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Effect of Sn addition on improving the stability of Ni-Ce_{0.8}Sm_{0.2}O_{1.9} anode material for solid oxide fuel cells fed with dry CH₄

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Abstract

Sn-NiO-Ce_{0.8}Sm_{0.2}O_{1.9} (SDC) is synthesized as an anode material for solid oxide fuel cells with H₂ and dry methane as fuels. Sn-Ni alloy is formed after reduction. The performances of anode-supported single cells with a configuration of Sn-Ni-SDC|SDC|Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-δ} are investigated in the range of 600-700 °C. With increasing Sn content of the anode, the performances of the cells fed with H₂ and dry methane both decrease slightly, indicating a reduced anodic catalytic activity. However, the stability of the cell with dry methane as fuel improves remarkably with the addition of Sn due to the suppression of carbon deposition on the anode.

Keywords: Solid oxide fuel cell; Nickel cermet anode; Methane; Tin; Carbon deposition

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1. Introduction

Solid oxide fuel cells (SOFCs) are electrochemical devices that convert the chemical energy of fuels into electrical energy with high system efficiency and low emission [1, 2]. SOFCs usually operate at high temperatures, e.g. 700-1000 °C, which benefits electrode reaction kinetics and thus leads to a high flexibility of fuel [3, 4]. Instead of hydrogen, carbon monoxide and hydrocarbons can be utilized as fuels, among which CH₄ is the most attractive one due to its abundant supply and low cost [5]. Various strategies have been explored to utilize CH₄ as fuel of SOFCs. Extensive studies have been focused on external and internal reforming of CH₄ with the goal to suppress carbon deposition at the anode side, but these approaches decrease the overall efficiency while simultaneously increase the complexity of the system [5, 6]. Instead, direct electrochemical oxidation of CH₄ has attracted much attention in recent years thanks to the system simplicity and cost effectiveness [7].

The most critical challenge to direct electrochemical oxidation of CH₄ is the degradation of anodes due to deposited carbon [8, 9]. Oxide anodes with various structures, such as perovskite [10], fluorite [11], pyrochlore [12], rutile [13] and tungsten bronze [14], have been extensively explored in recent years. Most of these oxides exhibit satisfactory resistance to carbon deposition. Oxides with a tetragonal rutile structure, e.g. Nb_{1-x}Ti_xO₂, or a tungsten bronze structure, e.g. Sr_{0.6}Ti_{0.2}Nb_{0.8}O₃, show promising electronic conductivities in a reducing atmosphere, but their catalytic activities are quite low [15]. Anodes with a fluorite structure, such as doped ceria, possess high oxygen ionic conductivity and catalytic activity towards the electrochemical oxidation of CH₄ [16, 17]. However, the electronic conductivity of these oxides is not sufficient, generally less than 1 S cm⁻¹ [18]. Most of the recent studies of oxide anodes have been focused on materials with a perovskite structure,

which exhibits modest electrical conductivity and catalytic activity [19, 20]. Huang et al. [21] investigated a double perovskite $\text{Sr}_2\text{MgMoO}_{6-\delta}$ as the anode of a single cell supported by a 300- μm -thick $\text{La}_{0.8}\text{Sr}_{0.2}\text{Ga}_{0.83}\text{Mg}_{0.17}\text{O}_{2.815}$ electrolyte layer. The cell exhibited a maximum power density (P_{max}) of 440 mW cm^{-2} with a promising stability at 800°C with dry CH_4 as the fuel. Recently, a layered oxygen-deficient $\text{PrBaMn}_2\text{O}_{5+\delta}$ anode showed efficient catalytic activity and stability with hydrocarbons as fuels at 850°C [10].

For further development and commercialization of SOFCs, it is important to find ways to lowering the operating temperature [22, 23]. Most oxide anodes are not suitable for hydrocarbon fueled SOFCs operated below 800°C due to their limited electrical conductivity and catalytic activity [24, 25]. An exception are Ni-based cermet anodes that show high electronic conductivity and excellent catalytic activity towards CH_4 oxidation at intermediate temperatures ($600\text{--}800^\circ\text{C}$) [26, 27]. In our previous work, $\text{Ni-Ce}_{0.8}\text{Sm}_{0.2}\text{O}_{1.9}$ (SDC) was employed as the anode material of a direct CH_4 SOFC. The SDC phase provided a high oxygen ionic conductivity and enlarged the region of three-phase boundaries [28]. A cell with a 120- μm -thick SDC electrolyte layer exhibited a P_{max} of 670 mW cm^{-2} at 700°C . Ni-SDC anodes have also been investigated with other hydrocarbon fuels such as methanol, ethanol and biomass gasification tar [29-32]. However, Ni-based anodes suffer from serious carbon deposition in hydrocarbon atmospheres, which is the main obstacle of their utilization.

Much effort has been made to improve the stability of cermet anodes with hydrocarbons as fuels. Park et al. [33] investigated the properties of Cu-SDC anode for direct hydrocarbon SOFCs. The anode showed high stability due to the low catalytic activity of Cu towards the formation of C-C bonds, but it exhibited slow

anodic reaction kinetics as well. Precious metals, such as Ru, Au and Rh, have been added to Ni-based cermets, and the carbon deposition is suppressed to an extent [34, 35]. Yang et al. [36] found that nanoscaled BaO in NiO-YSZ anode could absorb water, which facilitated the removal of deposited carbon.

In 2006, based on density functional theory (DFT) calculations, Nikolla et al. [37] demonstrated that alloying Ni with Sn could modify the carbon chemistry on the metal surface, improving the catalytic activity and the resistance to carbon deposition. From then on, Ni-Sn alloy has been intensively studied as an anode of direct hydrocarbon SOFCs [38, 39]. Nikolla and co-workers [40, 41] proved by both experimental and DFT calculation results that Ni-Sn alloy preferentially oxidizes carbon atoms rather than forming C-C bonds. Myung et al. [5] found that Sn modified the microstructure of Ni-GDC anode by inhibiting the coarsening of Ni nanoparticles. However, Park et al. [42] and Singh et al. [43] reported that Sn did not decrease the carbon deposition on the Ni-based cermet anodes in hydrocarbon atmosphere. Furthermore, contradictory results of the effect of Sn on the catalytic activity of Ni-based anodes have been reported. Nikolla et al. [41] and Singh et al. [43] found that Sn increased the activation barrier for the CH₄ activation and the anodic polarization resistance, while Yoon et al. [39] declared that the catalytic activity of Ni was not affected by a small amount of Sn. Therefore, more investigation is still needed to understand the effect of Sn on the properties of Ni-based anodes [44]. In this work, Sn is added to Ni-SDC anodes for SOFCs with CH₄ as fuel. The effect of Sn content on the performance and stability of the single cell is examined. The properties of the carbon deposits on the anodes after the stability test are investigated.

2. Experimental

2.1. Material preparation

An oxalate co-precipitation method was used to synthesize SDC powder [45]. SDC and NiO (Alfa Aesar) powders were mixed by ball-milling technique in ethanol for 24 h. The weight ratio of SDC to NiO is 1:1 [16, 46]. After that, the mixture was dried at 100 °C overnight and calcined at 1000 °C in air for 1 h to form NiO-SDC composite powder. Stoichiometric $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ (ALDRICH) was dissolved in ethanol, and then incipient-wetness impregnated into the NiO-SDC powder with molar ratios between Sn and Ni of 0.01:1; 0.03:1; and 0.05:1, respectively. After the calcination at 1000 °C in air for 1 h, composite anode materials were formed, named 1Sn-NiO-SDC, 3Sn-NiO-SDC and 5Sn-NiO-SDC, respectively. The powders were reduced in H_2 at 700 °C for 3 h for characterization. $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{Co}_{0.8}\text{Fe}_{0.2}\text{O}_{3-\delta}$ (BSCF) was used as the cathode material and the preparation procedure has been described in previous works [47].

2.2 Characterization

The X-ray diffraction (XRD) measurement was carried out on anode powders before and after reduction with a rotating-anode diffractometer (Rigaku Rotaflex RU-200B) with a $\text{Cu-K}\alpha$ source at 40 kV and 100 mA. The scanning rate was 2°min^{-1} . H_2 -temperature-programmed reduction (H_2 -TPR) was carried out with the reductant of 5% H_2/N_2 using a ChemBET3000 TPR/TPD instrument (QuantaChrome, America) equipped with a thermal conductivity detector from room temperature to 800 °C at a heating rate of $5^\circ \text{C min}^{-1}$.

2.3 Fuel cell test

The fabricating process of the anode-supported single cell has been described in our previous work [16]. Briefly, anode-electrolyte bilayers were fabricated through a co-pressing method. The bi-layer pellets were sintered at 1450 °C in air for 2 h. A mixture of 5 wt.% ethyl cellulose and 95 wt.% terpineol was used as a binder, which

was mixed with the BSCF powder to form a slurry. A Laurell WS-400A-6NPP/LITE spin coater was used to coat the BSCF slurry on the top of the electrolyte layer. The cell was dried at 85 °C in air for 2 h. The spin coating procedure was repeated twice, and then the cell was sintered at 1140 °C in air for 1 h. Au paste was used as the current collector on both anode and cathode sides. The geometric surface area of the electrodes was 1.654 cm². The anode of the single cell was reduced in H₂ at 700 °C for 3 h, and then a scanning electron microscope (FEI Nova 200 Nanolab) was used to investigate the cross-sectional morphology of the cell.

The *I-V* and *I-P* characteristics of the single cells were measured with an electrochemical workstation (Powerstat-05, Nuvant Systems Inc.) with dry H₂ (100 ml min⁻¹, STP) or dry CH₄ (70 ml min⁻¹, STP) as the fuel and air (350 ml min⁻¹, STP) as the oxidant. The output voltage is linearly scanned from the open circuit voltage (OCV) to 0 V at a rate of 0.01 V s⁻¹. The anode was exposed in H₂ at 700 °C for 3 h, and then the measurement was performed from 700 to 600 °C. The stability of the single cells with dry CH₄ as the fuel was tested at 600 °C for 72 h. After the stability test, the surface morphology of the anode was characterized with SEM. The carbon deposited on the anode surface of the tested single cells was studied with energy dispersive X-ray spectroscopy (EDS). The EDS measurement was carried out with a scanning electron microscope (Philips XL30 FEG/ Phoenix XEDS). The relative carbon deposition area was calculated according to the principle of pixel statistics. In addition, the properties of the deposited carbon were studied with temperature programmed oxidation mass spectrometry (TPO-MS) using a Micromeritics AutoChem 2910 instrument. The cathode layer was carefully removed by polishing, and then the remaining anode-electrolyte bilayer was ground to fine powder, which was first treated in He atmosphere at 200 °C for 1 h, and then cooled down to room

temperature. After that, the powder was oxidized in 1% O₂-99% He gas mixture with a flow rate of 70 ml min⁻¹ (STP) from room temperature to 700 °C at a heating rate of 10 °C min⁻¹. An online mass spectrometer was used to monitor the amount of CO₂ in the outlet gas.

3. Results and discussion

3.1. Characterization

Fig. 1. XRD patterns of (a) unreduced anodes, (b) reduced anodes and (c) partially magnified patterns of (b)

Fig. 1a shows the XRD patterns of the Sn-NiO-SDC powders with different Sn contents. All of the XRD patterns contain the peaks of SDC (JCPDS #075-0158) and NiO (JCPDS #073-1523), and the intensities of SnO₂ peaks (JCPDS #088-0287) become stronger with increasing Sn content. No other phase is observed, implying that no chemical reaction happens among NiO, SDC and SnO₂. The peaks of NiO and SnO₂ disappear after the samples were treated at 700 °C in H₂ (Fig. 1b), while those of Ni (JCPDS #087-0712 and #070-0989) and Ni₃Sn₂ (JCPDS #065-9650) are observed, which is probably due to the reduction of NiO and SnO₂. The peaks of Ni shift to smaller angles with the increase of Sn content due to the formation of Ni-Sn alloy (Fig. 1c) [37].

Fig. 2 exhibits the TPR curves of pure SDC, SnO₂ and anode powders with various contents of SnO₂. A slight consumption of H₂ at about 500 °C is observed during the reduction of pure SDC. The reduction of pure SnO₂ begins at about 500 °C, and the summit of the peak appears at 692 °C, which is consistent with the reported

data [48]. Two reduction peaks at 373 and 445 °C are observed in the curve of NiO-SDC, both of which correspond to the reduction of NiO. The reduction of SDC is not obvious in the curve since the consumption of H₂ by the reduction of Ce⁴⁺ is much smaller than that by the reduction of NiO. The addition of 1 wt.% Sn leads to the lowering of the reducing temperature of NiO by about 50-70 °C, implying the interaction between NiO and SnO₂ phases. Similar TPR results were obtained from Sn-Ni catalysts supported by α -Al₂O₃ [48, 49]. Results of DFT calculations show that the adsorption energy of oxygen on Sn-Ni alloy is lower than that on monometallic Sn and Ni, leading to the lowering of the reducing temperature [40]. With the further increase of the Sn content, the reducing temperature of NiO decreases slightly.

Fig. 2. TPR curves of (a) SDC, (b) SnO₂, (c) NiO-SDC, (d) 1Sn-NiO-SDC, (e) 3Sn-NiO-SDC and (f) 5Sn-NiO-SDC

Fig. 3 shows the cross-sectional microstructure of a single cell with 1Sn-Ni-SDC

anode. The thickness of the dense SDC electrolyte layer is 115-120 μm . Both of the anode and cathode layers adhere closely to the electrolyte. The thicknesses of the porous cathode and reduced anode layers are 43-46 and 488-492 μm , respectively.

Fig. 3. Cross-sectional SEM micrographs of (a) cathode and electrolyte layers and (b) the single cell with 1Sn-Ni-SDC anode

3.2. Single cell performance

Fig. 4. (a) OCV and (b) $P_{\max}$ of the single cells with various anodes with H₂ and CH₄ as fuels

The OCVs of single cells with various anodes are shown in Fig. 4a. For both H₂ and CH₄ as the fuels, the OCVs of the cells at 700 °C are around 0.83-0.85 V, lower than the theoretical values calculated by the Nernst equation (1.00 and 1.04 V for H₂ and CH₄ as the fuels, respectively) [50]. In the reducing atmosphere, Ce⁴⁺ in the SDC phase is partially reduced to Ce³⁺ [51], resulting in the mixed ionic and electronic conduction in SDC and the decrease of the OCVs of the cells. With the decrease of the operating temperature, the reduction of Ce⁴⁺ is alleviated, and the OCV increases gradually. The content of Sn in the anode shows no obvious effect on the OCV.

Fig. 4b illustrates the effect of the content of Sn in the anode on the $P_{\max}$ of the single cell. The cell with Ni-SDC as the anode reaches a $P_{\max}$ of 625 mW cm⁻² at 700 °C with H₂ as fuel. With increasing Sn content of the anode, the $P_{\max}$ decreases slightly. A $P_{\max}$ of 600 mW cm⁻² is achieved by the cell with the 5Sn-Ni-SDC anode.

It has been reported that a shell of Sn-Ni alloy is formed on the surface of Ni particles during the reduction, resulting in a decrease of the catalytic activity [37, 40]. Besides, the accumulation of Sn on the surface of the anode has been proved by XPS and STEM results [39, 52]. The $P_{\max}$ of the cells at 700 °C with CH₄ as fuel are higher than those with H₂ as fuel, probably due to the higher energy density of CH₄ [16], consistent with the results in previous reports [53, 54]. The decrease of the $P_{\max}$ with increasing Sn content in the anode is more obvious with CH₄ as fuel, from 670 mW cm⁻² for the cell with Ni-SDC anode to 605 mW cm⁻² for the one with 5Sn-Ni-SDC anode. Nikolla et al. [55] found that the breaking of C-H bond is the rate-limiting step in CH₄ activation, and the activation energy for CH₄ dissociation on Sn-Ni alloy is higher than that on monometallic Ni. With both H₂ and CH₄ fuels, the $P_{\max}$ decreases when the operating temperature is decreased, and the decrease with CH₄ fuel is more noticeable due to the higher activation energy for the oxidation of CH₄ than that of H₂.

Fig. 5. I - V and I - P characteristics of the single cell with 5Sn-Ni-SDC anode with (a) H_2 and (b) CH_4 as fuels at various temperatures

Fig. 5 shows the I - V and I - P characteristics of the single cell with 5Sn-Ni-SDC anode. With both H_2 and CH_4 fuels, the activation polarization in the low current region is not obvious, implying a promising catalytic activity of the anode towards the electrochemical oxidation of the fuels [56]. Meanwhile, the concentration polarization in the high current region is rather insignificant thanks to the porous structure of the electrodes, as shown in Fig. 3.

The stabilities of the cells with CH_4 as fuel under a constant current of 300 mA at 600 °C are shown in Fig. 6a. The initial output voltages of the cells are around 0.78-0.80 V. For all of the cells, the output voltages decrease gradually during the 72 h of operation. Fig. 6b displays the effect of the content of Sn in the anode on the performance drop of the cell. The performance drops of the cells with Ni-SDC, 1Sn-Ni-SDC, 3Sn-Ni-SDC and 5Sn-Ni-SDC anodes after 72 h are 3.7, 2.6, 1.8 and 1.5%, respectively, demonstrating that Sn improves the stability of Ni-SDC anode with CH_4 as fuel.

Fig. 6. (a) Chronopotentiometry results of single cells with various anodes under 300 mA at 600 °C; (b) drop of performance of the cells after 72 h discharge

Fig. 7. Surface SEM and EDS elemental mappings of tested anodes. (a) Ni-SDC; (b) 1Sn-Ni-SDC; (c) 3Sn-Ni-SDC; (d) 5Sn-Ni-SDC.

The distribution of carbon deposition on the surface of various anodes detected by EDS-element mapping after the stability test is shown in Fig. 7. Carbon deposits are observed on all of the anodes. The relative carbon deposition areas on the Ni-SDC, 1Sn-Ni-SDC, 3Sn-Ni-SDC and 5Sn-Ni-SDC anodes are 2.83, 2.11, 1.41 and 1.31%, respectively. The amount of carbon deposition decreases with increasing Sn content,

and this can be considered as the main reason for the improvement of the stability of the single cells.

Fig. 8. (a) TPO-MS results of the ground anode-electrolyte bilayer powders of the tested cells and (b) relationship between Sn content and the amount of carbon deposits

TPO-MS results of the ground anode-electrolyte bilayer powders of the tested cells are shown in Fig. 8a. Four deconvoluted peaks are obtained from each curve, at around 272-278 °C (peak I), 378-385 °C (peak II), 466-482 °C (peak III) and 522-531 °C (peak IV), respectively, suggesting the existence of four carbon species. The two low-temperature peaks (I and II) are probably due to the oxidation of poorly polymerized, H-rich carbon or amorphous carbon with a lower degree of graphitization [57, 58], while the two high-temperature peaks (III and IV) may be caused by the oxidation of carbon deposits with a higher degree of graphitization such as filamentous carbon [59]. It is well known that the carbon with a higher graphitization degree is more difficult to remove by electrochemical oxidation, and thus exhibit more negative impacts on the stability of the anode [60, 61].

The amounts of different carbon species on the anode materials are shown in Fig. 8b. Among all the types of carbon, type II carbon contributes the largest amount. Except type I carbon, the amounts of the other types of carbon deposits decrease with increasing Sn content. Demicheli et al. [62] proposed that the active C atom formed from the complete dissociation of CH₄ on Ni catalyst is in the form of C-Ni₃, which means that seven adjacent active Ni sites are involved for the complete dissociation of each CH₄ molecule. On the contrary, less adjacent Ni active sites are required for the formation of adsorbed CH_x, which is the intermediate in the electrochemical oxidation of CH₄. The addition of Sn into the Ni-SDC anode leads to the formation of Sn-Ni alloy on the surface during the reduction process. The surface-enriched Sn effectively reduces the number of Ni active sites adjacent to each other, which results in a remarkable suppression of carbon deposition and the improvement of the stability of the single cell, while leading to a slight decrease of the catalytic activity of the anode towards CH₄ electrochemical oxidation [37, 40].

4. Conclusion

A number of Sn-NiO-SDC composites have been investigated as anode materials of SOFCs with H₂ and dry CH₄ as fuels. The reducing temperature of NiO decreases with increasing Sn content. Sn-Ni alloy is formed after reduction. Anode-supported single cells with a configuration of Sn-Ni-SDC|SDC|BSCF are fabricated. The increase of Sn content in the anode leads to a slight decrease of cell performance with H₂ as fuel and a more noticeable decrease with CH₄ as fuel, attributed to the reduced anodic catalytic activity. The cell with 5Sn-Ni-SDC anode exhibits $P_{\max}$ of about 600 mW cm⁻² with both H₂ and CH₄ as fuels at 700 °C. Carbon deposition on the anode is significantly suppressed by the addition of Sn, leading to an improvement of the stability of the single cell with dry methane as fuel. The cell with 5Sn-Ni-SDC anode shows the highest durability at 600 °C. Its performance only drops by 1.5% during 72 h operation under a constant output current of 300 mA.

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