Sr₂Fe_{2-x}Mo_xO_{6-δ} perovskite as an anode in a solid oxide fuel cell: Effect of the substitution ratio

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Abstract:

Double perovskite, Sr₂Fe_{2-x}Mo_xO_{6-δ} (SFMO), as an anode material of the solid oxide fuel cell (SOFC) exhibits excellent performance. The effects of the substitution ratio of Mo on its properties and electro-catalytic activity are examined. **The SFMO anode shows a porous structure with a pore size of several micrometers.** Using hydrogen and dry methanol as the fuels, the single cell with the SFMO anode with x between 0.4 and 0.6 gives the maximum power outputs of 541 and 387 mW cm⁻² at 1073 K, respectively. The electro-catalytic activity of SFMO anodes exhibits an order of Sr₂Fe_{1.4}Mo_{0.6}O_{6-δ} > Sr₂Fe_{1.5}Mo_{0.5}O_{6-δ} > Sr₂Fe_{1.6}Mo_{0.4}O_{6-δ}. However, the overall conductivity of SFMO displays a reverse order. With the increase of the Mo content, the surface Fe²⁺/Fe³⁺ ratio increases regularly, but the Mo⁵⁺/Mo⁶⁺ ratio shows a peak in Sr₂Fe_{1.5}Mo_{0.5}O_{6-δ}. It is concluded that the electro-activity of the SFMO anodes for the electro-oxidation of hydrogen and methanol is not limited by their conductivity, but their surface Fe²⁺/Fe³⁺ redox couple.

Key Words: Solid oxide fuel cell; Perovskite anode; Redox couple; Methanol

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1. Introduction

The utilization of perovskite materials as anode catalysts in solid oxide fuel cells (SOFCs) fed with carbon-containing fuels becomes an interesting topic recently [1-6]. With a general formula of ABO_3 , perovskite materials include various oxides with different A and B metals, and their A and B sites can be further doped by other metals [7]. Compared to nickel based anode catalysts, perovskite materials have a great potential in coke tolerance [8-10]. For perovskite, the electronic conductivity and the surface composition have been taken as the most significant properties for its performance as the anode in SOFCs [3,10,11]. Ozkan *et al.* found that the activity of $La_{0.6}Sr_{0.4}FeO_3$ was strongly influenced by doping Co in it [12]. Bossche and McIntosh reported that the doping of Co and Ni in $La_{0.75}Sr_{0.25}Cr_{0.5}Mn_{0.4}X_{0.1}O_{3-\delta}$ (X=Co, Fe and Ni) enhanced the activity, while the doping of Fe had a negative effect [13]. Improvement of the SOFC performance was also reported with coating an additional electronic conductor on the surface of the $La_{0.75}Sr_{0.25}Cr_{0.5}Mn_{0.5}O_{6-\delta}$ (LSCM) anode, which had a low electronic conductivity, *i.e.* 1.5 S cm^{-1} in 5 % H_2 -95 % Ar atmosphere [9,10].

$Sr_2Fe_{2-x}Mo_xO_{6-\delta}$ (SFMO) has been recognized as a good anode material because it shows a high electro-catalytic activity and reasonable tolerance to coking [5,14]. With hydrogen as the fuel and Sr_2FeMoO_6 as the anode material, a single cell supported with $La_{0.6}Sr_{0.4}Ga_{0.8}Mg_{0.2}O_{3-\delta}$ (LSGM) electrolyte exhibited a peak power output (P_p) of 600 mW cm^{-2} at 1073 K [5,10]. The P_p faded only 0.7 % after 20 discharging cycles with hydrogen as

the fuel [5]. In our previous work, $\text{Sr}_2\text{Fe}_{1.5}\text{Mo}_{0.5}\text{O}_{6-\delta}$ anode showed the ability to avoid carbon formation under the open circuit condition with feeding methanol for 3 h [14]. Recently, $\text{Sr}_2\text{Fe}_{1.5}\text{Mo}_{0.5}\text{O}_{6-\delta}$ has been used as both anode and cathode materials in a symmetrical configuration, exhibiting not only chemical compatibility with the electrolyte but also remarkable electrocatalytic activity for both oxygen reduction and fuel oxidation [15]. Hou *et al.* partially replaced Mo in SFMO with Nb as the cathode of a SOFC, and obtained a maximum power density of 1.1 W cm^{-2} at 800°C [16].

Previous works suggest that B site metals in SFMO influence the catalytic activity [5,17]. However, the relationship between the activity and the properties of the material, especially the conductivity and the surface composition, is still unclear [18]. In this work, SFMO samples with different Mo contents are used as anodes in single cells fed with hydrogen and dry methanol. Effects of the substitution ratio on properties of anodes and performances of single cells are examined and discussed.

2. Experimental

2.1. Material preparation

SFMO powder was prepared by a solid-state reaction technique. Stoichiometric SrCO_3 , Fe_2O_3 and MoO_3 (all materials were 99.99 % from Guangfu fine chemical, Ltd.) were thoroughly mixed and then calcined at 1173 K for 10 h. The powder was pelletized at 200 MPa and annealed at 1523 K in air for 5 h. The pellets were ground and ball milled into very

fine powder. $\text{Sr}_2\text{Fe}_{1.6}\text{Mo}_{0.4}\text{O}_{6-\delta}$, $\text{Sr}_2\text{Fe}_{1.5}\text{Mo}_{0.5}\text{O}_{6-\delta}$ and $\text{Sr}_2\text{Fe}_{1.4}\text{Mo}_{0.6}\text{O}_{6-\delta}$ are denoted as sample 1, 2 and 3, respectively. The preparation details of $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{Co}_{0.8}\text{Fe}_{0.2}\text{O}_{3-\delta}$ (BSCF) cathode and LSGM electrolyte materials have been described elsewhere [19, 20].

2.2. Characterization

The powder X-ray diffraction (XRD) patterns of all three samples were recorded at room temperature using a D/max 2500 v/pc instrument (Rigaku Corp. Japan) with $\text{Cu-K}\alpha$ radiation, 40 kV and 200 mA, at a scanning rate of 5° min^{-1} . The surface property of fresh samples was measured with a PHI 1600 X-ray Photoelectron Spectroscopy (XPS) with $\text{Mg-K}\alpha$ radiation. Conductivities of samples in the hydrogen atmosphere were measured with a direct current four-probe method by an electrochemical workstation (VersaSTAT 3, Ametek) at 1023 K and 1073 K, respectively. The surface morphologies of the anodes were characterized by a Hitachi S-4800 scanning electron microscope (SEM).

2.3. Single fuel cell fabrication

The electrolyte-supported single cell was fabricated with a screen-printing technique. LSGM powder was pressed into a pellet with a diameter of 13 mm under 200 MPa and sintered at 1723 K for 20 h. The thickness of the obtained pellet was 300 μm . SFMO and BSCF powders were both mixed with a binder (V006, Heraeus Ltd.) to make into slurries. SFMO slurry was firstly coated on one side of the electrolyte and sintered at 1423 K in air for 1 h. BSCF slurry was then screen-printed on the other side of the electrolyte and sintered at

1273 K in air for 1 h. As indicated in our previous paper [5], the thicknesses of the sintered anode and cathode are around 30 μm and 50 μm , respectively. Ag paste was coated on both sides as the current collector. The effective surface area of the cell in each side was 0.5 cm^2 .

2.4. Test of the cell

The single cell was tested at 1023 K and 1073 K under atmospheric pressure with a homemade setup. Hydrogen was firstly used as the fuel. Then the fuel was switched to pure methanol, which had been gasified at 423 K before fed into the anode chamber through an alumina tube. The flow rates of both fuels were 80 ml min^{-1} (STP). Oxygen with a flow rate of 100 ml min^{-1} (STP) was used as the oxidant. The fuel cell *I-V* characteristics were measured by an IT-30 electronic load (Ningbo BaTe Technology Co., Ltd., China). For a typical measurement, the cell was stabilized under the operating temperature until reaching a constant open circuit voltage (OCV) value. Then the cell voltage was varied from OCV to a selected voltage with a stepwise of 50 mV and a holding time of 20 s for each measured step to get a stable performance. The measurement was done when the peak power output appeared. To distinguish catalytic effects of Ag paste and SFMO, a blank cell with only Ag paste as the anode was also tested.

The electrode polarization of the single cell was investigated by electrochemical impedance spectroscopy (EIS) with an electrochemical workstation (VersaSTAT 3, Ametek) at an open circuit condition with a frequency range of 10^4 -1 Hz and an amplitude of 10 mV.

3. Results and discussion

3.1. Characterization

The X-ray diffraction (XRD) results of all samples (Fig. 1) reveal a pure double-perovskite structure (JCPDS 70-4092). No other phases can be observed from the XRD patterns, implying the stability of the SFMO in an oxidative atmosphere since the samples were annealed in air. $\text{Sr}_2\text{Fe}_{1.5}\text{Mo}_{0.5}\text{O}_{6-\delta}$ also shows a good stability in a reducing atmosphere reported in our previous work [14]. A tiny expansion of unit cells is observed with the increase of Mo content as listed in Table 1. Since the ionic radii of Fe^{2+} (0.78 Å) and Fe^{3+} (0.65 Å) are larger than those of Mo^{5+} (0.61 Å) and Mo^{6+} (0.59 Å) [18], the expansion of the unit cell is most likely attributed to the transition of the cell structure driven by the variation of the metal centers [21].

The SEM images (Fig. 2) exhibit that the microstructures of the three anode surfaces are similar, with a sintered particle diameter of around 1 μm. The anode layer with a thickness of about 30 μm adheres to the electrolyte layer tightly. It is obvious from the XRD and SEM results that the microstructures of the sintered anodes are similar, and it is reasonable to assume that they will not lead to any significant differences in the cell power outputs.

The chemical states of Fe and Mo elements on SFMO surfaces at room temperature are obtained from XPS and determined by curve fitting of Fe-2p and Mo-3d core level spectra. Take sample 2 for instance (Fig. 3), the Fe-2p core level spectrum consists of Fe-2p 3/2 and

Fe-2p 1/2 excitations. The deconvoluted peaks at 709.2 eV for Fe-2p 3/2 and 723.0 eV for Fe-2p 1/2 are at 2⁺ valence, while peaks at 710.9 eV for Fe-2p 3/2 and 724.7 eV for Fe-2p 1/2 peaks are at 3⁺ valence. Similar to Fe atoms, surface Mo atoms are in the pairs of Mo⁵⁺/Mo⁶⁺ according to the core level spectrum of Mo-3d 5/2 and Mo-3d 3/2 shown in Fig. 3 (b). The binding energies are 230.9 eV and 234.6 eV for Mo⁵⁺ and 231.9 eV and 235.2 eV for Mo⁶⁺. Atom ratios of Fe and Mo in different valences and the calculated oxygen stoichiometry for all the three samples are summarized in Table 2. The ratio of Fe²⁺ rises with the increase of the Mo content, whereas Mo⁵⁺ reaches the highest content in sample 2. As the Mo content is increased (from 0.4 to 0.6), more Fe³⁺ are reduced to Fe²⁺ to keep electro-neutrality. The result is in agreement with ref. [5, 17] and it suggests that the surface redox couples strongly depend on the composition of SFMO.

3.2. Electrical conductivity

Electrical conductivities of all SFMO samples increase with the increase of the temperature in a reducing atmosphere (Fig. 4), which indicates a semiconductor property. The overall conductivity, which decreases obviously with the increase of the Mo content, is the combination of ionic and electronic conductivities of the sample, and the ratio between them is not clear based on existing results. However, since the ionic conductivity of SFMO is generally less than 0.1 S cm⁻¹ in the testing condition, the electrical conductivity of SFMO is dominated by the electronic conductivity. The electronic conductivity of SFMO derives from

the formation of Fe-O-Fe bond that forms the pathways for the movement of the electrons or electron holes [22]. $\text{Sr}_2\text{Fe}_{1.5}\text{Mo}_{0.5}\text{O}_6$ was reported to form the percolation path of Fe-O-Fe in both hydrogen and air atmospheres by Liu *et al.* [23]. It can be expected that the decrease of the Fe content in SFMO reduces the amount of Fe-O-Fe pathways and consequently leads to a drop in the electronic conductivity. Compared to the previous reports, the conductivities of SFMO obtained from the solid-state reaction is similar with those from the combustion method [16, 23].

3.3. Performance of the fuel cell

Since a thin layer of silver is coated on SFMO anodes as the electrical conductor, a single cell with the anode without SFMO but only Ag layer is built to test the contribution of Ag to the power output. With hydrogen as the fuel, such a “blank” cell exhibits an open circuit potential (OCP) of 0.8 V and P_p of 12 mW cm^{-2} at 1073 K (Fig. 5). Such a performance is much lower than those of normal cells that will be shown later, implying a poor catalytic activity of Ag used in this work. Therefore, it is reasonable to neglect the contribution of Ag layer to the power output of the tested normal cell.

The performances of single cells with SFMO anodes at 1023 K and 1073 K are shown in Fig. 6. With H_2 as the fuel, P_p of cells with sample 1, 2 and 3 as anodes are 380, 385 and 387 mW cm^{-2} at 1023 K and 482, 508 and 541 mW cm^{-2} at 1073 K, respectively. It is obvious that with the increase of the temperature, the power output increases significantly for all the three

cells. At 1023 K, only small differences in the power output for the three cells are observed. It is contrasted that at 1073 K the power output increases obviously with the increase of the Mo content. Since the polarization of BSCF cathode is quite low above 600 °C, a reasonable explanation is that at 1023 K the performance of the cell is not controlled by the fuel oxidation reaction, but by the transfer of the oxygen ion in the thick electrolyte layer. When the temperature increases to 1073 K, the transfer in the electrolyte is much faster, and the influence of the anode reacting rate on the cell performance becomes apparent. When the cells are fed with methanol, the maximum power densities are 205, 297 and 341 mW cm⁻² at 1023 K and 382, 395 and 415 mW cm⁻² at 1073 K, for cells with sample 1, 2 and 3 as anodes, respectively. With the increase of the Mo content, the power output increases obviously at both 1023 K and 1073 K, indicating that the anode property has a significant impact on the cell performance.

Noticeably, the OCP of the cells with H₂ as the fuel is stable at 1.10 ± 0.02 V, while it varies between 0.92 V to 1.10 V when the fuel is changed to methanol. The OCP variation of the cells fed with methanol implies that the compositions of the gas in three anode chambers are different due to the partial decomposition of methanol. With dry methanol as the fuel, reactions 1-6 take place in the anode:

As suggested by the mass spectra results in our previous work [14], both thermal decomposition and catalytic decomposition of methanol occurred at OCP at 1023 K, resulting in about 20 % and 15 % volume conversion ratios of methanol, respectively. CO_2 was also observed with a small amount, suggesting the appearance of the direct electro-oxidation and/or the reforming reactions. Based on the previous result [14], it is expected that the fuel gas in anode chamber is a mixture of 40% H_2 , 40% CH_3OH , 20% CO and a small amount of CO_2 at 1023 K. It is hard to distinguish the contributions of the electrochemical oxidations of the three fuels to the power output exactly. However, it is widely accepted that the electro-oxidation of hydrogen is the most facile one among them [1-6]. Therefore, it is reasonable to relate the power output with the partial pressure of hydrogen when the cell is fed with methanol. For the cells fed with hydrogen, it is clear that the increase of Mo content in SFMO benefits the power output at 1073 K, as shown in Fig. 6. Consequently, two apparent factors, *i.e.*, the partial pressure of hydrogen in the anode chamber and the Mo content in SFMO, determine the power output of the cells fed with methanol.

3.3.2. Impedance spectroscopy

EIS results of single cells with SFMO anodes are shown in Fig. 7. The intercepts of the semicircle at high and low frequency regions on Z_{re} axis are considered as the ohmic resistance and the overall resistance of the cell, respectively [24]. The difference between these two values is regarded as the reacting resistance of the electrode. The ohmic resistance was deducted in Fig. 7 for better comparison. The semicircle contains both anode and cathode reacting processes, which are difficult to distinguish from each other. However, since the cathodes are identical in all cells, the difference between the semicircles mainly comes from the different anodes. As summarized in Table 3, a regular decrease of the reacting resistance of the electrode with the increase of Mo content in SFMO anode is observed in both cells fed by hydrogen and methanol. The trend is consistent with that of the cell performance presented in Fig. 6. It is also shown in Fig. 7 that with the increase of the temperature, the semicircles for both fuels at 1073 K are obviously smaller than the corresponding ones at 1023 K, indicating the decrease of the reacting resistance with the increase of the temperature.

3.4. General discussion

An increase of the Mo/Fe ratio in SFMO materials leads to an improvement of their performances as anodes of SOFCs with hydrogen or methanol as the fuel. It is well known that a higher mixed ionic-electronic conductivity of an anode material would lead to a better performance due to the larger TPB area, the increased surface oxygen exchange rate and the reduced ohmic resistance [1,2]. However, in this study, the performance of the single cells and

the conductivity of SFMO have opposite trends with the increase of the Mo/Fe ratio, implying that the conductivity of the anode is not the main factor affecting the cell performance.

The EIS results present a reduced anode reacting resistance, *i.e.*, an enhancement of the catalytic activity, with the increase of the Mo/Fe ratio in SFMO anodes. Since the crystal structure and pore structure are quite similar for all the SFMO samples tested, these two features of SFMO are not the main reasons for the difference of the catalytic activity. We propose that the activity of SFMO is related to the $\text{Fe}^{2+}/\text{Fe}^{3+}$ couple, especially the amount of Fe^{2+} . It agrees with the common knowledge that the activity of perovskite depends on its B site metals [17]. Moreover, the $\text{Fe}^{2+}/\text{Fe}^{3+}$ pair is reported to play an important role in the oxidation of propane [25]. The substitution of Fe with Mo could generate or stabilize Fe^{2+} ion, and SFMO with a higher Fe^{2+} content is expected to possess a higher activity. This assumption is also supported by one previous report, in which a cell with a similar configuration with $\text{Sr}_2\text{FeMoO}_{6-\delta}$ anode presents a P_p of 600 mW cm^{-2} with hydrogen as the fuel at 1073 K, higher than 541 mW cm^{-2} for the cell with $\text{Sr}_2\text{Fe}_{1.4}\text{Mo}_{0.6}\text{O}_{6-\delta}$ anode in this work [5]. However, the enhancement of the Mo content leads to a reduced stability of the SFMO in oxidizing atmospheres, which increase the complexity of the fabricating procedure. Therefore, a careful balance between the activity and the stability of SFMO is still needed.

4. Conclusion

Effects of the substitution ratio of Mo in SFMO on its properties and its electro-catalytic

activity as the anode material of SOFCs have been studied. With an increase of the Mo/Fe ratio, the electrical conductivity of SFMO decreases. However, with the increase of the Mo content, the electro-catalytic activity of SFMO improves, leading to an enhanced performance of the single cell with H₂ or methanol as the fuel. The substitution of Fe by Mo brings an increase of the amount of Fe²⁺ ions and surface Fe²⁺/Fe³⁺ couples, which is the reason of the improved activity of SFMO. These results provide basic insights into the utilization of carbon-containing fuels and potentially provide promising ways for the optimization of perovskite anode materials.

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Table 1. Cell parameters of SFMO for the cubic model.

Table 2. Surface compositions (percentages of Fe and Mo redox couples and the oxygen stoichiometry) of SFMO samples obtained from XPS spectra at room temperature.

Table 3. Electrode reacting resistances of the single cells with SFMO anodes under open circuit condition.

Figure 1. XRD patterns of $\text{Sr}_2\text{Fe}_{2-x}\text{Mo}_x\text{O}_{6-\delta}$ samples at room temperature.

Figure 2. SEM images of the as-prepared anodes corresponding to (a) sample 1, (b) sample 2, (c) sample 3 and (d) cross-sectional image of the LSGM electrolyte/ $\text{Sr}_2\text{Fe}_{1.5}\text{Mo}_{0.5}\text{O}_{6-\delta}$ anode.

Figure 3. XPS curves for fresh $\text{Sr}_2\text{Fe}_{1.5}\text{Mo}_{0.5}\text{O}_{6-\delta}$; (a) Fe and (b) Mo.

Figure 4. Electrical conductivities of SFMO samples measured in H_2 . (■) sample 1; (●) sample 2; (▲) sample 3.

Figure 5. The performance of the single cell with silver as the anode. Fuel: hydrogen; T: 1073 K.

Figure 6. Performance of single cells with different SFMO anodes, (a) sample 1 as the anode; (b) sample 2 as the anode; (c) sample 3 as the anode.

Figure 7. Impedance spectra of single cells at open circuit condition. The ohmic resistance is deducted in all the cases. (a) sample 1 as the anode, (b) sample 2 as the anode, (c) sample 3 as the anode, (d) equivalent circuit. Frequency range: 10^4 -1 Hz.

Table 1. Cell parameters of SFMO for the cubic model.

Sample	a (Å)	b (Å)	c (Å)	Volume (Å³)
1	7.331	7.331	7.331	394.0
2	7.349	7.349	7.349	396.9
3	7.360	7.360	7.360	398.7

Table 2. Surface compositions (percentages of Fe and Mo redox couples and the oxygen stoichiometry) of SFMO samples obtained from XPS spectra at room temperature.

Sample	Fe²⁺	Fe³⁺	Mo⁶⁺	Mo⁵⁺	O_x
1	0.48	0.52	0.42	0.58	5.10
2	0.52	0.48	0.35	0.65	5.28
3	0.59	0.41	0.47	0.53	5.35

Table 3. Electrode reacting resistances of the single cells with SFMO anodes under open circuit condition.

Anode	Electrode reacting resistance /Ω			
	1023 K, H₂	1023 K, CH₃OH	1073 K, H₂	1073 K, CH₃OH
1	0.56	0.94	0.43	0.52
2	0.39	0.61	0.27	0.40
3	0.32	0.42	0.23	0.33

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Graphical abstract