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Review paper

Studies on Dual Phase Ceria-based Composites in Electrochemistry

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The ceria-based dual-phase composites have been recently developed as functional electrolytes successful for intermediate and low temperature solid oxide fuel cell applications. These composite materials showed many unique advantages over the conventional single-phase electrolytes, such as superionic conduction in two-phase interfaces, dual proton and oxygen ion conduction resulting in extremely high ion conductivity and high current outputs in fuel cell and other applications, e.g. electrolysis. Interfacial superionic conduction is a characteristic for high conducting dual-phase composites. The composite approach can combine or integrate multi-ion functions, typically, dual H^+ and O^{2-} conduction together to enhance the material conductivity and device performance. Dual or hybrid H^+ and O^{2-}conduction is based on a consideration that both proton (H^+) and oxygen ion (O^{2-}) are the fuel cell source ions. Proton conduction is important for LTSOFCs since it can be activated easier than oxygen ions in the low temperature (LT, 300-600°C) region. The superionic conduction, dual phase proton and oxygen ion transport make significant conduction and electrical contributions for electrochemical devices. This paper makes a review on these recent studies.

Keywords: fuel cell, ceria-composite electrolytes, proton and oxygen ion conduction

1. INTRODUCTION

Single-phase ceria-based electrolytes, e.g., ion doped ceria, GDC or SDC, are considered as the promising candidate for developing solid oxide fuel cell (SOFC) at intermediate temperatures (below 800ºC) since their ionic conductivity can reach 10^{-1} S/cm at 800ºC, two hundreds degrees lower than that of the conventional high temperature SOFC electrolyte, YSZ (Yttrium stabilized zirconia) having a O^{2-} conductivity of 10^{-1} S/cm at 1000ºC. The ceria-based single-phase electrolytes have been studies extensively for decades in IT (intermediate temperature (IT, 500-800ºC) SOFCs [1-6]. However, some challenges hinder their commercialization and practical applications. The single-phase ion doped ceria exhibits a certain electronic conduction (n-type semiconduction) in the reduced fuel environment, e.g., in a fuel cell (FC) device because of the instability of the ceria in reduced atmospheres [7-9]. Consequently, this n-type semiconduction drastically decreases the open circuit potential from the theoretical values [10]. In this case, some amount of fuel is consumed by leaked oxygen due to the internal short circuit state of electrolyte by formed electrons. Furthermore, this electronic reduction also causes mechanical problems in the electrolyte [11]. Many efforts have been made to overcome the ceria material instability with electronic conduction problem in FC operations. It was reported that adding some amount of the YSZ to the Sm-doped ceria (SDC) to form the composite-type electrolyte can effectively suppress electronic conduction [12]. In this composite electrolyte, SDC grains were dispersed in a YSZ matrix, so the electronic conduction caused by SDC can be effectively blocked by the YSZ matrix. A SOFC with this composite electrolyte offered the advantages of a higher cell voltage due to pure ionic conducting YSZ, and high conductivity from SDC. The SDC content and the particle size significantly affected the power generation characteristics of the cell, and the polarisation was significantly decreased.

In recent years the ceria-based dual-phase composite electrolytes have been investigated widely involving various ceria-based composites. The earlier attemps were tried to prepare two-phase composite ceramic materials, such as GDC-Al_2O_3 and GDC-NaCl etc. By studying their fuel cell applications, we found these composite materials can effectively suppress the electronic conduction, thus enhance the material stability in the fuel environment [13]. However, the conductivity of such composite materials was even decreased. In order to develop functional ceria-based electrolytes for ITSOFC applications, many efforts have been made for investigation of on various ceria-based-salt composite ceramics, such as SDC (samarium doped ceria), GDC (gadolinium doped ceria), YDC (yttrium doped ceria) and CDC (caesium doped ceria) etc composites with different salts and hydrates, such as chlorides [14-16], fluorites [14, 15], carbonates [15-18], sulphates [19] and sodium or potassium hydrates [14, 15, 20]. These recent ceria-based composite developments have grown promising Next generation fuel cell R&D [21].

Nanocomposite idea of Zhu and co-workers [14-21] substantially changed the direction of solid oxide fuel cell research. The nanocomposite idea is based on combining a ceria based nano powders with a second conducting phase. The bulk properties of the composite element not anymore dominant, but interface between two constituents becomes effective in materials or composition properties. Extensive studies of Zhu and co-workers [14-21] showed that nanocomposites exhibits super ionic conduction at much lower temperatures (300-600 °C) then operating temperatures of conventional LTSOFS. This introduces a new class of SOFC, low temperature SOFC (LTSOFC).

The LTSOFC is considered as new breakthrough in solid oxide fuel cell technology. Lower operational temperature will allow the usage of conventional stainless steels as interconnector material which substantially reduces the cost of fuel cell and conventional sealing materials will be used. The lower temperature will also greatly reduce the startup and shutdown time of SOFC and respond time to the changing power requirement (increasing or decreasing the power produced). The advantages and high efficiency of LTSOFC will broaden the application area of SOFCs.

This paper makes a brief review on these studies in electrochemistry.

The ceria dual/two-phase composites so far investigated can be classified as basically following four criteria according to the 2nd composite phase used, with discussions in following sections, respectively.

2.1. Ceria-salt composites

In general, proton conduction exists commonly in many types of salts, and it may often transport in the two-phase interfaces of the composites [22-25]. However, salts are not used in SOFC alone due to high operating temperature. The composite of ceria and salts enhance the conductivity of electrolytes used in SOFC. This solid-like, or semi-solid and soft-solid composite electrolyte with high ion conduction based on the composite containing one molten phase had been discovered as early as in 1994 [26]. A typical ceria-salt example is the ceria-carbonate composite system, e.g. SDC-NLCO often containing one molten phase in a fuel cell operating temperature. A certain amount of the molten carbonate highly distributed and incorporated in the interfacial regions of the ceria oxide grains/phases can form the composites with a controlling level of the microstructure. In this case a certain amount of the molten carbonate can cause extremely high conductivity due to an interfacial effects, but not weaken the mechanical strength. So the system can well remain a solid-like state. In the SDC-carbonate composites the ceria is the host O^{2-} conducting phase, while H^+ conduction may exist in the 2nd (guest) salt phase and in the two-phase interfaces. Proton and oxygen ion conductions take place respectively in the SDC and carbonate/or in the two-phase interfaces based on different mechanisms. This new material concept thus provides feasibility to achieve high ionic conductivity, > 10^{-1} S/cm, in the LT region. The chemical stability and strong mechanical strength of the oxide benefit the system at the same time. They can also provide advantages in less corrosion compared with the pure molten salt phase, higher conductivity than the solid state. Therefore, the SDC-NLCO are some kind intermediate phase between solid and molten (liquid) states, which can combine the advantages from the SOFCs and MCFCs (molten carbon fuel cells), see below, new fuel cell science.

Among these ceria composites the SDC (or GDC and CDC)-carbonate composites are most commonly used materials, which have been demonstrated with the best performances in many LTSOFC applications. The two-phase ceria composite electrolytes, especifically the ceria-carbonate (Li_2CO_3-Na_2CO_3) containing one molten phase realized the superionic conductivity of 0.1 Scm^{-1}at 600ºC.

On the other hand, the alkaline earth carbonates, MCO_3 (M = Ca, Sr, Ba) used are in the well solid state for the FC operation at intermediate temperatures, 400 – 700 °C, since their melting points, 1339 °C for $CaCO_3$, 1740 °C for $BaCO_3$ and 1497 °C for $SrCO_3$, are far above the operating temperatures between 400 to 700 °C. The ceria-solid carbonate have demonstrated excellent ITSOFC technology [27], also the solid carbonates can significantly reduce the material corrosion. Li_2SO_4 is another typical solid salt example to form the solid-ceria-salt composites for LTSOFC electrolytes. In Li_2SO_4 which has an anti-fluorite structure a number of ”foreign” cations as well as H^+ are mobile [28-30]. Li_2SO_4 has discovered to have high proton conductivity, 10-2 S/cm at 600 °C, incorporated with the SDC, a new SDC-sulphate composite electrolyte has also made successful LTSOFC applications [19].

While for ceria-carbonate containing a molten phase, e.g. Li, Na, K-carbonate or their mixtures in a high composition, e.g. weight ratio higher than 60% in the SDC-carbonate composites, $CO_3^{=}$ anions can become highly mobile. In this case, in addition to O^{2-} conduction form the SDC phase, the $CO_3^{=}$ ion conduction is also significant when the operational temperatures above the carbonate melting points. The composites for fuel cell application in this case, can act a multi-ion transport system, where H^+, O^{2-} and $CO_3^=$ can make fuel cell contributions if the H_2 and air/CO_2 are supplied in the fuel cell conditions.

Unlike the conventional superionic conduction/transition that appears in the single-phase bulk from low conductive phase transferred to the superionic one accompanying a structure change, the superionic conduction in the composites is determined by the interfaces, i.e., the change in the interfacial properties without changing the phase structures. The composite system conductivity thus strongly depends on the coupling effect between the constituent phases.

2.2. Ceria-hydrate composites

Ceria-hydrate composites have been developed in a much similar way to the ceria-carbonate composites just replacing the carbonates by hydrates. The hydrates, such as NaOH and KOH were discovered with also proton conduction [30]. It can be expected therefore that the ceria-hydrate composites may have both O^{2-} conduction from the ceria phase and proton conduction form the hydrate phase as well as in the interfaces between these two constituent phases. When the operation temperatures above the hydrate melting points, the OH^- ions become also mobile which can make also significant conduction contribution if its composition is sufficiently high, same as that happens in the ceria-carbonate composite systems. Both proton and oxygen ion conduction results successful LTSOFC applications, near 800 mWcm^2 at 600ºC [20]. It should be pointed out for the ceria-hydrate composites that metal hydrates may react with CO_2 to form metal carbonates as observed in AFC (alkaline fuel cell). It is a problem for AFCs which are based on OH^- conduction process. As long as hydrate is converted to that carbonates, the AFC performance is degraded. Therefore, the AFC needs pure oxygen as oxidant for operations. Anyway, in ceria-hydrate composites, this hydrate-carbonate process does not affect its fuel cell application, because the ceria-carbonate mentioned above is still functional electrolyte for the LTSOFCs.

2.3. Ceria-perovskite oxide proton conductor dual phase composites

In addition to the salt phase acting as the 2nd composite phase, proton conducting perovskite oxide can also act as the 2nd phase used in the ceria-composites. Using the SDC-BCY composites, we obtained successful fuel cell performance, > 300 W/cm^2 [32]. It was observed that the fuel cell performance enhanced significantly when temperature above 550ºC. Later, Schober et al [33] prepared again the SDC-BCY composites and performed the impedance analysis/measurements and found that there is a superionic conduction at temperature around 550 ^{o}C [33], see Figure 1 (with permission from T. Schober). There has been ever an argument that the ceria-salt composites may cause high conductivity due to the molten salt effect, however, both oxides, SDC and BCY composites prove that there is an interfacial superionic conduction mechanism which results higher conductivity then that of each individual phase.

2.4. Ceria thin film dual phase composites

Nanophase ceramics are inorganic materials with typical microstructural dimensions less than 100 nm. When the ceramic is formed of nanocrystallities less than 10 nm, surface atoms become preponderant in

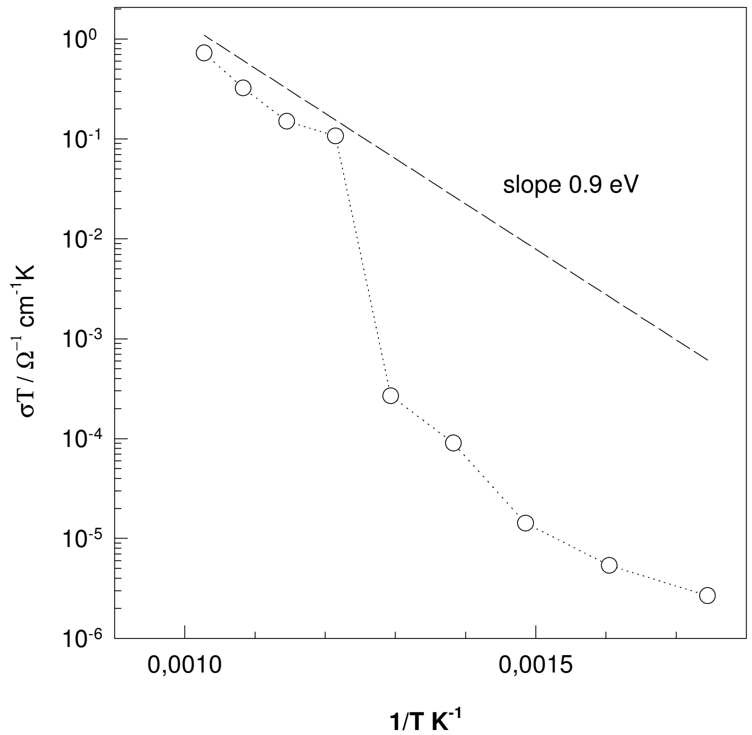

Figure 1. Impedance of a composite of the oxygen ion conductor $Ce_{0.8}Gd_{0.2}O_{1.9}$ (75%) and the proton conductor BCY15 (25%). Ag electrodes. Note superionic phase transition, with permission from Tillman Schober

the structure, yielding an improved surface adsorption, conduction and diffusion as well as catalytic and electrochemical properties towards gas phases and ionic/electronic transport processes. We have first developed various nanostructured thin film ionic-doped ceria, and composite CeO_2-SiO_2, CeO_2-Al_2O_3 and CeO_2-ZrO_2 [34-36]. These thin films were found to significantly enhance the ionic conductivity and also the chemical stability compared with their bulk/powder properties with great promise for ITSOFC applications. The unusual electrical properties and stability in the fuel cell are concluded to be the results of the nano-materials and nano-structured thin film.

The thin film structure which provides super function and significant improvement of the materials properties has revealed some new attributes of the nano-materials and brought new interesting academic subjects. The nanostructure-dependent properties of these thin film ceria-based materials differ much from those of crystals of the chemically identical bulk materials. High density of defects in nano-structured materials provides a large number of active sites for ionic conduction and high diffusivity through nanometer-sized interphase boundaries to promote fast kinetics and ion transportation. In the thin film the material; particles/grains are easy to form crosslinking framework and a special thin film two-dimension-like structure, which promotes the fast ionic transport and dynamic processes. This could be the reason why the nanostructured ceria-based thin films have demonstrated a number of great improvements compared with the bulk materials. This new phenomenon was not only discovered in the ceria-based but also in nano-thin Li_2SO_4-Al_2O_4 films [37].

Nanophase thin films based on ceria, e.g., $M_xCe_{1-x}O_2$, CeO_2-Al_2O_3 and CeO_2-SiO_2 a were successfully prepared via inorganic sol-gel process. Both ionic and mixed conducting properties can be designed targeting specific applications. The extent of the ionic and electronic conduction of the thin films can be adjusted through the material components and compositions. Such nanostructured thin films showed higher oxygen ion and mixed conduction at lower operating temperatures, which are of great interest for both fundamental and applied research. Especially, the thin films applied to the electrochromic devices, exhibit excellent electrochemical properties that could be attributed to the special nano- and thin film structure which is essentially different from the chemically identical bulk materials. The ion conduction in the ceria-based thin films and insertion/extraction in the CeO_2-composite thin films have proposed very interesting new areas and provided a basis for low (or two) dimensional-process and "thin film nano-electrolytes and nano-electrochemistry". This may be caused by the special bi-dimensional textural structure of the ultra-thin films [36]. The nano-structured thin films based on the ceria possess also great potential in film SOFC applications for intermediate temperature (400 to 700°C) or low temperature (below 400°C) operations.

3. Electrochemical studies

3.1. Gas concentration studies

In order to study proton and oxygen ion conduction and transport properties, the hydrogen concentration cells (HCCs) and oxygen concentration cells (OCCs) can be constructed. The results obtained from the respective HCC or OCC may not be directly compared with each other, since for some material, e.g. ceria, stoichiometry strongly depends on the in-situ gas atmosphere. This issue is specially addressed as follows [38]:"When speaking of the electrical properties of the halide-based electrolytes the gas atmosphere being employed must be specified." Indeed the employed gas atmosphere, e.g., the hydrogen, oxygen or fuel cell (FC) gas atmospheres, can change the sample's stoichiometry, ionic conduction and transport properties based on consideration of the defect chemistry described in section 3.2. In the hydrogen or oxygen concentration cells, the concentration of the mobile species, e.g., H^+ or O^{2-}, is not the same for the either case. For example, in the hydrogen (concentration cell), only H^+ is available from the external resources, while the O^{2-} ions are not available, converse case is true for the oxygen concentration cell case. In each specific case, the H^+ or O^{2-} is missing, but they can both be mobile if they are sufficiently generated from the supplied gas resources. On the other hand, we may not judge $t_{H+} + t_{O2-} = 1$ for individual measured results from the hydrogen and oxygen concentration cell. The key point here is that the studied materials do not possess of these H^+ and O^{2-} inherently, which are only generated from the provided external gas resources, see section 3.2. In addition, the results obtained from either hydrogen or oxygen concentration cell are under the specific conditions requested for eq. (1) and (2), i.e., residual water and oxygen (for the hydrogen cell) or hydrogen (for the oxygen cell) can be kept the same at both gas sides. Due to direct use of the commercial gases (different gases could have dissimilar standards for the residual water and other gas impurity), the above requested conditions can not be strictly followed. However, the obtained results are still useful to refer the properties of the respective ion species.

3.2. Fuel cell studies-Direct Characterization by Fuel Cells (FCs)

FCs have been used as a new method and standard procedure to evaluate the material properties. Both a.c. impedance analysis and fuel cell I-V characterization, i.e., the current density versus voltage has been suggested for characterization of the electrical properties of materials. Although the a.c. impedance measurements are a common way to acquire the material conductivity, the FCs are even better tool to directly characterize the electrolyte materials in-situ [38]. Through measurements of I-V characteristics, the conductivity of the fuel cell electrolyte can be determined after subtraction of the influence of the electrodes and electrolyte/electrode interfaces as described earlier [10]. The I-V plot shows the fuel cell voltage as a function of current. The current and voltage can be measured under various loads. The measurements give information about the electrolyte resistance, the reaction kinetics at the electrodes and gas diffusion limitations at the electrodes. In this work, the main experimental part of the I-V measurements is made in order to investigate the performance of the prepared fuel cell PEN, i.e. the anode/electrolyte/cathode assembly. We used electrolyte supported cell using Pt paste (Leitplatin 308A, Hanau) electrodes, where the electrolyte was about 1 mm thick. The fuel cell PEN assemblies were sandwiched between two gas distributing rings with an inner diameter of 0.95 mm and an effective gas area of 0.71 cm^2. The rings were made of stainless steel and painted with silver paste (Leitsilber 200, Hanau) which provides better contact and sealing between the electrodes and the gas distribution rings. The fuel, hydrogen, and the oxidant, air, were supplied via tubes to the anode and cathode chambers, respectively. A variable load unit was used to measure the current and voltage. The fuel cell was inserted into a cylinder furnace and the cell temperature was measured by a thermocouple. After introducing fuel at the set temperature, the OCV increased to a steady value. The current-voltage characteristic was obtained by drawing current at incremental steps and measuring the cell voltage at each step at steady state.

In some respect the conductivity obtained from the fuel cell study may more correctly depict the electrical property of the materials, especially when considering the material stability in-situ environment. Respective HCC and OCC studies may not provide correct material features because of the strong material stoichiometry dependence on the in-situ gas atmosphere. Following examples can provide a concrete picture for understanding the necessary for direct characterization by FCs. The same consideration is also needed for other stoichiometry dependent materials, e.g., ceria and related composites.

In FC atmosphere, the situation is different from the hydrogen and oxygen concentration cells, since in the FC case both H^+ and O^{2-} are available from external hydrogen (anode) and oxygen (cathode) resources. The situation here is somehow more complicated based on different mechanisms for H^+ and O^{2-} defect generation and transportation. There is a significant difference between oxygen ions and protons. The O^{2-} can replace F^- or Cl^- anion and occupy regular lattice sites, acting as normal ionic dopant. On the contrary, protons have very special qualities, such as being bare nuclei, extremely small, 10^{-5} Å in diameter, showing strong polarization ability etc. Protons are too small to occupy regular lattice sites. Instead they are easily attached or combined with anion groups or formed as proton-vacancy pairs [39]. Therefore, in

FC case, there is a competition between the H^+ and O^{2-} defects. From the defect chemistry point of view depicted in next chapter, H^+ defect is more easily generated than that of the O^{2-}. Thus the H^+ defect is usually predominating over the O^{2-} formation, making the proton transport number reasonably much higher than that of the O^{2-}. While in the hydrogen and oxygen concentration case, only one defect formation process exists, either for the H^+ (in the hydrogen cell) or O^{2-} formation in the oxygen cell since only one gas resource is supplied. As long as the external gas resources are available, and the time for the defect forming process is sufficient, the general defect chemistry eq. (1) - (3) should be followed. Therefore, each ionic defect concentration thus the transporting property is significantly different among FC, HCC and OCCs.

3.3. Electrolysis

The electrolysis experiment was performed using the fuel cell setup described above, but operated in a reverse process/mode. The electrolysis cell was connected to a constant voltage supply and a multimeter was used to measure the current through the circuit. The applied voltage was varied between 0.5-3.0 V and the current – voltage characteristics was obtained by drawing the voltage vs current in 0.5 V steps. When a more exact determination was needed, e.g. at the transition point of the electrolysis, smaller voltage steps, e.g., 0.2 V, was used. The current was measured at each step at steady state.

Water(steam) was supplied to one chamber, either to the anode or to the cathode, through an air flow saturated by means of a bubbler which contained boiling, or alternatively room tempered water. The other chamber (cathode or anode) was supplied by nitrogen gas in order to prevent the water (steam) from the air to enter the second chamber.

4. Results and Discussions

4.1. Structural characteristics

The ceria-salt or oxide, e.g., Al_2O_3 and SiO_2, composites consist of independent ceria and salt or other oxide phase as observed in XRD phase structure studies. Figure 2 and 3 show XRD patterns for respective ceria, GDC, mixed with NaCl, and CeO_2-Al_2O_3 or –SiO_2 composites. Distinctly separate diffraction patterns for GDC and NaCl can be distinguished as indicated in Figure 2. For CeO_2-Al_2O_3 or SiO_2 composites, due to amorphous Al_2O and siO_2 phase, their corresponding XRD patterns can not be observed, only CeO_2 phase is observed.

The SDC-carbonate composites are other typical ceria-composites containing either a solid $BaCO_3$-$CaCO_3$ (CBCO) or molten Li_2CO_3-Na_2CO_3 (LNCO) carbonate phase in the operating temperature range of fuel cell or electrolysis. Figure 3 shows the XRD results obtained from the SDC-carbonate composites. In the SDC-CBCO composite, where two separate phases of the SDC and carbonates were identified, see Fig. 3 (a). While for the SDC-LNCO composite containing the molten carbonate the XRD reflections only show the SDC phase, the molten carbonate is invisible from the XRD pattern, (Fig. 3 (b)). The EDX analysis, however, further proves the LiNa-carbonate co-existence in the SDC-NLCO composite, see Figure 4. The XRD results demonstrated that there was neither chemical reaction nor new compound between the SDC and carbonate phases. The carbonate component was in amorphous and highly distributed among the SDC.

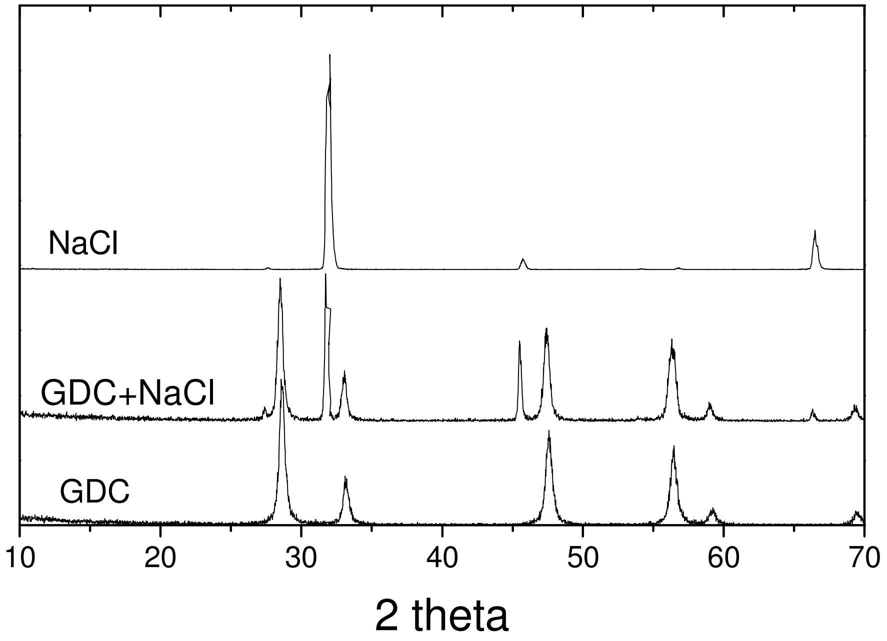

Figure 2. XRD patterns for ceria-composites: GDC-NaCl.

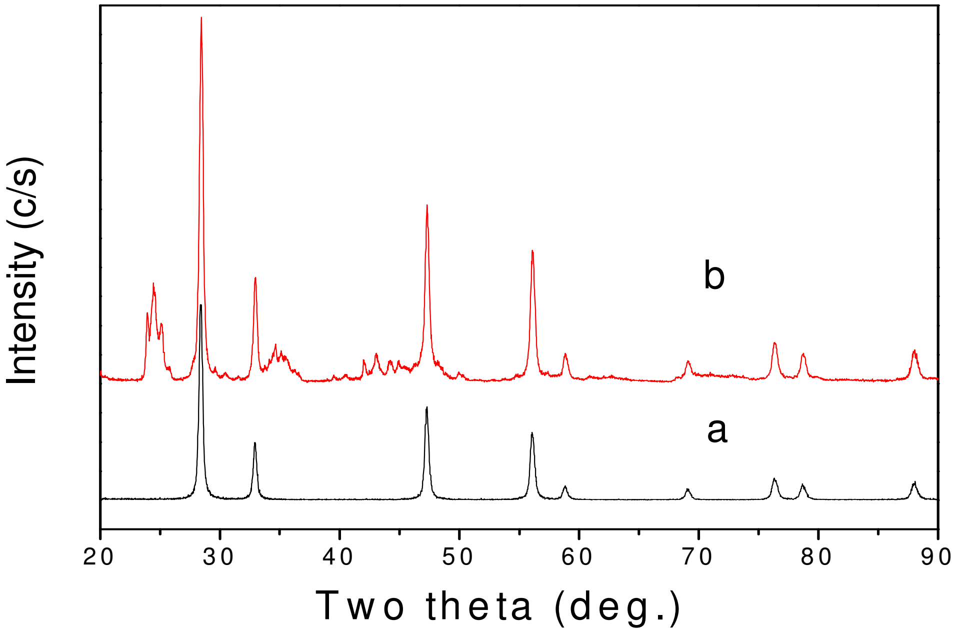

Figure 3. XRD patterns for ceria-carbonate composites, a) SDC-BaCO3 CaCO3; b) SDC-NLCO

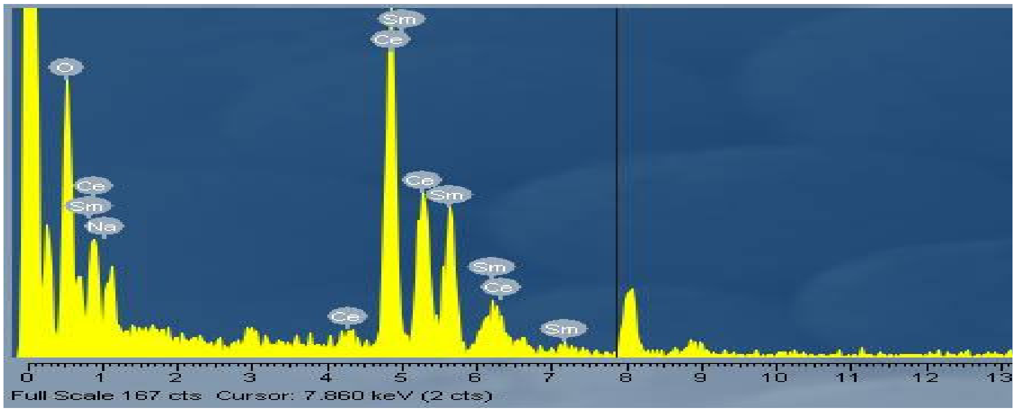

Figure 4 EDX for SDC-NLCO

4.2. Fuel cell studies

For the H_2/O_2 fuel cell with O^{2-} ion conducting electrolyte, oxygen is reduced at the cathode side to form oxygen ions and transported through the electrolyte to react with hydrogen at the anode side to form the water. When a proton conducting electrolyte is used, hydrogen will be oxidized at the anode side to form protons which are transported through the electrolyte to react with O_2 to produce water at the cathode. In the dual H^+/O^{2-} electrolyte, there are two ionic transporting processes, H^+ and O^{2-}, correspondingly, the following cell reactions take place:

at the anode: $H_2(a) \Leftrightarrow 2H^+ + 2e$ (1)

$H_2(a) + O^{2-} \Leftrightarrow H_2O(a) + 2e$ (2)

at the cathode $1/2O_2(c) + 2H^+ + 2e \Leftrightarrow H_2O(c)$ (3)

$1/2O_2(c) + 2e \Leftrightarrow O^{2-}$ (4)

(1) and (3) come to $H_2(a) + 1/2\ O_2(c) \Leftrightarrow H_2O(c)$ (5)

(2) and (4): $H_2(a) + 1/2\ O_2(c) \Leftrightarrow H_2O(a)$ (6)

Water is produced at both anode and cathode sides.

Figure 5 shows a typical fuel cell operation performance where the fuel cell is discharged under a constant load. The discharge curve shown in Fig. 5 displays a constant output under the current density of 600-800 mA/cm^2 between 520-580ºC. During the cell operation/discharge, water formations were tested at both anode and cathode sides. This is due to dual H^+ and O^{2-}conduction, thus allowing water produced at both the anode and the cathode according to above fuel cell reactions.

4.3. Electrolysis studies

In the electrolysis, i.e., the reverse operational mode of the fuel cell, the cell reactions are dependent on electrode which is supplied with water. Due to the changed polarities compared to the fuel cell, the

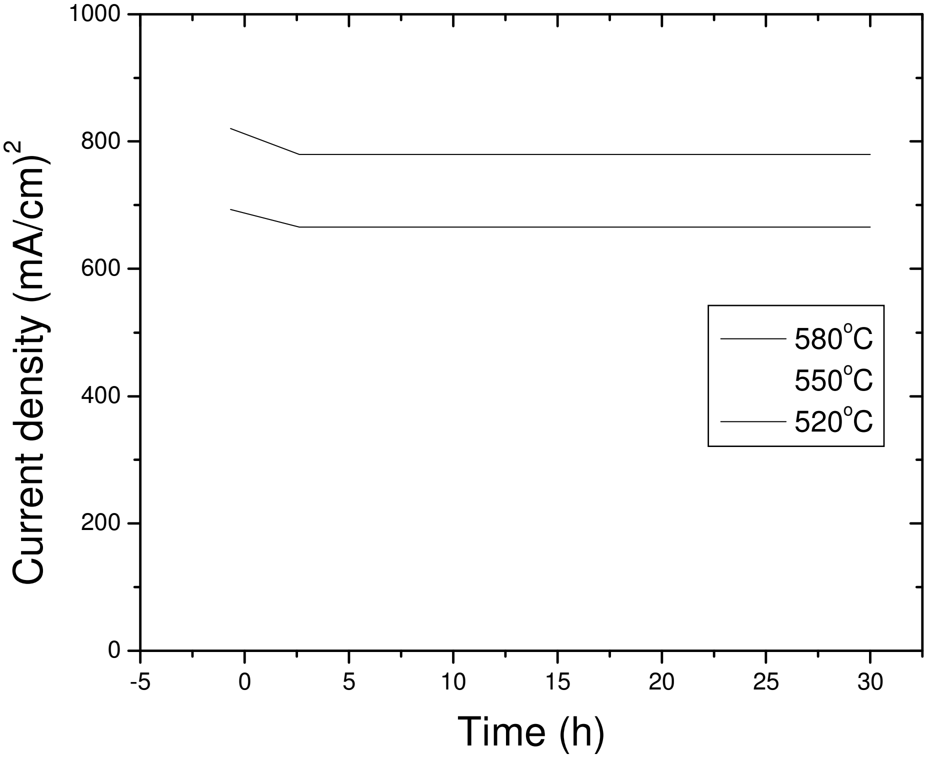

Figure 5. Discharge performances for the FC using the SDC-20 wt% carbonate electrolyte at 520-580°C.

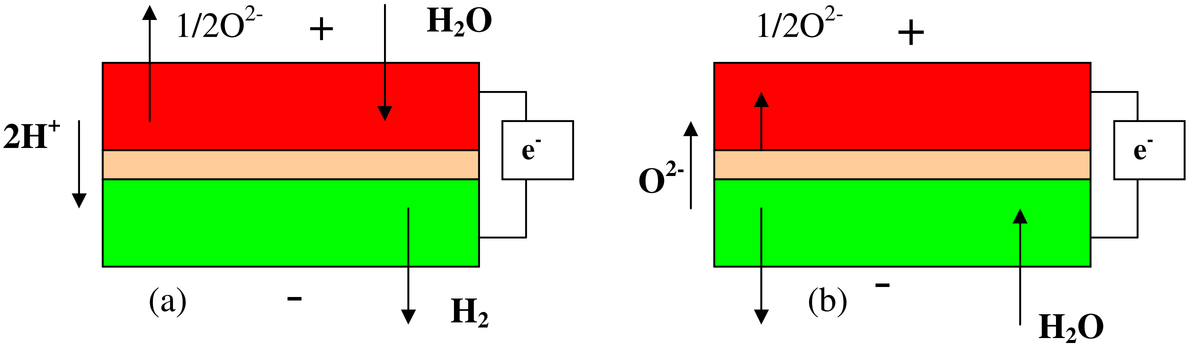

Figure 6. Electrolysis operation models for either H$^+$ or O^{2-} case, (a). Cell reactions taking place with water supplied at the positive electrode, in the H$^+$ conducting mode; and (b) cell reactions taking place when water is supplied at the negative electrode, in the O^{2-} conducting mode.

anode and the cathode defined in the electrolysis cell are just opposite to those of the fuel cell operating mode. In proton conduction case, water is supplied to the anode, protons are transported through the electrolyte from anode to the cathode, and the hydrogen is produced at the cathode side, Fig. 6 (a), while in the O^{2-} conduction case, water is supplied to the cathode, oxygen ions are transported through the electrolyte in the opposite direction compared to that of protons, i.e. from the cathode to the anode, thus producing the hydrogen again at the cathode side, see Figure 6 (b). These two kinds of electrolysis cell reactions are described below.

In case of water supplied at the cathode for a O^{2-} conductor, the reactions are:

Anode reaction: $O^{2-} \rightarrow 1/2O_2 + 2e^-$ (7)

Cathode reaction: $H_2O + 2e^- \rightarrow O^{2-} + H_2$ (8)

When water is supplied at the anode for a H+ conductor,

the following reactions take place:

Anode reaction: $H_2O \rightarrow 1/2O_2 + 2H^+ + 2e^-$ (9)

Cathode reaction: $2H^+ + 2e^- \rightarrow H_2$ (10)

The typical current–voltage curve, see Figure 7, of the electrolysis appears when the applied voltage is gradually increased. The current is small until a certain voltage, the decomposition voltage, is reached and thereafter the current increases more rapidly. The small current is caused by diffusion of ions away from the electrodes and a certain amount of external electric energy is needed to counterbalance this diffusion and to keep the electrodes polarized [40].

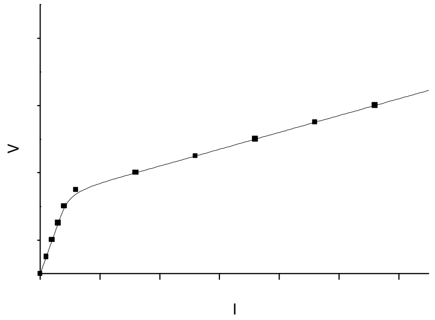

Figure 7. A typical current-voltage curve for an electrolysis cell.

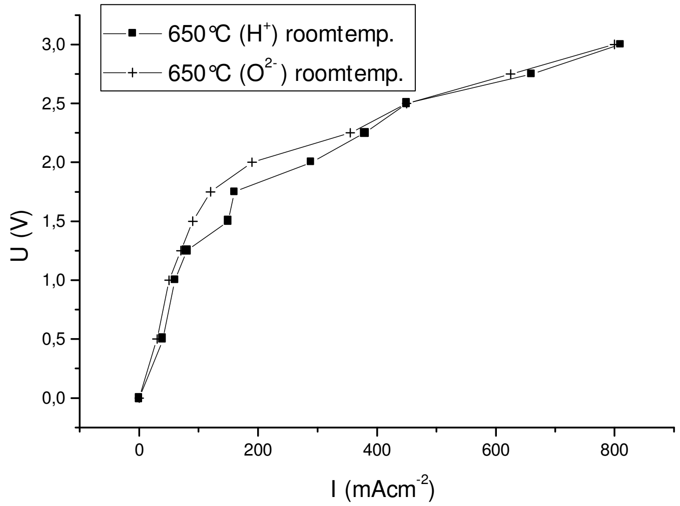

Figure 8. Electrolysis behaviors measured from the SDC-20 wt% carbonate electrolyte fuel cell at 650°C. Water saturated air (room temperature) and N_2 was supplied to the respective gas chambers during the process.

Figure 8 shows the typical electrolysis curves obtained for the electrolyte supported cell with Pt electrodes, where the typical current-voltage curve for the electrolysis cell (see Fig. 8) is seen with a clear electrolysis voltage transition, above 1.0 V for H^+ and 1.75V for O^{2-}. We see also that water saturated air (at room temperature) supplied to the electrolysis cell shows a lower current density than that of water saturated hot air. This could be due to that low temperature results to a low water pressure and consequently a low concentration of charge carriers. Finally, the cells showed significant current outputs both when water was supplied to the anode or to the cathode, respectively, which implies the two charge carriers, H^+ and O^{2-} are present. The plots related to either O^{2-} or H^+ transport results are indicated in Fig. 8 and the principal explanation is found in Figure 6.

4.4. Ionic conduction in composites

Significant enhancement is observed in the ionic conductivity and diffusivity in the interfaces between two phases in contrast to the single phase. This effect or conducting mechanism may be understood when CeO_2 exposed to the hydrogen of the fuel cell atmosphere which can cause a certain electronic conduction (n-type semi conduction) on the CeO_2 particle surface due to the reduction of Ce^{4+} to Ce^{3+}, where extra electrons were produced [10, 14, 41, 42]. These ceria particles thus form a semiconducting oxide. In the ceria-Ni-Al metal composites, the metal can promote this situation also directly bringing semiconducting sites to the composite material grains and interfaces. In either ceria-salt or ceria-metal composites for FC applications, there exist negatively charged oxygen adsorbents, such as O_2^-, O^-, and O^{2-}, could cover the surface of the ceria. These negatively charged oxygen adsorbents, especially, the additional oxygen ions on the surface of the ceria particles may essentially consist of an interfacial conducting path for oxygen ions. Consequently, some enhanced oxygen ionic conduction taking place. Thus, the nano-meter CeO_2-Al_2O_3, -SiO_2 are highly conductive though the CeO_2, Al_2O_3 and SiO_2 are insulators, respectively. This conducting mechanism is an essential consideration for the function and enhancement in the ITSOFC performance using ceria-based composites as the electrolytes.

4.5. Dual or hybrid H^+ and O^{2-}conduction

The ceria-based composite materials (usually with two/dual phases) have demonstrated major advantages in fuel cell applications over the single-phase electrolytes. Proton conduction is important for LTSOFCs because it can be thermally activated at low temperatures. The dual proton and oxygen ion conduction creates new advantages for LTSOFCs.

The O^{2-} conduction in ceria phase is determined by the oxygen ion vacancies (mechanism) in the ceria lattice; H^+ conduction may form in the carbonate through temporal bonding, H^+ - $CO_3^=$ (HCO_3^-) mechanism [26]. Both H^+ and O^{2-} conduction can be integrated in one composite to enhance the system conductivity based on the composite effect. This effect concerns the ion conduction at interfaces, or interfacial conduction, as the key. Figure 9 presents a schematic for such hybrid proton and oxygen ion conductor model and depicts also the hybrid/dual H^+/O^{2-} conduction routes and the conducting chain: H---O-H, H-O-H and O-H---O atoms/ions, which makes the H^+ (marked by two small bolls/dots in Fig. 9) and O^{2-} (larger boll) interfacial conducting path/mechanism.

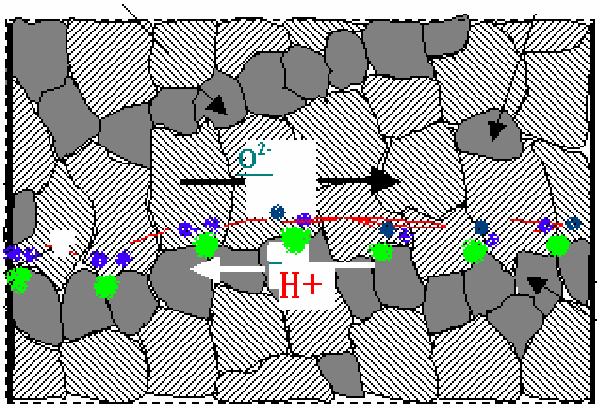

Figure 9. A schematic for such hybrid H^+/O^{2-} ion conductor model.

On one hand, it is highly possible for oxygen ions/atoms in the SDC particle/phase surfaces to meet and capture protons. This acts as a basic driving force for oxygen atom/ion on protons moving from one site to another in the interfacial range. On the other hand, because of certain high temperatures (hundreds of celsius), and high mobility of the oxygen ions in SDC, the captured protons cannot be stable with oxygen atoms/ions. There is a high tendency to release them. While at the same time, the neighbor oxygen atoms/ions being free from protons just wait for. Thus there is another driving force to push protons. Protons can only temporally stay with oxygen atoms/ions and then have to jump to another. The process of proton's capturing and releasing by oxygen atoms/ions results in an interfacial conducting chain/mechanism. Correspondingly this dynamic process/mechanism can also further promote oxygen ion mobility vice versa. Both H^+/O^{2-} conducting phases composing in one bulk are just good to excellent. This can never be the case when each phase are independent. This is an advanced function and mechanism of novel hybrid/dual composite conductors.

The combination of the H^+ and O^{2-} conduction can, on one hand, enhance transported ion concentrations/flows resulting in higher fuel cell current/power outputs; on the other hand, improve the electrode dynamics/kinetics and processes to create excellent fuel cell performances. These phenomena are significantly different from other fuel cells with only one kind of the ion function in/for the processes. Recent theoretical studies [43] have shown that SOFC-H^+ operation mode is more preferential than the SOFC-O^{2-} mode because the former can make a higher efficiency, especially for direct operation of the hydrocarbon fuels, such as methanol etc. Therefore, the combination of H^+/O^{2-} contributions creates another excellence and advance for the LTSOFC technology.

Although mixed H^+/O^{2-} conductions were discovered for some proton conducting perovskite oxides (PCPO) [44, 45], there are substantial differences between the PCPO and our materials. In the PCPO the H^+ and O^{2-} conductions are in a single phase based on the same oxygen vacancies. Consequently, the rule,

$$t_{H+} + t_{O2-} = 1 \qquad (11)$$

must be followed due to the same constituent, the oxygen vacancy to determine the conductivity. Thus, H^+ and O^{2-} conductions cannot enhance each other, but reversely, if one is weakened, the other is strengthened. Nevertheless the situation is completely different from our H^+ and O^{2-} conducting two-phase composites. Each conducting phase/species conducts through a different structure, phase and origin. In addition, the interfacial conduction processes/mechanisms play a key in the large conductivity enhancement. This applies not only to protons but also to oxygen ions because of some active interaction and interfacial mechanism between the constituent phases in the composite.

4.6. Multi-ion transport and New fuel cell sciences - combined fuel cell technologies

In addition to dual proton and oxygen ion conduction, there is a high possibility for $CO_3^=$ conduction in ceria-carbonate composites. But in order to conduct the carbonate anions as the functional fuel cell ions, two conditions have to be satisfied. *i)* Ceria-composites should provide sufficient mobility and conducting channels for $CO_3^=$ anions; *ii)* continuous $CO_3^=$ resources should be provided during the fuel cell operations. If any one is lacking the $CO_3^=$ effect on the fuel cell can be neglected when using the ceria-carbonate as the electrolyte. Otherwise, the $CO_3^=$ conduction and corresponding fuel cell effect/function will have to be taken into consideration.

In our current LTSOFCs, carbonate was used to form only the necessary shells for nano-ceria-composites, where the carbonate is in a solid or soften-solid state. The careful controlled the carbonate amount is in the level, just good for forming the percolative network and provide continuous ion conducting channels/framework. The carbonates are in stick or attached together with the nano-ceria core without flowing freedom. Therefore, the first condition is not satisfied; secondly, in our LTSOFC measurements, we always employed the hydrogen and air (or oxygen) gases to operate the fuel cell. This means that there is no sufficient or no external resources for $CO_3^=$ concentration to maintain the steady stable fuel cell current although there is little content of CO_2 in air. On the other hand, the fuel cell power output can reach 1000 mWcm^{-2}, much far higher than that can be obtained from the MCFC, this cannot be described by the $CO_3^=$ behavior. Finally, our fuel cell operation temperature in the 300-600ºC is lower than that of the MCFC (650ºC). At lower temperatures, the carbonate is well solidified. All these facts show unusual properties of the ceria-carbonate composites. Recent report on the super ion conduction transition in these composites is a typical example [46].

Of course, the ceria-carbonate composites can also be used as the MCFC electrolytes if the high carbonate contents (above 30 wt %), and MCFC operation conditions are supplied. It may benefit the MCFC using such kind composite electrolytes for multi-functions.

From the a.c. impedance and d.c. (fuel cell) conductivities we can further: electrical properties and multi-ion conduction functions of the ceria carbonate composites. Figure 10 shows conductivity-composition dependence for the SDC-20 wt% $LiNaCO_3$. It can be seen that the a.c. conductivity increases simply with the carbonate contents. Due to the solid state limit of the tested samples and the a.c. conductivity testing cell holder, we could only measure the carbonate contents up to 40 wt%. However, it can reasonably extend the result to higher carbonate content reaching the molten carbonate conductivity in the 1 S/cm level. The ceria-carbonate composite containing 35 wt% carbonate showed an a.c. conductivity already close to this level. But keep in mind that the a.c. conductivity reflects not only $CO_3^=$, but also all mobile ion conductivities, e.g., Li^+, Na^+ cations. In this case, the system acts as a multi-ion transport system, while M^+ (Li^+ and Na^+) are actually more mobile than $CO_3^=$. In this case, more mobile M^+ cations may result a side effect to additional potential polarization due to blocking or non-resourced mobile ions.

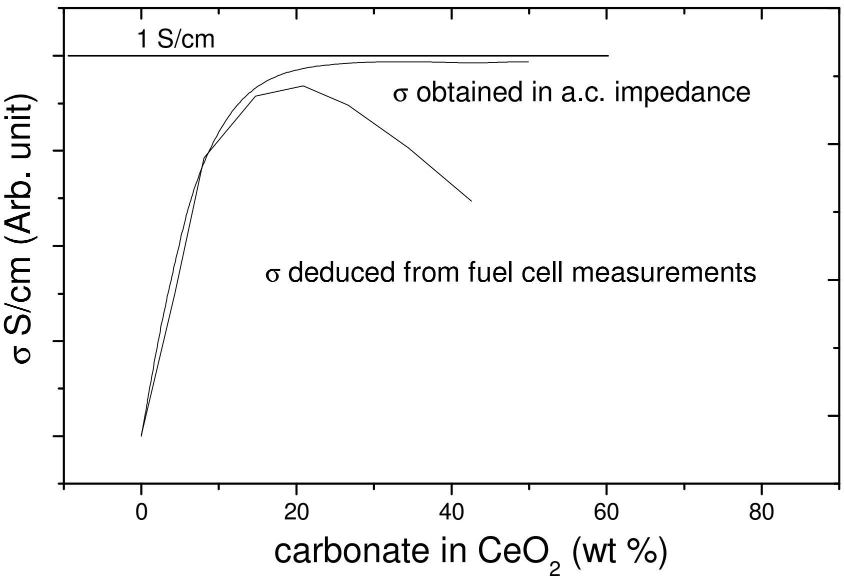

Figure 10. Composition dependence of the A.C. and D.C. conductivities for various SDC-carbonate composites

Conversely, the d.c. conductivity of the same sample showed only an initial increase with the carbonate composition up to about 20 wt%. Further increase the carbonates, the d.c. conductivity drops dramatically. This phenomenon may be explained as the conflict between the H_2/O_2 fuel cell source ions, H^+ and O^{2-} and blocking $CO_3^=$ ions mobility. The d.c. conductivity reflects only the source ions contributions. The $CO_3^=$ anions are huge mobile ions but blocking in H_2/O_2 fuel cell. The increase of their mobility and concentration can certainly destroy or hinder the fuel cell source ions, H^+ and O^{2-}, mobility and transport, thus cause the conductivity decrease.

These multi-ion transporting electrolyte and combining their conductivities together in one fuel cell device if it can be, we would create a new advanced fuel cell technology and high performance as the fuel cell power output is proportional to the transported ion concentrations. The ceria-carbonate electrolytes and its proton oxygen ion conduction property which results in excellent LTSOFC performances are the typical example.

In the early studies we found dual or hybrid O^{2-} and H^+ conduction combined in ceria-carbonate composites when employed as the fuel cell electrolytes. Based on this fact, we further investigated the similarities between the SOFC and MCFC to find possible common ionic conduction and transport mechanisms for such new fuel cell phenomena.

From the solid electrolyte and ionics point of view, the ceria-carbonate system is a multi-ion transport electrolyte system when used in fuel cell applications. It contains both intrinsic and extrinsic moving/transporting ion species depending on which fuel cell mode operated or which atmosphere provided. E.g., M^+(M= Li, Na, K), CO_3^{2-} and O^{2-} ions are intrinsic mobile species, while H^+ is extrinsic

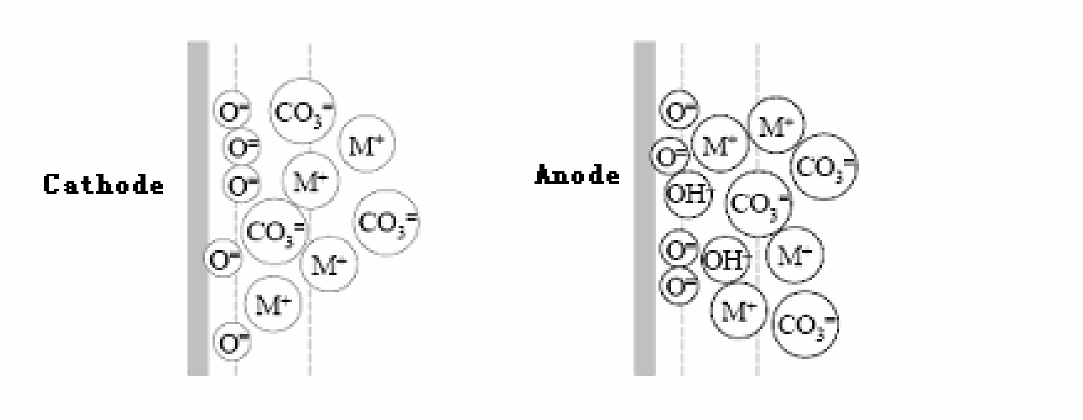

Figure 11. Double layer structure formed by various mobile ions at interfaces of the ceria-carbonate composite electrolyte and electrode in fuel cells

ions. Clearly Li^+/Na^+ are more mobile than any other ions, but they are blocking in either MCFC or SOFC operation due to no charge carriers' source M^+ ions provided, so they cannot contribute to fuel cell current outputs. However, the concentration gradient of these Li^+/Na^+ blocking mobile ions will be formed to make contributions or influences on the source ions transportation, see Figure 11. If under a hydrogen/oxygen (air) e.g. SOFC operation mode/environment, M^+ and CO_3^{2-} are both blocking mobile species due to no resources to supply. In this case, we may call it is SOFC technology based on O^{2-}/H^+ contributions; while in the MCFC case, CO_3^{2-} can make contribution, not M^+; however, it will be further determined by the operation conditions, e.g. the carbonate in the composite, i.e. how much carbonate contained in the ceria-carbonate composites which can supply sufficient mobile CO_3^{2-} concentrations, how high operation temperature is, above or below the carbonate melting points etc. In any cases, the O^{2-}/H^+ can exist as basic mobile species, resulted in a new combined SOFC/MCFC technology. All these will make different judgments on which fuel cell technology and processes based on the final results obtained. Therefore, the ceria-carbonate composite electrolytes have provided a very interesting fundamental research from material, ionics, electrochemical and fuel cell to device, technologies and applications. It opens a new field with significant importance for both fundamental and applied researches.

5. **Summary and Conclusions**

Ceria-salts and ceria-oxides, e.g., Al_2O_3 and SiO_2 as well as ceria-metal composites are advanced composite materials with vast application for developing new marketable ITSOFC materials and technologies. The new materials are super conductive (0.1 - 1.0 Scm^{-1}) for successful ITSOFCs applications. Conventional SOFC technology using ultra-thin YSZ (yttrium stabilized zirconia) layer electrolyte may reach the similar performance above temperature 750°C. It should be commented that our ITSOFCs have adopted thick layer electrolytes (around 400-500 μm thick), while YSZ SOFC for 750°C operation has to use ultra thin, several μm thick, electrolyte in order to achieve the same performance. This addresses two issues, *i)* The ceria-composite ITSOFC technology has a big potential for technical development by employing film technologies to prepare the thinner electrolyte to 20-50 μm thick preferably; *ii)* Several μm thick layer YSZ electrolyte SOFCs can not guarantee long life time operation, because the interfacial layers formed between the electrolyte and electrodes in SOFCs are at least several μm thick.

Compared with conventional SOFCs, challenge for the ceria-Salt/oxide composites mainly concerns Materials Science. It Concerns: i) advanced oxide synthesis uses the molecular engineering, designing the lattice defects, vacancies or interstitial atoms, in the crystal structure; *ii)* Soft chemical technology, e.g., *precipitation (sol-suspension)* and *sol-gel* processes, have been widely adopted to synthesis successfully various advanced ceramic powders and film membranes; *iii)* Nano-materials and technologies. The nano-technology for preparation of the ceria-based composites, especially in a good controlling level both for microstructure and molecule for the oxide phase. The properties of these ceria-composites prepared by the nano-technology are significantly different from those of the conventional bulk materials in many cases. High defect concentration in the nano-structured host oxide phase can provide a large number of active sites for protonic conduction as well as gas-solid catalysis. In addition, high diffusivity through nanometer-sized interphase boundaries promotes fast kinetics of catalyst activation and proton transportation. Even more, large fraction of interphase/grain boundaries in the nanostructures may effectively suppress the cationic conduction due to the fact that the cations are far larger than protons. The development regarding fully functional ceria-salt or oxide composites with advanced applications has made a good contribution to Materials Science and also certainly provided new opportunities for future LTSOFC commercialization.

Material R&D focusing on the IT/LTSOFCs has been concentrated in various new composite materials, although there are strong developments in parallel for technical development of the thin film YSZ SOFCs. The new materials are based on ceramic-composites, especially various ceria-based composites, have demonstrated promising material properties and their application for IT/LTSOFCs are very successfully. It can be believed these innovations reported in this review and its continuous development in materials will accelerate the fuel cell commercialization. The fuel cell technology, one of the greatest high technologies for the 21st century today still faces many challenges, among them, the material is eventually a critical issue.

The materials and their R&D for IT/LTSOFC can be classified as several groups, i) oxygen ion conduction dominating conductors; ii) proton conduction dominating conductors; iii) dual H^+/O^{2-} ion conductors and iv) oxygen ion and electronic mixed conductors. The latest group has only employed for IT/LTSOFC electrode application, while the former three groups are functional IT/LTSOFC electrolytes. The materials, especially, various ceria-based composites reviewed in this paper are growing of great interest in electrochemistry.

Use of dual proton and oxygen ion conducting ceria-based composite electrolytes has several advantages over oxides, e.g., high overall fuel cell system efficiency can be expected. Being different from the oxygen ion conducting YSZ and pure ion-doped ceria electrolytes used in the conventional SOFC, the new composite ceramic materials reported here are the two-phase composite ceramics 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. 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 fuel cell performance as observed for other SOFCs using the pure oxygen ion conducting electrolytes, e.g., YSZ.

The innovative dual phase ceria-based composites/materials offer solutions overcoming the drawbacks of the single-phase materials, such as interfacial superionic conduction, i.e. the superionic conduction created by the interfaces between the constituent phases, and dual proton and oxygen ion conduction. This field demonstrates also a new promising technology to produce hydrogen in the revised electrolysis process with the ceria-based dual-phase composite electrolyte fuel cell technology. The device can operate either in the fuel cell mode to produce electricity from hydrogen and oxygen or in the electrolysis mode to produce hydrogen and oxygen from electricity and steam.

Our dual H^+/O^{2-} conductors are based on proton and oxygen ion two-phase conduction in addition to the interfacial mechanism. It can enhance greatly the electrolyte material conductivity resulting in the high current outputs, and exhibits an enormous potential. On the other hand, deep understanding on multi-ion transport phenomena and corresponding electrochemical behavious/processes, such as double layer structure, polarization, effects caused by the blocking mobile and non-blocking species etc. fundamental studies are needed in order to develop successful advanced LTSOFC technology for practical applications and next generation fuel clel technology.

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