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Short communication

In operando optical study of active three phase boundary of nickel-yttria stabilized zirconia solid-oxide fuel cell anode under polarization

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HIGHLIGHTS

- Patterned Ni-film anode is used to facilitate the direct observation of TPB.
- In operando observation of Ni morphological change using laser microscope.
- Ni wettability on YSZ surface can be enhanced during operation.
- Ni-film spreading and breaking phenomena compete during operation.

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ABSTRACT

Degradation of solid oxide fuel cell (SOFC) anode always takes place during long-term high temperature operation because of the decrease in three phase boundary (TPB) density and loss of nickel (Ni) network percolation due to Ni coarsening. In the present study, for the first time, an *in operando* observation technology using optical laser microscope is developed to demonstrate the real-time local morphological change of Ni at active TPB under polarization conditions. The local morphological change, which is determined by the competition between the mechanisms of enhanced Ni wettability on yttria-stabilized zirconia (YSZ) surface and thin Ni-film break up caused by Ni coarsening are observed. *In operando* observation reveals the reason of rapid performance degradation of SOFC anode under sever operation conditions. It is expected that the *in operando* observation of Ni morphological change can largely enrich our understanding of the SOFC anode microstructure change, which may further supply precious opportunities to investigate sever degradation mechanisms.

1. Introductions

Solid-oxide fuel cells (SOFCs) have emerged and attracted great interest to improve energy conversion efficiency and to reduce environmental impact. Most of the current SOFC anodes exhibit degradation in long-term operations, which is one of the challenges for the industrial applications. Rapid degradation of anode may take place during high current density operation [1]. The coarsening of nickel (Ni) in conventional Ni-yttria-stabilized zirconia (YSZ) anode has been considered as one of the main reasons for the degradation of SOFC anode because it results in decreases of both three phase boundary (TPB) density and Ni network connectivity [2–4]. SOFC performance and degradation under severe operating conditions have been studied and a critical anode-cathode (A-C) voltage was found, below which the degradation rate was significant [2,5]. It is reported that the degradation of Ni-YSZ composite anode cannot be explained only by the simple Ostwald ripening mechanism. With high overpotential, it is possible that the critical A-C voltage is related to the Ni redox potential. However, no solid evidence supports this assumption. Patterned Ni-film electrode has been applied as a promising approach which facilitates the direct observation of Ni at TPB [6–8]. Ni spreading phenomena on YSZ surface during operation has been reported at active TPB using patterned Ni-film anode [9]. It was found that Ni wettability on YSZ can be enhanced during operation. A theory of competition between the mechanisms of Ni-film spreading and the thin Ni-film break up was proposed to explain the dynamic morphological change of Ni and the corresponding anode polarization resistance variation.

At present, most of the investigations on SOFC anode microstructure change were carried out using scanning electron microscope (SEM) at room temperature. *In operando* reduction of NiO and redox of Ni have been investigated by Jeangros et al. in an environmental transmission electron microscope (ETEM) [10,11]. The limitation of the TEM is that it requires an extremely low hydrogen (H_2) pressure which is several orders of magnitude lower than that in the usual SOFC anode operation.

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Real-time thermal imaging technique has been applied across a SOFC electrode at a temperatures over 600° C [12]. However, the observation scale was limited in millimeters and the microstructure change can not be observed.

In order to observe the real-time Ni morphological change at active TPB *in operando*, we report an unique observation technology using optical laser microscope technique. With this technique, the observations on Ni morphological change in conventional SOFC operational conditions thus can be realized. Compared to conventional SEM micron-scale observation, the current optical laser microscope technique is limited to a 100 μm observation scale. For a patterned Ni-film anode, all the TPBs concentrate at Ni-film edges on YSZ substrate with an uniform microstructure. In order to facilitate the observation, a stripe-net-patterned Ni-film anode was fabricated to compensate the observation scale limitation of optical laser microscope technique. To the best knowledge of the authors, this is the first time such an *in operando* observation technique has been reported on the investigation of SOFC anode microstructure change within conventional operational conditions.

2. Experimental section

Ni-film preparation. The Ni-film anode was prepared by DC Ni sputtering method (CANON-ANELVA E−200S, 1 Pa, 300 W) on mechanically polished dense YSZ pellet (diameter 24 mm, thickness 0.5 mm, Fine Ceramics Corp., Japan). The YSZ pellet was then sandwiched by a magnetic substrate and a thin steel mask (thickness 0.1 mm) with patterned slots [9]. The sputtering was repeated with the mask rotated 90° after the first sputtering. Grid like Ni-film network was obtained to ensure the connectivity as shown in Fig. 1 (a). After pumping to a base pressure of 1×10^{-4} Pa, the deposition was carried out in argon at 1 Pa with a plasma power of 300 W at room temperature. The deposited Ni-film with a thickness of about 1 μm was then sintered in air at 1400° C for 3 h to obtain the patterned NiO-film. The specific Ni-film thickness was chosen based the conventional composite Ni-YSZ anode particle size [1]. Pt paste was printed on the counter side of the YSZ pellet as cathode. Pt mesh (50 mesh/inch, Nilaco, Japan) was used as current collector for both anode and cathode. The bottom of the cathode chamber was initially heated up to 250° C and kept for 2 h, and then heated up to 500° C and kept for 2 h to enhance the bonding of glass seal. Then, the bottom of the cathode chamber was heated to 1000° C for both reduction and operation of anode. Without direct contact with thermocouple, it was difficult to obtain the exact temperature of the anode top-surface during operation as the cell is heated only from the bottom side. The anode temperature is estimated to be about 850° C based on the color and the brightness observed through the observation window.

In operando observation. In operando observation of Ni morphological change at active TPB was carried out inside a self-designed stainless steel chamber, as shown in Fig. 1 (b). The anode and cathode gas flows were separated by a steel sub-chamber which was heated by silicon carbide (SiC) electric substrate heater. Since the reduction environment results in the performance degradation of the heater in a higher temperature environment, the experiment time was limited in 48 h to protect the heater. The temperature of the stainless steel chamber bottom was monitored through a Pt thermocouple plate as shown in Fig. 1 (b). The anode top-surface temperature was not monitored so that the current generated in operation did not influence the accuracy of the thermocouple. Glass paste was used to seal the gaps between the YSZ pellet and the steel sub-chamber as shown in Fig. 1 (a). The performance of cell was evaluated in a gas composed of 10 vol% H_2, 87 vol% N_2 and 3 vol% H_2O as a fuel and pure O_2 as an oxidant. Video images and surface profiles were captured by a high-resolution 3D laser scanning confocal microscope (VK-X1000, KEYENCE, Japan) *in operando* with A-C voltage fixed at 0.5 V as a sever operation condition. By combining conventional white light with a laser light source, laser scanning microscope is able to scan a surface and collect both an optical image and surface profile data with nanometer-level resolution on any material or shape by analyzing the intensity of the returned laser light relative to the z-position of the laser. The real-time images of Ni morphological change *in operando* thus can be captured subsequently with a time interval of 480 s. Since the Ni-film thickness is out of the accurate measurement range of the 3D laser scanning microscope, qualitative Ni height profiles were measured as shown in Fig. 1 (f)-(h).

3. Results and discussions

Fig. 1 (c)-(e) show the *in operando* top-view images and the corresponding 3D surface profiles of a specific anode area before reduction, after reduction and after a 48 h operation. The anode gas was 10 vol% H_2, 87 vol% N_2 and 3 vol% H_2O. It is seen that the morphology of Ni-film after reduction showed no large difference compared to the NiO-film, except for the change in grain size from larger NiO to smaller Ni. The TPB kept the original length after reduction. After applying an A-C voltage of 0.5 V, a Ni spreading phenomenon is observed moving from the original TPB position toward the center of the open square surface of YSZ. A transient structural change from dense Ni-film near the original TPB position to isolated Ni droplets at the spreading front can be observed. Fig. 2 (a) shows the corresponding change of current density during 48 h operation. It is seen that the current density showed a relatively large degradation rate in the initial 2.5 h. Then the anode performance was enhanced from 2.5 to 5 h and degraded again with a relatively moderate rate until 15 h. Finally, the anode performance entered a stable stage until the end of the operation. Oscillation of current density is observed throughout the operation.

Jiao et al. [9] reported the Ni spreading phenomenon based on the *ex situ* SEM observation. In order to study the dynamic process of the complicated Ni spreading in details, the *in operando* top-view video observation using high-resolution 3D laser scanning confocal microscope was conducted. The top-views and corresponding 3D surface profiles shown in color at different times are shown in Fig. 2 (b)-(h). (See supplemental video for details. Note that the video has been accelerated to show 48 h operation). In the initial 2.5 h, dense Ni-film spread continuously along the YSZ surface starting from the original TPB edge. From 2.5 h, the Ni front broke into isolate Ni droplets. The breaking up occurred in a very short time less than 8 min. After the breaking up, the motion of isolated Ni droplets stopped and changed into sphere shape by sintering mechanism. Another Ni spreading starting from the Ni phase percolated to the main Ni network merged with the isolated droplets formed previously. The cycle of spreading-breaking up repeated continuously. In each cycle, the Ni spreading process took much longer time than the breaking up of the Ni-film. During the cycle, spreading of Ni covered the open YSZ surface between the isolated Ni droplets. With this repeated cycle, the Ni phase moved towards the center of the square YSZ surface with an average speed of about 2.4 $\mu m h^{-1}$ during the initial stage of operation. Most of the break up of Ni-film took place before the spreading Ni covered all of the isolated Ni droplets. The Ni spreading speed after the initial 5 h to the end of the operation was obviously slowed down with an average speed of about 0.4 $\mu m h^{-1}$. It was observed that after every breaking up of the Ni-film, newly formed Ni droplets kept immobile until they merged with the next Ni spreading. A percolated Ni net-work from the dense Ni-film to the isolated Ni droplets dynamically changed in time and space.

Supplementary video related to this article can be found at http://dx.doi.org/10.1016/j.jpowsour.2018.06.001

It is known that the local humidity at active TPB under polarization can be much higher than that in the bulk gas phase, especially at high current density conditions [14]. The adsorbed oxygen concentration on Ni surface close to active TPB can differ from the thermodynamic equilibrium by up to 2 orders of magnitude [13]. Jiao et al. [9] investigated the effects of oxygen adsorption on Ni surface tension using Belton's equation. It was predicted that the equilibrium contact angle of