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Fast ionic conduction in semiconductor $\text{CeO}_{2-\delta}$ electrolyte fuel cells

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Abstract

Producing electrolytes with high ionic conductivity has been a critical challenge in the progressive development of solid oxide fuel cells (SOFCs) for practical applications. The conventional methodology uses the ion doping method to develop electrolyte materials, e.g., samarium-doped ceria (SDC) and yttrium-stabilized zirconia (YSZ), but challenges remain. In the present work, we introduce a logical design of non-stoichiometric $\text{CeO}_{2-\delta}$ based on non-doped ceria with a focus on the surface properties of the particles. The $\text{CeO}_{2-\delta}$ reached an ionic conductivity of 0.1 S/cm and was used as the electrolyte in a fuel cell, resulting in a remarkable power output of 660 mW/cm² at 550 °C. Scanning transmission electron microscopy (STEM) combined with electron energy-loss spectroscopy (EELS) clearly clarified that a surface buried layer on the order of a few nanometers was composed of Ce^{3+} on ceria particles to form a $\text{CeO}_{2-\delta}$ @ CeO_2 core-shell heterostructure. The oxygen deficient layer on the surface provided ionic transport pathways. Simultaneously, band energy alignment is proposed to address the short circuiting issue. This work provides a simple and feasible methodology beyond common structural (bulk) doping to produce sufficient ionic conductivity. This work also demonstrates a new approach to progress from material fundamentals to an advanced low-temperature SOFC technology.

Introduction

Surface/interface structures are found to play a vital role in producing exceptional material properties. For example, topological insulators with an insulating core and electron conducting surface^{1–3} displayed unique electrical conducting properties. The interface between two insulating oxides can produce superconductivity^{4,5}. In addition, semiconductor/ion conductor heterointerfaces, such as YSZ/SrTiO₃^{6,8,10} and $\text{Ce}_{0.8}\text{Gd}_{0.2}\text{O}_{2-\delta}$ - CoFe_2O_4 ¹¹ composites, can enhance the ionic conductivity through two material interfaces by several orders of magnitude^{6–10}.

These extraordinary properties on surfaces or at interfaces indicate a new strategy to develop material functionality. Thus, a new emerging approach for oxide interfaces was established^{12,13}. By tuning the electronic states, oxygen ion conducting properties can be modified at interfaces¹⁴.

Ceria (CeO_2) has attracted extensive interest and demonstrated multifunctionality in many fields, such as catalytic applications^{15–17}, solar cells and photoelectrochemistry^{18–20}, lithium batteries^{21,22}, fuel cells^{23–26} and a variety of other energy-related applications^{25,26}. The most important characteristic of ceria is the capacity to store and release oxygen via facile $\text{Ce}^{4+}/\text{Ce}^{3+}$ redox cycles, which largely depends on the concentration and types of oxygen vacancies in the lattice as well as surface structures and states. Unique physical properties are associated with Ce^{3+} ions and oxygen vacancies. Especially from the nanoscale perspective, non-stoichiometric oxygen atoms are present at the grain boundaries or surface, and these concomitant vacancies play an

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important role in determining the various chemical and physical properties of ceria. The surface state is fundamental^{27,28} and demonstrates significantly different physical and chemical properties when compared to those of the bulk matrix. The role of vacancy dynamics may be very important at interfaces and on surfaces because of the high mobility and redistribution of charged vacancies²⁹. Ceria can be easily reduced from CeO₂ to CeO_{2-δ} through surface reduction at low oxygen partial pressures. The changes in surface oxygen vacancies often dramatically alter material physical and electrochemical properties, especially when the ceria particle size is less than 100 nm.

It is well known that CeO₂ itself is an insulator. To improve the ionic conductivity of cerium-based oxides, aliovalent doping with rare earths and alkaline cations, such as Gd, Sm, Ca and La, introduces oxygen vacancies in the lattice as charge compensating defects and increases the ionic conductivity, where the highest level of oxide-ion conductivity was reported for Gd- and Sm-doped Ce_{1-x}M_xO_{2-δ} (M = Gd and Sm)^{30,31}. Although extensive efforts have been made to utilize doped ceria as an alternative electrolyte in solid oxide fuel cells (SOFCs), several critical challenges have hindered practical application of this material as reported extensively in the literature. (i) Ceria-based electrolytes under fuel cell conditions are reduced by H₂, which can be accompanied by significant electronic conductivity to further deteriorate the open-circuit voltage (OCV) and power output³². (ii) Once the ceria size is in nanometer scale, the electronic conduction is dominant; e.g., an enhancement of four orders of magnitude in the electronic conductivity was observed for CeO₂ when the particle size transitioned from the micro- to nanoscale³³. There were two approaches published in *Nature* in 2000 for high ionic conduction that were based on structural doping³⁴ and surface mechanisms³⁵. Doping to create bulk ionic conduction in a material is a central methodology in SOFC material research and development. However, alternative materials that can replace YSZ have not yet been successful; on the other hand, the surface approach has not been seriously developed in the current SOFC framework. This study highlights a new conceptual method to develop high electrical conductivity in CeO₂ without doping based on characteristic surface defects (Ce³⁺, oxygen vacancies and superoxide radicals) combined with band energy alignment to avoid the formation of short circuits.

The CeO₂ surface approach presented in this work addresses challenges based on recent scientific understanding and results achieved on this material. In our approach, we take advantage of the ceria electronic conduction and surface defects for the successful demonstration of new advanced SOFC materials and technologies. Through simple heat treatment processes,

we created different surface defects and electrical properties to investigate the correlation between the conductivities and surface state of the CeO₂. The presence of oxygen vacancies and defects on the CeO₂ surface resulted in new electrical and band gap properties and successful SOFC application. Our study presents a new design concept for both materials and devices that will have a great impact on the next generation of advanced SOFCs.

Experimental section

Synthesis of CeO₂ powder

CeO₂ powders were prepared using the wet chemical precipitation method. In a typical synthesis procedure, 5.43 g cerium nitrate hexahydrate (Ce(NO₃)₃·6H₂O) and 1.98 g ammonium bicarbonate (NH₄HCO₃) were separately dissolved in 200 ml deionized water under magnetic stirring. Then, the NH₄HCO₃ solution was used as the deposition agent and poured slowly (10 ml min⁻¹) into the Ce(NO₃)₃·6H₂O solution, which was stirred for 2 h and statically aged for 12 h at room temperature. Following filtration, the material was washed with deionized water to remove any possible ionic remnants and then a pure CeO₂ precursor was obtained. The CeO₂ precursor was dried at 120 °C for 24 h and calcined in air at 900 °C for 4 h to obtain CeO₂ powder.

Characterization

The X-ray diffraction (XRD) patterns of the as-prepared CeO₂ samples were analyzed to determine the crystallographic phases via a Bruker D8 X-ray diffractometer (XRD, Germany, Bruker Corporation) operating at 45 kV and 40 mA with Cu Kα radiation (λ = 1.54060 Å). The morphology of the samples were investigated using a JSM7100F field emission scanning electron microscope (FESEM, Japan) operating at 15 kV. To further characterize the microstructures, scanning transmission electron microscope (STEM) was performed on a JEOL ARM-200CF field emission microscope with a probe corrector and Gatan imaging filter (GIF) electron energy-loss spectrometer (EELS) operating with an accelerating voltage of 200 kV. Collection semi angle of 57.1 mrad was used to record the EELS line scan. The high angle annular dark field (HAADF) image was simulated using a multi-slice method implemented in QSTEM image simulation software. Ultraviolet photoelectron spectroscopy (UPS) measurements were performed to obtain the valence band level. The UV-vis diffused reflection spectra of the materials were tested on a UV3600 spectrometer (MIOSTECHPTY Ltd.).

Cell construction and measurement

The devices used for measurements were constructed using 0.2 g CeO₂ powder sandwiched between two thin

layers of $\text{LiNi}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$ semiconductor pasted on nickel foam and pelletized at room temperature under a hydraulic press pressure of 200 MPa to obtain a simple symmetric configuration device of (Ni)NCAL/CeO₂/NCAL(Ni). Two nickel foam acted as current collectors. The device was shaped as 13 mm in diameter, around 1.0 mm in thickness with an effective area of 0.64 cm². Pure hydrogen and ambient air were supplied to each side of the cells as fuel and oxidant, respectively. The flow rates were controlled in the range of 80–120 ml min⁻¹ for H₂ and 150–200 ml min⁻¹ for air under 1 atm. To analyze the cell performance, the voltage and current readings were collected using a programmable electronic load (IT8511, ITECH Electrical Co., Ltd.) to plot the I - V and I - P characteristics.

Electrochemical impedance spectroscopy (EIS) was carried out by using an electrochemical workstation (Gamry Reference 3000, USA) in both air and fuel cell operation atmospheres, and the frequency ranged from 0.1 Hz to 1 MHz with an amplitude of 10 mV.

Results and discussion

Figure 1 shows the XRD pattern of the CeO₂ powder synthesized at 900 °C for 4 h compared with that of CeO₂ reduced in H₂ at 550 °C for 1 h (R-CeO₂). The patterns exhibit the same fluorite structure. However, a shift towards lower angle is observed for R-CeO₂ sample in the expanded XRD pattern, as shown in the inset. The lattice parameters for the CeO₂ powder and R-CeO₂ calculated by Scherrer equation were 5.403 Å and 5.452 Å, respectively, suggesting a slight CeO₂ local lattice expansion. The XRD analysis indicates that i) the CeO₂ obtained at 900 °C had a normal lattice structure that agreed with the

standard lattice parameter of 0.5410 nm indicated in the JCPDS card; and ii) the hydrogen treatment led to a reduction of Ce⁴⁺ to Ce³⁺, thereby causing lattice structural changes, i.e., the lattice expanded significantly from 5.403 to 5.452 Å. The large Ce³⁺ radius can bring about lattice expansion by forming non-stoichiometric CeO_{2-δ} in the CeO₂ fluorite structure within tolerance limitations. The effect is similar to that of large Sm³⁺ and Gd³⁺ rare earth ions doping into CeO₂ and cause corresponding lattice expansion.

Along with the production of Ce³⁺, oxygen vacancies are also created in the CeO₂ lattice. This process can be described by:



This is a fundamental way to improve CeO₂ electrical properties. CeO₂ has stoichiometry valence of Ce⁴⁺ which is located in the grain interior³⁶. Hydrogen treatment leads to chemical defects on the CeO₂ particle surfaces. This process can be deemed as a surface doping process due to the replacement of Ce⁴⁺ by Ce³⁺. The introduction of oxygen vacancies and accompanying large-sized Ce³⁺ ions leads to a distortion of the local symmetry and results in an increased lattice expansion, thus causing strain and surface stresses. This speculation can be directly observed in the high-resolution STEM images and is discussed in the next section. The hydrogen reduction process, e.g., during fuel cell operation or at a low oxygen partial pressure, starts from CeO₂ particle surfaces and approaches to the bulk, it is reasonable to consider a different surface state from the bulk to be further characterized in the following sections. The production of Ce³⁺ in CeO₂ can have the same effect as trivalent rare earth ions, e.g., replacing Ce⁴⁺ with Sm³⁺ or Gd³⁺, that are doped in CeO₂ to cause CeO₂ a lattice expansion. We noticed that Ce³⁺ ions have an ionic radius of 1.03 Å that is larger than the value of Ce⁴⁺ (0.92 Å), Gd³⁺ (1.05 Å) and Sm³⁺ (1.08 Å), respectively. Therefore, producing Ce³⁺ in CeO₂ may result in doping effects, similar to Sm³⁺ and Gd³⁺, and impact not only the lattice but also the ionic conductivity. However, it should be noted that Ce³⁺ is on the surface, while Sm³⁺ and Gd³⁺ are doped in the bulk³⁷.

We adjusted the synthesis conditions and found that the sintering temperature can play a role in determining the microstructure and electrical properties of as-prepared ceria. The detailed work with regard to sintering temperature was added in supplementary information (SI) and can be described as follows. The XRD patterns of the CeO₂ powder sintered at various temperatures are presented as Fig. S1 in the SI. The results can be summarized: i) different temperatures led to the same fluorite structure; ii) the CeO₂ crystallinity was enhanced with the sintering temperature; iii) the lattice constant decreased as the sintering temperature increased, indicating a change in

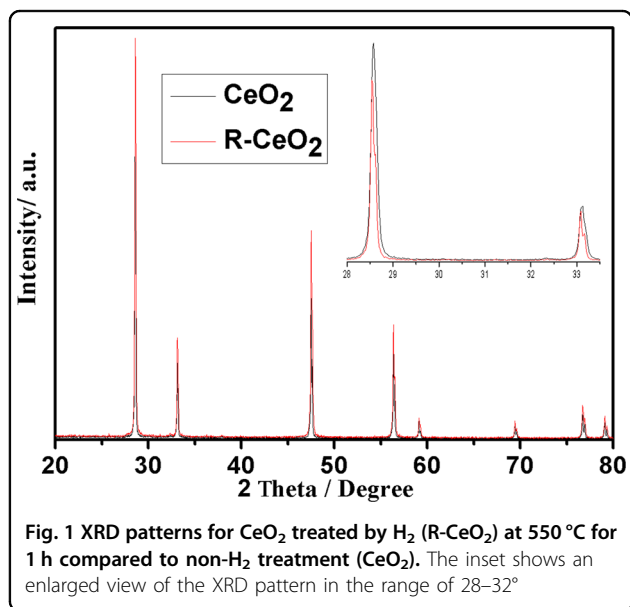


Fig. 1 XRD patterns for CeO₂ treated by H₂ (R-CeO₂) at 550 °C for 1 h compared to non-H₂ treatment (CeO₂). The inset shows an enlarged view of the XRD pattern in the range of 28–32°

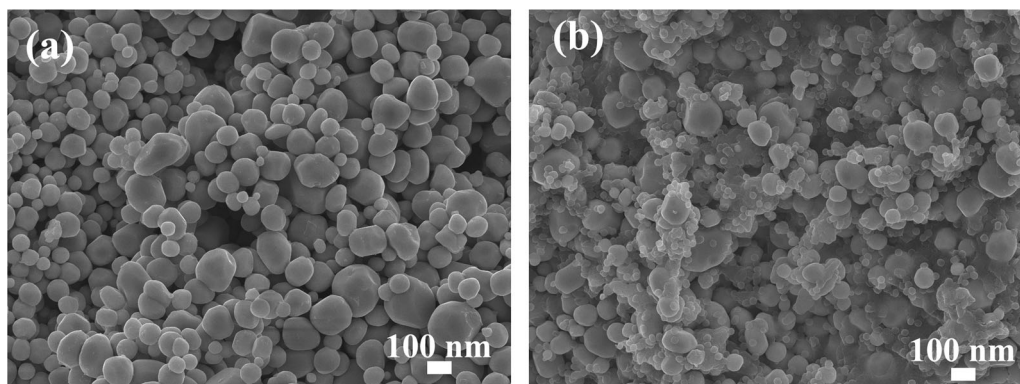


Fig. 2 SEM images of the CeO₂ powder (a) before and (b) after fuel cell measurements

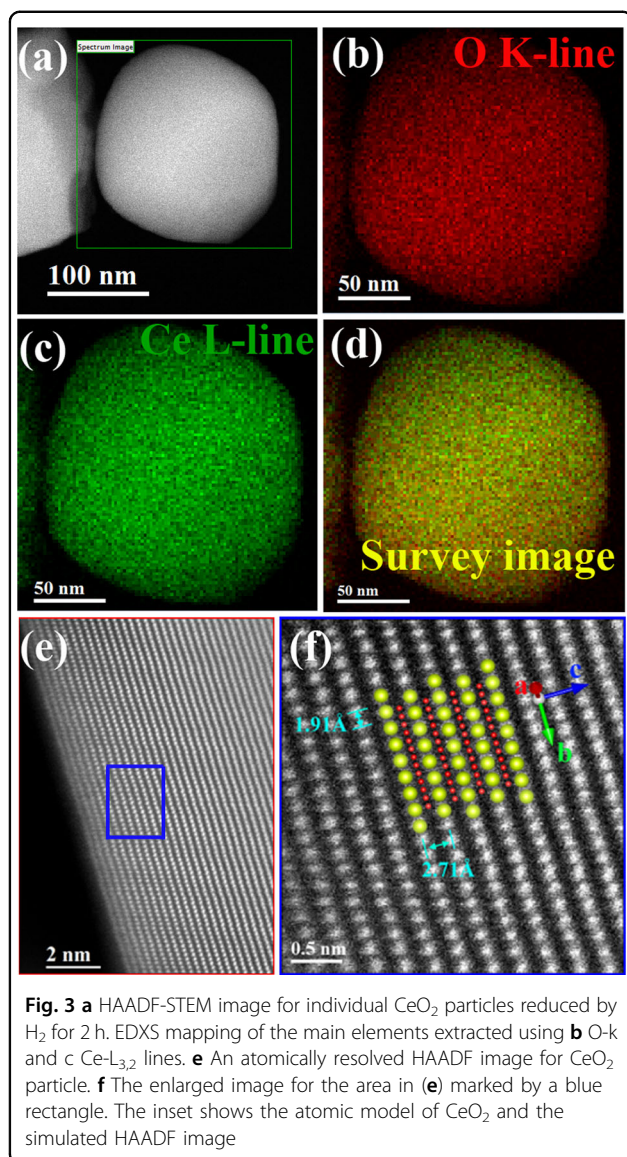
the Ce³⁺/Ce⁴⁺ ratio. Upon increasing the sintering temperature from 500 to 900 °C, the lattice parameters decreased correspondingly from 5.416 to 5.403 Å, which was deduced from the XRD patterns. This may be due to Ce ions not being fully oxidized at low sintering temperature, i.e., some Ce³⁺ coexisted with Ce⁴⁺. The large Ce³⁺ can expand the ceria lattice, while sintering at increased temperatures can fully oxidize the Ce ions, converting Ce³⁺ to Ce⁴⁺, and lead to a normal lattice constant that agrees with standard JCDPS data. Figure S2 shows the morphology evolution of the CeO₂ powder with sintering temperature through SEM characterization. A clear trend is discernible indicating that the grain size increased with the sintering temperature from several nanometers (500 °C) to 200–300 nm (1000 °C), which is closely related to the electrical conductivity and activation energy of ceria. The particular sintering temperature resulted in the formation of nanoscale CeO₂, and the size effect possibly extended the interfacial area accompanying with a reduced enthalpy of defect formation on the CeO₂ crystallizes and caused a high oxygen deficiency on the ceria particle surfaces, significantly enhancing the electrochemical performance of the cells. While focusing on low-temperature (<600 °C) SOFC electrolyte applications, we carefully optimized the synthesis conditions and fixed the sintering temperature at a sufficiently high temperature of 900 °C for 4 h to address the material stability and produce excellent electrochemical performance.

Figures 2a, b display the morphological change of the CeO₂ particles before and after fuel cell measurements. The original CeO₂ particles displayed a spherical shape with a 20–200 nm size distribution, and some pores were observed in the electrolyte layer, but the pores were enclosed without penetrating through the CeO₂-electrolyte membrane. After the FC measurements, the gaps between the particles were filled, and the CeO₂ electrolyte layer presented a fair density and good gas-tightness, thus ensuring that the assembled cells possessed high OCVs

(above 1 V) and excellent power outputs (see the cell performance section below) compared with conventional cells based on a dense doped ceria electrolyte.

Figure 3a shows the HAADF-STEM image for individual CeO₂ particles reduced by H₂ for 2 h. The particle was an irregular sphere with a diameter of 190 nm. The energy dispersive X-ray spectrometer (EDXS) mapping of the main elements using O-k and Ce-L_{3,2} lines for the CeO₂ particle is shown in Fig. 3b, c, and Fig. 3d is the survey image, which indicates an almost uniform element distribution throughout the entire particle. Figure 3e and f shows the atomically resolved HAADF-STEM image for the reduced CeO₂ particles. A high-resolution image is displayed in Fig. 3d, showing the atomic arrangement. An atomic structure model of the cubic phase of the CeO₂ along the [211] projection and a simulated HAADF image are superimposed on the HAADF image.

To further investigate the surface state of the reduced CeO₂ particles, the high spatial resolution of aberration-corrected STEM combined with EELS analysis were allowed to detect the valence variations of superficial Ce at the atomic scale. Figure 4a displays the particle area for EELS analysis and the blue arrow indicates the line scan direction. The plot of EELS scan signal from surface (point A) to grain interior (point B) was presented in Figure 4b. The Ce M₅/M₄ ratio is sensitive to the chemical state of Ce; therefore, the oxidation state of Ce can be determined quantitatively from the M₅/M₄ ratio using the positive part of the second derivative of the experimental spectra. Figure 4c gives the Ce M_{5,4} edges extracted from particle surface and 20 nm away from the surface. The resultant intensity ratios are listed in the inserted table. It can be found that the M₅/M₄ ratio on the surface is higher than that of the interior grain. As reported, a small M₅/M₄ ratio corresponds to Ce⁴⁺ and a large ratio is associated with Ce³⁺. Therefore, Ce³⁺ was produced on the surface of the CeO₂ particle, indicating the formation of a thin layer of oxygen-deficient CeO_{2-δ} on the surface. EELS

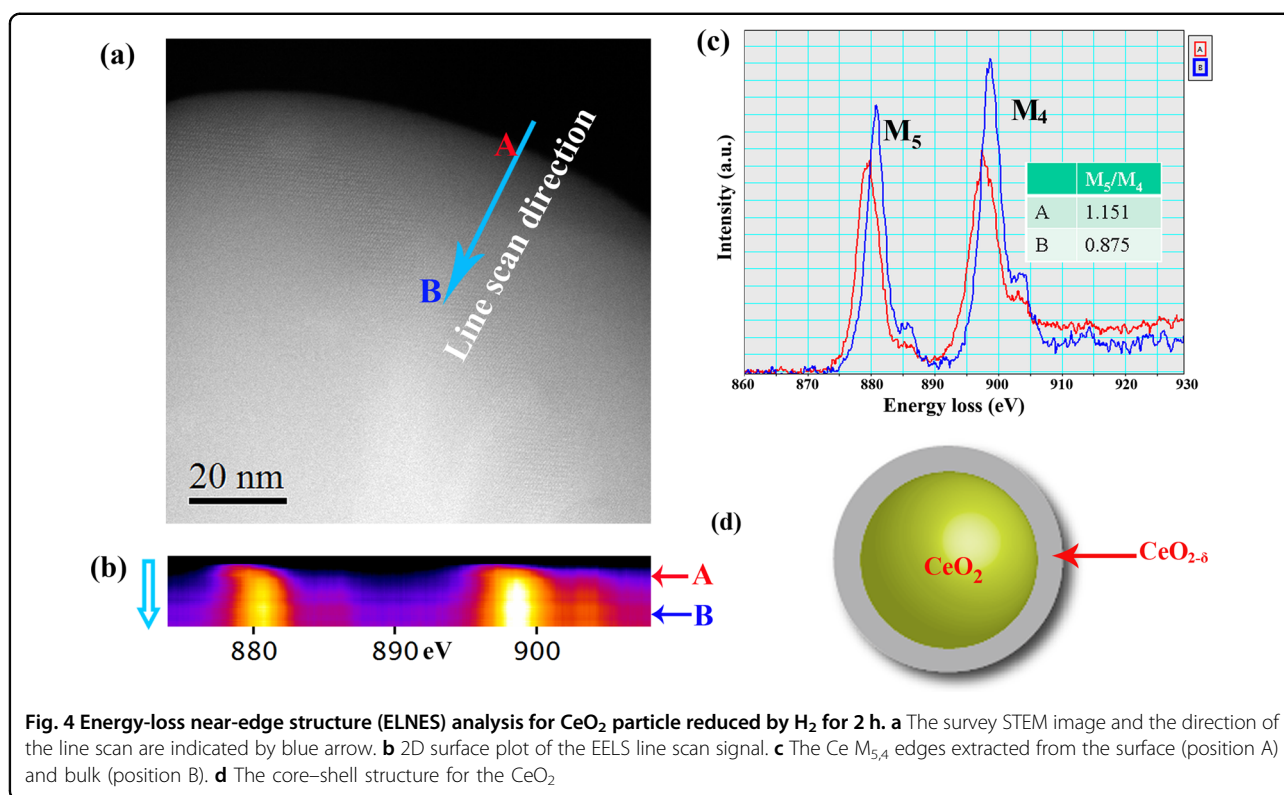


measurements confirmed the presence of oxygen vacancies on the particle surface. When a neutral oxygen vacancy is formed, two electrons are left behind. It is generally accepted that these electrons are localized in the *f*-state of the nearest Ce atoms³⁸, which changes their valence state from +4 to +3. In other words, the presence of Ce³⁺ could be evidence of oxygen vacancy formation, which significantly improves ion conductivity on the surface. Therefore, the stoichiometric CeO₂ in the interior grains is an insulator, and the oxygen-deficient CeO_{2-δ} on the surface possesses promising electrical conducting properties. Therefore, a novel CeO_{2-δ}@CeO₂ structure with a topological configuration, i.e., an insulating core and high conducting shell, was formed as illustrated in Fig. 4d. This evidence clearly indicates that

there is strong ionic conductivity for the reduced CeO₂, which was reflected by the great power output of the fuel cells assembled from pure CeO₂. In fact, it was reported that a surface layer of CeO_{1.5} is formed on the nano-CeO₂ particles, and the CeO_{1.5} fraction presented a significant increase when the particle sizes were below 15 nm and reached up to 90% at 3 nm³⁹.

The electron core level XPS spectra of the reduced and as-prepared CeO₂ were obtained to peer the chemical composition and valence states of the elements. Figure 5a shows the Ce 3d spectra collected from the as-prepared CeO₂. The spectrum is composed of two multiplets identified as V and U. These multiplets correspond to the spin-orbit split 3d 5/2 and 3d 3/2 core holes. The u''' and v''' peaks with a high binding energy indicate the final state of Ce 3d⁹ 4f⁰ O2P⁶, and the peaks labeled as u, v, u'' and v'' with a low binding energy are attributed to the Ce 3d⁹ 4f² O2P⁴ and Ce 3d⁹ 4f¹ O2P⁵ final states. The six characteristic peaks can be indexed as the Ce 3d spectrum for Ce⁴⁺, which is consistent with previous reports^{40,41}. Besides the six characteristic peaks of Ce⁴⁺, three extra peaks marked as u₀, u' and v' appeared in the Ce 3d XPS of the R-CeO₂ sample as Fig. 5b shown, demonstrating the existence of the Ce³⁺ oxidation state. The energy split between the v and v' peaks is ~3.0 eV, which is close to the value observed for the Ce³⁺ compound⁴². Figure 5c, d presents the O1s XPS spectrum of the as-prepared and R-CeO₂, which delivered an asymmetric feature that could be deconvoluted into different symmetrical signal. The spectrum for the as-prepared CeO₂ sample is fitted by two peaks centered at 529.5 eV and 530.5 eV, which are attributed to the lattice oxygen (marked as O_I) and surface adsorbed oxygen (marked as O_{II}), respectively. For the R-CeO₂ sample, the asymmetric O1s spectrum is deconvoluted into three peaks denoted as O_I, O_{II} and O_{III}. The new peak (O_{III}) with a higher binding energy is related to the presence of the oxygen vacancies, possibly due to the existence of Ce³⁺ produced by H₂ reduction, which is crucial for ionic conduction and dominated the electrochemical performance of the assembled fuel cell.

This surface layer of the core-shell structure was further characterized to understand the boundaries and buried interface effects on the ionic conduction origin and enhancement. We carried out more careful characterization to identify and determine the tension of the grain boundaries with agglomerated CeO_{2-δ} particles through STEM in combination with the EELS, as shown in Fig. 6. The HAADF images a and b show that the particle size was in the range of 10–200 nm. It is clear that all of the particles closely contacted each other, and the color of the interface region between the particles is different from the interior of the particles, indicating stress accumulation at the interface. As Fig. 6c shows, neither disordered nor amorphous structures are present at the grain boundaries,

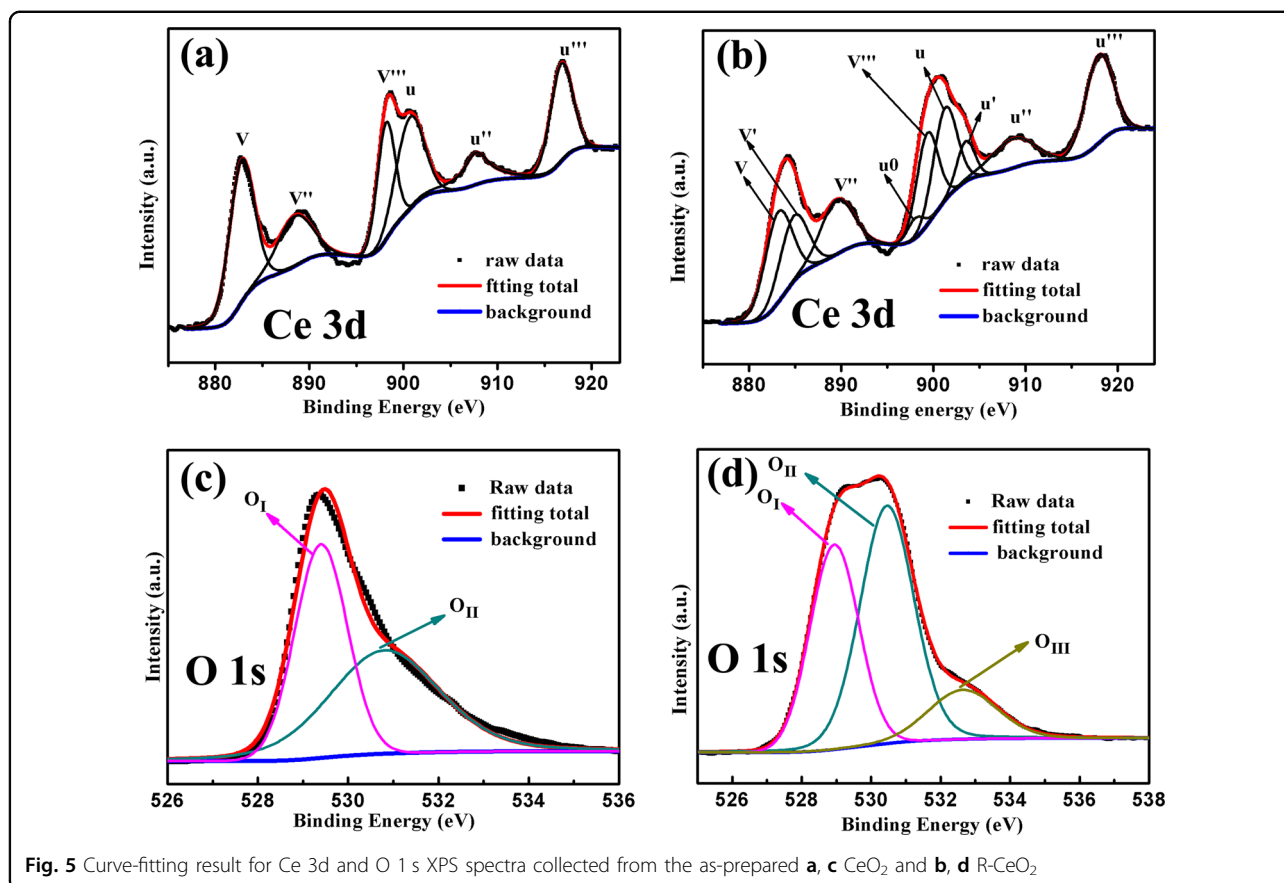


indicating that the boundaries are successfully joined at the atomic level.

In Fig. 6, there are two direct pieces of evidence to support the interfacial conduction mechanism. (i) First, an analysis of the stress was carried out at the interfaces. As shown in Fig. 6a, b for the HAADF images, the contrast is bright at the interfaces, which indicates that there was an accumulation of stress. (ii) An emphasis is paid on analysis of the valency state at the interfaces. The Ce valence state changes were extracted using Ce-M_{5,4} edges in atomic resolution, as shown in Fig. 6e. Both the chemical shift and white-line ratio methods and analyses prove that there was an ~1.5 nm buried interface, where Ce was in the 3+ valence state and is highlighted in red in Fig. 6d. This implies that oxygen vacancies were created in the buried interfaces. Because accompanying with the Ce³⁺ formation, the oxygen vacancy generation process can be described by equation (1). The experimental evidence indicates that the surface and grain boundaries play a dominant role in ionic transport; it is well understood and reported in the literature^{43–45} that stress and tension generate vacancies at interfaces to promote ion transport.

The electrical behavior of the CeO₂ pellets was examined by EIS analysis under air and H₂/air FC environment at a device measuring temperature of 550 °C. The EIS results are shown in Fig. 7. To understand the EIS behavior in more detail, a simulation was carried out using the equivalent circuit models of R_o(R₁-QPE₁)(R₂-QPE₂)

(Insets of Fig. 7), where R is the resistance and QPE represents the constant phase element. The high-frequency intercept on the Z'-axis, as shown in the enlarged inset, reflects the entire ohmic resistance of the device, including the resistance of CeO₂ bulk, electrodes and connecting wires. Both EIS results were characterized as a semicircle followed by an inclined line, and the flat semicircle in the medium-frequency region could be superimposed by two standard semicircles. One is attributed to the grain boundary/surface effect in the middle-frequency range, and the other is due to the charge-transfer impedance on the electrode/CeO₂ interface. In addition, the inclined line in the low-frequency region corresponds to the ion-diffusion process in the electrode process. These processes also commonly exist in fuel cells based on doped ceria electrolytes⁴⁶. It can be seen clearly that the CeO₂ based device under an air atmosphere exhibited a typical ion conducting nature and low conductivity, which are reflected by a large semicircle due to grain boundary and charge transfer processes. In the FC condition, the device immediately shows a mixed electron-ion conducting behavior and a rapid decrease in resistance of more than two orders of magnitude (see the inset of Fig. 7). The diameter of the semicircle in the medium-frequency region for the CeO₂ under FC conditions is much smaller than that of the CeO₂ device in air, indicating much lower grain boundary and charge-transfer resistances. The result suggests that the

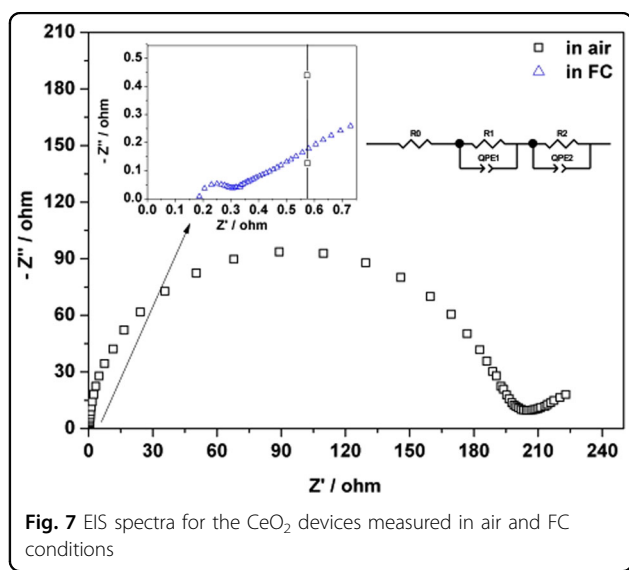
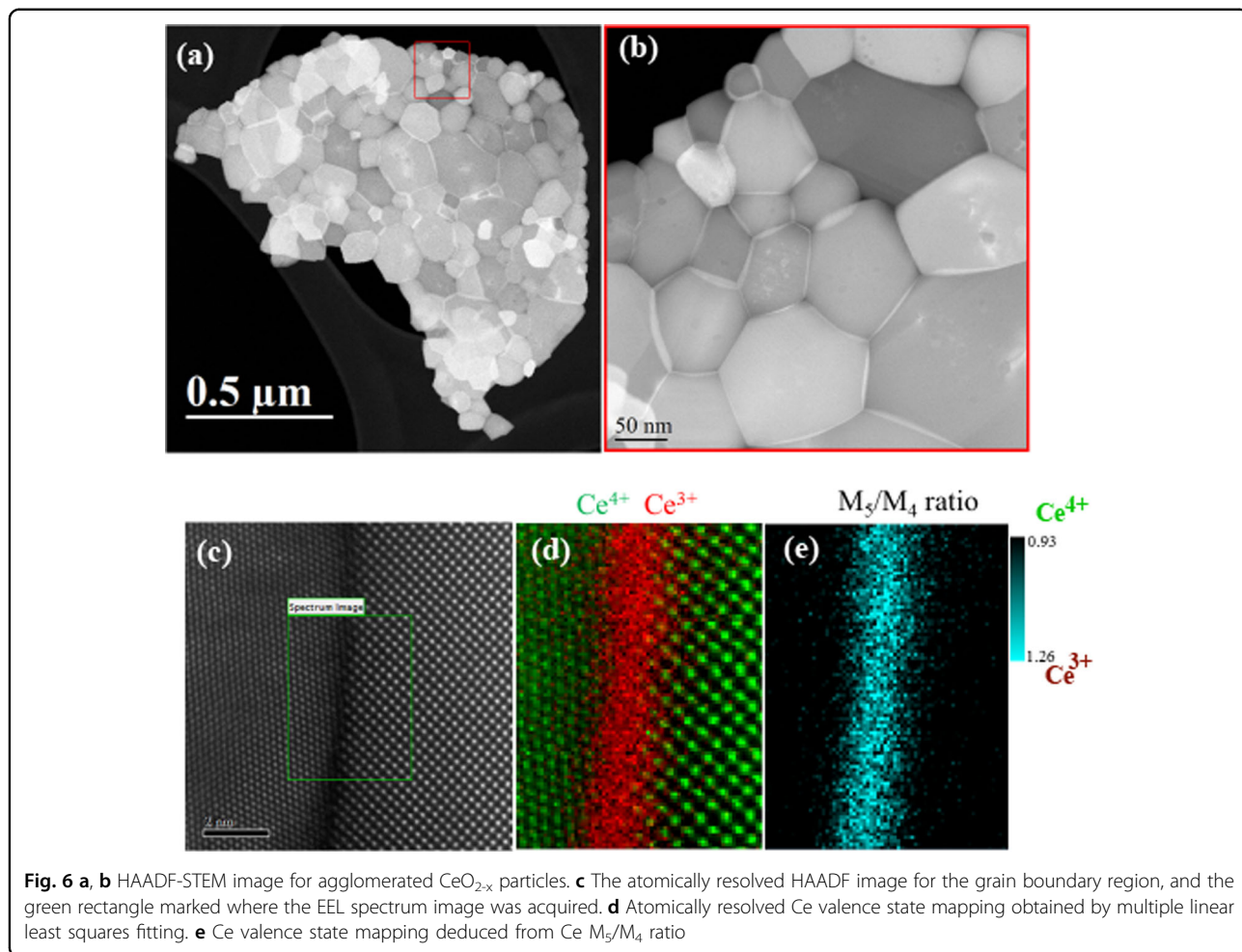


conductivity (both ions and electrons) of CeO₂ under FC conditions was significantly enhanced in comparison with that under an air atmosphere. The fitting results show that the total electrical conductivity of the CeO₂ in air was low, $\sim 10^{-4}$ s/cm, as estimated from the EIS result in air; in contrast, a drastic change occurred to bring about a high conductivity state under FC conditions, and the conductivity exceeded 10^{-1} s/cm. In addition, the obtained capacitances displayed low values, revealing the rate-determining processes in the fuel cell. This result is consistent with the reduction of the Ce⁴⁺ to Ce³⁺ in the H₂/air environment. This occurred because H₂ can reduce CeO₂ and form large oxygen vacancies, further resulting in significant enhancement of both oxygen ion and electronic conduction.

The oxygen deficient layer on the surface can function as an oxygen ion transport pathway and significantly dominate the charge conduction, especially the grain boundary conductivity, which was deduced from the EIS plot of the pellet. To further verify the surface conduction, we specifically separated the grain boundary resistance from the EIS results and converted the resistance to conductivity by using the pellet dimensions. Figure 8 shows the grain boundary conductivity (σ_{gb}) of CeO₂ as a function of temperature obtained in air and H₂/air

atmospheres. The noteworthy point is that the σ_{gb} obtained in the H₂/air atmosphere was significantly higher than that in the air, possibly due to the formation of an oxygen-deficient layer on the particle surface under the H₂/air atmosphere, which provided a pathway for oxygen transport to significantly enhance σ_{gb} .

Based on the excellent electrical properties, the CeO₂ samples were used as the electrolytes for fuel cells, and the cell performances are shown in Fig. 9. It can be seen clearly that high OCV values (1.0 to 1.12 V) and power outputs (140–660 mW/cm²) was achieved at operational temperatures of 400–550 °C. To verify the reproducibility of the performance, we fabricated 8 cells from non-doped CeO₂ and evaluated their electrochemical performance. A box plot diagram was chosen to present the power maximum of the measured 8 cells at various testing temperatures, as shown in Fig. 10. The horizontal lines in the box denote the 25th, 50th and 75th percentile values. Obviously, the performance presented in Fig. 9 is close to the mean value; therefore, the value is representative. Although there was high electronic conduction, as discussed above, the CeO₂ electrolyte exhibited no any electronic short-circuiting problem. These results obtained from non-doped CeO₂ surface conduction demonstrated significant advantages over doped ceria



electrolyte fuel cells from both the OCV and power output perspectives. For example, samarium-doped ceria (SDC) electrolyte fuel cell devices have demonstrated OCVs < 0.9 V and output powers < 100 mW/cm^2 at 600°C , while non-doped CeO_2 achieved 660 mW/cm^2 at 550°C ³². This indicates a very different ionic conduction mechanism and fuel cell principles between the doped bulk conducting SDC and non-doped surface conducting CeO_2 , which deserves further study.

It has been reported that nanoscale CeO_2 shows strong or dominant electronic conductivity, giving nanosized CeO_2 a mixed ionic and electronic conductivity (MIEC) state³³. The grain boundary-enhanced electron concentration corresponding to depression in the positively charged ionic (oxygen vacancy) species is expected from space charge theory. It should be pointed out if the fuel cell electrolyte has significant electronic conductivity, i.e., a typical MIEC electrolyte, which will make significant

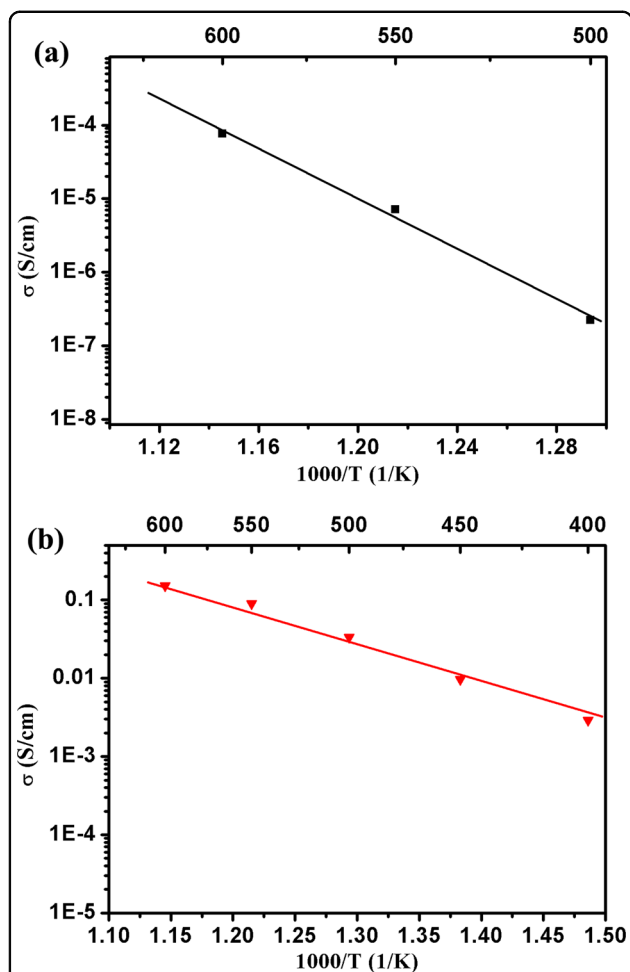


Fig. 8 The grain boundary conductivity of CeO_2 as a function of temperature obtained in (a) air and (b) H_2/air atmospheres

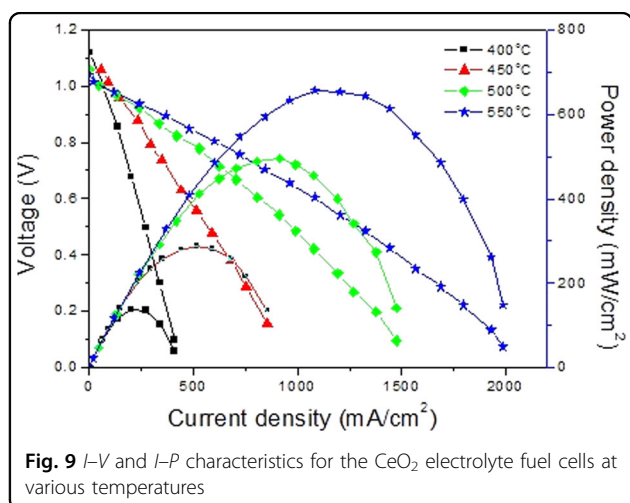


Fig. 9 I - V and I - P characteristics for the CeO_2 electrolyte fuel cells at various temperatures

device OCV and power losses. However, our case represents the opposite situation because excellent fuel cell performances were obtained for the OCV, which

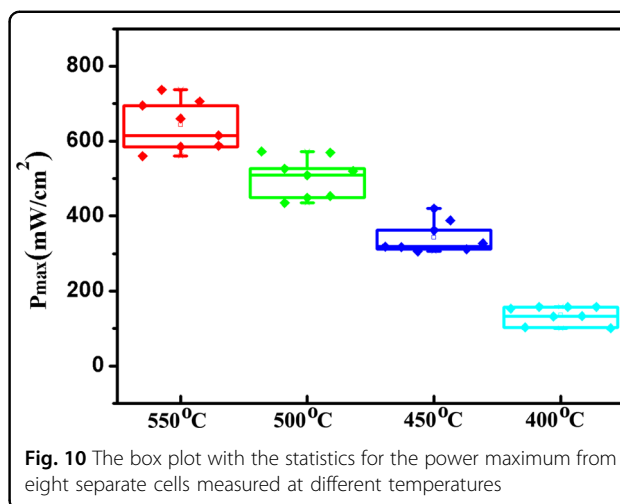
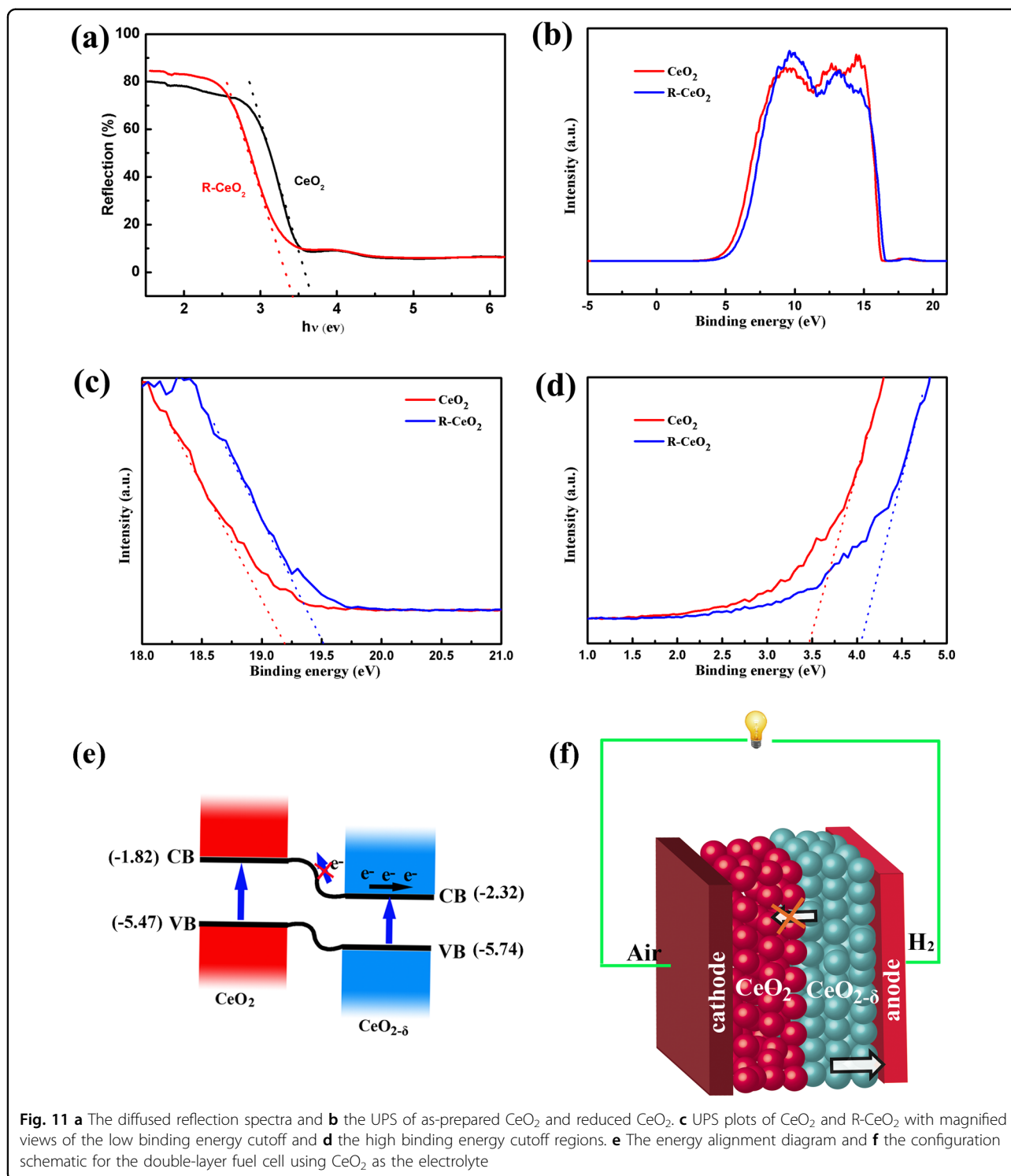


Fig. 10 The box plot with the statistics for the power maximum from eight separate cells measured at different temperatures

exceeded 1.0 V and even reached 1.12 V, and for the power output, which reached 660 mW/cm^2 at 550°C .

How can the MIEC type CeO_2 be used as a fuel cell electrolyte and cause no additional losses in the OCV and power output? These conflict with conventional MIEC theory and SOFC devices for a doped ceria electrolyte fuel cell³³. We propose a new scientific principle for a semiconductor junction combined with energy band alignment, which has been reported in other semiconductor-ionic membrane fuel cell systems^{47,48}. In this case, the contacted CeO_2 on the anode side was reduced by H_2 to form Ce^{3+} and released free electrons. The surface conduction was formed, and the extra electrons simultaneously brought about n-type conduction for the CeO_2 on the anode side. Martin and Duprez determined the oxygen and hydrogen surface diffusion on the oxide surfaces, and pointed out that both oxygen and hydrogen can transport rapidly on the CeO_2 surface^{49,50}. Lai et al. reported that a Sm-doped CeO_2 thin film exhibited mixed ionic and electronic conductivity with a bulk ionic conductivity of 7 mScm^{-1} and an electronic conductivity of 6 mScm^{-1} under open-circuit conditions at 500°C ⁵¹. These data agree well with our fuel cell results, although we used the pure CeO_2 phase, which possessed sufficient surface electron and ionic conductivities.

On the other hand, CeO_2 on the air side showed hole conduction⁵², i.e., p-type conduction, while the CeO_2 on the anode side reduced by H_2 turns to electron (n-type) conduction. Naturally, a p-n junction was formed between two parts of the CeO_2 electrolyte. In this case, we propose a double-layer electrolyte model for the fuel cell, as shown in Fig. 11f. Band energy alignment between the CeO_2 and R- CeO_2 is proposed to clarify the charge separation and barrier to block the electron passing through the CeO_2 electrolyte, even though it is an MIEC-type electrolyte. An oxygen vacancy is associated with the formation of two Ce^{3+} ions and is a two-electron donor center, which can



lead to significant electronic conduction. Concerning the formation of double-charged oxygen vacancies, electrons in the conduction band were composed of Ce 4f energy states. The electrons formed during reduction were treated as being localized on the cerium, thereby converting Ce^{4+} to Ce^{3+} ions. To verify this assumption, the accurate

band energy of the $\text{CeO}_2/\text{R-CeO}_2$ was determined by UPS combined with UV-vis diffused reflection. UPS of the CeO_2 and R-CeO_2 were carried out to determine their valence band. In the UPS spectra presented in Fig. 11b, the energy was calibrated with respect to He I photon energy (21.21 eV). As Fig. 11c, d shows, by defining the

low-binding and high-energy cutoff, the valence band maximum below vacuum level was obtained to be -5.47 eV for CeO_2 and -5.74 eV for the R- CeO_2 sample. These band gaps were determined from the diffused reflection measurements (Fig. 11a) to be 3.65 eV and 3.42 eV for CeO_2 and R- CeO_2 , respectively. On the basis of these results, we can further deduce the corresponding conduction band (CB) levels to be 1.85 eV for CeO_2 and 2.32 eV for R- CeO_2 . The final band alignment is sketched in Fig. 11e and clearly reveals that the CB position of CeO_2 is higher than that of R- CeO_2 , the extra electrons produced by the reduction atmosphere should aggregate in the CB of the R- CeO_2 , further decreasing the CB position. The conduction band offset formed potential barriers to prevent the electrons generated on the anode side from passing through the interface between CeO_2 and R- CeO_2 , thus avoiding a short-circuiting problem. In addition, the built-in field formed by the CeO_2 /R- CeO_2 band energy alignment should promote oxygen ion transport.

In the present work, we discovered that CeO_2 without doping can create much better electrical properties and fuel cell performance than those of conventional cation doped ceria, e.g., samarium-doped ceria (SDC) based on bulk ionic conduction. The possible underlying mechanism involves the formation of a surface oxygen-deficient layer and core-shell architecture for reduced CeO_2 that is accompanied by band energy alignment to avoid shorting, which is a novel mechanism for ceria electrolyte materials and a novel fuel cell principle. On the other hand, the H_2 supplied as fuel reduces the Ce^{4+} into Ce^{3+} , which has the same doping effect as Sm^{3+} and improves the ionic conductivity, namely, “self-doping” occurs. However, cation doping and self-doping are different. For example, cation doping, such as with Sm^{3+} or Gd^{3+} takes place in the CeO_2 particle bulk to create oxygen vacancies, further developing bulk conduction, while self-doping occurs at the particle surface accompanied by oxygen vacancies, leading to different surface conduction mechanisms. Surface conduction has unique advantages, including low activation energy and fast ionic mobility. Both of these advantages contribute to better ionic conductivity and fuel cell performance than conventional cation doped cerium-based electrolytes. For example, Shen et al. reported a Gd-doped ceria (GDC) electrolyte for SOFCs with mixed electronic conduction, resulting in an OCV < 0.9 V and power output < 100 mW/cm².³² In other words, the surface conduction induced by fuel cell conditions is distinct from the ordinary O^{2-} conduction mechanism in bulk doped ceria and appears to be a new methodology for the design of new functionalities for advanced technologies in the energy sector, especially for next generation SOFCs.

Conclusions

The occurrence of charged defects and the control of stoichiometry in fluorite CeO_2 materials can be accomplished by a reduction treatment, which can strongly affect the CeO_2 surface defects. Reducing and oxidizing conditions during cell operation produce CeO_2 semi-conducting (n-type at the anode and p-type at the cathode)-ionic properties and greatly enhance both the electronic and ionic conductivities. Ionic conductivity may play a dominant role in fuel cell processes and device performance accompanied by sufficient electron conduction. High ionic conductivities have been realized by creating surface defects, e.g., oxygen vacancies and surface pathways. The CeO_2 should be reduced to non-stoichiometric $\text{CeO}_{2-\delta}$ at the anode region and combined with CeO_2 at the cathode side to form a double-layer device. The energy band alignment between $\text{CeO}_{2-\delta}$ / CeO_2 can produce efficient charge separation and avoid the device short circuiting problem, while charge separation is an enormous challenge for conventional SOFCs based on a doped ceria electrolyte, where OCV and power losses generally occur to some extent due to the existence of electronic conduction. The semi-conducting and ionic properties take advantage of the semiconductor energy band to prevent the electrons from internally migrated simultaneously enhance the ionic transport. The synergistic effect to enhance the ionic conductivity is also observed above 0.1 S/cm at 550 °C. The non-doped CeO_2 approach may instigate very interesting new fundamental understanding of the science and promote SOFC development.

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Conflict of interest

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