity for various ceria-based thin films.

The conductivity of the CSCs was determined from both ac impedance and direct FC  $I$ - $V$  measurements. Both measurements displayed a fair agreement. The agreement may be due to an entire ionic conduction in the electrolytes. In order to give an overview and a picture of these new composite ceramic electrolytes, Fig. 9 depicts a range to represent

improvements of these new materials compared with the conventional SOFC electrolytes, e.g. GDC and YSZ without composing. It can be seen clearly from Fig. 9 that the ionic conductivity,  $10^{-2}$  to  $1 \text{ S cm}^{-1}$ , is obtained for various CSCs between 400 and 600 °C. This conductivity value is  $10^4$  times higher than that of the zirconia-based electrolyte, YSZ, used in HT SOFCs and 10–100 times higher than that of the non-composing ceria, e.g. GDC at the same temperatures. Table 1 summarizes the conductivity and relevant fuel cell performance for various CSC electrolytes studied in this work.

Being different from the oxygen ion conducting YSZ and pure ion-doped ceria electrolytes used in the conventional

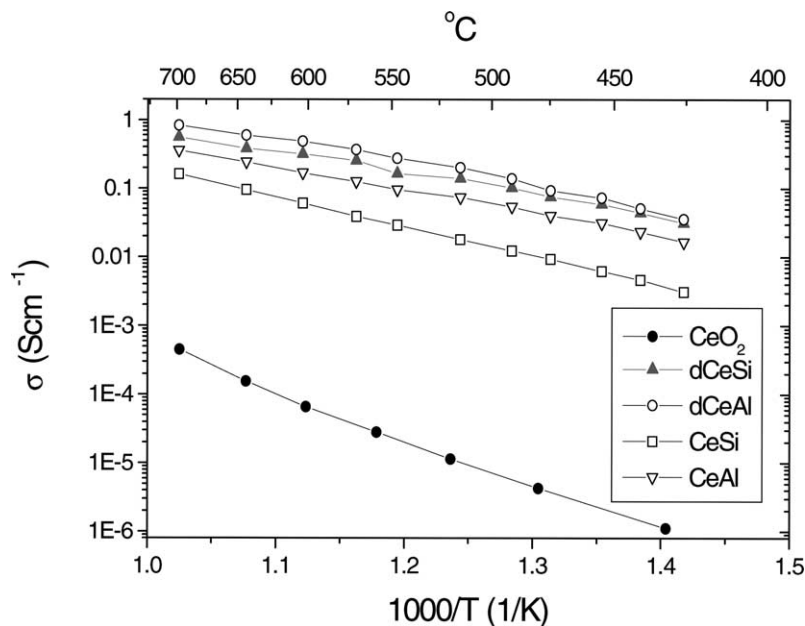


Fig. 8. Temperature dependence of conductivity for various ceria-based thin films, where dCeSi is the sample with 10 mol% Na-doped  $\text{CeO}_2$  composing with 50 mol%  $\text{SiO}_2$ ; dCeAl is 10 mol% Na-doped  $\text{CeO}_2$  with 30 mol%  $\text{Al}_2\text{O}_3$ ; CeSi and CeAl are the films for 0.5  $\text{CeO}_2$ -0.5  $\text{SiO}_2$  and 0.7  $\text{CeO}_2$ -0.3  $\text{Al}_2\text{O}_3$  (in molar ratios), respectively.

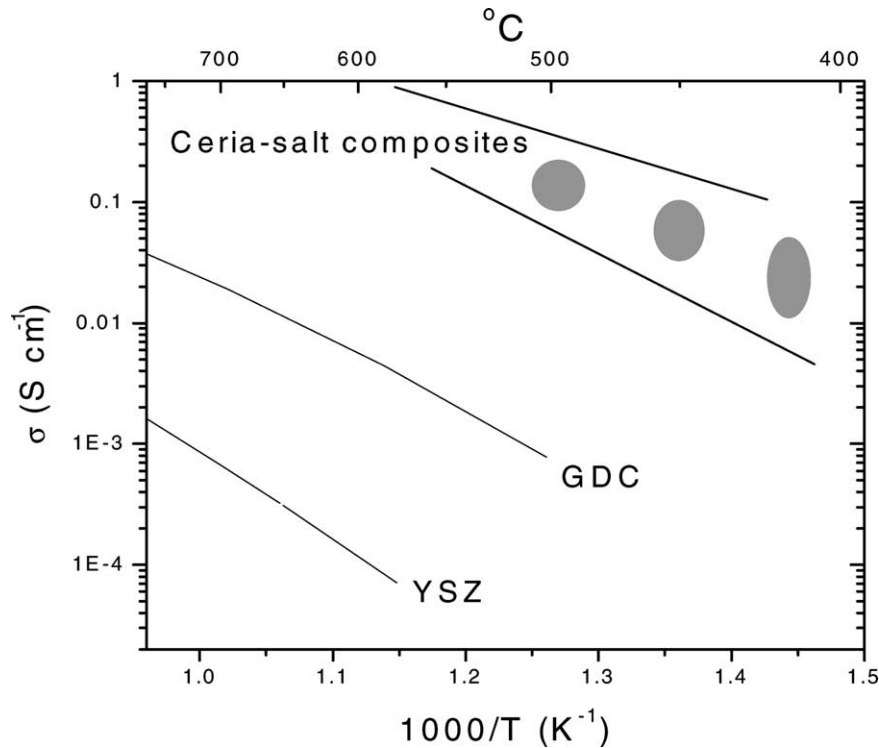


Fig. 9. Temperature dependence of conductivity for various CSC electrolytes compared to conventional SOFC electrolytes, e.g. non-composing YSZ and GDC. Typical CSC compositions are listed in Table 1.

SOFC, the new CSCs reported here are the two-phase composite materials with both oxygen ion and proton conduction. One phase, e.g. ion-doped ceria, has high oxygen ion conductivity; while the other, the salt, has significant proton conductivity as reported before [26–28]. Fig. 10 shows a schematic drawing of the proton and oxygen ion conduction and paths in the CSC two-phase materials. Certain proton conduction may promote the electrode reaction and the kinetics between the electrolyte and electrode interfaces, consequently enhance the current exchange rate resulting in the high current outputs. In fact the electrode–electrolyte interfaces are keys to determine the FC performance as observed for other SOFCs using the pure oxygen ion conducting electrolytes, e.g. YSZ.

These new materials have provided some important and interesting subjects concerning both fundamental and applied research. In conventional composite materials the significant conductivity enhancement, so-called composite effect, occurs usually for a system containing two solid-phase components, where one component has a moderate ionic conductivity while the other is non-conducting. The conductivity enhancement is suggested to be due to high conductivity in the interface layers between the conducting and the insulating phase, and has been observed in many materials [29–37]. Typical examples are LiX (X = I, Cl, F)–Al<sub>2</sub>O<sub>3</sub> and other oxyacid salts, such as Li<sub>2</sub>SO<sub>4</sub>, etc. mixed with alumina. The conventional composite theory [38–43] established on the material with the conducting and insulating phases cannot

Table 1  
Conductivity and fuel cell performance of the CSC electrolyte samples with three typical salt compositions

| Ceria | Salts                                                                                  | Conductivity (S cm <sup>-1</sup> ) | Fuel cell performance (mW cm <sup>-2</sup> ) | Temperature (°C) |
|-------|----------------------------------------------------------------------------------------|------------------------------------|----------------------------------------------|------------------|
| GDC   | 20 wt.% of 1 LiCl:1 SrCl <sub>2</sub> (mol%)                                           | 0.015–0.21                         | 0.1–0.58                                     | 400–660          |
| GDC   | 15 wt.% NaOH                                                                           | 0.02–0.45                          | 0.1–0.62                                     | 380–620          |
| GDC   | 22 wt.% of 2 Li <sub>2</sub> CO <sub>3</sub> :1 Na <sub>2</sub> CO <sub>3</sub> (mol%) | 0.01–0.80                          | 0.2–0.78                                     | 400–660          |
| SDC   | 20 wt.% of 1 LiCl:1 SrCl <sub>2</sub> (mol%)                                           | 0.02–0.24                          | 0.1–0.60                                     | 400–660          |
| SDC   | 15 wt.% NaOH                                                                           | 0.03–0.50                          | 0.2–0.66                                     | 380–620          |
| SDC   | 22 wt.% of 2 Li <sub>2</sub> CO <sub>3</sub> :1 Na <sub>2</sub> CO <sub>3</sub> (mol%) | 0.02–0.90                          | 0.2–0.80                                     | 400–660          |
| YDC   | 22 wt.% of 1 LiCl:1 SrCl <sub>2</sub> (mol%)                                           | 0.01–0.18                          | 0.1–0.52                                     | 400–660          |
| YDC   | 15 wt.% NaOH                                                                           | 0.02–0.4                           | 0.2–0.58                                     | 380–620          |
| YDC   | 22 wt.% of 2 Li <sub>2</sub> CO <sub>3</sub> :1 Na <sub>2</sub> CO <sub>3</sub> (mol%) | 0.01–0.78                          | 0.2–0.70                                     | 400–660          |

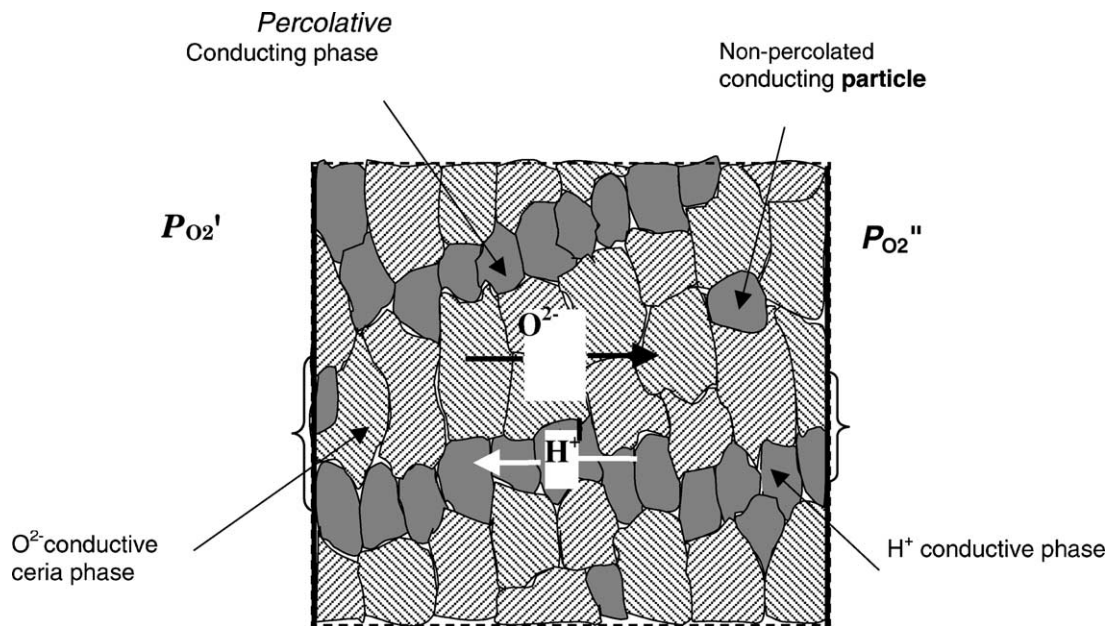


Fig. 10. Two interpenetrated percolative phases between the oxygen ion conducting ceria and proton conducting salt.

fully explain the new CSC materials that possess two conducting phases. Following the conventional way, the GDC–Al<sub>2</sub>O<sub>3</sub> does not make the conduction enhanced, but rather decreased [25]. At present stage, the detailed mechanism of the oxygen ion and proton conduction in these new CSC materials is still not clear, such as how the conductivity is enhanced once two conducting solid phases are involved in the material, especially, the GDC, YDC and SDC have already high defect concentration within its structure; what is the nature of the interfaces, thus the conducting mechanism, between the two conducting phases of the ceria and salts; and the knowledge of the ionic transport process for the oxygen ions and protons moving from the opposite directions in the FC process. All these and other related questions are still open. More fundamental studies are currently undertaking.

#### 4. Conclusions

The current SOFC commercialization faces a serious material R&D challenge. New materials R&D are essential to open the door for market-competitive ITSOFC technologies. Two-phase CSC electrolytes show conductivities in the range of 0.01–1 S cm<sup>-1</sup> in the IT region. The best ceria–salt-composites were found for the GDC– and SDC–MCO<sub>3</sub> (M = Li, Na, K, single or mixture of carbonates), both GDC and SDC composites show close electrical properties and ITSOFC performances. These ceria–salt-composite electrolyte ITSOFCs reach the power densities, 300–800 mW cm<sup>-2</sup> in the IT region. These ceria–salt-composites are thus new advanced materials. Based on them, various techniques, e.g. hot-pressing, tape-casting, screen-printing and sol–gel were developed to prepare and scale-up CSCs

for advanced ITSOFC applications. There is no doubt that continuous technical developments are valuable for obtaining a better and sounder energy alternative.

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