

Short communication

Carbon doped MO–SDC material as an SOFC anode

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Abstract

Oxide mixtures MO–SDC, M = Cu, Ni, Co, SDC = Ce_{0.9}Sm_{0.1}O_{1.95} were synthesized by employing a citrate/nitrate combustion technique. Two kinds of Carbon materials, activated carbon (AC) and vapor grown carbon fiber (VGCF) were homogeneously dispersed into the MO–SDC. The materials can be used as anodes to fabricate single cells using a uniaxial die-press method. The sintering temperature was studied to optimize cell performance. Experimental results showed that cells sintered at 700 °C had better performance. When the temperature was above 750 °C, the cells were severely distorted, and cannot be tested. Compared with the basic MO–SDC anode, AC and VGCF improve the solid oxide fuel cell (SOFC) anode properties, due to a change of the microstructures of the anode materials which enhance their electron conductivity. Single cell performances were evaluated by I–V measurements, and when 1.25 wt.% VGCF was introduced into the MO–SDC by ball-milling, termed: 1.25 wt.% VGCF–MO–SDC, the 1.25 wt.% VGCF–MO–SDC anode material could achieve the highest power density of up to 0.326 W cm⁻² with H₂ as fuel. The calcination temperature of the MO–SDC dry gel also strongly influenced the electrochemical performance of the 1.25 wt.% VGCF–MO–SDC material. XRD spectra for each calcined temperature and the I–V measurement both suggest that calcinations at 550 °C for 1 h are suitable. 1.0 wt.% AC–MO–SDC and 1.25 wt.% VGCF–MO–SDC have similar performance when the cell was fed in methanol/3% H₂O, and the corresponding power density was up to 0.253 W cm⁻². Traces of carbon were found in the off-gases.

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1. Introduction

Low-temperature solid oxide fuel cells (LTSOFCs), i.e. operating at 400–600 °C, have demonstrated a promising high performance for different fuels. Compared with traditional high temperature (HT) devices, they have lower operating costs and possess special advantages for transportation and for distributed power applications [1–5]. Ohara et al. has reported a doped lanthanum gallate electrolyte Ni–SDC cermet anode had very stable performance [10]. A Ni–SDC anode for direct oxidation of methane in SOFCs was also studied, compared with Ni–YSZ, the Ni–SDC anode exhibited higher open-circuit voltages (OCVs) and a lower degree of polarization [11]. Ni–SDC anode material exhibits excellent performance with H₂ as fuel. Elemental Co was introduced into the Ni–YSZ anode, and the partial substitu-

tion of Ni with Co lowers the polarization resistance, especially the main contribution which is usually most dependent on the cermet microstructure [12]. Additionally, Cu–CeO₂ (YSZ) is used as an anode avoiding carbon deposition because Cu is a less active catalyst for C–C bond formation, unlike Ni [5]. A doped Ni–SDC anode was shown to be a promising material in LTSOFC devices. H₂ is the most efficient fuel in a SOFC; it can be directly fed in with no reforming process. Gorte et al. [1] found that the Cu–YSZ anode had a poor performance with a hydrocarbons feed, and when a catalytic oxide, like ceria, was used as the addition with the Cu cermet, reasonable power densities could be achieved. The electrolyte with high ionic conductivity and an active thickness of the electrolyte are essential. In recent years, Zhu et al. devoted themselves to developing LTSOFCs, resulting in novel functional ceria-salt composite CSCs electrolyte materials [6–9].

One of the CSCs [7] was BaCO₃–SrCO₃, which was used as the electrolyte in this paper, which aims at exploring a kind of suitable and non-noble catalyst anode material in LTSOFCs.

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In the present work, a novel anode catalyst VGCF–MO–SDC; $M = \text{Cu}, \text{Ni}, \text{Co}$; $\text{SDC} = \text{Ce}_{0.9}\text{Sm}_{0.1}\text{O}_{1.95}$ was synthesized by employing a citrate/nitrate combustion technique. The single cell was fabricated using a uniaxial die-press and different anode catalyst was measured in the LTSOFC device for comparison. The following discussions are based on the experimental results.

2. Experiment

2.1. Preparation of anode materials

In this paper, anode materials were prepared employing combustion synthesis of citrate–nitrate gels. Appropriate amounts of $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$, $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, and fine SDC powder were added to distilled water, into which 1.5 mol citric acid per mole nitrate was added. The solid–solution mixture was heated and converted to a gel as the solvent was evaporated. Then the gel was dried fully in an oven at 110°C and, in the following step, fired at 500°C in air for 1 h to form a porous dry gel of MO–SDC. 0.75, 1.00, 1.25, 1.5, 1.75 wt.% VGCF was mixed to the fresh MO–SDC ash and the whole mixtures was together ball-milled for 5 h, respectively. Then the relative homogeneous mixture was sintered at 680°C in N_2 for 1 h to form VGCF–MO–SDC anode catalyst material. One weight percent AC–MO–SDC anode material was prepared by the same method as the one stated above.

2.2. Fuel cell arrangements

The single cell was fabricated using a uniaxial die-press [13]. Fig. 1 shows the microstructure of cell after being sintered. The materials from top to bottom were: the current collector, the lithiated NiO cathode, the CSC electrolyte, prepared anode materials, current collector. The lithiated NiO cathode, CSC electrolyte, prepared anode materials and the current collector materials were directly cold Co-pressed under 30 MPa into

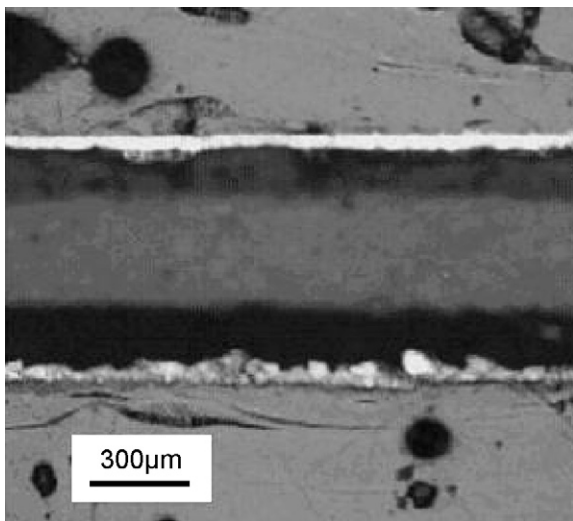


Fig. 1. Microstructure of cell after being sintered.

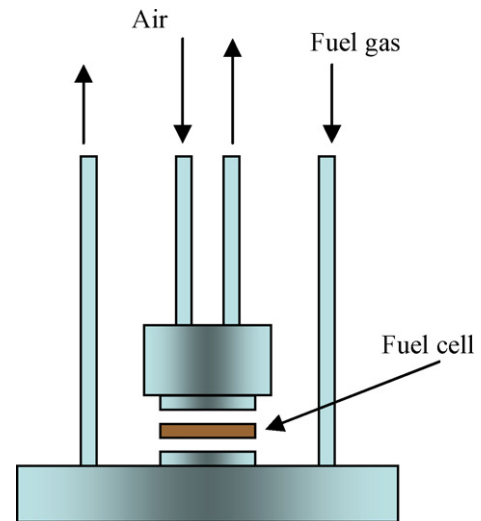


Fig. 2. Schematic for testing device of fuel cells (partly).

cylindrical pellets in one step. The dense electrolyte was sandwiched between the two porous electrodes, the anode and the cathode. The FC was placed between two alloy pipes (also of 12 mm diameter) with the cathode facing outwards in order to be exposed to air and the anode facing into the pipe in order to be exposed to fuel contained within the pipe. The schematic device is shown in Fig. 2, the symmetrical pipe of the feed-in gas is the off-gas pipe; the two pipes were skillfully designed to be a clamp that was convenient for the flows of fuels and air. The cell-clamp assembly was placed into a tubular furnace for measurements. The fuel gas is H_2 or methanol gas/3% H_2O .

2.3. Suitable sintered temperature of single cell

MO–SDC single cells were sintered at 650, 675, 700, 725 and 750°C in a muffle furnace to select the most suitable temperature for high power density and current–voltage performance. Other thermal influences during the sintering process were also considered, for example, the cells would be distorted above 750°C .

2.4. Suitable calcined temperature of MO–SDC dry gel

MO–SDC dry gel was prepared by the citrate/nitrate combustion technique, and then was calcined at 500, 550, 600, 700°C for 1 h. Afterwards, 1.25 wt.% VGCF was introduced to the calcined powder to use as anode materials. The best calcination temperature was selected using the corresponding I–V measurement results.

2.5. Feeding with methanol gas

The cells were made using the optimized operation obtained above. Methanol as the fuel was evaporated at 150°C in a quartz heater, and subsequently flowed through the pipe into the cell anode chamber in a gaseous state. The fuel gas was methanol/3% H_2O .

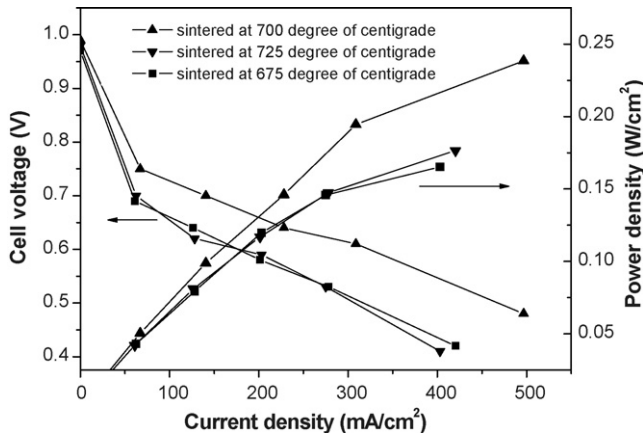


Fig. 3. MO-SDC anode material performance vs. different sintering temperatures.

2.6. Characterization of anode materials

Ball-milled and calcined anode powder was dispersed with ethanol as the dispersant in a KQ318 super sonic dispersion analyzer. The microstructure of the dispersed samples was revealed with a Philips XL30 (Netherlands, Philips XL30) scanning electron microscope (SEM). The powder X-ray diffraction analysis was carried out using a Rigaku X-ray diffractometer (ModelDMax-2500) equipped with a Ni-filtered Cu K α (1.542 Å) radiation and a graphite crystal monochromator.

3. Results and discussions

3.1. Suitable sintered temperature of single cell

Pure H₂ was used as the fuel for the cell and air as the oxidant. MO-SDC material was used as the anode to make a single cell, which was sintered at different temperatures, then the best sintering temperature was selected according to the power density-T curve, which is shown in Fig. 2.

As shown in Fig. 3, the temperature strongly influences the performance. Cells sintered at 700 °C had a superior performance, achieving 0.239 W cm⁻². The cell sintered at 750 °C was severely distorted. The cell would be cracked when it was

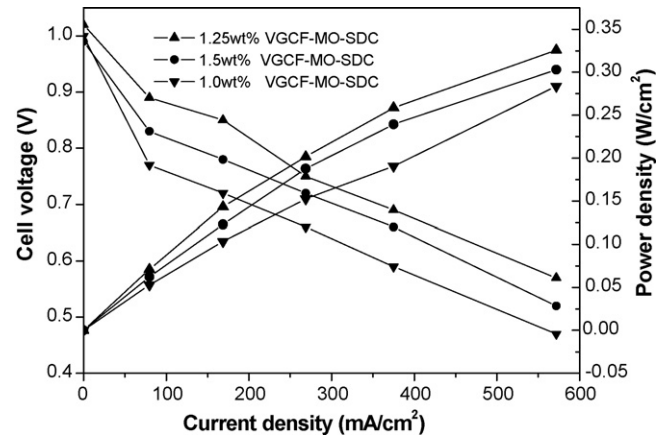


Fig. 4. Performance of different VGCF weight percent in VGCF-MO-SDC anode materials.

sandwiched between two pipes, so it cannot be tested. Because a phase interface between each electrode exists, a suitable temperature can separate each material area with a clear interface and the material also can be activated. If the temperature was too high, above 750 °C for example, the cells were destroyed by the thermal stresses caused by the difference in thermal expansion coefficients between the anode, electrolyte and cathode. If the temperature was too low, then there was no clear phase interface between the electrode materials or the material had a low activity so the cell performance was poor. So 700 °C was selected as the most suitable sintering temperature.

3.2. Suitable VGCF quantity used in anode material

VGCF was introduced to the MO-SDC material at 0.75, 1.00, 1.25, 1.5, 1.75 wt.%. The cell performance is shown in Fig. 4. 0.75 wt.% VGCF-MO-SDC, 1.75 wt.% VGCF-MO-SDC were also measured, and the power density was 0.257 and 0.278 W cm⁻² respectively, both less than the 1.25 wt.% VGCF-MO-SDC anode material. SEM studies of these powders were conducted to reveal the morphology (Fig. 5).

As shown in Fig5 the VGCF was homogeneously dispersed in the MO-SDC powder, this can enhance the electrochemical performance and adjust the thermal performance of the MO-SDC

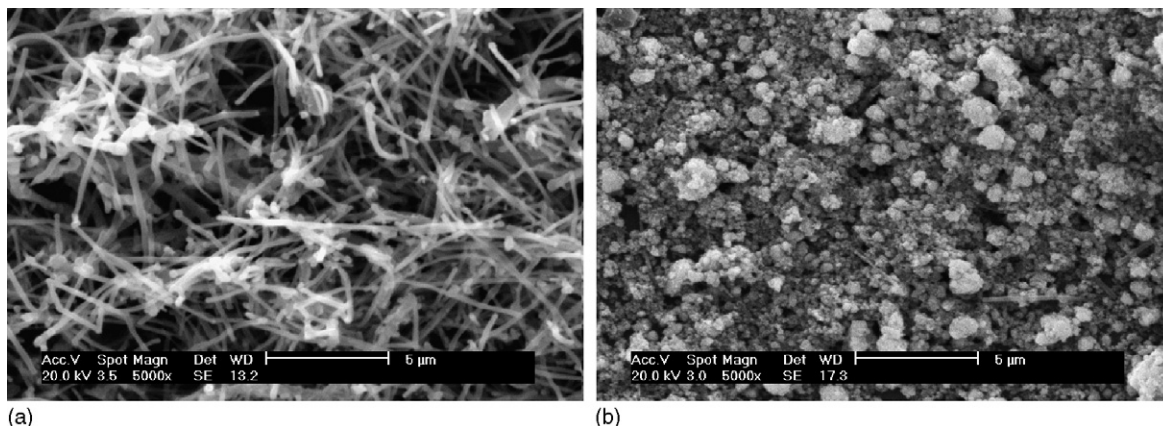


Fig. 5. Morphologies of VGCF-MO-SDC materials with VGCF (a) and 1.25 wt.% VGCF-MO-SDC (b).

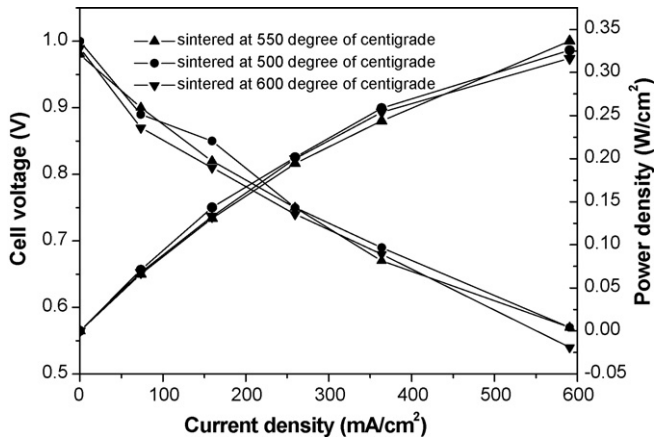


Fig. 6. Performance of 1.25 wt.%VGCF-MO-SDC anode material at different calcined temperature of MO-SDC dry gel.

anode material. The 1.25 wt.%VGCF-MO-SDC anode material can achieve a power density of 0.326 W cm^{-2} , which is much higher than 0.239 W cm^{-2} with the MO-SDC as anode.

3.3. Calcined temperature of MO-SDC dry gel

The MO-SDC ash was calcined at 500, 550, 600, 700 °C in a muffle furnace for 1 h. Then 1.25 wt.%VGCF was mixed into the calcined powder uniformly to use as the anode material. The sintering temperature of the single cell was selected as 700 °C. Fuel cell performance is shown in Fig. 6.

As shown in Fig. 6, the MO-SDC dry gel calcined at 550 °C temperature gives the best performance, and achieves a power density of 0.337 W cm^{-2} , which is higher than 0.326 W cm^{-2} after calcination at 500 °C. But in the medium current zone, the cells had better performance when the MO-SDC dry gel was calcined at a lower temperature. XRD patterns of these materials are shown in Fig. 7. The carbon material (VGCF) peak was not apparent in the figure, and perhaps it was obscured by other elements.

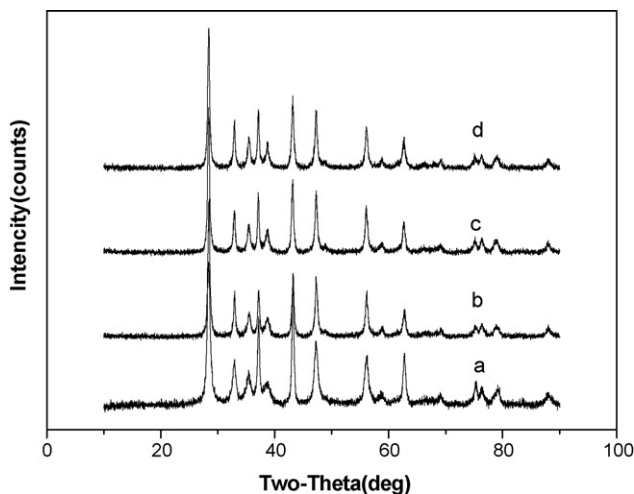


Fig. 7. X-ray patterns of calcined 1.25 wt.%VGCF-MO-SDC anode material at different calcined temperature of MO-SDC dry gel: 500 °C (a), 550 °C (b), 600 °C (c) and 700 °C (d).

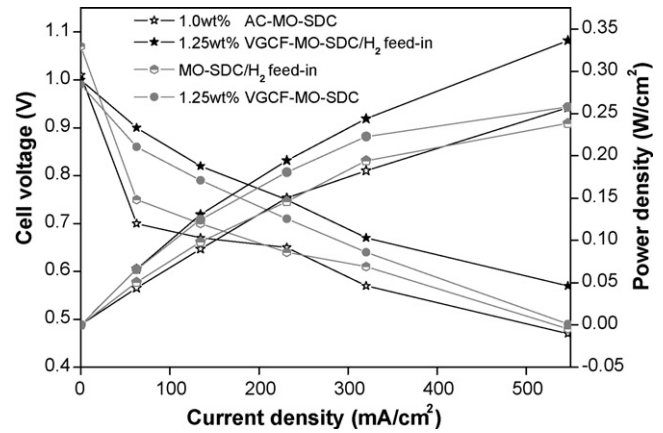


Fig. 8. I-V measurement of 1.25 wt.%VGCF-MO-SDC and 1.0 wt.% AC-MO-SDC feeding in methanol/3% water; along with 1.25 wt.%VGCF-MO-SDC, MO-SDC by using H_2 as fuel.

3.4. Feeding with methanol gas

All of the cells above were tested with H_2 as the fuel. 1.25 wt.%VGCF-MO-SDC was also used as an anode when gaseous methanol was employed as the fuel in which MO-SDC dry gel was calcined at 550 °C for 1 h, and the cells were sintered at 700 for 1 h with N_2 as protect gas. I-V measurement results are shown in Fig. 8.

As shown in Fig. 8, 1.0 wt.%AC-MO-SDC and 1.25 wt.% VGCF-MO-SDC give similar power densities with methanol gas as fuel, and achieved 0.257 and 0.258 W cm^{-2} , respectively, but the latter worked better in medium current density ranges. In the MO-SDC based anode materials, transition metal oxides of CuO with n-type conductivity and NiO, CoO with p-type conductivity, have good catalytic activities for the electrochemical oxidation of H_2 , and also have potential catalytic activity for hydrocarbon fuels. Unfortunately, a carbon deposit was found in the exhaust.

In this work, the focus and tasks were set for the exploitation of new catalyst anode materials that can function in LTSOFC devices. But there is a lack of effort for improving the long-term performance of the anode and device. At this stage of our work, the material stability was not good enough, perhaps due to the carbon materials destroyed at above 500 °C after long-term operation. Therefore, by incorporating other materials into MO-SDC it is expected that continued work will lead to better properties in the anode materials.

4. Conclusions

In this work, it was found that the sintering temperature of a single cell strongly influenced the performance of the anode materials with or without carbons. A suitable sintering temperature was 700 °C. The relatively higher electrochemical performance of the VGCF-MO-SDC anode material was attributed to the improvement of electron conductivity by adding carbon. A novel 1.25%VGCF-MO-SDC anode material was developed, which had the highest power density of 0.326 W cm^{-2} and which worked in LTSOFC devices with

H₂ as fuel. The calcination temperature of MO–SDC dry gel impacted the performance of 1.25 wt.%VGCF–MO–SDC and a power density of 0.337 W cm⁻² was achieved when the gel was calcined at 550 °C for 1 h. The anode material also worked well when fed with methanol gas. Compared with the 1.0 wt.%AC–MO–SDC anode, they both achieved 0.253 W cm⁻² power densities, but the VGCF containing anode worked better in the medium current density range. Unfortunately, a carbon deposit was found in the off-gas.

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