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ORIGINAL PAPER

Effect of pretreatments on the anode structure of solid oxide fuel cells

Guo-Bin Jung · Kai-Fan Lo · Shih-Hung Chan

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Abstract An important objective in the development of solid oxide fuel cell (SOFC) is to produce thin stabilized zirconia electrolytes that are supported upon the nickel–zirconia composite anode. Although this will reduce some of the problems associated with SOFCs by permitting lower temperature operation, this design may encounter problems during start- up. The first step in a start-up involves the reduction of nickel oxide in the anode to metallic nickel and increase of three-phase boundary will be beneficial for further reaction. In this study, two pretreatment methods are investigated for their effects on the performances of SOFC. Performances of the SOFCs are influenced by the pretreatment conditions, which included exposure of the cells to dilute H_2/O_2 either under open-circuit or closed-circuit conditions before their performance studies. By carrying out the methods, the pretreatment using the closed circuit is found to attain much higher performances effectively and efficiently. Accompanying with SEM and element analysis, increase of three-phase boundary is considered to give rise to changes in the anode microstructure, leading to activation of the anode. Mechanisms of NiO in anode reducing to Ni and porous structure via different pretreatments and their effects on the anode microstructure are proposed.

Keywords Pretreatment · Anode-supported · Triple-phase boundary (TPB) · Solid oxide fuel cell (SOFC) · Proton exchange membrane fuel cell (PEMFC) · Direct methanol fuel cell (DMFC) · Oxygen vacancy

G.-B. Jung (✉) · K.-F. Lo · S.-H. Chan
Department of Mechanical Engineering and Fuel Cell Center,
Yuan Ze University,
135 Far East Road, NeiLi,
TaoYuan 320, Taiwan
e-mail: guobin@saturn.yzu.edu.tw

Introduction

Because of their potential to reduce the environmental impact and geopolitical consequences of the use of fossil fuels, fuel cells have emerged as tantalizing alternatives to combustion engines. Like a combustion engine, a fuel cell uses some sort of chemical fuel as its energy source, but, like a battery, the chemical energy is directly converted to electrical energy, without an often messy and relatively inefficient combustion step. In addition to high efficiency and low emissions, fuel cells are attractive for their modular and distributed nature and zero-noise pollution. They will also play an essential role in any future hydrogen fuel economy. Among all the popular fuel cells developed internationally, solid oxide fuel cell (SOFC) provide high-energy-conversion efficiency due to direct conversion of fuels into electric power at high temperature in a cogeneration system compared to that of proton exchange membrane fuel cells (PEMFC) and direct methanol fuel cells (DMFC).

Conventional SOFC with an YSZ electrolyte are now being operated at 900 °C or higher temperature to attain power density sufficient to use in the system. However, the high-temperature operation causes serious problems such as internal mechanical stress due to the difference in the thermal expansion coefficients of the materials and chemical reactions. Therefore, operating temperature lower than 700 °C is desirable. As chemical and conduction processes in SOFC are strongly thermally activated, a reduced operating temperature leads to another difficulty in large voltage losses due to the ohmic resistance of the materials and the polarization at the electrodes. Most of the voltage losses are generated from the ohmic resistance of the electrolyte. A number of approaches have been reported preparing a thinner electrolyte that reduces the corresponding resistance [1, 2], and high power density was obtained using YSZ thin film electrolytes [3, 4].

There are generally two categories making a robust three-layer membrane while maintaining thin electrolyte layer: cathode supported cell [5] and anode supported cell [6]. Although cathode-supported cell can be produced by ceramic process (Toho) and by atmospheric plasma spraying (Siemens-Westinghouse) with scalable processes, most studies focus on anode-supported cell structure because thicker anode can be designed with good TCE match to the electrolyte, and it has excellent conductivity. In addition, an anode-supporting structure presents advantages in terms of cost, conductivity, and mechanical strength. Moreover, the anode support allows for film deposition of the electrolyte by easily scalable and automated (high temperature) ceramic processes, as opposed to expensive and production limiting vapor deposition techniques (PVD, EVD) of thin YSZ used at necessarily lower temperature for cathode supports. Although anode-supported cell possesses advantages compared to that of cathode- and electrolyte-supported cell, some disadvantages exist, which include high NiO content, lack of redox stability, low mechanical stability needed to be overcome for ultimately commercialization.

When a fuel cell is tested, it usually takes some time to reach a steady state, at which the cell yields its best performance. Therefore, a pretreatment or break-in period is needed to reach the full performance of the fuel cell. There are several reports on this matter, and the pretreatment methods generally depend on the type of fuel cell (such as PEMFC, DMFC, SOFC) and perhaps the developer's preference. For example, Plug Power has developed a method for enhancing cell performance by steaming or boiling the electrode for PEMFC performance improvement [7]. Kho et al. [8] have found that conditioning of the cell in methanol results in a substantial increase in the performance of a DMFC.

Although anode-supported cell presents more benefits than cathode- and electrolyte-supported cells as shown previously, thicker anode structure might be obstructive for high power output due to longer transport path or less three-phase boundary (TPB) for all species, including oxygen ion, electron, and H_2 fuel. Therefore, anode pretreatment will be more critical for anode-supported SOFC because anode is ten times thicker than that of PEMFC and DMFC. Traditionally, H_2 is usually guided into anode section for NiO reduction to Ni under open circuit as pretreatment or break-in [9–11]. However, we found that the effect is less pronounced and limited especially under low-temperature circumstances. Different pretreatment processes of the anode might lead to dissimilar anode structure and result in performance difference as has been found in low-temperature fuel cell.

The aim of this study was to obtain more information about the contribution of anode pretreatment to the electrochemical performance of anode-supported SOFC currently manufactured as standard cells of Leatech in Taiwan. Two pretreatment procedures were executed in relation to application of a constant current or not. The reaction mechanisms of anode resulted from different pretreatment processes are proposed to understand how the pretreatments lead to variation of anode microstructure.

Experimental

Cell fabrication

YSZ and NiO powders were used to prepare porous anode substrates. A mixture containing approximately 51 mass% NiO powder, 34 mass% commercial YSZ (Y0.1ZrO2) powder, and 15 mass% pore former (poly-methyl-metha-acrylate) was ball-milled in EtOH solvent. After drying, the mixture was uniaxially pressed into squares of 30 mm in length, then calcined at 900 °C for 2 h in air. Green film of the YSZ electrolyte was prepared onto the anode substrates from electrolyte slurry by a dip-coating method. The electrolyte film and anode substrate were co-fired at 1,400 °C for 2–5 h in air with a controlled heating rate of 3 °C /min. The electrolyte slurry was prepared by ball-milling YSZ powder with isopropanol and oil. After that, (La, Sr)MnO3 (LSM) powder, which was selected as a cathode material, was printed onto the YSZ electrolyte pellets, and they were fired at 1,200 °C. Figure 1 shows a photograph of the anode-supported SOFC in this study.

Anode pretreatment and cell testing

Electrochemical measurements of the single cells were performed in a stainless steel test fixture placed inside the furnace. To obtain sufficient electronic contact between the cell and the electronic devices, Au meshes were used on both sides of the anode and the cathode. Sealing of the gas compartment was performed by a YSZ fiber doped with YSZ powder (Z-Car, USA). At the beginning of the tests, an argon flow was introduced at the anode side and an air flow at the cathode side. The temperature was then slowly increased to the desired temperature for anode pretreatment (Fig. 2). After reaching this temperature, the anode of the single cells was reduced by a stepwise replacement of argon by 10 vol% hydrogen.

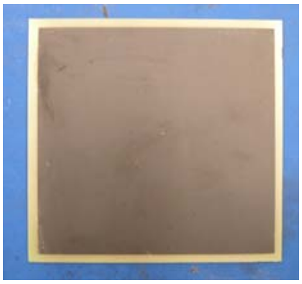


Fig. 1 Photograph of anode supported cell (as-prepared)

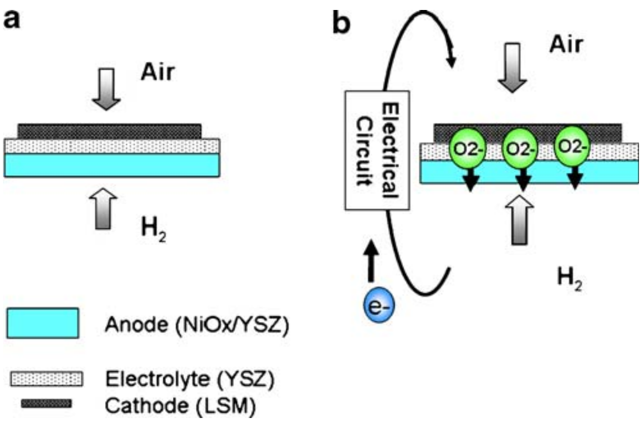


Fig. 2 Anode pretreatment via **a** open circuit, **b** closed circuit proposed by this study

The total gas flows of hydrogen and air were both set at 150 ml/min (standard temperature and pressure [STP]) using mass flow controllers. Before cell testing, two methods were utilized for anode pretreatment. Figure 2a shows anode pretreatment via open circuit and Fig. 2b shows anode pretreatment via closed circuit with constant current (50 mA). The biggest difference of these two pretreatments was to let the oxygen ion move freely within anode structure via closed circuit. All electrochemical data obtained during the pretreatments were by DC methods using a current-controlled power supply and a computer-controlled data acquisition system. The current–voltage characteristics were measured with increasing current load by a sequential step change of 0.05 V starting from 1.0 V until the voltage dropped below 0.2 V.

Microstructural characterization

The morphology of the surfaces of the composite membranes was studied by means of a scanning electron microscope (SEM, model JSM-5600, Jeol, Japan) equipped with EDS. The sample surface was coated with gold powder under vacuum.

Results and discussion

Effect of pretreatments

The SOFCs that run at high temperature do not yield any performances immediately upon start-up and they need pretreatment to attain stable and high performances. In our experiments, the anode structures were at an almost completely oxide state when they were fabricated. Therefore, we first tested the effect of pretreatment by placing an anode-supported cell in dilute H_2 at 500 °C for 12 h and measuring its performance for every 2 h. Figure 3 compares the changes in performance during continuous pretreatment via open circuit. *I–V* curves of the cell were measured repeatedly under air and dilute H_2 circulating conditions at 500 °C as described in the experimental section. It took about 5 min to get every data point because the *I–V* curves were collected at each run.

As shown in Fig. 3, performance of the initially treated anode-supported cell was very poor. After it was pretreated for 4 h under open-circuit condition, its performance increased steadily from 14 to 16 mA/cm^2 at 0.4 V. Although the cell performance increased gently after further pretreatment for 8 and 12 h, the improvements are less pronounced and limited. The performance increased by about 21% through the pretreatment via open-circuit condition with overall 12 h. The improvement in performance by pretreatment with open-circuit condition is ascribed to changes in the anode structure caused by reduction of NiO to Ni under chemical reduction environment [7].

With this transition, the dense NiO/YSZ anode layer changes to less dense one. The pores appeared in the

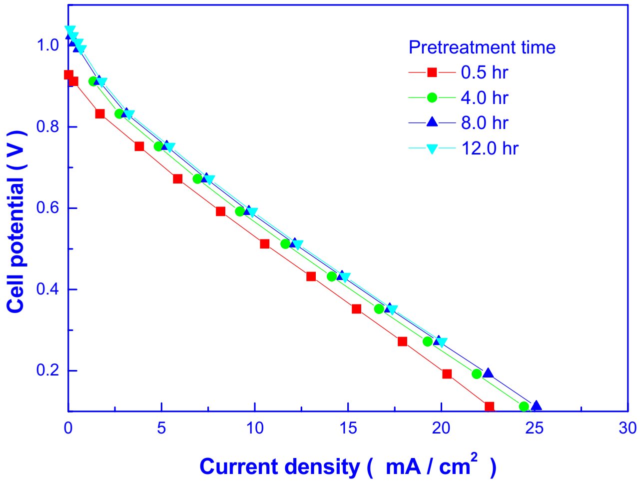


Fig. 3 Performance variation of SOFC during pretreatment via open circuit

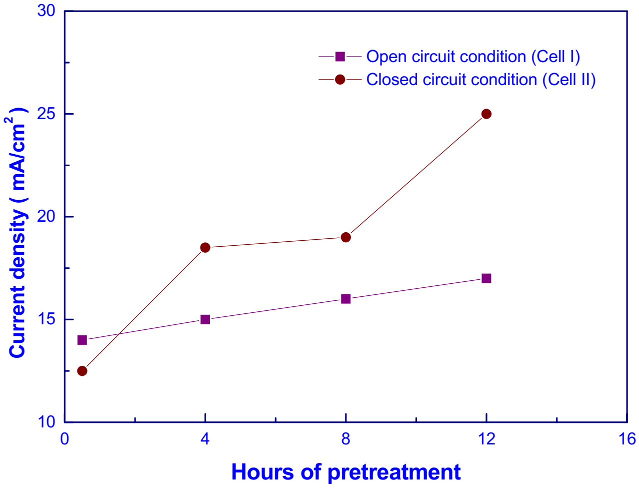


Fig. 4 Effect of pretreatment time on the performance of SOFC

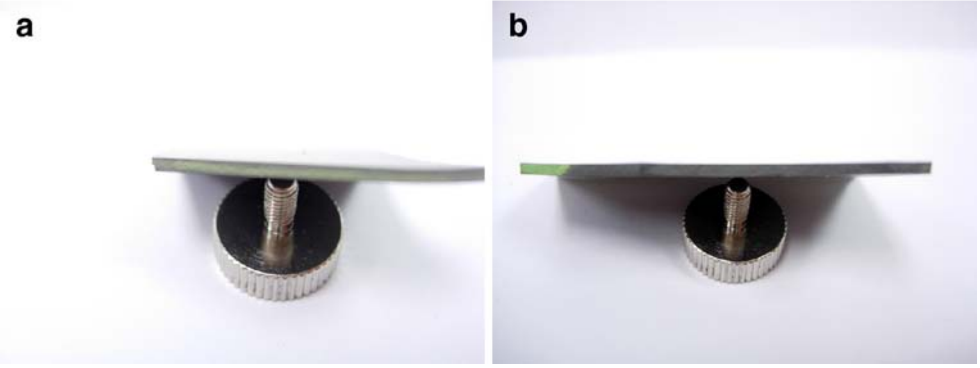


Fig. 5 Photographs of anode (lateral view) after pretreatment via **a** open circuit, **b** closed circuit

neighborhood of Ni particles, which can promote the diffusion of fuel gas. In addition, the increase of cell voltage from 0.9 to 1.05 V under open circuit in the beginning of the pretreatment, meaning Ni particles are put into function once reduced from NiO. In addition, the polarization is believed to be reduced by increasing triple phase boundary (TPB) at which an electrochemical reaction occurs. Gradually, the anode inner-layer morphology, including the TPB lengths, determine the cell performance.

In addition to force, the air and dilute H_2 through cathode and anode side, the connection between two platinum wires (connecting cathode and anode) is established with a constant resistance, making oxygen ion transportation freely and NiO reduction electrochemically. The external resistance between anode and cathode was chosen so that the current was maintained at 50 mA for the entire pretreatment. As shown in Fig. 3, performance of cell II at initial stage was very poor. After it was pretreated for 4 h under closed-circuit condition, its performance increased sharply from 12.5 to 18.5 mA/cm^2 at 0.4 V. With overall 12 h pretreatment under closed-circuit condition, the cell performance increased to 25 mA/cm^2, almost 100% performance increase through pretreatment via closed-circuit condition (Fig. 4).

Although both methods are positive to increase cell performance, pretreatment via closed circuit demonstrates higher potential to activate the cell effectively and efficiently. The possible reason that the pretreatment via closed circuit is more effective than that via open circuit indicates that changes in the anode structure and its morphology might be the most important factor. The structural changes may include changes in NiO to Ni, porosity (pore distribution), and connectivity between electrolyte and catalyst particles. The initial performance difference of the two cells is caused by slight variation of the original cell material. The anode-supported cells after pretreatment were removed out of the test fixture for further comparison as shown in Fig. 5. The color of anode via open circuit did not present much difference. However, the one via closed circuit changed greatly and uniformly from green to gray, meaning a more efficient method than that of open circuit.

Microstructure and element analysis

To further investigate the effects of the pretreatment, the anode structures were further compared via microstructure and element analysis. Figure 6 shows an SEM micrograph

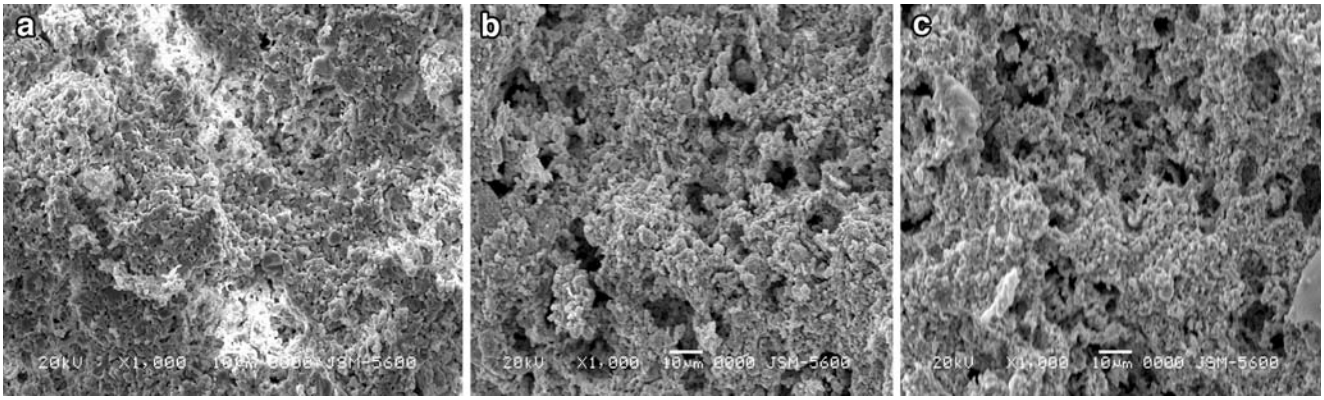


Fig. 6 SEM micrographs of anode as prepared (**a**), pretreatment via open circuit (**b**), pretreatment via close circuit (**c**)

Table 1 Element analysis of anode sub-layer

Methods	O/Ni+Zr (L1, surface layer)	O/Ni+Zr (L2)	O/Ni+Zr (L3)	O/Ni+Zr (L4)
As prepared	1.85	–	–	–
Open circuit	1.66	1.76	1.80	1.79
Closed circuit	1.43	1.6	1.62	1.67

of surface of a typical cell before and after testing. Note that the anode is essentially fully dense before pretreatment (as prepared), as evidenced by the existence of only a few isolated pores as shown in Fig. 6a. After the sample is reduced in dilute H2 at 500 °C as shown in Fig. 6b, the micrograph shows lots of pores were generated, which were the free spaces left when NiO reduced to Ni. Moreover, we found that these pores generated via open circuit are surfaced and concentrated. However, the pores were generated more uniform and interior (deeper) as shown in Fig. 6c.

The uniform and discrete distribution of the porous sections inside the anode structure demonstrates that pretreatment via closed circuit is an effective method for reducing NiO/YSZ electrodes of solid oxide fuel cells. To further investigate the effects of pretreatment on anode, the element distribution of anode was studied. Table 1 shows the atomic ratio variations in anode region before and after pretreatment. As shown in Table 1, element analysis indicated significant O enrichment at the anode surface (L1) associated with the sample as prepared. The percentage loss on O was minor with pretreatment via open circuit, as evidenced by decrease from 1.85 to 1.66 relative to the metal (Ni+Zr) atom.

For the pretreatment via closed circuit, however, the O/Ni+Zr ratio decreased apparently to 1.43 with the same pretreatment time. To further examine the effect of pretreatment on anode structure with different depth, the anode structure was polished to three sublayers (L2–L4) as shown in Fig. 7. The element analysis of each layer was investigated and calculated as shown in Table 1. In addition to original anode surface layer (L1), each sublayer also presents a decrease in O/Ni+Zr ratio after pretreatment. In the case of pretreatment via open circuit, the percentage loss of O increase from L1 to L4 after a sudden decrease of L1 after pretreatment. Variations of percentage loss of O

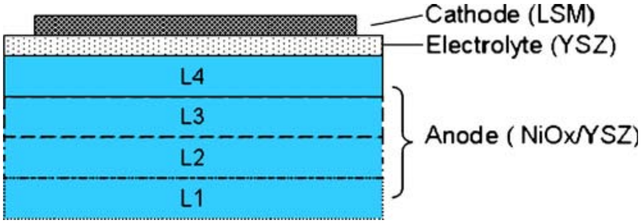
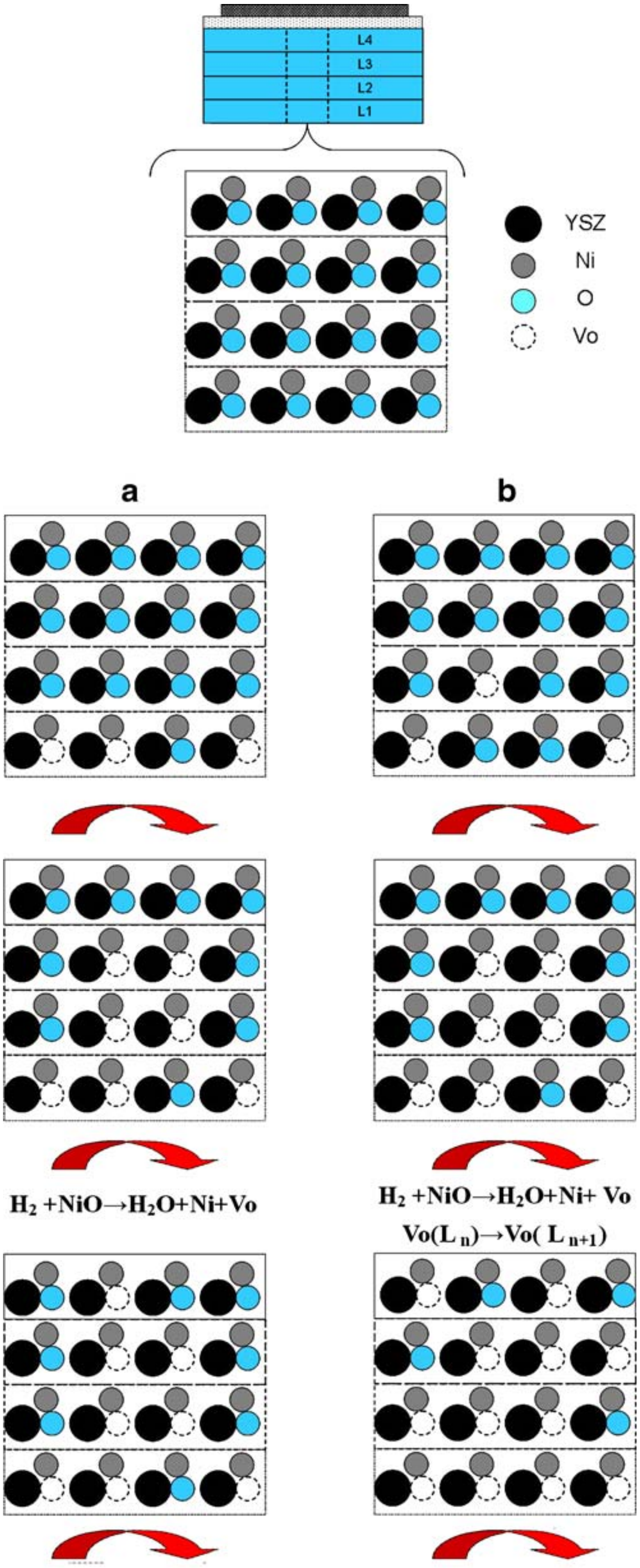


Fig. 7 Schematic diagram of anode sublayer



$H_2 + NiO \rightarrow H_2O + Ni + Vo$

$H_2 + NiO \rightarrow H_2O + Ni + Vo$

$Vo(L_n) \rightarrow Vo(L_{n+1})$

Fig. 8 Proposed mechanisms of anode structure with pretreatment via **a** open circuit, **b** closed circuit with anode depth imply the difficulties of NiO reduction increase with depth. The trend of percentage loss of O presents similarly for pretreatment via closed circuit. However, pretreatment via closed circuit appears to be more efficient of oxygen removal or reduction of NiO for each sublayer.

From the SEM and EDX measurements, pretreatments on anode have shown Ni, YSZ, and porosity form contiguous, three-dimensional interpenetrating networks, and there is a certain amount of Ni–YSZ–pore three-phase boundary (TPB) present. The existence of TPB is critical, as these are the physical locations where the electrochemical reaction of hydrogen oxidation occurs. Pretreatment via closed circuit presents a more prominent effect on the generation of TPB. Similar interpenetrating networks exist between LSM–YSZ–pores with TPB in the cathode interlayer, where the electrochemical reaction of oxygen reduction occurs. Recent work has shown a profound effect of TPB length in composite cathodes on cell performance [12].

Mechanisms of anode reduction

According to this study, the changes of the anode structure during pretreatment may be explained stepwise as shown in Fig. 8. For dilute H_2 pretreatment under open-circuit condition, NiO particles in the anode surface tend to reduce to Ni easily with the production of porosities (or oxygen vacancy, Vo) in the beginning as shown in Fig. 8a. However, the reduction becomes slower because H_2 penetration through the dense NiO/YSZ meet higher difficulties. Therefore, only NiO exist in the few sublayers close to the anode surface is capable of reducing to Ni and comes up with limited triple-phase boundary in the anode structure. However, with the help of closed circuit, oxygen vacancies are transported from anode to cathode (opposite to that of oxygen ions, O^{2-}) within the anode structure freely.

Therefore, reduced Ni on the surface may be further transferred to NiO ($Ni + O^{2-} \rightarrow NiO + 2e^-$), while the NiO in the deeper interlayer may reduce to Ni ($NiO \rightarrow Ni + Vo + 2e^-$). In other words, the oxygen vacancies moves from surface layer (L_n) to inner layer (L_{n+1}) as shown in Fig. 8b and c.Therefore, a broader porosity is generated within the anode resulting in an increase in the triple-phase boundary length in the structure and an enhancement in the diffusivity of fuel gas and electrode conductivity. These multiple-positive reasons resulted in an enhancement of the cell performance.

Conclusions

At this point of the study, performances are not optimized and low power densities are available, due to dilute H_2 used and lower operation temperature in this study. However, the results confirm the feasibility of SOFC being activated via different pretreatment methods. The fact that pretreatment via closed circuit was more effective than that of traditional open-circuit condition indicates that gradually deeper changes accompanying with both chemical reaction and electrochemical transfer in anodes resulted in an increase in the triple-phase boundary length in the structure and an enhancement in the diffusivity of fuel gas and electrode conductivity, resulting in an enhancement in the performance of the anode.

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