Improved activity and stability of Ni-Ce_{0.8}Sm_{0.2}O_{1.9} anode for solid oxide fuel cells fed with methanol through addition of molybdenum

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Abstract

Ni-Mo-Ce_{0.8}Sm_{0.2}O_{1.9} (SDC) composites are prepared and investigated as anodes of solid oxide fuel cells with methanol as fuel. The addition of Mo improves the catalytic activity for methanol pyrolysis and the resistance to carbon deposition of Ni-SDC anode. The anode with a mole ratio of Mo to Ni of 0.03:1 exhibits the lowest polarization resistance. The cell with that anode and SDC-carbonate composite electrolyte shows a maximum power density of 680 mW cm⁻² at 700 °C. The stability of the cell is enhanced with the increase of the content of Mo in the anode, which is mainly attributed to the decreased amount of carbon deposits with a high graphitization degree.

Keywords: Solid oxide fuel cell; Nickel Anode; Molybdenum; Methanol; Carbon deposition; Electrochemical performance

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1. Introduction

A solid oxide fuel cell (SOFC) converts chemical energy in fuels to electrical energy directly with high system efficiency and low emissions [1-3]. Fast electrode reacting kinetics of SOFCs because of their high operating temperature allows the utilization of readily available fuels, such as natural gas, coal gas, gasoline, jet fuel, diesel and even solid carbon, instead of hydrogen [4-8]. Liquid fuels are considered as promising fuels for portable applications due to their high volumetric energy density [9, 10]. For small-scale portable applications, it is meaningful to directly use methanol in SOFCs because methanol has low content of impurities which can poison the anode [11, 12]. Meanwhile, pyrolysis and catalytic decomposition of methanol can be readily achieved at typical SOFC anodic conditions [13], favoring subsequent electrochemical oxidation of the products of these reactions, which are mainly CO and H₂ [14, 15].

Conventional Ni-yttria stabilized zirconia (Ni-YSZ) cermet anode [16], which has excellent catalytic properties for fuel oxidation and high electrical conductivity, is not suitable for SOFCs fed with carbon-containing fuels including methanol because it suffers from serious carbon deposition. Ni is a good catalyst not only for the breaking of C-H bonds but also for the formation of C-C bonds [17]. The accumulation of deposited carbon leads to the blockage of anode pores and hinders gas diffusion. In addition, the deposited carbon will destroy the anode structure, causing a permanent damage of the cell [18-20].

Aliovalent cation doped ceria materials, such as Ce_{0.8}Sm_{0.2}O_{1.9} (SDC), have been used as anode materials for SOFCs because of their efficient mixed electronic-ionic conductivity in reducing atmospheres, which expands the active region for the electrochemical oxidation of the fuels [21, 22]. The partial reduction of Ce⁴⁺ to Ce³⁺ in a reducing atmosphere allows SDC to storage/release oxygen, facilitating the oxidation of adjacent deposited carbon [23]. Therefore, compared with Ni-YSZ, Ni-SDC shows a higher resistance to carbon deposition [20, 24]. SDC also exhibits a good electrocatalytic activity for the oxidation of methanol [25], making it a promising anode component in SOFCs with methanol as the fuel.

Recently, Escudero *et al.* [26] found that doping Mo into Ni-CeO₂ anode lowers the activation energy for breaking C-H bond and reduces carbon deposits with methane as fuel. In this work, Mo is added into Ni-SDC anodes for SOFCs fed with methanol. The effect of Mo content on the catalytic activity of the anode for methanol decomposition is examined. The properties of the carbon deposited at the anodes and the performance of the single cells are investigated.

2. Experimental

2.1. Material preparation

SDC powder was prepared with an oxalate co-precipitation technique [27]. SDC and NiO powders with a weight ratio of 1:1 were mixed thoroughly by ball milling for 24 h and then calcined at 1000 °C for 1 h to form a composite anode. Ammonium molybdatetetrahydrate (NH₄)₂MoO₇ (> 99.0 %, Guangfu fine chemical, Ltd., China) was dissolved in aqueous solution of ammonia. Then the solution was impregnated into the NiO-SDC powder. The impregnated material was calcined at 500 °C for 1 h. The mole ratios of Mo to Ni in the anodes were 0.01:1, 0.03:1 and 0.05:1, which were marked as NiO-1Mo-SDC, NiO-3Mo-SDC and NiO-5Mo-SDC, respectively. To characterize the structure of the anodes with different contents of Mo in the anode atmosphere, the powders were reduced in H₂ at 700 °C for 2 h, named Ni-SDC, Ni-1Mo-SDC, Ni-3Mo-SDC and Ni-5Mo-SDC, respectively.

The electrolyte was a composite of SDC and (Li_{0.67}Na_{0.33})₂CO₃ with a weight ratio of 7:3. The cathode was composed of 30 wt% composite electrolyte and 70 wt% lithiated NiO. Detailed preparing processes of the electrolyte and cathode materials were described in previous works [7, 8, 28].

2.2. Characterization

The X-ray diffraction (XRD) patterns of the powders were recorded at room temperature using a D8 Focus diffractometer (Bruker Corp., Germany) with Cu-K α radiation, 40 kV and 200 mA, at a scanning rate of 8° min⁻¹. To analyze the Mo-3d state in the anode materials after reduced in H₂, X-ray photoelectron spectroscopy (XPS) was recorded using a PHI1600 XPS system with Al-K α

radiation. The catalytic activities of the various anodes for methanol pyrolysis and carbon deposition were evaluated in a tubular quartz reactor. In a typical test, 0.1 g of anode particles (40-60 mesh) was reduced by hydrogen at 700 °C for 2 h before gasified anhydrous methanol with a flow rate of 100 mL min⁻¹ (STP) was fed in the reactor at the same temperature. When the system reached a quasi-steady state, the content of H₂ in the outlet gas was analyzed with a gas chromatograph (Clarus 500, Perkin Elemer) with a thermal conductivity detector. The methanol flow was kept for 300 min for carbon deposition, and then the sample cooled down to room temperature in Ar atmosphere. The mass of the deposited carbon was measured with a PerkinElmer Diamond Thermogravimetric analyzer (TGA) in air from 30 to 900 °C with a heating rate of 10 °C min⁻¹. The structure of the carbon was analyzed with a Raman spectrometer (Renishaw inVia) under a 633 nm He-Ne laser excitation source at room temperature. The deposited carbon was also analyzed with oxygen temperature programmed oxidation (O₂-TPO) combined with an online mass spectrometer (HidenHPR-20) to monitor the amount of CO₂ in the outlet gas. The cross-section morphology of the single cell was observed with a Hitachi S-4800 scanning electron microscope (SEM). The energy dispersive X-ray spectroscopy (EDX) test was performed on the anode surface of the single cells after reduced in H₂ to determine the contents of Ni and Mo by using a Genesis XM2 instrument.

2.3. Fuel cell test

The pellet containing an electrolyte layer and a cathode layer was fabricated with a co-pressing method followed by sintering, as described in previous works [7, 29]. The cathode was composed of 30 wt% composite electrolyte and 70 wt% lithiated NiO. The thicknesses of the electrolyte and the cathode layers were 0.65 and 0.35 mm, respectively. The anode materials were made into slurries with a binder (V006, Heraeus Ltd.), and then screen-printed on the electrolyte layer followed by sintering at 700 °C in air for 1 h. Ag paste was coated on both sides of the cell as a current collector. The effective area of the electrodes was 0.64 cm².

The performance of the single cell was measured in a homemade device. Before the test, the anode side of the cell was exposed to H₂ for 2 h at 700 °C. Gasified anhydrous methanol (100 ml

min^{-1} , STP) and O_2 (30ml min^{-1} , STP) were used as fuel and oxidant, respectively. The I - V and I - P curves of the cell were measured at $700\text{ }^\circ\text{C}$ with an electrochemical workstation (VersaSTAT 3, Ametek). The electrochemical impedance spectrum (EIS) of the cell was recorded under the open circuit voltage (OCV) in the frequency range from 1 M to 0.1 Hz with an amplitude of 10 mV . The stability of the cell was tested under a constant current of 300 mA cm^{-2} at $700\text{ }^\circ\text{C}$ with methanol as the fuel. SEM-EDX test was performed on the surface of Ni-3Mo-SDC anode after the stability test.

3. Results and discussion

3.1. Characterization

The characteristic peaks of SDC (JCPDS #075-0158) and NiO (JCPDS #073-1523) are observed in the XRD patterns of NiO-Mo-SDC powders, as shown in Fig. 1a, and the peaks of MoO_3 (JCPDS#075-0912) appear in the pattern of NiO-5Mo-SDC, which are relatively weak due to the low content of Mo [26]. After the powders were reduced in H_2 at $700\text{ }^\circ\text{C}$, the peaks of Ni (JCPDS #065-2865) were observed instead of those of NiO and MoO_3 (Fig. 1b). With the increase of Mo content, a slight left shift of Ni peaks is observed (Fig. 1c), indicating a tiny expansion of unit cells, which is probably due to the formation of Ni-Mo alloy [30].

Fig. S1 shows the Mo-3d core-level spectrum consisting of Mo-3d_{3/2} and Mo-3d_{5/2} excitations on the surface of the Ni-3Mo-SDC powder. For Mo-3d_{3/2} excitation, four deconvoluted peaks are obtained at 236.1, 235.4, 234.7 and 231.0 eV, corresponding to Mo^{6+} , Mo^{5+} , Mo^{4+} and Mo^0 , respectively. The binding energies for Mo-3d_{5/2} excitation at 6+, 5+, 4+ and 0 valences are 233.2, 232.4, 231.4 and 227.0 eV, respectively. The XPS result shows that four valence states of Mo co-exist in the anode after reduced, as reported by other researchers [31].

3.2. Catalytic activity

As mentioned above, methanol can be pyrolyzed at the operating temperature of the SOFC. The major products are H_2 and CO, which could be electrochemically oxidized at anode. The influence of the Mo content in the anode on the yield of H_2 is shown in Fig. 2. The yield of H_2 is about 89.4 % at $700\text{ }^\circ\text{C}$ with Ni-SDC as the catalyst. It increases with the raise of Mo content, indicating that the addition of Mo accelerates the pyrolysis of methanol. The yield of H_2 reaches

96.2 % with Ni-3Mo-SDC as the catalyst, which keeps almost constant when Mo content is further increased.

Fig.1 XRD patterns of (a) unreduced anodes; (b) anodes reduced in H_2 at 700 °C for 2 h and (c) partially magnified patterns of (b).

Fig.2 H₂ yields of methanol pyrolysis with different anodes as catalysts at 700 °C.

3.3. Carbon deposition analysis

Fig. 3a shows the TGA curves of various anode powders after carbon deposition. The weight loss begins at about 500 °C corresponding to the oxidation of the deposited carbon. The weight loss of the anode without Mo is about 56 % at 900 °C, much higher than those of the anodes containing Mo, which only lose about 43 %, demonstrating that the addition of Mo increases the coking resistance of Ni-SDC anode in methanol atmosphere.

Fig. 3b shows the Raman spectra of various anodes after carbon deposition. Two Raman characteristic peaks at around 1360 cm⁻¹ (band D) and 1580 cm⁻¹ (band G) are observed. Band D reflects the disorder of the structure of the deposited carbon and band G is due to C–C stretching [32, 33]. The degree of graphitization of a carbon material is defined as R .

$$R = I_D / I_G \quad (1)$$

I_D and I_G are intensities of D-peak and G-peak, respectively. The carbon with a lower R value shows a higher graphitization degree [34, 35]. The R values of the carbon formed on Ni-SDC, Ni-1Mo-SDC, Ni-3Mo-SDC and Ni-5Mo-SDC are 1.06, 1.19, 1.37 and 1.45, respectively, implying the carbon formed on the anode with a higher Mo content has a lower graphitization degree.

a

b

Fig.3 (a) TGA curves and (b) Raman spectra of anodes with different Mo contents after carbon deposition.

TPO-MS results of the various anode powders after carbon deposition are shown in Fig. 4. Two deconvoluted peaks are obtained from each curve, suggesting the existence of two carbon species. The peak around 500-600 °C (peak I) with a higher intensity is probably due to the oxidation of poorly polymerized whisker carbon adsorbed mainly on the surface of the catalyst [36-38]. The other peak around 550-700 °C (peak II) with a lower intensity could be attributed to the oxidation of pyrolytic carbon with a higher degree of graphitization, which first deposits as soot-like particles on the surface of the catalyst [36, 39]. Then the accumulated carbon would encapsulate the entire catalyst pellet and fill the voids among particles, eventually leading to deactivation of the catalyst and blockage of the reactor [36, 40, 41].

Fig.4 TPO-MS results of anode powders with different Mo contents after carbon deposition. o: raw data; solid line: peak I fitting result; dash line: peak II fitting result.

Fig. 5 shows the mass fractions of different carbons deposited on the anodes, which are determined based on the TPO-MS results. Type I carbon contributes a larger portion of the total amount. The mass fraction of type I carbon is around 80 % of the total carbon deposits on Ni-SDC and Ni-1Mo-SDC anodes, and it reaches about 99% on Ni-5Mo-SDC anode. Furthermore, according to the total amount of the deposited carbon obtained from the TGA results (Fig. 3a), the amounts of different carbon deposits can be calculated, which are also illustrated in Fig. 5. The amount of type I carbon deposited on the Ni-SDC anode decreases rapidly with a little addition of Mo in the anode, and rises slightly when the amount of Mo is further increased. On the contrary, the amount of type II carbon decreases monotonically with the increase of the Mo content in the anode. It has been pointed out that carbon with a higher degree of graphitization is more difficult to be removed during the electrochemical oxidation reaction, which is the main reason for the decreased stability of the fuel cell with hydrocarbon as fuel [40, 42]. Therefore, it is expected that the increase of Mo content in the Ni-Mo-SDC anode would lead to a better stability of the SOFC fed with methanol.

Fig.5 Mass fractions and weights of different types of carbon deposits on anode powders with various Mo contents.

Fig.6 SEM images of the cell with Ni-3Mo-SDC anode before the cell test. (a) anode and electrolyte interface and (b) cathode and electrolyte interface.

3.4. The microstructure of the single cell

Fig. 6 shows the cross-section morphology of the single cell with Ni-3Mo-SDC as the anode. The thickness of the printed anode layer is 24-30 μm . Both the anode and the cathode layers are porous, which adhere closely to the dense electrolyte layer. The porous structure of the electrodes facilitates the diffusion of the gasified methanol and oxygen to the reacting sites, reducing the concentration polarization of the cell [15]. The SEM-EDX images of Ni-1Mo-SDC, Ni-3Mo-SDC and Ni-5Mo-SDC anode surface of the single cells after reduced in H_2 are shown in Fig. S2. The mole ratios of Mo to Ni are 0.012, 0.030 and 0.052, respectively, which are similar to the ratios of Mo to Ni in the anode powders before the reduction.

Fig.7 (a) I - V and I - P curves and (b) impedance spectra of the fuel cells with various anodes at 700 °C with methanol as fuel.

3.5. Single cell performance

Fig. 7a displays I - V and I - P characteristics of the fuel cells with various anodes fed with gasified methanol. The maximum output power densities ($P_{\max}$) of 425, 486, 680 and 643 mW cm⁻² are achieved at 700 °C by the fuel cells with the Ni-SDC, Ni-1Mo-SDC, Ni-3Mo-SDC and Ni-5Mo-SDC anodes, respectively. The highest $P_{\max}$ of the single cell with the Ni-3Mo-SDC anode could be attributed to the high catalytic activity of the Ni-3Mo-SDC anode for the decomposition reaction of methanol, as demonstrated in Fig. 2. The EIS results of the single cells at 700 °C are shown in Fig. 7b. The high-frequency intercepts on the real axis are mainly result from the ohmic resistances, while the arcs reflect the influence of electrode polarization [43]. In the I - V curves and EIS results of the cells, the influence of concentration polarization is not obvious, which is due to the porous structure of the electrodes, as shown in Fig. 6. Since the cathode and electrolyte are identical for all cells, the differences in the EIS results could be attributed only to the differences of the anodes. The ohmic resistances of all the anodes are similar, while the anode polarization resistance shows an order of NiO-SDC > NiO-1Mo-SDC > NiO-5Mo-SDC > NiO-3Mo-SDC, contrary to the order of catalytic activity of the anodes for methanol pyrolysis. Therefore, the lowest polarization resistance of Ni-3Mo-SDC anode and the highest performance of the corresponding cell could be attributed to the rapid pyrolysis of methanol at the anode, leading to a high H₂ content in the fuel.

Fig. 8a shows the output voltage of the cells at 700 °C as a function of time under a current density of 300 mA cm⁻². The voltage of the cell with the Ni-SDC anode decreases gradually from about 0.86 V at the beginning to about 0.82 V after 240-minute discharge, and then drops sharply to about 0.75 V during the next 60 minutes probably due to the accumulation of carbon. For the cells with the addition of Mo in the anodes, their performances decrease at slower rates. The relationship between the content of Mo in the anode and the drop of the performance of the cell is shown in Fig. 8b. After operating with methanol as fuel for 300 min, the performances of the cells with Ni-SDC, Ni-1Mo-SDC, Ni-3Mo-SDC, and Ni-5Mo-SDC anodes drop by 12.4, 10.0, 5.7 and 4.8 %, respectively.

respectively. There is still carbon deposition on the surface of Mo-added anodes, which is detected by EDX-element mapping, as shown in Fig.S3. However, the addition of Mo in the Ni-SDC anode significantly improves the stability of cells with methanol as fuel. Combining with the results of Raman analysis (Fig. 3b) and carbon-type analysis (Fig. 5), we believe that the improvement of the cell stability is due to the suppressed deposition of carbon with a high degree of graphitization.

Fig.8 (a) Chronopotentiometry results of single cells with different anodes under 300 mA cm^{-2} at 700°C ; (b) drop of performance of the cells after 300-minute discharge.

4. Conclusion

Ni-Mo-SDC composite has been investigated as an anode material of an SOFC with methanol as fuel. The addition of Mo into Ni-SDC improves the catalytic activity for methanol pyrolysis, which produces H₂ as a fuel of SOFCs. The Ni-3Mo-SDC composite anode shows the lowest anodic polarization. The single cell with Ni-3Mo-SDC anode and SDC-carbonate composite electrolyte exhibits the highest $P_{\max}$ of 680 mW cm⁻² at 700 °C. The addition of Mo also enhances the resistance to carbon deposition of Ni-SDC in methanol atmosphere. The amount of deposited carbon with a high degree of graphitization, which is the main reason for the degradation of the cell, decreases with the increase of the content of Mo in the anode. The cell with Ni-5Mo-SDC anode shows the most stable performance, which drops by 4.8 % during 300-minute operation.

Acknowledgments

The financial support of NSF of China under contract number 51402210 and 21120102039, the support of Tianjin Municipal Science and Technology Commission under contract number 15JCQNJC06500 and 13JCZDJC26600, and the support of the Ministry of Education of China under contract number 20130032120023 are gratefully acknowledged. The work has been also supported by the Program of Introducing Talents to the University Disciplines under file number B06006, and the Program for Changjiang Scholars and Innovative Research Teams in Universities under file number IRT 0641.

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