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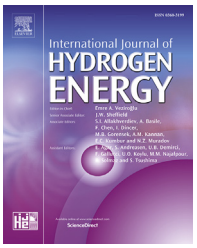

Coking-resistant NbO_x-Ni-$Ce_{0.8}Sm_{0.2}O_{1.9}$ anode material for methanol-fueled solid oxide fuel cells

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ABSTRACT

NbO_x is added in Ni-$Ce_{0.8}Sm_{0.2}O_{1.9}$ by impregnation as an anode material for solid oxide fuel cells fed with methanol. Nb (IV) and Nb (V) exist in the reduced anode. The addition of Nb reduces the binding energy of Ni. The catalytic activity of the anode and the performance of the single cell both increase with the increase of Nb. At 700 °C, the cell with 5NbO_x-Ni-$Ce_{0.8}Sm_{0.2}O_{1.9}$ anode and $Ce_{0.8}Sm_{0.2}O_{1.9}$-carbonate electrolyte shows a output power density of 687 mW cm^{-2}. Meanwhile, water produced in the anode is absorbed by NbO_x and forms surface hydroxyl groups, which facilitates the removal of carbon. The addition of NbO_x decreases the amount of deposited carbon in the humidified methanol atmosphere significantly, and an improved stability of the single cell is achieved.

Introduction

Solid oxide fuel cells (SOFCs) are promising energy converting devices with a high efficiency [1–3]. Working at a high operating temperature (typically 600–1000 °C), SOFCs exhibit rapid electrode kinetics, which avoids the use of noble metal electrode materials and thus reducing the manufacturing cost [4,5]. Furthermore, SOFCs can directly utilize various complex fuels such as biogas, alcohols and carbon, which are much readily available and safer to store, instead of hydrogen [6–8]. Methanol is regarded as a prospective renewable fuel for SOFCs which could be obtained from biomass directly. Moreover, methanol tends to pyrolyse and thermally decompose above 700 °C, forming H_2 and CO which could be utilized as the fuels [9,10].

Ni-based cermet anodes are not suitable for SOFCs fed with hydrocarbons due to serious carbon deposition. As an early attempt to replace Ni, Park et al. [11] reported a Cu-doped ceria composite anode which exhibited a sufficient electronic conductivity and a promising stability with butane as the fuel. However, the low catalytic activity and low melting point of

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Cu impede its further development. The activity of Cu-based cermet anode could be improved by adding a certain amount of precious metals such as Ru [12], while the cost of the anode is increased simultaneously. Metal oxides generally exhibit a good thermal stability and a high resistance to carbon deposition compared with metal-based anodes. Rutile-type oxides, e.g. $Ti_{1-2x}Cr_xNb_xO_2$, show a sufficient electronic conductivity in a reducing atmosphere, while their catalytic activity towards electrochemical oxidation is limited by the low mobility of oxygen ions [13]. The oxides with a pyrochlore structure, such as $Gd_2Ti_{2-x}Mo_xO_7$ and $Pr_2Zr_2O_7$, are either unstable in a reducing atmosphere or poorly conductive [14,15]. In recent years, a series of manganite-based double perovskites with a layered structure possess a promising electrical conductivity and a high catalytic activity for the oxidation of hydrocarbons [16–18]. However, impure phases inclined to be formed in the complex structure during the preparation process hinder the application of these materials on a large scale [19,20].

Though novel anode materials for SOFCs fed with hydrocarbons have been extensively explored, few of them are comparable with Ni in terms of electronic conductivity, catalytic activity and price. Therefore, much attention has been focused on improving the resistance to carbon deposition of Ni-based anodes. Nikolla et al. [21] introduced Sn in Ni as a catalyst for methane steam reforming, leading to the decrease of the binding energy of carbon on the nucleation centers and the facilitated oxidation of deposited carbon. The formation of Ni-Co and Ni-Mo alloys in cermet anodes decreases the amount and the graphitization degree of carbon deposited in methanol atmosphere, which improves the stability of the single cells [22]. Yoon et al. [23] reported that incorporating W to the Ni-based cermet anodes formed hydrogen tungsten bronze (H_xWO_3), the hydroxyl groups in which promoted the oxidation of deposited carbon, resulting in an improved stability of cells fed with natural gas. Choi et al. [24] demonstrated that coating Nb_2O_5 on Ni-YSZ anode remarkably enhanced the power output of cells with H_2 as fuel due to the high electrical conductivity of NbO_2 formed in the reducing atmosphere and the excellent catalytic activity of niobium oxides for the dissociative adsorption of H_2. Justin et al. [25] found that doping Nb_2O_5 in Pt/C catalyst significantly enhanced the methanol electro-oxidation activity. In this work, NbO_x is added in the Ni-$Ce_{0.8}Sm_{0.2}O_{1.9}$ (SDC) anode by impregnation. The anodic activity towards the electrochemical oxidation of methanol is investigated. The effects of NbO_x on the coking resistance to carbon deposition are studied.

Experimental

Materials preparation

NiO-SDC composite powder with a mole ratio of 7:3 was synthesized through a hydrothermal method, which is described in detail in a previous work [26]. Ammonium niobate oxalate hydrate $C_4NH_4NbO_9 \cdot H_2O$ was dissolved in deionized water. Then the NiO-SDC powder was impregnated with the $C_4NH_4NbO_9 \cdot H_2O$ solution and calcined in air at 700 °C for 1 h subsequently. The mole ratios between Nb and Ni were 0.01, 0.03 and 0.05, noted as 1NbO_x-NiO-SDC, 3NbO_x-NiO-SDC and 5NbO_x-NiO-SDC, respectively. For characterization, the powders were treated in H_2 at 700 °C for 2 h, noted as 1NbO_x-Ni-SDC, 3NbO_x-Ni-SDC and 5NbO_x-Ni-SDC, respectively.

The composite electrolyte was prepared by mixing SDC powder and binary eutectic carbonate $(Li_{0.67}Na_{0.33})_2CO_3$ [27]. The SDC powder was also synthesized with the hydrothermal method. The weight ratio of SDC in the electrolyte was 70 wt%. 70 wt% lithiated NiO and 30 wt% composite electrolyte were ball milled for 4 h, followed by calcination at 700 °C for 1 h to obtain the cathode powder.

Characterization

The crystal structure of the anode powders were studied using an X-ray diffractometer (D8-S4, Bruker AXS). The surface properties of the reduced powders were investigated with an X-ray photoelectron spectrometer (XPS, PHI 600). The functional groups on the surface of the anode powders were examined with a Fourier transform infrared spectrometer (FTIR, Nicolet Nexus).

In order to investigate the influence of NbO_x on the coking resistance, the reduced NbO_x-Ni-SDC powders were treated in a 99.6 vol% CH_3OH-0.4 vol% H_2O gas mixture (corresponding to the anode atmosphere with 80 ml min^{-1} CH_3OH as the fuel under 100 mA cm^{-2}) at 700 °C for 6 h. The amount of carbon was measured through thermogravimetric analysis (TGA, Netzsch STA449F3).

Fabrication and test of single cells

The 0.6 mm-thick electrolyte and 0.3 mm-thick cathode bilayer was fabricated through a co-pressing approach and subsequently sintered at 700 °C for 1 h. A slurry consisting of the NbO_x-NiO-SDC anode powder and a binder (V006, Heraeus, Ltd.) with a weight ratio of 1:1 was printed onto the surface of the electrolyte layer, which was sintered at 700 °C for 1 h. The thickness of the anode layer was 20 μm. Silver was used as current collector.

For the test of the single cells, the anodes were treated in H_2 at 700 °C for 2 h, and then *I-V* curves of the cells were measured using an electrochemical work station (VersaSTAT3, Ametek). Gasified methanol (80 ml min^{-1}, STP) and O_2 (20 ml min^{-1}, STP) were used as the anode and cathode gases, respectively. Electrochemical impedance spectra (EIS) of the cells were collected with the electrochemical workstation from 1 M to 0.1 Hz. The stability of the cell was measured at 700 °C under 100 mA cm^{-2}. The anode surface of the single cell after the stability test was observed with a scanning electron microscope (SEM, S-4800, Hitachi).

Results and discussion

Characterization

XRD results of the powders before the reduction are illustrated in Fig. 1a. The peaks of NiO (JCPDS#71-1179) and the cubic fluorite structure of SDC (JCPDS#75-0158) are observed

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