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Coking-resistant $Ce_{0.8}Ni_{0.2}O_{2-\delta}$ internal reforming layer for direct methane solid oxide fuel cells

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ABSTRACT

The development of direct methane solid oxide fuel cells (SOFCs) is severely hindered by the deactivation of conventional Ni-based anodes due to carbon fouling. Here, a $Ce_{0.8}Ni_{0.2}O_{2-\delta}$ (CNO) internal reforming layer is imposed on conventional Ni-$Sm_{0.2}Ce_{0.8}O_{2-x}$ (SDC) anodes for direct methane SOFCs. In CNO, there are two types of Ni species which are segregated NiO dispersed over the CNO and incorporated Ni^{2+} in the ceria lattice, respectively. The Ni^{2+} dopants are stable in wet hydrogen at 650 °C; however, the segregated NiO is reduced into Ni under the same conditions. With the doping of Ni^{2+} into the ceria lattice, surface oxygen vacancies are generated in CNO. For the stability testing in wet methane (~3 mol% H_2O in methane) at 650 °C and 0.2 A cm^{-2}, the voltage of the conventional Ni-SDC anode decreases by 43.1% in approximately 26 h, whereas the CNO internal reforming layer operates stably for 40 h. In wet methane at 650 °C, with the addition of the CNO internal reforming layer, the polarization resistance of the Ni-SDC anode reduces by 22.3% from 0.0917 to 0.0712 Ω cm^2, and the maximum current density of it increases from 614 to 664 mW cm^{-2}.

1. Introduction

Solid oxide fuel cells (SOFCs) have been regarded as one of the most promising alternative solutions for power generation with high efficiency, low emissions and fuel flexibility [1,2]. Due to the elimination of Carnot cycle, SOFCs can generate electricity with high efficiency as well as other types of fuel cells [3]. As the SOFCs operate at high temperatures, high-quality waste heat generated during their operation can be recovered for co-generation [4], which can further enhance the energy conversion efficiency and therefore enable to save energy and reduce the greenhouse gas emissions. Another advantage of SOFCs is their high fuel flexibility: any fuel including hydrogen and hydrocarbons can be used for them [3,5]. Methane, the main component of natural gas, would be the most promising source of fuel for SOFCs as it is abundantly available on earth [1].

Regarding the anode materials of direct methane SOFCs, Ni-based cermets are preferably used due to the low cost of Ni and its high activity for methane reforming and oxidation [5]. However, carbon deposition over Ni catalyst during long-term operation is a disturbing problem that impedes the development of direct methane SOFCs [6]. To address this issue, several approaches have been proposed. Decorating Ni-based anodes with other materials can effectively alleviate carbon accumulation on them. For example, modifying them with proper amount of transition metal Fe or Cu can improve methane oxidation and so enhance their stability and electrochemical performance in methane [7,8]. When tungsten was adopted to decorate Ni-Gd-doped ceria anodes, the stability of them was significantly improved, attributing to the formation of $H_xWO_{3-\delta}$ which can eliminate carbon deposition [9]. Alkaline-earth metal oxides, which are all basic oxides and well known for their water [10] and carbon dioxide [11] adsorption capacities, are also utilized to decorate conventional Ni-based anodes to enhance their stability in methane [12–17]. Cu-based cermets have been investigated and believed to be alternative anodes for direct methane SOFCs because Cu is relatively sluggish to break C—C and C—H bonds [5,18]. For instance, methane can be directly oxidized on Cu/CeO_2/yttria-stabilized zirconia (YSZ) anode; no

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carbon deposition was observed after testing for 3 days [19]. However, the method usually used for the preparation of Ni-based cermets cannot be used for the preparation of the Cu-based anodes due to the low melting point of copper and copper oxide as compared to that of nickel and nickel oxide [5]. The Ni-based anodes can also be replaced by mixed ionic and electronic conductors such as single and double perovskites, etc. For example, a single perovskite $La_{0.75}Sr_{0.25}Cr_{0.5}Mn_{0.5}O_{3-\delta}$ (LSCM) displayed comparable performance with a Ni-YSZ anode and operated stably in methane; nevertheless, it showed low electrical conductivity in reducing conditions [20]. A layered double perovskite $PrBaMn_2O_{5+\delta}$ (PBM) exhibited higher electrical conductivity than LSCM in wet 5% H_2 and showed excellent electrochemical performance in H_2 and C_3H_8 [21]. However, it was inactive for methane oxidation. To acquire a relatively high maximum power density in methane, a Co–Fe catalyst had to be added into the PBM anode. Similarly, double perovskites $Sr_2Fe_{1.5}Mn_{0.5}O_{6-\delta}$ (SFM) [22] and $Sr_2Mg_{1-x}Mn_xMoO_{6-\delta}$ [23] had a relatively low catalytic activity for methane oxidation as well.

Apart from the methods above, covering an internal reforming layer over conventional Ni-based anodes has been proved to be an effective strategy to improve their stability in hydrocarbons as well. Zhan and Barnett initially proposed this method by applying a Ru–CeO_2 layer over the Ni-YSZ or Ni-Sm-doped ceria anode [24]. The SOFC with this layer operated stably in octane-containing fuel for 50 h, while the single cell without it failed quickly in approximately 20 h. Subsequently, various catalyst layers were investigated. For example, MnO–Co [25], Ni–MnO [26] and Cu–MnO [27] composite catalyst layers improved the stability and electrochemical performance of their corresponding pristine anodes. Coating a pure ceria functional layer over a Ni-Gd-doped ceria anode significantly boosted its power density in humidified methane at 449 °C as methane can be steam-reformed on this layer [28]. A catalyst layer, consisting of Li^+-conductor: $Li_{0.33}La_{0.56}TiO_3$ (LLT) and Ni, greatly improved the stability of the Ni-based anode in wet methane, and the Li^+ evaporation during the operation was compensated from the bulk LLT [29]. Other catalyst layers such as $La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-\delta}/Al_2O_3$ bilayer [30] and Ni–$La_2Ce_2O_7$ [31] were also investigated to improve the stability of the Ni-based anodes.

Ni-doped ceria ($Ce_{1-x}Ni_xO_{2-\delta}$) had been extensively investigated as catalysts for dry reforming of methane [32], ethanol steam reforming [33], CO oxidation [34], water gas shift reaction [35], and the anode functional layer applied between the Ni-SDC anode and the SDC electrolyte [36]. Doping Ni into the ceria lattice creates oxygen vacancies and therefore promotes methane oxidation [37]. Ni/$Ce_{1-x}Ni_xO_{2-\delta}$ [32] and $Ce_{0.8}Ni_{0.2}O_{2-\delta}$ (CNO) [33] showed much better catalytic activity and stability than Ni/CeO_2 for dry reforming of methane at 700 °C and H_2 production through ethanol steam reforming at temperatures above 350 °C, respectively. Moreover, the CNO also showed much higher catalytic activity than $Ce_{0.9}Ni_{0.1}O_{2-\delta}$ at temperatures high than 400 °C because of the metallic Ni formed from segregated NiO in the CNO during ethanol reforming [33]. However, until now, no one has employed the CNO as an internal reforming layer for conventional Ni-based anodes.

Herein, in this study, CNO was employed as the internal reforming layer of the Ni-SDC anode for direct methane SOFCs. The stability and electrochemical performance of the single cells with and without CNO internal reforming layer were evaluated and compared in wet methane at 650 °C. It was found that the addition of the internal reforming layer not only improved the stability but also decreased the polarization resistance and enhanced the maximum power density of the Ni-SDC anode.

2. Experimental

An EDTA (Ethylene diamine tetra-acetic acid)-citrate method [36] was used to synthesis CNO. Pure ceria was also prepared using the same method as a reference. The fabrication of the CNO is introduced as an example. Metal nitrates $Ni(NO_3)_2 \cdot 6H_2O$ (Strem Chemicals) and $Ce(NO_3)_3 \cdot 6H_2O$ (Aldrich) were used as the starting materials. They were dissolved in deionized water stoichiometrically. EDTA and citric acid were then added into this solution. The mole ratio of the overall metal ions: EDTA: citric acid was 1:1:2. The pH value of the solution was adjusted by $NH_3 \cdot H_2O$. After the evaporation of the water on a hot plate under stirring, a clear gel was obtained and then heated at 240 °C for several hours to get a solid black precursor. Fine CNO powders were acquired after the calcination of the precursor at 800 °C for 3 h. The CNO powders were then ball-milled with some binder in ethanol for 2 h to obtain the CNO slurry.

The fabrication of the single cell with the configuration of CNO reforming layer/NiO-SDC anode support/SDC electrolyte/BSCF cathode is introduced as follows. First of all, the mixture of NiO (JT. Baker), SDC (Fuel cell materials) and dextrin (Sigma) with the weight ratio of 60:40:10 was pressed into a pellet in a circular steel mould at 68 MPa. After that, the SDC electrolyte powders were distributed over the pellet and co-pressed with it at 204 MPa to form a bilayer. Subsequently, the bilayer was calcined at 1400 °C for 5 h to get a dense-enough SDC electrolyte. In the following stage, the CNO slurry was spray-coated onto the surface of the Ni-SDC anode support, and then the support with the CNO layer was calcined at 1100 °C for 2 h. Eventually, BSCF slurry was spray-coated onto the SDC electrolyte and calcined at 1000 °C for 2 h. The active area of the cathode was 0.28 cm^2.

The single cell is assembled according to the following procedures. Initially, silver wires were fixed on both anode and cathode electrodes by silver paste for current collection, and silver ink was brushed onto the cathode for current collection as well. After that, the single cell was assembled onto an alumina tube using silver paste.

For evaluation, the assembled single cell was loaded into a furnace and heated to the required temperature. The electrochemical performance of the single cell was investigated using a four-electrode method. After reduction, the current-voltage (I–V) curve and impedance spectrum of the single cell were tested using an Autolab PGSTAT30 workstation in wet methane (~3 mol% H_2O in CH_4) at 650 °C. The frequency range for the impedance spectrum testing was from 100 kHz to 0.1 Hz under open circuit voltage (OCV). The stability testing was performed in wet methane at 650 °C at 0.2 A cm^{-2}.

The features of the as-prepared and reduced CNO powders, and the carbon deposition of the single cells after stability testing were characterized using the following means. X-ray diffraction (XRD, Bruker D8 Advance) was employed to identify the crystal structure of as-synthesised CNO powders and CNO powders reduced in wet hydrogen (~3 mol% H_2O in H_2) at 650 °C for 3 h. To identify the structural parameters of the CNO, powder XRD Rietveld refinement (Topas software, Bruker) was used. The pure ceria was also refined for comparison. For the temperature-programmed reduction (TPR) profile of the CNO, it was investigated under 5 v% H_2 in argon using BELCAT (BEL Japan, Inc.). The SEM of JEOL JSM-7001F was used to investigate the CNO/Ni-SDC interface and the microstructure of the CNO internal reforming layer, while the SEM of JEOL JSM-7100F was used to check the morphology of the fresh ceria, CNO and reduced CNO powders, and the carbon deposition of the single cells with and without the CNO reforming layer.