



Short communication

Ceria-based nanocomposite with simultaneous proton and oxygen ion conductivity for low-temperature solid oxide fuel cells

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ABSTRACT

The samarium doped ceria-carbonate (SDC/Na₂CO₃) nanocomposite systems have shown to be excellent electrolyte materials for low-temperature SOFCs, yet, the conduction mechanism is not well understood. In this study, a four-probe d.c. technique has been successfully employed to study the conduction behavior of proton and oxygen ion in SDC/Na₂CO₃ nanocomposite electrolyte. The results demonstrated that the SDC/Na₂CO₃ nanocomposite electrolyte possesses unique simultaneous proton and oxygen ion conduction property, with the proton conductivity 1–2 orders of magnitude higher than the oxygen ion conductivity in the temperature range of 200–600 °C, indicating the proton conduction in the nanocomposite mainly accounts for the enhanced total ionic conductivity. It is suggested that the interface in composite electrolyte supplies high conductive path for proton, while oxygen ions are probably transported by the SDC grain interiors. An empirical “Swing Model” has been proposed as a possible mechanism of superior proton conduction.

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1. Introduction

Solid oxide fuel cells (SOFCs) have attracted much attention because of their high potential for providing efficient, environmentally friendly, and fuel-flexible power generation systems that can be adapted for both small power units and large scale power plants [1,2]. Besides, they are the only fuel cell systems that can directly utilize combustible fuels, such as hydrocarbon fuels, biogas, coal gas, etc., without the need for external reforming [3]. There have been several prototypes of SOFCs successfully demonstrated by companies such as Siemens Westinghouse and Rolls-Royce [4]. However, such SOFCs systems require high operation temperature (800–1000 °C), which causes several problems, e.g. material degradation [5], as well as other technological complications and economic obstacles. Therefore, there is a broad interest in reducing the operation temperature of SOFCs, e.g. in the range below 600 °C [6]. A key requirement is to improve the performance of the electrolyte of SOFCs at such low temperature. This requires development of new materials or material architecture for achieving reasonable ionic conductivity of the electrolyte in this temperature range. Doped ceria is considered as a good candidate for low-temperature SOFCs (LTSOFCs) [7], besides it has been widely used as oxygen sensor, and three-way catalyst [8–11], etc. However, doped ceria shows electronic conductivity at lower oxygen

partial pressure which results in a significant power loss, thus preventing its further commercialization. The development of new electrolyte materials for LTSOFCs is a great challenge for SOFC community.

Earlier, we suggested novel ceria-based composites as promising alternative electrolyte materials for LTSOFC in 2001 [12]. In later reports, we have demonstrated that enhanced ionic conductivity can be achieved in the ceria-based composite systems, resulting in superior fuel cell performances, as reviewed in Ref. [13]. This composite approach was designed and fabricated based on the utilization of the interface as express path for ionic conduction. Recently, some new composite electrolytes with unique nanostructures, i.e. core-shell SDC/Na₂CO₃ nanocomposite [14], and SDC nanowires based nanocomposite [15] were designed by the novel nanocomposite approach, since the interface region is dominant in overall transport in these nanostructured composite materials. Two main functions were achieved by using carbonate as inclusion in the nanocomposites: (1) the ionic conductivity of the electrolyte was enhanced, and (2) the thermal stability of the nanostructure was improved [16]. However, up to now, the exact conduction mechanism for the enhanced ionic conductivity remained unclear, especially in terms of charge carriers (proton or O²⁻).

In the present study, the proton and oxygen ion conductivity of SDC/Na₂CO₃ nanocomposite electrolyte has been carefully investigated by employing a four-probe d.c. technique under different gas atmospheres in the temperature range of 200–600 °C. The conductivity data were analyzed to identify the possible conduction pathways for proton and oxygen ion in the nanocomposite.

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2. Experimental

The SDC/ Na_2CO_3 nanocomposite system investigated in this study is the same as in our previous report [14]. The SDC/ Na_2CO_3 nanocomposite material was prepared as described elsewhere [14] and pressed under 300 MPa into pellets, followed by sintering at 680 °C for 30 min. The d.c. conductivity of the nanocomposite electrolyte was measured by the four-probe technique in a temperature range of 200–600 °C. Pt paste was painted on both surfaces of pellet in aligned ring shape as current probes. A pair of Pt points was painted by Pt paste at the center of Pt rings, which served as voltage probes. The distance between voltage probe and current probe was kept as 1 mm. Thereafter, the pellet with Pt painting was heated at 700 °C for 30 min. A slurry, made by mixing Pyrex® glass powder and commercial binder with acetone, was pasted on the exposed part of sample and baked at 700 °C to serve as the external sealing. The conductivity under reducing or oxidizing atmosphere was monitored by continuously supplying anode gas (5% H_2 , 95% N_2) or cathode gas (synthetic air, 21% O_2 , 79% N_2) to both sides of the pellet. A typical excitation of 1 mA was applied from EG&G 366 current source. The potential drop across the sample was measured using a HP 3478A digital multimeter.

The ion blocking cell is employed for the Wagner–Hebb measurement. Pt paste and Pt foil were used as reversible electrode and blocking electrode respectively. The cell was sealed by Pyrex® glass as well. A constant voltage from EG&G 366 potentiostat was applied to the cell, and the current was measured by a HP 3478A multimeter.

3. Results and discussion

Electrical conductivity of a solid electrolyte at different temperature is, in general, the most important factor to be used to evaluate its property. For polycrystalline electrolytes, electrical conductivity can be studied by electrochemical impedance spectroscopy (EIS), especially when grain interior and grain boundary conductivities have to be separated [17]. In SOFC field, EIS is extensively used to determine the conductivity of all types of solid electrolytes. As an example, Boden et al. have reported an extensive study on the conductivity of SDC-carbonate composite with different composition under several gas atmospheres measured by EIS [18]. However, despite its versatility, EIS is not very suitable for studying composite systems, where multiple mobile charge carriers will contribute to the overall measured conductivity, e.g. O^{2-} , H^+ , Na^+ , and CO_3^{2-} [19]. Hence the contribution of the specific ions of interest in SOFC operation, i.e. O^{2-} and H^+ , cannot be distinguished from contributions of other ions when studied by EIS. This is probably the reason that the exact conduction mechanism for SDC composite systems remained unclear in spite of many reported studies. The four-probe d.c. conductivity measurement, employed in this study, on the other hand, gives an unequivocal conductivity measure of mobile ions under different gas atmospheres over a wide temperature range. Furthermore, from a practical point of view, d.c. measurements are more close to the actual application regime of SOFCs. Therefore, we suggest the use of four-probe d.c. measurement as a good alternative to determine the contribution of each charge carrier (O^{2-} and H^+) in the SDC/ Na_2CO_3 nanocomposite system. The four-probe d.c. technique is not a new method for investigating solid electrolytes [20], but there has been limited reports on study of electrolytes using this technique during the past decades.

Fig. 1 shows the total conductivity of the SDC/ Na_2CO_3 nanocomposite electrolyte obtained from three different techniques. The EIS data is taken from our previous work [14], and the conductivity calculated from the slope of fuel cell current–voltage characteristics is shown as well. It is seen that the conductivity measured by four-

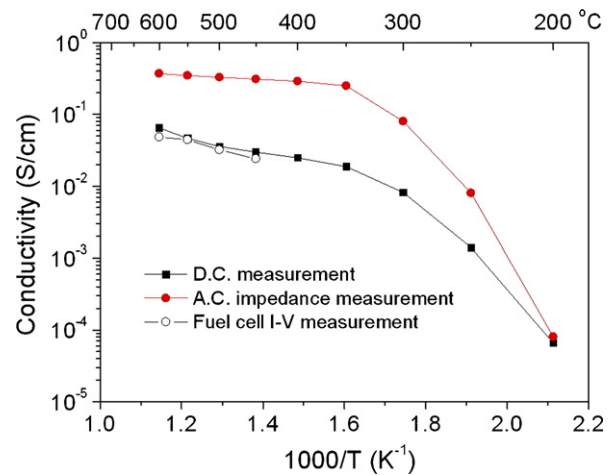


Fig. 1. Conductivity of SDC/ Na_2CO_3 nanocomposite electrolyte obtained from d.c. measurement (the sum of proton conductivity and oxygen ion conductivity), a.c. impedance spectroscopy, and derived from fuel cell I - V curve.

probe d.c. technique, which is the sum of the proton conductivity and oxygen ion conductivity, is much closer to that derived from the slope of fuel cell I - V curve representing the actual fuel cell performance [21], whereas the conductivity data of the SDC/ Na_2CO_3 nanocomposite measured by EIS show much higher values because of contributions from other ions, like Na^+ , CO_3^{2-} . This confirms that d.c. technique more objectively reveals actual performance of the composite electrolyte systems. In the d.c. measurement, only ions associated with fuels (O^{2-} and H^+) can contribute to the measured conductivity, while ions that are not actually contributing to the measured conductivity are blocked in a “static status”. It is worth noting that there is a sharp increase in the conductivity measured by both d.c. and EIS around 350 °C. This phenomenon which has been reported in our previous study can be explained to be due to the glass transition of amorphous Na_2CO_3 phase [14]. It is expected that glass phase transition allows more freedom for ion transportation in the interface region existing between Na_2CO_3 and SDC, thus resulting in much lower activation energy above T_g of carbonate (less steep slope).

Fig. 2 displays the temperature dependence of conductivity of SDC/ Na_2CO_3 nanocomposite electrolyte under two different gas atmosphere, 5% H_2 and air, as determined by the four-probe d.c. measurements. Under hydrogen gas atmosphere only proton conductivity (σ_{H^+}) makes a significant contribution to the overall

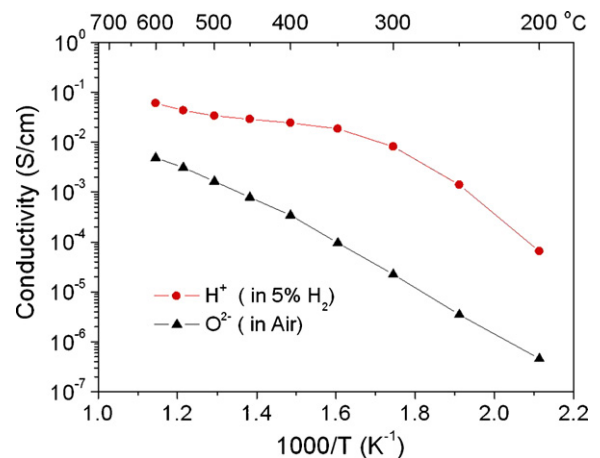


Fig. 2. Conductivity of SDC/ Na_2CO_3 nanocomposite electrolyte under 5% H_2 and air atmosphere measured by four-probe d.c. technique.

measured conductivity, as electronic conductivity can be neglected (this will be elaborated later). Similarly, the conductivity measured under air is mainly resulting from oxygen ion conductivity ($\sigma_{O^{2-}}$). It is shown in Fig. 2 that σ_{H^+} of SDC/ Na_2CO_3 nanocomposite electrolyte is much higher than $\sigma_{O^{2-}}$ with 1–2 orders of magnitude over the whole temperature range (200–600 °C). For example, at 600 °C σ_{H^+} is approximately 0.06 S cm⁻¹ while $\sigma_{O^{2-}}$ is 0.005 S cm⁻¹. These results demonstrate for the first time that proton conduction mainly accounts for the enhanced ionic conductivity in the nanocomposite electrolyte. The proton conductivity curve (—●—) shows a change of the slope at around 350 °C, corresponding to activation energy of 0.272 eV above 350 °C and 1.018 eV below 350 °C. It is obvious that the transition point is just above the glass transition of carbonate. On the other hand, the oxygen ion conductivity has a nearly constant slope over the whole temperature range, corresponding to an activation energy of 0.896 eV. This is comparable to the value obtained for heavily doped nanostructured ceria electrolytes reported by Bellino et al. [22]. From these data it is clearly demonstrated that the interface introduced by carbonate in the SDC/ Na_2CO_3 nanocomposite enhances the protons conduction, while it seems not to have any effect on the oxygen ions transportation, whose path is expected to be the grains of SDC. The interface introduced by carbonate as inclusion acts as pathway for proton transport since proton has a higher limit of ionic diffusivity and mobility than O^{2-} , resulting in an enhanced ion transportation.

On the other hand, there is a general concern that the high conductivity obtained for SDC/ Na_2CO_3 nanocomposite under reducing atmosphere may be related to an increase of the electronic conductivity due to reduction of doped ceria. However, the electronic conductivity in the SDC/ Na_2CO_3 nanocomposite system is negligible in the temperature range considered. Firstly, it has been verified, in our previous reports [16], that the electronic conductivity of SDC was reduced effectively by the introduction of carbonate, as the open-circuit voltage (OCV) of cells based on the SDC-carbonate electrolyte was clearly higher than typical SDC film single cells. Secondly, it is widely accepted and demonstrated that electronic conductivity of doped ceria is negligible at temperatures lower than 600 °C [23]. In order to further confirm this hypothesis, the electronic conductivity, σ_e , of the composite electrolyte was measured by Wagner-Hebb method with an ion-blocking electrode [24], and was determined to be 3×10^{-4} and 2×10^{-4} S cm⁻¹ at 600 °C and 550 °C. From these measurements, σ_e/σ_{H^+} is less than 0.5%, which confirms that electronic conductivity of SDC/ Na_2CO_3 nanocomposite electrolyte is quite negligible below 600 °C and its high conductivity under 5% H_2 atmosphere is due to enhanced proton conductivity.

From the above, the electrode reactions of SDC/ Na_2CO_3 nanocomposite SOFCs during operation of the fuel cell can be expressed as:

Anode reactions:



Cathode reactions:



where H^{\bullet} , $V_0^{\bullet\bullet}$, O_0^{\times} , e^{-} denote a proton, an oxygen vacancy, a lattice oxide ion and an electron, respectively. Thus, different to conventional electrolytes in SOFCs, the novel SDC/ Na_2CO_3 nanocomposite electrolyte possesses the unique simultaneous H^+/O^{2-} dual ion conduction property. This unique behavior has been further substantiated by the experimental observation of H_2O generation on both electrodes. Fig. 3a gives a schematic illustration of the dual

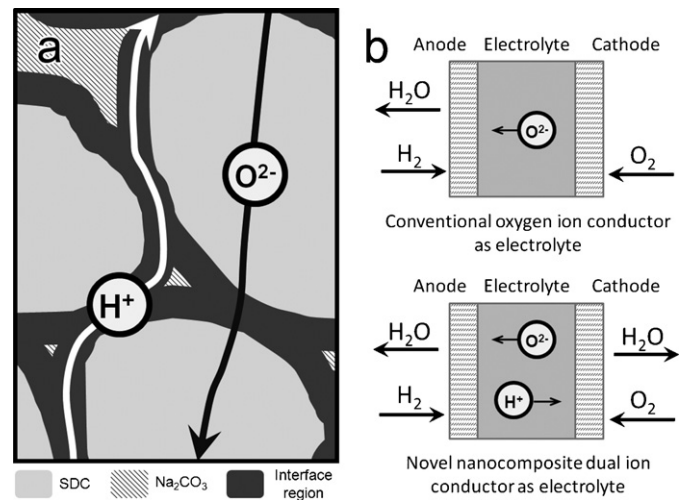


Fig. 3. (a) A schematic illustration of dual H^+/O^{2-} conduction pathways: the protons are transported by the interface in the SDC/ Na_2CO_3 nanocomposite, while oxygen ion conduction is through the grains of SDC, (b) comparison of conventional oxygen ion conductor and SDC/ Na_2CO_3 nanocomposite as electrolyte for SOFCs.

ion conduction, where the protons are transported in the interface region of the composite, while the oxygen ions are conducted through the SDC grains. The dual ion conduction of protons and oxygen ions not only enhances the total ionic conductivity, but also promotes reactions at both electrodes, resulting in improved fuel cell output, as shown in Fig. 3b. Furthermore, proton conduction seems to be thermally activated at lower temperature than that of O^{2-} as revealed by above calculated activation energy. For instance, the SDC/ Na_2CO_3 electrolyte can retain a high σ_{H^+} (ca. 10^{-2} S cm⁻¹) at 350 °C. Therefore, it is expected that SOFCs based on the nanocomposite electrolyte can operate at temperature as low as 400 °C, if performances of electrodes could be improved at such low temperature.

It is widely accepted that hydrogen bond is involved in almost all proton conduction processes [25,26]. For example, the mechanism for proton transport in complex oxides with perovskite structure (e.g. $BaCeO_3$) involves the hydroxyl group (O–H) formation and followed by proton hopping between two neighboring oxygen atoms [27]. Strong hydrogen bonding is considered to be a precursor of proton transfer reaction; however, long-range proton transport also requires rapid bond breaking and forming processes, which are expected to occur only in meta-stable hydrogen bonded systems [26]. In some recent studies, proton conduction was also reported in the grain boundary of nanostructured oxides, i.e. doped ceria [28,29], and YSZ [29–31]. Kim et al. reported that the grain boundaries in nano-crystalline YSZ are highly selective for ion transport, being conductive for proton but resistive for oxygen ion [32]. They explained the proton transportation by hydrogen bond (O–H) formation via dynamic chemical and physical adsorption of water molecules in the grain boundary of SDC or YSZ, with similar mechanism as above for perovskite oxides [31].

We therefore can attribute the superior proton conduction of the SDC/ Na_2CO_3 nanocomposite system to formation of meta-stable hydrogen bonds on the surface of SDC nanoparticles. The presence of sodium carbonate as the inclusion/secondary phase plays an important role in the enhancement of the proton conductivity, which results in several orders of magnitude higher conductivity than that of the reported single-phase nanostructured SDC. Since pure sodium carbonate is not a good proton conductor, we consider that there is an interaction at the interface of SDC nanoparticles and sodium carbonate phase, leading to the superior proton conduction. At temperatures (400–600 °C) above the T_g , SDC nanoparticles

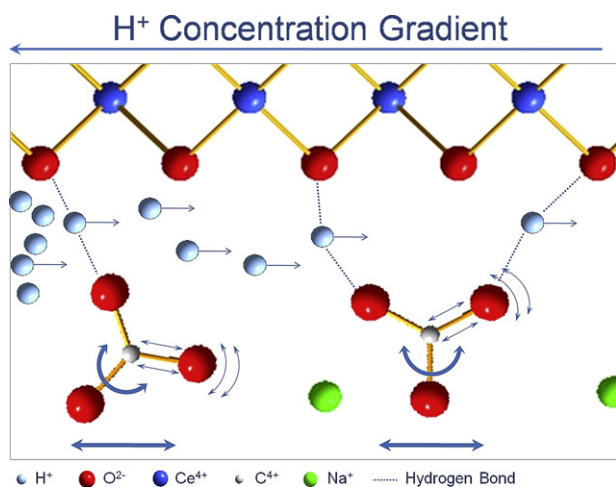


Fig. 4. “Swing Model” pathway for proton conduction in SDC/Na₂CO₃ nanocomposite.

are surrounded by sodium carbonate phase with high mobility of carbonate ions [14], constructing unique two-phase (Ce–O, C–O) interface, which is expected to be responsible for the proton pathway.

It may be difficult to determine the exact mechanism of the proton transportation at the interface of SDC nanoparticles and sodium carbonate, however, we propose an empirical “Swing Model” to interpret the proton conduction mechanism in our nanocomposite system. As illustrated in Fig. 4, when protons approach the composite electrolyte from anode, it can form meta-stable hydrogen bonds with oxygen ions from both SDC surface and CO₃²⁻ group. When the operating temperature is above the glass transition temperature of amorphous carbonate phase, the bending and stretching vibration of C–O bonds are enhanced, as well as the mobility and rotation of CO₃²⁻ group. These enhanced movements facilitate rapid breaking and forming of hydrogen bonds in the interface region, leading to effective long-range proton transportation driven by proton concentration gradient. In this process, carbonate serves as a “bridge” for protons to move from one hydrogen bond to another. A very good support to this conduction mechanism is found in Nolan and Watson’s work [33], where CO can be absorbed on the ceria surface to form CO₃ group. This indicates that on the surface of ceria nanoparticles, there are plenty of oxygen pairs with the same distance as that in CO₃²⁻ group. Therefore, when the special oxygen pairs on the ceria surface form hydrogen bonds with proton in the nanocomposite electrolyte, the bonds can be easily transferred by CO₃²⁻ groups, resulting in meta-stable hydrogen bond breaking and re-forming. The suggested “Swing Model” of the proton conduction mechanism for the SDC/Na₂CO₃ nanocomposite can explain the following experimental observations:

1. Other than Sm-doped ceria, the nanocomposite prepared by other heavily rare earth doped ceria (La: 36%, Pr: 6%, Ce: 58%) and carbonate showed also excellent ionic conduction [34]. On the other hand, for the composite made by other oxides (YSZ, TiO₂, and ZrO₂), the proton conductivity is extremely low. The interaction between carbonate and the surface of ceria, i.e. the local resemblance of special oxygen pairs on SDC surface and in CO₃²⁻ group, is crucial for the superior proton conduction.
2. Pellets made of SDC nanoparticles without carbonate have very low proton conductivity.
3. Measurements on pure Na₂CO₃ pellets showed extremely low proton conduction.
4. The activation energy of proton conductivity changes around T_g of amorphous sodium carbonate [14].

Using the “Swing Model”, the observed proton conduction in nanostructured SDC and YSZ reported by Kim et al. can be understood to be due to significantly larger area of grain boundary than their bulk analogues. However, compared to SDC/Na₂CO₃ nanocomposite system, the proton conductivity of single-phase nanostructured SDC or YSZ is much lower because of the lack of bridge carrier which can significantly enhance proton transportation. Another reason is that the proton conductivity in nanostructured SDC and YSZ only can be detected below 120 °C, since high operating temperature will promote the grain growth of the nanoparticles. This problem has also been solved by using carbonate as the inclusion which preserves the nanostructures of SDC nanocomposite even up to 700 °C [16]. To further improve the “Swing Model”, more efforts are needed on the molecular dynamic studies as well as design of experiments on other nanocomposite system with controlled properties.

4. Conclusions

In summary, it has been proved by the four-probe d.c. conductivity measurement that the SDC/Na₂CO₃ nanocomposite electrolyte possesses the unique simultaneous H⁺/O²⁻ conduction property. The measurements reveal that the proton conductivity in SDC/Na₂CO₃ nanocomposite electrolyte is 1–2 orders of magnitude higher than oxygen ion conductivity in the temperature range of 200–600 °C, which confirms that proton conduction mainly accounts for the significantly enhanced total ionic conductivity, resulting in an excellent fuel cell performance. It can be further concluded that the interface introduced by adding sodium carbonate phase supplies high conductive paths for proton transport, while oxygen ions are most probably transported within SDC phase. An empirical “Swing Model” has been proposed for the mechanism of superior proton conduction.

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