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Nickel-based anode with microstructured molybdenum dioxide internal reformer for liquid hydrocarbon-fueled solid oxide fuel cells

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ABSTRACT

The present paper describes the fabrication of a bilayer structured solid oxide fuel cell (SOFC). Its anode consists of molybdenum dioxide (MoO_2)-based internal micro-reformer in the form of a porous thin film deposited over conventional Ni/YSZ cermet. Cell performance was measured by directly feeding a mixture of *n*-dodecane and air at different O_2/C ratios to the anode at 750 °C. Our findings show that the bilayer structured SOFC operating at an O_2/C ratio of 0.64 led to the highest initial cell performance with an initial maximum power density >4.0 W cm^{-2}. At a constant voltage of 0.7 V and O_2/C ratio of 0.64, the bilayer structured SOFC showed a gradual increase in power density output over the first 2 h, followed by a stable output of 3.6 W cm^{-2} for the next 10 h. The tested cell showed no indication of coking and phase transformation. When a conventional Ni-based SOFC without the internal micro-reformer was operated under similar conditions, its initial performance and long-term stability were found to be significantly lower than that of bilayer structured SOFC due to Ni oxidation under high O_2/C ratio or coking under the low O_2/C ratio. These results open up new opportunities for efficiently generating electrical power from various types of high energy density liquid fuels using SOFCs with an integrated MoO_2 micro- reformer.

1. Introduction

Solid oxide fuel cells (SOFCs) are a promising technology because they can efficiently and directly convert the chemical energy of fuels into electrical energy [1–3]. Due to the high operating temperatures (typically 600–1000 °C), SOFCs hold particular promise because of their ability to use a variety of complex liquid fuels, such as conventional liquid transportation fuels (e.g., gasoline, diesel-like fuels and jet fuels) and next generation liquid bio-fuels (e.g., biodiesel), either by using external reforming systems or directly feeding these fuels into their inexpensive transition metal-based anodes [4,5].

Nickel (Ni)-based anodes are commonly used in SOFCs owing to their low cost, good chemical stability, and excellent catalytic activity toward hydrogen oxidation and reforming of small hydrocarbon molecules. However, Ni-based anodes are well known for promoting severe surface carbon deposition. Excessive formation of carbon deposits on the anode leads to a rapid deterioration of the cell performance by physically blocking access of the reactants to the active catalyst sites [6–11]. To operate Ni-based SOFCs by directly feeding liquid hydrocarbon fuels, a thin catalytic layer can be deposited over the Ni-based anode to act as an internal micro-reformer. In previous work conducted by Zhan and Barnett, a ruthenium oxide-based internal micro-reformer was used to directly operate a SOFC with complex liquid fuels at the O_2/C ratios ranging from 0.66 to 0.88 [12]. However, ruthenium oxide is expensive and its use would significantly increase the overall cost of SOFCs. Thus, an alternative and inexpensive catalytic material with high reforming activity and good stability toward complex liquid fuels is required to fabricate the internal micro-reformer over a Ni-based anode.

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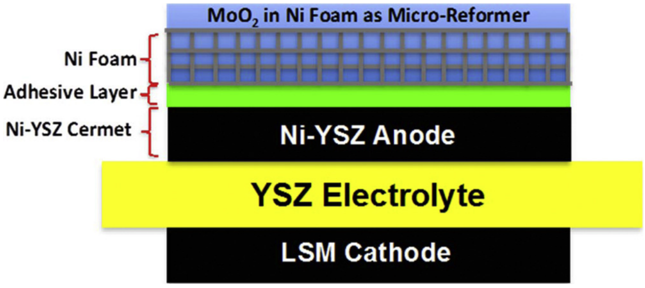

Fig. 1. Schematic of Ni-based SOFC with an internal MoO_2 micro-reformer layer.

In previous work, we successfully synthesized nanoparticle molybdenum dioxide (MoO_2) that displays not only high reforming activity for various liquid hydrocarbons but also excellent coking tolerance [13,14]. The catalytic activity has been explained in terms of a reaction mechanism similar to that proposed by Mars and van Krevelen [13]. The capability of MoO_2 to selectively transfer lattice oxygen to hydrocarbon molecules is believed to reduce the amount of carbon accumulated on the catalyst surface, thus minimizing coke formation during the reformation of logistics fuels [13,15,16]. In addition, MoO_2 possesses a significant metallic component to its interatomic bonding and displays metallic-like electronic conductivity comparable to that of highly conductive oxides such as ReO_3, as a result of a relatively high density of states in the valence band [17–19].

In the present paper, we describe the fabrication and performance of MoO_2-based internal micro-reformer, which consists of a porous thin film deposited over the conventional Ni-based anode. The results of operating the cell with *n*-dodecane are compared with a conventional Ni-based SOFC without internal micro-reformer. The tested cells are characterized using various analytical techniques including scanning electron microscopy (SEM) with energy dispersive X-ray analysis (EDX), X-ray diffraction (XRD), and X-ray photoelectron spectroscopy (XPS).

2. Experimental

The anode of our bilayer structured SOFC consisted of three major components: the Ni-YSZ cermet, an adhesive layer, and the MoO_2-covered Ni foam, as shown in Fig. 1. The Ni foam with a thickness of 0.72 mm was mechanically cut into a $1 \times 1\ cm^2$ square shape. A slurry was prepared to serve as an adhesive layer, which allows one to physically attach the Ni foam over the Ni-YSZ cermet. The composition of the slurry was 3 wt.% binder (Butvar B-98; Sigma–Aldrich, St. Louis, MO), 5 wt.% dispersant (polyvinylpyrrolidone; Sigma–Aldrich, St. Louis, MO), 3 wt.% pore former (polyvinyl alcohol; Sigma–Aldrich, St. Louis, MO), 50 wt.% solvent (isopropyl alcohol; Sigma–Aldrich, St. Louis, MO), and appropriate amounts of NiO and YSZ powders. All the components were physically mixed to form the adhesive slurry. A commercial half-cell consisting of a Ni-YSZ cermet (anode) and YSZ electrolyte (Fuel Cell Materials, Lewis Center, OH) was used to fabricate the bilayer structure SOFC. The thicknesses of the YSZ electrolyte and the Ni-based anode for the commercial half-cell were 150 μm and 50 μm, respectively. The electrode diameter was 12.5 mm, while that of the electrolyte was 25 mm.

The adhesive slurry and Ni-foam were applied to the Ni-YSZ cermet of the half-cell and calcined at 900 °C for 2 h in static air to burn out the organic compounds. Subsequently, the calcined body was sintered at 1400 °C for 10 h to achieve good adhesion between the different layers [20]. Without the Ni foam, the MoO_2 in the micro-reformer layer oxidizes to the inactive MoO_3 phase by reacting with lattice oxygen from the YSZ electrolyte during the cell operation. Since the Ni foam cannot conduct oxygen ions, it acts as a protective layer to prevent the MoO_2 reforming layer from oxidizing. Sr-doped $LaMnO_3$ (LSM) (Fuel Cell Materials, Lewis Center, OH) and an organic binder (V-006A; Heraeus, W. Conshohocken, PA) were mixed in a ratio of 60:40 (by weight) to prepare a slurry, which was painted as the cathode on the YSZ electrolyte surface of the half-cell followed by drying at 120 °C. The cathode was further sintered at 1100 °C for 2 h in air. Before preparing the internal MoO_2 micro-reformer, the Ni-based anode was completely reduced in flowing H_2 at 850 °C for 7 h.

Once the Ni foam was incorporated into the button cell, a nanoparticle MoO_2 catalyst ink was electrosprayed over the Ni foam [21]. To obtain the MoO_2 thin film with the necessary pore structure and morphology, the deposition parameters were kept at the following values: substrate temperature at 300 °C; flow rate of suspension at $2\ mL\ h^{-1}$; nozzle-to- substrate distance of 6 cm; applied voltage at 10 kV; deposition time for 1 h. During electrospraying, the MoO_2 nanoparticles filled and eventually covered the Ni foam. Subsequently, an additional layer of MoO_2 catalyst ink was painted on the surface of the MoO_2-filled Ni foam. This catalyst ink was prepared by mixing commercial MoO_2 particles (Alfa Aesar, Ward Hill, MA) with a solution of nanopure water and polyvinyl alcohol [22].

The cell testing system used in this work consisted of two concentric quartz tubes with two furnaces. The fuel mixture was introduced through the inner tube, while the outer tube served as an exhaust line. The lower furnace was used to vaporize the fuel at 350 °C, whereas the upper furnace was used to heat the cell to 750 °C. Air was used as the oxygen source for the cathode and was allowed to flow through the insulation on the upper furnace into the cathode via natural convection. The fuel mixture that was directly fed to the anode consisted of mixtures of *n*-dodecane and air at oxygen- to-carbon molar ratios (O_2/C) of 0.60, 0.64, and 0.70. The flow rate of *n*-dodecane was maintained at $0.3\ mL\ h^{-1}$. Based on our previous works, the range of O_2/C ratios used for this study was determined to prevent an undesired phase transformation of MoO_2 into either Mo_2C or MoO_3 [13–16]. If the O_2/C ratio is lower than this range at 750 °C, MoO_2 would reduce to Mo_2C and eventually lead to the severe carbon deposition. On the other hand, if the O_2/C ratio is higher than this range at 750 °C, MoO_2 would oxidize to inactive MoO_3. After operating Ni-based SOFCs with and without the MoO_2 internal micro-reformer, the tested anode layers were analyzed to determine the degree of coke formation using SEM (FEI Sirion operated at 15 kV) with EDX, XRD (Philips diffractometer using Co Kα radiation with an Fe filter), and XPS (AXIS-165 using achromatic MgKα (1254 eV) X-ray radiation with a power of 210 W). For these measurements, we used a blade to carefully remove the tested anode layers from the electrolyte surface. For the bilayer structured SOFC operating at the O_2/C ratio of 0.64, we could separate the MoO_2-based internal micro-reformer layer from the Ni-based electrode layer. Thus, we crushed each layer into the power form without mixing them up for the measurements.

3. Results and discussion

Fig. 2 shows initial cell voltage and power density as a function of the current density for the bilayer structured SOFCs operated at 750 °C using O_2/C ratios of 0.60, 0.64, and 0.70. According to Fig. 2, the initial OCV of the bilayer structured SOFC decreases from 1.065 to 0.944 V as the O_2/C ratio increases from 0.60 to 0.70. As the mixture of *n*-dodecane and air is directly fed into the bilayer structured anode, syngas is being produced through the partial oxidation process. However, as the O_2/C ratio increases, full oxidation of the fuel becomes dominant and the amount of syngas decreases. As the reforming gas stream with a lower concentration of syngas (i.e.,