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Charge separation and transport in $\text{La}_{0.6}\text{Sr}_{0.4}\text{Co}_{0.2}\text{Fe}_{0.8}\text{O}_{3-\delta}$ and ion-doping ceria heterostructure material for new generation fuel cell

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Abstract

Functionalities in heterostructure oxide material interfaces are an emerging subject resulting in extraordinary material properties such as great enhancement in the ionic conductivity in a heterostructure between a semiconductor SrTiO_3 and an ionic

¹ These authors contributed equally to this work.

conductor YSZ (yttrium stabilized zirconia), which can be expected to have a profound effect in oxygen ion conductors and solid oxide fuel cells [1-4]. Hereby we report a semiconductor-ionic heterostructure $\text{La}_{0.6}\text{Sr}_{0.4}\text{Co}_{0.2}\text{Fe}_{0.8}\text{O}_{3-\delta}$ (LSCF) and Sm-Ca-co-doped ceria (SCDC) material possessing unique properties for new generation fuel cells using semiconductor-ionic heterostructure composite materials. The LSCF-SCDC system contains both ionic and electronic conductivities, above 0.1 S/cm, but used as the electrolyte for the fuel cell it has displayed promising performance in terms of OCV (above 1.0V) and enhanced power density (ca. 1000 mW cm⁻² at 550°C). Such high electronic conduction in the electrolyte membrane does not cause any short-circuiting problem in the device, instead delivering enhanced power output. Thus, the study of the charge separation/transport and electron blocking mechanism is crucial and can play a vital role in understanding the resulting physical properties and physics of the materials and device. With atomic level resolution ARM 200CF microscope equipped with the electron energy-loss spectroscopy (EELS) analysis, we can characterize more accurately the buried interface between the LSCF and SCDC further reveal the properties and distribution of charge carriers in the heterostructures. This phenomenon constrains the carrier mobility and determines the charge separation and devices' fundamental working mechanism; continued exploration of this frontier can fulfill a next generation fuel cell based on the new concept of semiconductor-ionic fuel cells (SIFCs).

Graphical Abstract

The charge separation processes, from nano-particle level to the device level, are key to the scientific understanding of the SIFCs. The synergistic effect of junction and energy band alignment towards the charge separation from particle to device level, in particular blocking electron crossover, as well as the promotion of ion transport by built-in field, contribute to the working principle and facilitates high power output in the SIFC. Thus, it can realize fuel cell functions and fuel-to-electricity conversion through different means from the conventional fuel cell, wherein the semiconductor-ionic heterostructure, charge separation and junction play key roles, and joining physics and electrochemical processes are in force.

Keywords

Fuel cell device; semiconductor ionic fuel cell; charge separation, ionic transport; heterostructure; composite; semiconductor-ion material

Introduction

Since their invention and demonstration in 1839 by Sir Grove [5], all fuel cells (FCs) have used a construction with three functional components: anode, electrolyte and cathode. The anode and cathode need hydrogen and oxygen catalysts properties and sufficient ionic and electronic conductivity to accomplish the fuel (e.g. H_2) oxidation and oxidant (e.g. O_2) reduction processes. H^+ or O^{2-} ions subsequently are transported through the electrolyte to convert the fuel's chemical energy into electricity. The three-component technology requires a complex FC structure and stringent material selection such that all components must be stable and compatible with each other. Interfaces between electrolyte and the electrodes contribute to the major polarization losses [6]. Furthermore, the complex technology leads to high capital cost resulting in further delay of FC commercialization.

Among the three components, the key is the electrolyte [7] which governs the type and operating temperature of fuel cells. FCs have been developed based on various types of electrolytes, such as PEMFC (polymer electrolyte membrane fuel cell), AFC (alkaline fuel cell), PAFC (phosphoric acid fuel cell), MCFC (molten carbonate fuel cell), and SOFC (solid oxide fuel cell) [6-9]. The electrolyte type and its electrical properties identify the type of FC and determine the likely operating temperature ranges. For instance, a high temperature of 1000 °C is typically needed for the current YSZ (yttrium stabilized zirconia) being used as an electrolyte in order to obtain a sufficiently high ionic conductivity, which restricts the choice of the FC component materials and results in high cost, introducing an extra barrier to commercialization [8-10].

Recently, a new technology has been developed which eliminates the need of the electrolyte layer, demonstrating an electrolyte-layer free fuel cell (EFFC). This can be regarded as a breakthrough in the history of fuel cell development [11-13]. The 'electrolyte-free' term implies that a non- electrolyte separator/layer is needed for this device. The current fuel cell science (conventional) is insufficient to explain and understand the working principle of EFFCs. In particular, the pertinent question of "how short-circuiting is prevented without an electrolyte separating layer?" is not satisfactorily addressed. A similar question could be also raised for solar cells. Today,

the semiconductor and its physical properties are well understood thus various junctions are realized for successful understanding and progress in solar cell applications. This hints that similar scientific principles could be functional in the successful operation of EFFC that involves the semiconductor material. The semiconductor-ionic materials play a vital role in EFFC functions, which is a new type of functional material. It can function, on one hand, for semiconducting physical properties and junctions, and on the other hand, for ion electrochemical properties. The semiconductor-ionic approach provides a new way to realize the challenge for current SOFCs caused by the poor ionic conductivity of electrolyte at low temperatures. A strong ionic conductivity enhancement (two or more orders of the magnitudes) was found between a semiconductor SrTiO_3 (a semiconducting perovskite) and ionic electrolyte YSZ [1-3]. A similar phenomenon has been also observed for samarium doped ceria (SDC) and SrTiO_3 [3]. Although great enhancement in ionic conductivity has been found in these heterostructure semiconductor-ion materials, their performance in SOFCs is still a question. One of the reasons may be due to the presence of strong electronic conduction in such heterostructure materials due to SrTiO_3 [14]. According to the fuel cell science the existence of the electronic conduction in the membrane can cause serious OCV and power losses [15-18].

Recently, Singh et al [19] has pointed out that n- and p-type oxides could fulfill the role of anode and cathode quite beautifully, giving a new scientific view from a semiconducting physical aspect, as shown in Figure 1. This shows a potential to understand the fuel cell science from conventional electrochemical to a semiconductor-ionic device, i.e. anode is actually an n-semiconductor; while cathode is a p-semiconductor and an ion conductor as the electrolyte is in between. It has been recently reported [20] that nano-redox processes exist in EFFCs which is built through bulk heterojunction (BHJ), i.e. by the semiconductor (n- and p-) particles. In this case the macroscopical anode, cathode and ionic electrolyte functions can be replaced by n, p and ionic particles as illustrated in Fig. 1 (b), so that the FC redox is realized at nano-particles level. For better understanding, we may simply consider that Fig. 1(a) could be compacted from macro-to nano-scale, i.e. Fig. 1(b). By removing the electrolyte layer between the anode and cathode, the fuel cell turns into a n/p junction device that is well-known for the solar cell. We have reported the functioning of such a device (named as the bilayer fuel cell) using the n and p type semiconductor materials mixed with ion

conducting ceria, leading to good performance comparable to the conventional device with anode/electrolyte/cathode configuration [12]. This bilayer fuel cell is the first prototype of this n/p junction device and has been demonstrated again recently based on the p-n junction principle [21]. Following this line, we have further developed semiconductor-ionic fuel cells (SIFCs) to construct a novel device with the junction type designed by energy band alignment. The elegance in this strategy lies in the fact that the fuel cell ionic functions and processes are maintained at the same time with an even simpler non- electrolyte configuration.

Fig. 1. (a) A new recognition of SOFC science from ref 19; (b) Nano redox process in the EFC

In the present study, the semiconductor-ionic material $\text{La}_{0.6}\text{Sr}_{0.4}\text{Co}_{0.2}\text{Fe}_{0.8}\text{O}_{3-\delta}$ (LSCF) and the ion conductor, Sm^{3+} and Ca^{2+} co-doped ceria (SCDC) were selected to prepare a type of the semiconductor-ionic material (SIM), i.e. LSCF-SCDC to investigate further on the fundamental issues of charge separation and transport in a SIFC device. The device was constructed by sandwiching the LSCF-SCDC between two semiconducting oxide $\text{Ni}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}\text{Li}$ -oxide (NCAL) thin layers. In this way, a new concept of a fuel conversion device has been explored that operates in an analogous way to a fuel cell using a purely ion conducting electrolyte added by p and n-blocking layers to prevent electrons from short-circuit. Such materials and devices have been reported as a new generation fuel-to-electricity conversion technology [22] resulting in a simplified system with high performance. This strategy of SIFC has a great potential for fundamental research and applications as well as advanced technologies to

overcome the inherent fuel cell challenges. Therefore, there are strong needs for continuous research on fundamental issues along with more scientific support and greater understanding. The current work is for a deep understanding and characterizing core scientific mechanism on the charge separation and transportation of our previous work [22]. Especially, by employing electron energy-loss spectroscopy (EELS) analysis, we can characterize more accurately the buried interface between the LSCF and SCDC further reveal the properties and distribution of charge carriers in the heterostructures.

Results and Discussion

As observed from transmission electron microscopy (TEM), both LSCF and SCDC are in nano-scale as shown in Fig. 2. There are clearly buried interfaces between two phase particles, which will be further investigated and analyzed later (see Fig. 4). The physical properties on these interfaces are important to determine the charge separation and ionic transport properties.

Fig. 2. (a) TEM images for the LSCF- SCDC nanocomposite

We have measured the I-V and I-P characteristics for fuel cells, which show a maximum power density of about 1000 mW/cm^2 at 550°C for LSCF-SCDC based SIFC while the SOFC using the SCDC electrolyte only reached 325 mW/cm^2 under the same conditions. The SIFC shows even higher OCV, 1.08V in comparison with 0.91 V obtained from the SCDC-electrolyte based fuel cell. The lower OCV for the SCDC electrolyte based SOFCs is a common consequence resulting from reduced ceria

providing leakage of electronic conduction in the fuel cell environment. These results are comparable with those published before [22].

It is well known from the fuel cell science that the electrolyte having the electronic-ionic mixed conduction can immediately cause the internal short circuiting problem which restricts the use of mixed conductors. For example, doped ceria, despite having good oxide ion conductivity, has limited use as the electrolyte due to its significant electronic conduction, which is caused by partial reduction of Ce^{4+} to Ce^{3+} in fuel atmospheres at elevated temperatures, e.g. above 500 °C [15, 23, 24]. Thus the lower OCV obtained from the SCDC electrolyte fuel cell can be explained primarily as a result of some electronic conduction effects. This is also a limit to the successful usage of ceria for SOFC technologies, although significant R&D effort has been expended in this field [25]. In comparison, the SIFC device fabricated from LSCF and SCDC semiconductor-ionic layer replacing the SCDC electrolyte yields higher OCV and higher power output. The SIFC device does not display any short circuiting problem, which does not synchronize with the existing fuel cell science, because the introduction of electronic conductivity into the electrolyte will certainly cause short circuiting within the fuel cell [15-18]. In parallel, the SIFC device has generated significantly high power output (about 300% of that of the SCDC electrolyte fuel cell). The scientific principle for this semiconductor LSCF and ionic SCDC membrane fuel cell has been reported and described in our previous work [22]. It is designed by the energy band alignment to block electron short circuiting problem based on the solar cell principle, therefore, the LSCF-SCDC device can display an OCV above 1.0V. It is true that the LSCF-SCDC composite layer with proper LSCF and SCDC contents acting as the electrolyte can reach always above 1.0V OCV as reported [22]. The present work has continued to study the charge separation and transport processes in such novel fuel cell device.

In order to further reveal the underlying processes in the device, electrochemical impedance spectroscopy (EIS) measurements were carried out for the SCDC based fuel cell and LSCF-SCDC based SIFC devices, and the results are included in SI Fig. S3. Based on theoretical simulations, the results suggest that in conventional fuel cell device, the electrode/electrolyte interface charge transfer process is the rate-determining step for ORR process, while this is turned to the surface oxygen diffusion, adsorption and dissociation processes for the LSCF-SCDC based SIFC device. From the viewpoint of the clearly different configurations between fuel cell and

SIFC devices, the separation of anode and cathode by the ion-conductive SCDC electrolyte layer in FC forms two electrolyte/electrode interfaces, which cause distinct anodic and cathodic polarizations. In comparison, the SIFC device has semiconducting and ionic conductivities liberated from the constraint of electrode/electrolyte interfaces. Combined with the DC electronic conductivity measurement with the Hebb-Wagner polarization method (details are presented in SI), the electronic conductivity was obtained as 0.18 S/cm, while the total conductivity can be calculated from EIS to be 0.29 S/cm. We can thus get ionic conductivity for the LSCF-SCDC to be 0.11 S/cm by subtracting the electronic part from the total conductivity. All data is with reference to temperature at 500 °C. These indicate that the LSCF-SCDC possesses highly comparable electronic and ionic conductivities; this is due to a balanced conductivity request [26].

For further analysis of the LSCF-SCDC composite, element mapping was performed (see SI Figure S2). It was found that two phase materials were homogeneously distributed in a complementary way to form percolating networks and charge transport paths for electrons (in LSCF phase) and ions (in SCDC phase and LSCF-SCDC interfaces). The interest is that such well distributed electrons do not cause any internal short circuiting for the device. There must be a charge separation for electrons (holes) that is fundamental and warrants a deep scientific consider the underlying processes and mechanisms.

As reported, a bulk-heterojunction (BHJ) plays a key role in dictating the high performance in EFC devices [20]. BHJ is formed when p and n type semiconductors make intimate contact with each other, where the energy level difference between the n and p semiconductors contributes to charge separation and thus prevents the electron cross over the device.

At low oxygen, partial pressures ceria is partially reduced and develops n-type electronic conductivity according to

With the law of mass action, it follows, that

$$n = K_e N_{intr}^{-1/2} p(O_2)^{-1/4} \quad (2)$$

Where n denotes electron concentration and K_e is a constant. N_{intr} is the number of additional oxygen vacancies introduced by partial reduction which increases at low

oxygen partial pressures, e.g. on the H_2 site. Considering this fact, we assume that ceria can cause significant electron (n type) conductivity resulting in a thin n-type surface layer in the H_2 diffusion of the anode zone in contact with the LSCF-SCDC layer. Thus, a n (SCDC)- p (LSCF) bulk heterojunction structure may be formed to separate the electrons and holes, i.e. SCDC as shown in Fig. 3a where well distributed nano-particles for both SCDC and LSCF phases can be noticed. The corresponding energy diagram in the H_2 contacting site is shown in Fig. 3b. Following this BHJ, the p-type LSCF zone is extended to the cathode since the SCDC can maintain its O^{2-} conducting phase, thus the electrons are discontinued due to: i) SCDC not being reduced in oxygen (air) side and ii) the p-type conduction of LSCF. In addition, the p type-NCAL buffer layer also impedes the electrons path and completely avoids the electron short circuiting problem. The whole process can be expressed by an energy diagram for such an SIFC device as shown in Fig. 3c. These diagrams are supported by experimental UPS and UV-vis spectra results shown in SI (Fig. S6). In the SIFC device, by supplying H_2 and air on opposite sides, the BHJ is distributed in the H_2 contact site followed by the n-p junction as shown and the built-in field is denoted by the arrows.

Figure 3. (a) Nano-particles contacts between the LSCF and SCDC (b) energy diagram of p-n BHJ for charge separation on H_2 contact side at particle level and (c) energy band diagram at device level

The situation could be considered as similar to a solar cell, in that the electron is separated due to the energy band alignment avoiding the device short circuiting problem. From the energy alignment diagram, at the device level, the most important characteristic is that the electrons are generated in anode reaction by H₂ oxidation and contacted with ceria (SCDC), but the electrons could not pass through the LSCF(p)-SCDC (ion)/NCAL (p) layers and the energy band alignment drives the electrons towards the anode side. Once the device is loaded, the electrons will conduct directly through external circuit to air contact side, in order to contribute to the oxygen reduction process, i.e.

This is a normal SOFC cathode reaction.

Moreover, it can be noticed that the built-in field formed by the junction, indicated in Fig. 3 (c), on one hand, can facilitate the charge (electron and hole) separation, while on the other hand, promote ion (e.g. O²⁻) mobility, which may act as a secondary driving force to improve the ion transport, thus enhancing the device power output. This is the different underlying process for this physical–electrochemical mechanism compared to the conventional fuel cell electrochemical process. It could be called a synergistic effect in the SIFC device, in which ions may be promoted by semiconducting property with high mobility. Without using the ionic electrolyte separator, the limitation of the electrolyte ion conductivity has been removed. It is well known that the SOFC needs high operational temperature due to the poor ionic conductivity of YSZ electrolyte at lower temperatures which in turn poses a technical challenge for commercialization thus far. The SIFCs may provide a good solution and a new path to succeed in the SOFC mission.

To further analyse the interfaces between the semiconductor LSCF and ionic SCDC is vital to understand the charge distribution and separation mechanisms. Therefore, the electron microscopy and spectroscopy has been carried out by the ARM 200CF. The equipment was operated at 200 kV using a semi-convergence angle of 20.4 mrad, giving rise to a probe size of 0.8 °A (1 °A for the analytical analyses), while 90–370 mrad collection angles were used to obtain high angle annular dark field (HAADF)

images. Collection semi angles of 111.5 mrad and 57.1 mrad were used to record the EELS elemental mappings and line scans, respectively.

Figure 4 shows the low angle annular dark field (LAADF) scanning transmission electron microscopy (STEM) image of LSCF-SCDC. The position for EELS mapping are marked by the red rectangle. EELS mapping of the main elements was extracted using La-M5,4 (c), Ce-M5.4 (d), Fe-L3.2 (e), Co-L3.2 (e) and O K edge. The color map of La (red), Ce (green), Fe (dark-blue), Co (yellow) and O (blue) is superimposed in the survey image (b).

Figure 4 Image obtained by ARM 200CF and EELS mapping for elements

Fig.5 shows up close the compositional and charge distribution variations for the LSCF-SCDC interface acquired by EELS line scan in the STEM mode. Fig. 5 (a) are EELS line scan signal profiles presented in three-dimensional mode. As shown in Fig.5 (b) the STEM-EELS line scan analyses were performed across the boundaries of the particles, the green line indicates the position for line scan.. The extracted profiles of O, Fe, Co, La and Ce across the grain boundaries are presented in Fig.5 (c). It can be found

that Ce concentration decreases and Fe, La and Co concentrations increase as the line scans along the left to right direction, indicating that the left particle is SCDC and the right is LSCF. Moreover, the interface region with 11 nm width is formed between LSCF and SCDC particles, which was highlighted by two red lines. As shown by Fig.5 (c), a peak according to the presence of O was detected in the interface region, demonstrating that some O diffuses from particle interior towards the interface region. It is well known that O movement is closely correlated to oxide conduction, which is a key factor for determining the fuel cell performance. In addition, the O segregation in the interface region will block the electron across the interface due to the electrostatic position.

The Ce M5/M4 ratio is sensitive to the chemical state of Ce, therefore, the oxidation state of the Ce can be determined quantitatively from M5/M4 ratio using the positive part of second derivative of the experimental spectra. The resultant intensity ratio are shown in Fig. 5 (d), where the small ratio corresponds to the Ce^{4+} and the bigger one associated to Ce^{3+} [27, 28]. A significant difference of Ce M₅/M₄ intensity ratio can be observed between the LSCF-SCDC interface region and the SCDC particle interior. The ratio in the grain interior is higher than that of the interface region, reflecting that more Ce^{4+} has been converted to Ce^{3+} for the grain interior in comparison with the interface region; such a conversion is accompanied by the following reaction:

Where $V_o^{\cdot\cdot}$ denote oxygen vacancies. Thus, the higher oxygen vacancy concentration is attained in bulk. This may be attributed to interactions between the LSCF and SCDC which can cause such changes for the SCDC. This indicates that there is not any simple physical mixture or contact between the LSCF and SCDC. The Ce valence change indicates relevance to oxygen vacancies and electron formation, described in eq. (1) at the interface. Such a mechanism can thus enhance the O^{2-} conduction and the electron mobility simultaneously in the LSCF-SCDC heterostructure material. This study further supports the energy band between the LSCF and SCDC described in Fig.3 (b). The electrons produced at the interfaces can be driven by built-in field formed between the n-type ceria (due to produced electrons as discussed above) and p-type LSCF to realize the charge separation.

Fig 5 (a) 3D surface plot of the EELS scan signal across the LSCF-SCDC interface. (b) The STEM image of LSCF-SCDC particles and the position for line scan analysis are marked by the green lines. (c) The elemental distribution across the LSCF-SCDC interface. (d) profile of Ce M₅/M₄ ratio near the LSCF-SCDC interface.

Charge transport properties

From fundamentals of the electrochemistry the EIS can determine the materials' total conductivity for all mobile charge carriers, in our case, electrons and ions for the LSCF-SCDC; DC polarization can determine the electronic conductivity by blocking ionic sources, and the fuel cell I-V polarization curves can deduce the ionic transportation/conductivity. The results obtained from these methods are further discussed below. The EIS were measured under fuel cell operating atmosphere. As can be seen from Fig. S4 in SI, for the LSCF-SCDC device represented by red curve in Fig. S3, the interaction on Z'' axis to represent the LSCF-SCDC resistance of around 0.5 Ω corresponding to a total conductivity of the LSCF-SCDC to be 0.26 S/cm. Fig. 6 displays the D.C. polarization I-t curve, i.e. the current decreases with time in a certain period until a steady stable plateau can be reached. A polarization behavior can be observed in the initial stage of the I-t curve which can be attributed to the movement of ions, i.e. O^{2-} in the sample when the measurement starts. Since the O^{2-} ions are blocked by the Pt foil, the mobile oxygen ions would be exhausted with time and would not contribute to the current subsequently. Finally, the current reached a steady state in which the electrons were

the only source of charge carriers. In this way, the electronic conductivity was thus obtained from the stable current based on the basic calculation $R_e = V/I$. Subsequently the electronic conductivity is calculated to be 0.15 S/cm according to geometric parameters. Thus, the ionic conductivity can be estimated by subtracting the electronic one from the total conductivity 0.26 S/cm obtained from the EIS and is determined to be 0.11 S/cm at 550 °C. Though pure LSCF has excellent electronic conductivity, e.g. 215.58 S cm⁻¹ in the temperature range of 373-1023 K [3], in the LSCF-SCDC system, the electronic and ionic conductivities are comparable which are agreed with that reported before [22]. The balanced electronic and ionic conductivities are the key to make such mixed conducting semiconductor-ionic membrane fuel cell functions and also investigated by other groups, e.g. for the Ce_{0.8}Sm_{0.2}O_{2-δ}-Li_{0.15}Ni_{0.45}Zn_{0.4}(LiNiCuZn-oxide) fuel cell working principle, and the Sr₂Fe_{1.5}Mo_{0.5}O_{6-δ}-NSDC (Ce_{0.8}Sm_{0.2}O_{2-δ}-Na₂CO₃ as the electrolyte fuel cells [26, 29].

Fig. 6. DC polarization plot I-t for cell Pt (foil)/ LSCF-SCDC/Pt (foil) at 550 °C

On the other hand, the ionic conductivity of the LSCF-SCDC material used as the membrane in the SIFC device. Figure 7 displays typical I-V characteristics obtained for

the LSCF-SCDC device at 550°C. It can be seen the device can reach the max. power density of over 1000 mW/cm².

Fig. 7 Typical I-V characteristic for the LSCF-SCDC fuel cell at 550 °C

Following basic fuel cell electrochemistry, it is well explained that the linear part of the I-V characteristic as shown Fig.7, reflects the electrolyte or membrane ohmic resistance, [30-32], further described in SI, Fig. S5. Thus, we can calculate the ionic conductivity for the LSCF-SCDC used as the device membrane. In this way, we may obtain directly the ionic conductivity to compare with that obtained from EIS and DC polarization methods. Thus, we can be more certain about the charge transport properties in semiconductor-ionic materials, e.g. LSCF-SCDC studied in this work. From the I-V method the ionic conductivity was calculated to be 0.098 S/cm by considering the device geometrical parameters. This value is in a good agreement to 0.11 S/cm obtained from above EIS&DC method. The difference could be understood that different charge transport processes, e.g. in both ions and electrons are mobile in EIS, but electrons in DC polarization and ions in the fuel cell I-V method by blocking electrons passing. In summary, results obtained from above three methods exhibit a comparable conductivity between the electrons and ions, 0.15 S/cm vs 0.098-0.11S/cm at 550 °C. This agrees to a requirement of the balance electronic and ionic conducting situation reported for the electrolyte-free fuel cell. [33]

Fig. 8 displays the morphology of a cross section of the SIFC device after 50 hours of successful operation at 0.82 V under a current density of 120 mA/cm². Good adherence

and stability among the layers (NCAL and LSCF-SCDC composite) could be seen even after testing in actual fuel cell conditions.

Fig. 8. Cross-sectional image of SIFC device after 50 hours successful operation at 0.82V under current density of 120 mA/cm².

The stability for using the LSCF in hydrogen reduced atmosphere or anode environment is an issue. However, by literature review, we have found lots of works published to support the LSCF to be stable [33-35]. Anyway, the durability is a long time strategy and engineering issue to develop material and technology for applications. Even if the YSZ SOFC technology to demonstrate such a long time operation life, it has taken many years tremendous engineering efforts and huge investments. Moreover, the LSCF is one of the most commonly used electrode materials for SOFCs, it is meaningful to study this material to exploring its new technology and application from

this work. Most importantly, the fundamental understanding and science are important for following engineering efforts and technical developments.

Conclusions

The SIFCs based on novel functional SIM materials are a new type of advanced SOFCs without the electrolyte layer constraint, which has dominated SOFC history over last 100 years. The charge separation processes, from nano-particle level to the device level, is key to the scientific understanding of the SIFCs. The synergistic effect of junction and energy band alignment towards the charge separation from particle to device level, in particular blocking electron crossover, as well as the promotion of ion transport by built-in field, contribute to the working principle and facilitates high power output in the SIFC. Various methods were employed to determine the charge transportation properties for both electrons and ions, which confirmed the exhibition of comparable conductivities between them. This is reasonable given the actual LSCF-SCDC heterostructure material, where both LSCF and SCDC form the percolating phases. Thus, it can realize fuel cell functions and fuel-to-electricity conversion through different means from the conventional fuel cell, wherein the semiconductor-ionic heterostructure, charge separation and junction play key roles, and joining physics and electrochemical processes are in force. A derived benefit is accrued in the use of simplified construction and operation compared to fuel cells with anode/electrolyte/cathode configuration, thereby avoiding the major power losses caused by the electrode/electrolyte interfaces and getting rid of the electrolyte constraint. The associated benefits of this include cost-effective materials, simple technology and cheap fabrication processes, which along with deep scientific understanding, may in turn realize and accelerate fuel cell commercialization, and open up hitherto unidentified applications by using the new semiconductor-ionic functionalities and principles.

Experimental section

The $\text{La}_{0.6}\text{Sr}_{0.4}\text{Co}_{0.2}\text{Fe}_{0.8}\text{O}_{3-\delta}$ (LSCF) was purchased from Sigma Aldrich, USA, and the $\text{Ni}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}\text{Li}$ -oxide (NCAL) was purchased from Tianjin Baomo Joint Hi-Tech. venture, China. The synthesis of Sm^{3+} and Ca^{2+} co-doped ceria (SCDC) is given in supplementary information (see section S1). The nanocomposite LSCF-SCDC was

obtained by mixing nano-LSCF with SCDC materials in an optimized mass ratio of 40:60, then followed by sintering at 600 °C for 1 hour. Material and experimental details along with some characterization results are given in supplementary information.

Material characterizations were carried out as follows:

The morphology of the powder and pellets was analyzed with JSM7100F field emission scanning electron microscope (FESEM, JEOL Ltd., Japan) at 15 kV and with transmission electron microscopy (JEOL 2100F TEM, accelerating voltage 200 keV).

STEM observation and EELS analysis. Special microscopy information on grain boundaries were observed using STEM (JEM-ARM200CF, JEOL Co. Ltd) operated at 200 keV. EEL spectra were acquired in STEM mode by an Enfina spectrometer (GatanInc). The STEM-EELS characterization was performed on the ARM 200CF microscope equipped with a cold field emission electron source, a DCOR probe corrector (CEOS GmbH), a 100 mm² JEOL Centurio EDS detector, and a Gatan imaging filter (GIF) quantum ERS electron energy-loss spectrometer.

The optical properties of the samples were characterized with UV–vis–IR absorption (UV360 spectrometer, MIOSTECH PTY Ltd.). Optical band gap and valence band maximum of core materials were determined with ultraviolet photoelectron spectroscopy (UPS) measurements.

The fuel cell was constructed by using the LSCF-SCDC as the membrane which was sandwiched between two semiconducting NCAL layers pasted on the nickel foam in configuration of Ni (f)-NCAL/LSCF-SCDC/NCAL-Ni(f). The fuel cell device was fabricated by using dry-powder pressing process. The fuel cells were mounted in a stainless-steel testing holder by using silver paste for sealing. Hydrogen and ambient air were used as fuel and oxidant, respectively. The flow rates were controlled in the range of 80-120 ml min⁻¹ for H₂ and 150-180 ml min⁻¹ for air at 1 atm to the cells. To evaluate the device performance, a computerized instrument (IT8511, ITECH) was used to probe the I-V (current density-voltage) and I-P (current density-power density) characteristics.

EIS and DC polarization and fuel cell I-V characterization measurement

In order to determine the charge transport properties, electrochemical impedance spectroscopy (EIS) and DC polarization were carried out as well as fuel cell I-V characterization methods. More details about the I-V characteristic method are included

in SI. The EIS was carried out by using an electrochemical workstation (Gamry Reference 3000, USA) in fuel cell open circuit voltage (OCV) condition; the frequency ranged from 0.1 Hz to 1 MHz with an amplitude of 10 mV. In order to determine the electronic conductivity of the LSCF–SCDC composites, the Hebb-Wagner polarization method was employed in conjunction with EIS measurement. The measurements were performed with a digital micrometer (KD2531, Kangda Electrical Co., Ltd.). In this method, constant voltage of 0.2 V was applied using a potentiostat on a Pt (foil)/LSCF–SCDC/Pt (foil) cell and the current as a function of time ($I-t$) was recorded at 550 °C. The measured cell has the geometric parameters of 13 mm in diameter and 3.0 mm in thickness. The measured sample was placed in environment of an inert gas Ar.

Author Contributions

B.Z, A.Y. and R.R, J.-S. Kim conceived and designed the project, analyzed all the experiment data and wrote the main part of the manuscript. B.W. and C.X carried out experiments and measurements. Y. W. and P.A. for part of material characterizations. P.L. supervised the project and contributed to review involving also writing the paper.

Additional Information

The authors declare no competing financial interests

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Highlights

- Functionalities in heterostructure oxide material interfaces
- The LSCF-SCDC system contains both ionic and electronic conductivities
- Enhanced power density (ca. 1000 mW cm^{-2} at 550°C)
- Next generation fuel cell will be based on the new concept of semiconductor-ionic

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