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Non-doped CeO₂-carbonate nanocomposite electrolyte for low temperature solid oxide fuel cells

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Abstract

CeO₂ is an oxygen nonstoichiometric material for the coexistence of redox pair of Ce³⁺ and Ce⁴⁺, even under an oxidizing atmosphere, and its self-doping is fulfilled bases on the multivalence characteristics. It has been served in versatile applications, including fuel cells and catalysis. Excellent solid oxide fuel cell performances have been achieved at intermediate and low-temperature range based on doped cerium oxide electrolyte. In this study, we utilize its self-doping form to prepare core-shell structure bi-phase nano-composite of CeO₂ and alkali carbonate (Li₂CO₃, Na₂CO₃, and K₂CO₃) through a two-step synthesis method. SEM, TEM, XRD, and EIS measurements were applied to characterize the morphology, crystal size, the ionic conductivity of the electrolyte, and the electrochemical performance of resulting ceramic fuel cells. An exceptional ionic conductivity of 0.34 S cm⁻¹ was generated at 550 °C in air, significantly different from its insulating property of the perfect CeO₂ phase. A power density of 910 mW cm⁻² was also achieved as the highest electrochemical performance of a single cell. The multi-ionic conduction behavior of CeO₂-carbonate is also discussed. The results reveal an effective approach to develop alternative SOFC electrolyte materials for low-temperature, high-performance energy conversion applications.

Keywords: Low temperature solid oxide fuel cell; Core-shell; Ceria-carbonate composite electrolyte; interface conductivity; Self-doping; hybrid ionic conduction

1 Introduction

With the development of hydrogen energy economy, solid oxide fuel cell (SOFC) turns into one kind of fuel cell that is potentially industrialized in prospect due to the high efficiency, fuel flexibility, and sustainable characteristics [1-5]. The electrolyte is the key component determines operating that the system temperature and electrode/interconnect/sealant material and other balance of plants [6]. Generally, the classic ionic transportation of conventional SOFC electrolytes, like yttria-stabilized zirconium (YSZ), is highly relied on the inner oxygen vacancies of the atomic lattice which was created through heteroelement doping methodology [7-10]. Such an ionic transportation rate, however, is limited due to the strong interaction of the charge carrier with the cations on the lattice and between each charge carrier [1,11-13]. That requires a high operating temperature (700-1000 °C) to reach sufficient ionic conductivity. Therefore, the marketization of related SOFC technology was restricted by the necessary and rigorous performance of equipment/components, like sealing and the degradation of cell components or fuel cell performance with extended time.

Cerium-based oxides are one of the kinds most promising alternative electrolyte materials to replace doped zirconia for intermediate temperature solid oxide fuel cells. Excellent activity of cerium based oxide electrolyte materials through heteroelements such as Sm, Ca and/or Gd doping has been well-documented in the literature with exceptional fuel cell performance [14-16]. However, its electronic conductivity under reducing atmosphere, such as the typical fuel cell anodic condition, impedes such a promise. Ceria-based composite is therefore proposed to overcome the intrinsic drawback

while improving its ionic conductivity, with a particular interest in the ceria-carbonate composite [17-22]. The latter has displayed remarkable ionic conductivity and electrochemical performance at low temperatures (300-600 °C) [23,24]. For example, ionic conductivity records of Sm_{0.2}Ce_{0.8}O₂-carbonate composite reached 0.5 S cm⁻¹ at 600 ^{o}C by Peter Lund et al. [19], and that of CeO_2/CeO_{2-\delta} reached 0.16 S cm $^{-1}$ at 520 ^{o}C [17,18,25]. The prominent performance record of SOFC with ceria based nanocomposite material as the electrolyte of 1004 mW cm⁻² at 470 °C was reported in our previous work [26]. It has been reported that the high ionic conductivity of cerium based oxide material highly relies on the bi-phase and interface structure [21,27,28]. The required ionic transfer energy on the particle surface/interface is significantly lower than that of bulk oxygen ions conduction through the intentionally created oxygen vacancies, for the incomplete atomic lattice with less hindrance from atoms and chemical bonds at the surface [29]. Generally, the grain boundary resistance is three orders of magnitude larger than the grain bulk resistance [30]. But in this bi-phase nanocomposite, the grain boundary gaps are complemented by other elements/the second phase, and the diverse potential among elements in the interface will promote ionic transportation [27,29]. A more informative case by Li S. et al. [31] tested the electrochemical performance of a conventional molten carbonate fuel cell with LiAlO₂-carbonate composite electrolyte under the typical SOFC conditions i.e without the recycling of CO₂ in the cathode condition. A peak output of 466 mW cm⁻² at 650 °C was obtained in SOFC condition, which is significantly larger than the normal values for MCFCs. The absence of CO₂ excluded the fuel cell performance contribution from charge carrier of CO_3^{2-} , while it is owing to protons or oxygen ions.

Also considering the insulating property of LiAlO₂, and traditional bulk CO_3^{2-} ionic-conducting behavior of carbonate, the interface ionic conduction behavior is therefore deduced. However, the direct evidence of ionic conducting highways at the bi-phase interfaces is not vet confirmed. More recent work by Wang and Xing et al. [25,32] reported nonstoichiometric of CeO_{2-x} without any heteroelement dopants provides proton shuttle effect under fuel cell condition and super electrochemical performance, indirectly proving the surface or interface ionic conduction pathway. Moreover, the charge carriers in transportation in nanocomposite electrolytes include proton, oxygen ions, and CO_3^{2-} [22,33-38]. Multiple ion transfer (MIT) gives rise to the outstanding electrochemical performance, other than that caused by single ions (O^{2}) transmission through bulk atomic lattice [9,10]. The introduction of extrinsic ionic conduction (H^+) in the composite besides the intrinsic ones (O^{2-} and CO_3^{2-}) makes the study of ionic transportation more interesting but complicated. Hence, in this work, a non-doped ceria-carbonate composite was achieved through a precisely controlled two-step synthesis method [18,21,27]. A perfect interface is expected to form between alkali carbonate and CeO₂/CeO_{2-δ} in the form of a core-shell structure. In general, MIT, core-shell structure, ionic high-way interface and self-dope $CeO_2/CeO_{2-\delta}$ as core functionality facilitate the ionic conductivity of electrolyte materials and fuel cell electrochemical performance [15,25,27,39]. This work again highlights the high efficient interfacial ionic conduction for a high-performance fuel cell application and suggests an alternative method to further overcome the ionic conduction barrier which could not be realized by the normal bulk doping approach.

2 **Experimental**

2.1 Material and pellets preparation

Cerium nitrate (Ce(NO₃)₃•6H₂O), ammonium bicarbonate (NH₄HCO₃), alkali carbonate (Na₂CO₃ and K₂CO₃), nickel nitrate (Ni(NO₃)₂•6H₂O) and LiNO₃ were bought from Aladdin-e (www.aladdin-e.com, China) and used without purification. All chemicals are analytic reagents.

The electrolyte material was prepared through a two-step synthesis method includes a co-precipitation procedure followed by thermal evaporation and calcination. The amount of Ce(NO₃)₃•6H₂O was dissolved into deionized water to form a 0.5 M solution, and 0.5 M NH₄HCO₃ solution was achieved through the same method. A white precipitated precursor was immediately obtained from the mixing of the two solutions with continuous stirring at 1200 rpm for 2 hours and followed by 12 hours aging at room temperature. Then a specific amount of Na₂CO₃, K₂CO₃ and LiNO₃ were made into 0.5 M solution according to the molar ratio Li: Na: K = 0.5: 0.26: 0.24, and keep the atomic ratio between cerium and the total amount of alkali elements (Li, Na, K) is 7:6, then the solution was impregnated into the precursor precipitate. The above-mentioned mixture was aged 5 hours after a 2-hour continuous stirring at 1000 rpm, then dried at 90 °C. The dry precursor was calcinated at 800 °C for 3 hours and naturally cooled in air.

 $Ni(NO_3)_2$ •6H₂O and LiNO₃ were dissolved in deionized water together at molar ratio 7 : 3, then evaporated, dried and calcined at 800 °C in air for 4 hours, then cooling with the furnace naturally to form the symmetric electrode catalyst.

Electrode free electrolyte pellets and symmetric electrode sandwiched single SOFC pellets with a 13 mm in diameter were prepared through a cold-pressing method as reported in the literature [40]. Electrolyte pellets (the electrolyte thickness is 2.1 mm for ionic conductivity in air and 1.35 mm in hydrogen gas), and electrode sandwiched single SOFC pellets in a thickness of ~1.1 mm were prepared by dry-pressing under a 300 MPa pressure intensity, then both sides are covered with silver paste before being in-situ annealed for both pellets at 600 °C for 1 hour to increase its mechanical strength. The presence of carbonate acts as a high temperature glue to increase interaction between the electrode and electrolyte layer, and to form a 3D alkali carbonate network spreads through the whole pellet [41], so that an ever low sintering temperature of 600 °C is applied. After that, we adjusted the temperature of the furnace to targeting value by an amplitude of 2 °C min⁻¹, maintaining for at least 30 minutes before performing the electrochemical impedance spectroscopy and fuel cell voltage-current density characterizations.

2.2 Material characterization & electrochemical measurement

X-ray diffractometer (XRD) was used to characterize the electrolyte and electrode material crystal structure on a PANalytical X'Pert PRO MPD Alpha-1 Diffractometer, with Cu Ka radiation (λ = 1.5418 Å), 45 kV and 40 mA. The 2 θ was ranged from 20 – 90° at a measuring speed of 0.2° per second. Both electrode and electrolyte material surface morphology and particle size were examined by a scanning electron microscope (SEM, FEI APREO S).

The ionic conductivities of the electrolyte pellet measured by AC impedance spectroscopy method through a Reference 3000 -Potentiostat, the applied AC frequency

range is 1 MHz~0.1 Hz, with a 10 mV amplitude. A symmetric single fuel cell pellet with silver paste painting layer as a current collector was used to measure the electrochemical performance. The fuel cell performance is achieved through a home-made stainless steel fuel cell sample holder, with a programmable electronic load (IT8511, ITECH Electrical Co., Ltd.). The flowing H₂ and air are used as fuel and oxidant, respectively, for fuel cell demonstration and performance study. The I–V and I–P characteristics are then obtained at a linear scanning rate of 5 mV S⁻¹ from open-circuit voltage to 0.2 V. Two different applied gas atmospheres, static air, and hydrogen gas (10vol.% H₂ balanced with highly purified N₂), are used in the electrochemical impedance spectroscopy (EIS) study to reveal the hybrid ionic conduction behaviors of composite electrolyte pellet.

3 Results and discussion

3.1 XRD analysis

XRD pattern of electrolyte material is shown in **Fig. 1**a, which is fully indexed to be CeO₂, no crystal phase of alkali carbonate in the pattern could be observed. It has been reported that the alkali carbonate is an amorphous state in compositing with cerium based oxide [29]. The amorphous alkali carbonate exists as a shell on the CeO₂ particle since carbonate adsorbed on the surface of nanoceria particles with strong interaction. The ionic highway is therefore built with the presence of an amorphous alkali carbonate layer and gives outstanding ionic conductivity and fuel cell electrochemical performance [29]. The peaks of electrode material XRD pattern (**Fig.1**b) are indexed to Li_{0.28}Ni_{0.72}O crystal structure, which anastomoses with the element content from material synthesis. Nickel

oxide is one kind of remarkable catalyst for the electrochemical hydrogen oxidation reaction, and the lithium doping reduces the bandgap value and increases the electronic conductivity to improve the oxygen reduction activity [42].

The crystal sizes (D) of electrolyte and electrode material are calculated from XRD spectra according to Scherrer formula: $D = K\lambda/\beta \cos\theta$. Here D is the crystal size, λ is the wavelength, in this case, it's 0.154056 nm, β : FWHM 0.101. The crystal sizes of ceria based electrolyte material is therefore calculated: D₁=0.89*0.154056 nm/(0.101/180*3.14*cos14.2775) = 80.3 nm, and lattice size of LiNiO₂ is D₂=0.89*0.154056 nm/(0.231/180*3.14*cos21.9885) = 36.7 nm. Both give severe aggregation under typical fabrication conditions.



Fig. 1. XRD spectra of electrolyte and electrode material, (a) composite electrolyte, (b)

LiNiO*x* electrode

3.2 Structure and morphology studies

The morphology of the electrode material is shown in **Fig. 2**a; the uniform polyhedron particle with a grain size of 0.5-1 μ m has been obtained. Spherical particles with a grain size of 5-10 μ m for electrolyte materials are shown in **Fig. 2**b; and **Fig.2**c is

the SEM image of the part of the light blue **Scheme 1** in **Fig. 2**b. The shell of particles in scheme 1 melts after the continuous electron beam exposure during SEM observation. The window shape molten area formed by the high energy of the SEM electron beam irradiation when the single-particle was measured under a 100 nm resolution, with a high applied voltage 15.0 kV voltage, 93.6 μ A current and 10.2 mm measuring distance, and the temperature of radiation area may reach several hundred degrees [43]. The crystal size of electrolyte material is about 80 nm from the calculation by Sherrer formula, which constitutes the larger sized particles, as shown in **Fig. 2**.



Fig. 2. SEM images of electrolyte and electrode materials, (a) electrode, (b) electrolyte materials, (c) enlarged morphology of electrolyte material from area 1 after in-plant scanning by an electron beam in Fig. 2 (b).

From **Fig. 2** and **3**, we know that the particle of electrolyte material is of a micrometer size level, the TEM beam can not get through such thick matrix, as shown in **Fig. 3**a, a dark shadow like a black ball is observed under TEM recording condition. The magnified TEM images (**Fig. 3**b and c) show that the electrolyte particle is a composite of the well-crystallized phase plus an amorphous layer (**Fig. 3**c). Based on the applied material composition and literature, we can conclude that the crystal material is CeO₂, and

the amorphous layer is composed of alkaline carbonate. They form a typical core-shell structure, which is consistent with previous works, the amorphous alkali carbonate as shell and CeO₂ crystal as core in it. The alkali carbonate shell with a low melting point of 400-450 $^{\circ}$ C is easy to melt or be evaporated under SEM and TEM beam, while the CeO₂ with a high melting point will not [18,29]. Besides, such a core-shell structure with an enormous interface will endow outstanding ionic conductivity to electrolyte material, as recorded in previous works [27,28,35,44].



Fig. 3. TEM images of electrolyte materials, (a) single-particle (b) enlarged area 1 in Fig.

3a, (c) Enlarged area 2 in Fig. 3b.

3.3 Electrical and electrochemical performance

The electrochemical impedance spectra (EIS) of electrolyte pellets with silver paste current collectors in air and hydrogen gases, respectively, were recorded from 450 - 550 ^oC and the results are shown in Fig. 4. To better obtain the necessary ionic transport resistance and electrochemical process, an empirical equivalent circuit composing with R₁ series connects with several series-parallel connections include one resistor and one CPE is applied to simulate the impedance spectra. In the equivalent circuit, the R1 and R2 correspond to resistors and GPE1 to constant phase element; R0 represents the resistance to ionic transmission of electrolyte, R1-R3 and CPE1-CPE3 are related to the mass transportation, ionic diffusion from an electrolyte to an electrode, and the electrode reaction processes. Generally, the impedance spectra of the conventional oxide electrolyte ceramics compose of two semicircles and one tail; the two semicircles correspond to bulk resistance and grain boundary resistance, and the tail is the emblem of ionic diffusion in electrodes [13,45]. Normally, the ceramic grain boundary resistance is two~three orders of magnitude larger than that of grain bulk resistance [30,45]. To the electrolyte material which is composited by cerium oxide and alkali carbonate, there is only one semicircle in the high frequency range and followed by one tail in the low frequency range, which is frequently observed in other literature with similar material composition [19,23,35,40,46,47]. This is affected by the interface resistance between the cerium oxide grain and the alkali carbonate layer before carbonate melting [18,27,48]. And the mono semicircle vanished when the operating temperature reaches to the softening point (396 ^oC) of the amorphous layer, for the interface gap of grains disappeared, and the curve tail

represented redox reaction speed and gas diffusion mechanism in electrode [<u>17</u>]. From the above, we are aware of that the molten process of the amorphous alkali carbonate starts from ~400 °C, the grain boundary gaps got filled by the molten carbonate, leading to quite different grain boundary atmosphere compared with the oxide-oxide grain boundary one, that caused the grain boundary resistance disappeared in EIS. The composite electrolyte shows similar electrochemical responses in oxidizing air and reducing hydrogen gas, a high frequency intercept on the real axis plus a long tail, the later is caused by ionic diffusion from the electrolyte into silver paste electrode because of the ionic and electronic conduction nature between two different materials. The semicircles corresponding to bulk/grain boundary resistance disappear when the alkali carbonate is melted. Besides, you may see that the tail in hydrogen gas is larger than that in air, probably is due to the lower electrocatalytic activity of Ag toward hydrogen oxidation reaction (HOR) compared with that of oxygen reduction reaction (ORR).



Fig. 4. Temperature dependence of the electrochemical impedance spectra of the electrolyte material in air (a) and H_2 (b) at the temperature range of 450-600 °C.

At the elevated temperature above the carbonate melting point, ~400 °C, the enlarged interface with the melting carbonate can provide ionic conduction highway since the ionic conduction of the interface is much higher than the bulk conduction without structure limitation because of the increased charge carrier concentration and charge mobility at the interface. The ionic conductivity of the electrolyte pellet is then calculated based on the equation: $\sigma = L/(AR)$, where L is electrolyte thickness, A is the current collector and reaction area, 0.64 cm^2 in this case, and R is the resistance (R₀); and the results are shown in Fig. 5. Both ionic conductivity increases with the rise of operating temperature, showing ionic conduction thermal activation characteristics. Splendid ionic conductivity of the electrolyte pellet of 0.225 S cm⁻¹ at 450 °C and 0.34 S cm⁻¹ at 550 °C in air, and of 0.07 S cm⁻¹ at 450 °C and 0.20 S cm⁻¹ at 550 °C in hydrogen, were achieved. It is mentioned above that the alkali carbonate starts to soften from about 400 °C, the molten carbonate fills the grain boundary gap, which will generate a mass of mobile ions sourced from the soften carbonate, including carbonate (CO_3^{2-}) and M⁺ (M = Li, Na, and K); all will contribute to the total ionic conductivity. Plus the possible O^{2-} and H^+ conduction in air and hydrogen or water containing atmosphere, the hybrid ionic conduction is the unique characteristics over the common ceramic electrolyte material, in which only one, maximum of two ions, are included. The multi-ionic transportation, no grain boundary gap, and huge interface from the core-shell structure of both proton "shuttle" effect in core-shell $CeO_2/CeO_{2-\delta}$ [25] and $CeO_{2-\delta}$ -carbonate raise the exceptional ionic conductivity. It should be mentioned that in our case the oxide core we used is the undoped CeO₂, which could be considered as an insulator under the ideal condition. Such

an excellent ionic conductivity should, therefore, be ascribed to the addition of carbonate, which creates abundant interfaces for the superionic conduction pathway without lattice structure limitation. Considering that all contain the CO_3^{2-} and alkaline earth metallic (M⁺) conductivity, and higher total ionic conductivity in air vs. in hydrogen, we can conclude that the proton conductivity is lower than the oxygen conductivity during 450-550 °C, which is consistent with previous studies on ceria-carbonate composite electrolyte [49,50]. The promoted catalytic effect of alkali carbonate toward ORR may be credited [51]. Any, the ionic conductivity at the level of 10^{-1} S cm⁻¹ is still much higher than that of typical ceramic ionic conductivity. In particular, the applied operational temperature is 450-550 °C, making it a potential electrolyte for low temperature SOFCs.



Fig. 5. The calculated ionic conductivity of composite electrolyte material in air and H_2 separately at the temperature range of 450-550 °C.

With the excellent ionic conductivity of electrolyte material, plus the highly active and hybrid $H^+/O^{2-}/e^-$ conductive LiNiO₂ electrode catalyst that enables the enlarged electrochemical reaction active sites, the triple-phase boundaries, for high electrode activity [52,53], the assembled symmetric cell with LiNiO₂ electrode gives excellent electrochemical performance at the temperature range of 450-550°C (Fig. 6). The peak power output reaches to 499.8 mW cm⁻² at 450 °C, already reaching to the benchmarking industrial applicable fuel cell performance value [54], which is further increased to 910 mW cm⁻² at 550 °C. The outstanding performance is comparable to the current best fuel cell performance working at low temperatures reported in the literature [5,55,56], while we adopted a much simpler single-cell fabrication procedure with the additional virtue of low material cost. The performance is also superior to that with only the self-doped CeO₂ electrolyte under similar conditions [25,32]. Besides, it should be noted that the single symmetric cell in our case has a thick electrolyte layer up to 300 µm, therefore, it is expected that ever improved fuel cell power density can be obtained with a reduced electrolyte layer thickness. Theoretically, the peak power output could be improved to 1218 mW cm⁻² at 550 °C if the electrolyte thickness is reduced to 10 µm of the common ceramic electrolyte layer, given the same electrode catalyst and open-circuit voltage as well as fuel cell test condition. Such an excellent peak power output is one of the highest values in the literature, and it still holds a large room since the electrode polarization resistance still dominates the total polarization resistance.



Fig. 6. The electrochemical performance of fuel cells from 450-550 °C.

It should be noted that the ideal cubic cerium oxide gives a low ionic conductivity due to the insulator nature with limited surface/bulk defects such as oxygen vacancy that serves as a charge carrier for ionic transportation. The introduction of self-doping $CeO_2@CeO_{2-\delta}$ induces richens surface oxygen non-stoichiometry and yields constrained surface region which creates interesting surface ionic conduction behavior, as reported proton "shuttle effect" in the literature [25]. However, such a material may be limited to the nanoscale electrolytes that can not be fully adopted in high temperatures and stabilized under extended operational times. Besides, we should remember though the molten carbonate gives excellent carbonate and alkaline ionic conductivity due to the liquid phase structure under the elevated temperature, its composite with LiAlO₂ under the typical molten carbonate fuel cell atmosphere displays a much lower fuel cell peak power density, normally lower than 300 mW cm⁻² [57] with the average value of 120-150 mW cm⁻² for the commercial system at 650 °C [58], 3-6 times lower than that of our case. The excellent

fuel cell performance, therefore, should be ascribed to the excellent ionic conductivity of CeO_2 -carbonate composite. The surface proton shuttle created by the self-doping in non-stoichiometrical nanoscale ceria [25,32] and hybrid oxygen ionic and proton conduction along the huge oxide-carbonate interface [10,22,33,40,59] provide ionic transportation highway in the composite electrolyte and subsequently contribute the prominent fuel cell performance. Of course, we must admit that more sophisticated characterization techniques and in-depth process understanding are needed to reveal the exact ionic conduction mechanism in such a complex composite system.

4 Conclusions

In this work, a two-step method was implemented to prepare a core-shell structure composite of undoped CeO₂ and alkali carbonate (Li/Na/K₂CO₃) as electrolyte materials to low temperature SOFCs. The core-shell structure, integrating with the melting of carbonate above 400 °C which eliminates the grain boundary resistance and enlarges the interface area between CeO₂ and carbonate, generates the ionic conduction highway with a mass of mobile ions as the charge carrier, leading to striking ionic conductivity at the temperature range of 450~550 °C. Exceptional ionic conductivity of 0.34 S cm⁻¹ in air and 0.20 S cm⁻¹ in hydrogen gas at low temperature (550 °C) was aroused. Noticeable electrochemical performance of 910~499.8 mW cm⁻² on a single SOFC was reached in the hydrogen/air atmosphere at the temperature range of 550~450 °C. Besides, the ionic conductivity of 0.225 S cm⁻¹ remained at 450 °C in air, which may open an avenue to develop super low temperature SOFC.

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Declaration of interests

 \boxtimes The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

The authors declare the following financial interests/personal relationships which may be considered as potential competing interests: