Analytical TEM/STEM Characterization of Mutual Diffusions Occurred at the Electrolyte-Electrode Interfaces in the Intermediate Temperature Solid Oxide Fuel Cells

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The microstructure and local chemistry of the interfaces between electrolyte and electrode in intermediate temperature solid oxide fuel cell have been comprehensively investigated by a combination of a variety of analytical transmission electron microscopy (TEM) and scanning TEM techniques: high resolution TEM, selected area electron diffraction, energy dispersive X-ray spectroscopy, electron energy loss spectroscopy. It was demonstrated that mutual diffusions will occur at both electrolyte-anode and electrolyte-cathode interfaces. This type of diffusion would result in not only the changes of element spatial distributions and their valence states, but also microstructural evolution (i.e., superstructure formation). Moreover, the interfacial layers would be formed at the electrolyte-electrode interfaces arising from such diffusions, which is believed to be detrimental to fuel cell efficiency and should be suppressed by lowering cell fabrication temperatures.

Keywords Diffusion; Energy-dispersive X-ray Spectroscopy; Electron Energy Loss Spectroscopy; Interface; Microstructure; Solid Oxide Fuel Cell

1. Introduction
A solid oxide fuel cell (SOFC) is an electrochemical device that directly converts chemical energy into electrical energy and heat with high efficiency, quiet operation and little pollution [1,2]. Nevertheless, the high operation temperatures of traditional SOFCs, i.e., 900 – 1000 °C, usually result in complex problems, such as cell degradation, high cost of cell materials and interconnect components, reduced longevity and other technical or cost-effect problems [3,4]. In order to address such issues, it motivates the efforts to decrease the operation temperature to intermediate temperatures (500 – 700 °C), and lead to the development of intermediate temperature SOFCs (IT-SOFCs) in the past decade [2,5,6]. Two possible strategies have been put forward to decrease the operation temperatures: one is to use alternative electrolyte materials, and the other is to decrease the thickness of electrolyte to obtain lower ohmic resistance [2,7-9]. The rare-earth-doped ceria are more favourable and considered to be a better candidate for ionic conductors that can be used in IT-SOFCs, due to their better thermal stability and higher oxygen ion conductivity at intermediate temperatures [10,11]. Another efficient way is to use thin film electrolytes. Among various thin film deposition techniques, electrophoretic deposition (EPD) has been regarded as a promising way due to its low manufacturing cost, simple and fast deposition procedure, and more flexibility in substrate choice [12].

Nevertheless, one dilemma facing the IT-SOFCs development is that the sintering temperature of ceramics cell components. As for the compromise, the sintering temperature should be neither too low to synthesize a fully dense electrolyte, nor too high to lead to interactions or interdiffusions among constituent species. It can be noticed that, even though it is for IT-SOFC cell fabrication, high fabrication temperature is generally inevitable. Therefore, interdiffusion among cell components may occur during cell fabrication process, which would subsequently result in certain changes of compositions, element spatial distributions and microstructures. These changes should not be neglected when considering IT-SOFCs performance, especially when compositional and microstructural stabilities are some of the main concerns for IT-SOFCs applications [13,14]. Since the chemical compatibilities of cell materials and the interfaces between them is a prerequisite to any further cell testing or operation, it is essential to obtain fundamental understanding of the interaction or interdiffusion at the interfacial regions. In this study, the microstructure, elemental spatial distribution, interdiffusion and related evolution of valence state at both electrolyte-anode and electrolyte-cathode interfaces have been comprehensively investigated by using various techniques, including scanning electron microscopy (SEM), high resolution transmission electron microscope (HR-TEM), Energy-filtered TEM (EF-TEM) and scanning TEM (STEM). In the light of such a detailed study, fundamental knowledge on the local chemistry, element spatial distribution, microstructure evolution can be obtained accordingly, leading to the development of high quality electrolyte-electrode interfaces for IT-SOFC applications.
2. Experimental section

Different methods have been used to fabricate anode supported thin film electrolyte half-cell and the electrolyte supported cathode half-cell. Thin film electrolyte of 20 at.% Gd-doped ceria (20GDC) has been deposited onto anode substrate by EPD technique, more details about this fabrication procedure has been reported elsewhere [15,16]. The thin film \( \text{La}_{0.6}\text{Sr}_{0.4}\text{Co}_{0.8}\text{Fe}_{0.2}\text{O}_3 \) (LSCF) cathode was screen printed onto 20GDC electrolyte substrate as described in Ref. [17,18].

The morphology and microstructural features of electrolyte-electrode interfaces have been initially observed by field emission gun (FEG) SEM (Hitachi S-5000). Detailed microstructures of interfacial regions were further characterized by HR-TEM and STEM. HR-TEM observations were performed on a JEOL JEM-2000EX TEM operated at 200 kV. The chemical composition, elemental spatial distribution and valence state change of constituents were comprehensively investigated by a FEI Tecnai F20 STEM with operation voltage of 200 kV. The FEG nanoprobe STEM has a Gatan image filter which incorporates energy-dispersive X-ray spectroscopy (EDX), and electron energy loss spectroscopy (EELS) detectors. The FEG with highly coherent and strong electron beam source can provide high-resolution EDX and EELS detections from nanometer-scale regions. For STEM EDX, the FEG source was operated with a 4500 V extraction voltage, with the gun lens setting of 3 in nanoprobe mode with a spot size of 3. For high spatial resolution, EELS was also performed in STEM mode, with a reduced extraction voltage of 4200 V, gun lens setting of 6 and spot size 8. By using lower extraction voltage for EELS performance, less electrons are emitted, which will yield a finer zero loss peak as well as a better energy resolution. In order to avoid the strong elastic scattered peaks interference with EELS spectra, the observed region was tilted off-zone to minimize the strong Bragg reflections. Also, for accurate EELS analysis, the target area was detected at ultrathin crystalline areas with a relative thickness of 0.2 to 0.3 mean free path to minimize multiple scattering.

3. Results and discussion

Initial observations of electrolyte-electrode interfacial morphologies of half-cells were conducted by SEM. Fig. 1a is the cross-sectional view of the interface of thin-film GDC electrolyte supported by porous Ni-GDC anode. The well-adhered dense thin film was deposited on the porous substrate by using EPD technique. Fig. 1b shows the interface between thin film LSCF cathode and GDC electrolyte. More detailed observations of interfacial regions between electrolyte and electrode were further performed by TEM. Figs. 1c and d are low magnification TEM bright field (BF) images of interfaces of electrolyte-anode and electrolyte-cathode, respectively. HR-TEM observations have comprehensively conducted at electrolyte, anode and cathode. Interestingly, superstructures can be widely observed at electrolyte-electrode interfacial regions, while there are no superstructures at all at electrode sides.

Figure 1 SEM micrographs of cross-sectional views of (a) the interface between thin film GDC electrolyte and porous Ni-GDC anode, (b) the interface between thin film LSCF cathode and dense GDC electrolyte; the corresponding cross-sectional views of interfaces of (a) and (b) observed by TEM are shown in (c) and (d), respectively.

Fig. 2a is a typical HR-TEM micrograph of GDC grain detected at the electrolyte-anode interface. Besides the typical ceria fluorite lattice, a different microstructure feature can also be noticed, which has a periodic lattice fringe distance.
around 0.81 nm. This periodic interval is about five times of \{113\} lattice spacing of ceria, which can be verified by the corresponding optical diffractogram (Fig. 2b). As aforementioned, more investigations show that such kind of superstructures can only be observed at interfacial region, and seldom can be observed at anode or electrolyte regions far away from interface. Similarly, superstructures can also be widely observed at the interface between LSCF cathode and GDC electrolyte, as show in Fig. 2c. The interval of such long-range ordered structures is around 0.76 nm, which is about four times that of ceria \{220\} lattice spacing. This HR-TEM result can be confirmed by the corresponding diffractogram as shown in Fig. 2d. Also, it needs to emphasize that such superstructures can only be observed at the cathode-electrolyte interface. Different from the anode-electrolyte half-cell sample which has been treated by H₂ gas, the cathode-electrolyte sample has never been treated by reductive gas. Therefore, the superstructure formation at the interfacial region of cathode-electrolyte sample should not be attributed to the reduction of Ce⁴⁺ to Ce³⁺ due to H₂ gas treatment, as illustrated in previous reports [19].

**Figure 2** (a) HR-TEM micrograph of one typical GDC grain with superstructure formation observed at the anode-electrolyte interface, the corresponding diffractogram is shown in (b). (c) HR-TEM image of detailed microstructures in a GDC grain observed at the cathode-electrolyte interface, (d) is the corresponding diffractogram, indicating the superstructure formation.

EF-TEM mapping was further employed to investigate the spatial distribution of constituent elements at anode-electrolyte interfacial region. As shown in Fig. 3a, the interfacial morphology can be clearly distinguished by the EF-TEM observation. Figs. 3b and c are the enlarged area that is assigned as the dot square in Fig. 3a, representing the corresponding EF-TEM elemental maps of Ni L edge (855 eV) and Ce M edge (883 eV) respectively. Not that the grain boundaries between Ni and GDC are not sharp any more, compared to those contacting grains at the anode and electrolyte bulk area. There are considerable overlapping areas between contacted Ni and GDC grain, which implies possible interdiffusions may take place at the anode-electrolyte interfacial region.

**Figure 3** (a) The cross-sectional morphology of thin film GDC electrolyte on porous Ni-GDC anode observed by EF-TEM. The enlarged image of the dot square assigned in (a) is shown in (b) and (c), respectively, which are EF-TEM elemental maps of Ni and Ce correspondingly.

This type of two-dimensional elemental distribution has also been characterized at the interface between LSCF cathode and GDC electrolyte, while using a different technique. Fig. 4a is a STEM BF image of two edge-on grains at the cathode-electrolyte interface. The corresponding elemental compositions were qualitatively determined by STEM
EDX mapping. From the respective elemental maps of Ce, Gd, La, Sr, Co and Fe as shown from Figs. 4b to g, the GDC grain at the electrolyte and LSCF grain at the cathode can be clearly distinguished. It can be noticed that the sharp grain boundary observed in the STEM BF image (Fig. 4a) disappeared in all elemental maps, instead, there is considerable overlap and contrast gradient of element distributions at the GDC-LSCF grain boundary. This can be clearly seen from the reconstructed elemental maps shown in Fig. 4h.

Figure 4 (a) STEM BF image of two contacting grains observed at the cathode-electrolyte interface. (b) to (g) are elemental maps acquired at the same region of (a) by STEM EDX mapping. (h) is the reconstructed image combing all the elemental maps from (b) to (g).

Subsequently, quantitative analysis of elemental distributions at the electrolyte-electrode interfaces can be obtained from STEM EDX line scans. Fig. 5a is a typical STEM EDX line scan conducted exactly across the anode-electrolyte interface. It clearly demonstrates that Ni in the anode side can diffuse into GDC grains located at the electrolyte side. Moreover, note that the concentrations of rare earth elements Ce and Gd also decrease gradually across the interface and fade away in the adjacent Ni grain. This phenomenon clearly illustrates that Ce and Gd can diffuse from the electrolyte into the metallic Ni grains in the anode. This finding is quite different from previous reports, which demonstrated that the diffusion of rare earth element can be neglected at the interfacial region [19,20,21]. Therefore, all the Ni, Ce and Gd commix and mutually diffuse into contacted neighbours, with an average mutual diffusion region around 200 nm as assigned in blue in Fig. 5a. Furthermore, according to all STEM EDX line scans conducted at the electrolyte-anode interface, it reveals that all the constituent elements at the interfaces can mutually diffuse into adjacent contacted grains, with similar diffusion lengths. This implies that such type of mutual diffusion is independent of ionic radii of diffusion elements.

Analogous STEM EDX line scan analysis was also performed at the cathode-electrolyte interface, the corresponding concentration profile of elements at the interface is shown in Fig. 5b. Both LSCF and GDC grain interiors have homogenous chemical compositions. Nevertheless, at the grain boundary region, there is an overlap among different elements. This can be interpreted that constituent elements in LSCF and GDC grains were transported from one phase to the other, accompanied with similar diffusion lengths and leading to the formation of mutual diffusion zone with an average width around 200 nm.

Figure 5 Concentration profiles of STEM EDX line scans conducted across the (a) anode-electrolyte interface, and (b) cathode-electrolyte interface.

As above mentioned, due to the mutual diffusion detected at the electrolyte-electrode interface, the mutual diffusion zone will form in terms of the mixture of diffused ions. It is anticipated that the valence state of constituent elements may change at the mixed ionic environment. To verify this suspicion, it needs to examine the detailed valence state of constituent elements at the interface.
Figs. 6a to c display the EELS spectra of fine structures of Ce M_{4,5} adsorption edges acquired at the electrolyte, interface and anode, respectively. The EELS spectra acquired at the electrolyte and anode clearly demonstrate that the predominant Ce at these sides are in tetravalent state, which can be clearly verified by the satellite structures of post-edge peaks assigned by arrows in Figs. 6a and c. Moreover, the relative intensity ratio of M_{5}/M_{4} can be used for the quantification of Ce^{3+} and Ce^{4+}. Such type of fine structure has been well established as a fingerprint for the valence determination in EELS spectra analysis [22]. Interestingly, the fine structure of Ce M_{4,5} is quite different at the interface compared to that acquired at the electrolyte and anode. The relative intensity ratio of M_{5}/M_{4} significantly changed from original ~0.9 (at both electrolyte and anode) to ~1.16 (at the interface). This fine structure change of Ce M_{4,5} peaks indicates that trivalent Ce is predominant at the electrolyte-anode interface. Besides the Ce valence state change at the interface, the fine structure evolution of oxygen K-edge can also be detected at the interfacial region, as demonstrated in Figs. d to f. Similar oxygen K-edge EELS spectra can be acquired at both electrolyte and anode sides. Nevertheless, obvious fine structure evolution can be obtained in the EELS spectra of oxygen K-edge acquired at the interface. As shown in Fig. 6e, the intensity ration of I_{B}/I_{A} has significantly increase at the interface, suggesting that there is an obvious increase of the oxygen vacancy ordering at the interfacial region [22,23].

It is also worth analysing the valence state at the mutual diffusion zone formed at the cathode-electrolyte interface, the corresponding results are shown in Fig. 7. Fig. 7a compares the EELS spectra of Ce M_{4,5} peaks acquired at
electrolyte and the cathode-electrolyte interface, respectively. The clear evolution of intensity of M₄ and M₅ indicates that, at the interfacial region, trivalent Ce is predominant rather that tetravalent Ce. Similar to that observed in anode-electrolyte interface, the EELS spectrum of B peak of oxygen K-edge acquired at the cathode-electrolyte interface is significantly enhanced and is also higher than peak C. This again suggests that the oxygen vacancy ordering level is enhanced at the interfacial region.

According to the STEM EDX and EELS analyses, it allows us to evaluate the diffusion process and related evolution of microstructural features detected at the electrolyte-electrode interface. Previous reports demonstrated that dense GDC can be used as the diffusion barrier layer to inhibit the interdiffusion between electrolyte and electrode [24,25]. However, our investigation illustrates that mutual diffusions can still occur at both electrolyte-anode and electrolyte-cathode interfaces, even though dense GDC electrolytes are used in the cells. All cations in either LSCF or Ni can diffuse into contacting GDC grains, and Ce/Gd can also mutually diffuse into neighbouring LSCF or metallic Ni particles at the interfacial region. More important, such type of diffusion is independent of ionic radius of diffusing ions, resulting in the phenomenon that all ions have similar diffusion lengths. It is reasonable believed that such type of mutual diffusion is substitution diffusion between contacting materials. Also, because of the variation in the radius of substituted cations, this may act as a trigger for the valence state evolution of diffusing ions by compensation through substitution mismatch. As verified by EELS analyses, trivalent Ce is the predominant only within the mutual diffusion zone at both electrolyte-electrode interfaces.

Due to the mutual diffusion occurred at both electrolyte-electrode interfaces, the formation of a diffusion zone will subsequently appear at the interfacial region. It hence suggests that such mutual diffusion and related diffusion zone formation are the dominant factors that lead to microstructural feature changes, like the superstructure formation, at the interfacial region. As aforementioned, substitution of cations with different ionic radii can easily cause lattice mismatch. Such accumulated mismatch can be released by rearrangement of ions at the interfacial region and lead to long-range ordered structure formation. This situation may be revealed by the enhancement of oxygen vacancy ordering at the diffusion zone. Moreover, it can be anticipated that the changes in composition, as a result of elements mutual diffusion between electrolyte and electrode, may lead to changes in not only the microstructures but also the electrical properties of the materials. Take the superstructure formed at the interface for example, such type of highly ordered ion lattice may inhibit the free movement of cations or oxygen vacancies around this region and act as a blocking structure, which can lower the conductivity accordingly.

4. Conclusions

The interfaces between electrolyte (dense GDC) and electrode (LSCF cathode, Ni-GDC anode) have been comprehensively investigated in this study. The interfacial morphologies of LSCF/GDC and Ni-GDC/GDC were characterized by both SEM and TEM. STEM EDX studies demonstrate that mutual diffusion can take place at both electrolyte-anode and electrolyte-cathode interfaces. All diffusing ions have equal diffusion length, demonstrating that such type of diffusions are independent of ionic radii and can be considered as substitutional diffusions. Moreover, EELS analyses verified that the mutual diffusion would lead to a valence state change among diffusion ions. The typical phenomenon is the reduction of tetravalent Ce to trivalent one, mainly attributed to the compensation for radius variation during substitution. Enhanced oxygen vacancy ordering has also been detected at the interfacial region. It is concluded that the substitution of different ions with large radius difference and the enhanced vacancy ordering are predominant factors that lead to superstructure formation at the interfacial region. The mutual diffusion zone and superstructure formation are believed to be detrimental for ions/charge carriers transport across the electrolyte-electrode interfaces. Therefore, such mutual diffusion occurred during cell preparation should be suppressed/avoided in order to prepare high quality electrolyte-electrode interfaces.

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