NdFeO$_3$ as anode material for S/O$_2$ solid oxide fuel cells

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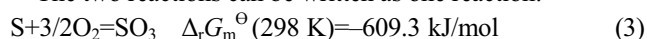
Abstract: Sulfur-oxygen solid oxide fuel cells (S/O$_2$-SOFCs) can improve the utilization ratio of energy via converting the combustion heat of sulfur into electrical energy directly, and sulfur trioxide which is an intermediate in sulfuric acid industry can be obtained directly via S/O$_2$-SOFCs. The anode material NdFeO$_3$ was prepared via sol-gel method, the phase stability of NdFeO$_3$ in sulfur vapor or sulfur dioxide atmosphere was investigated. The single cell, consisting of NdFeO$_3$-SDC/SDC/LSM-SDC structure, was fabricated by the screen-printing method and tested by the home-built equipment with sulfur vapor or sulfur dioxide as the fuel. As indicated by X-ray diffraction (XRD) analysis, NdFeO$_3$ was stable in sulfur vapor or sulfur dioxide atmosphere at 800 ºC, the phase composition of the mixture of NdFeO$_3$ and SDC (Sm doped CeO$_2$) did not change after the mixture was calcined at 800 ºC for 4 h. The transmission electron microscope (TEM) photograph revealed that the average grain size of NdFeO$_3$ powder was about 80 nm. With sulfur vapor or SO$_2$ as the fuel, the maximum open circuit voltages (OCVs) of the single cell were 409 mV at 620 ºC and 474 mV at 650 ºC, respectively; the maximum power densities of single cell were 0.154 mW/cm^2 at 620 ºC and 0.265 mW/cm^2 at 650 ºC, respectively.

Keywords: NdFeO$_3$; anode; sulfur; solid oxide fuel cell; rare earths

Sulfuric acid is an important chemical raw material, and the annual output of sulfuric acid in China reached 70 millions tons in 2010[1]. Sulfur is a main raw material for the production of sulfuric acid, about 50% of the sulfuric acid output in China was produced by using sulfur as the raw material in 2010. The preparation process of sulfuric acid using sulfur as the raw material is closely related to the following two reactions:

$$1/nS_n+O_2=SO_2 \qquad (1)$$
$$SO_2+1/2O_2=SO_3 \qquad (2)$$

The two reactions can be written as one reaction:

$$S+3/2O_2=SO_3 \quad \Delta_rG_m^\Theta(298\ K)=-609.3\ kJ/mol \qquad (3)$$

At present, the heat energy given by the reaction (3) cannot be utilized totally, because most of the combustion heat of sulfur is lost in the form of heat. Nowadays, solid oxide fuel cells (SOFCs) are attracting more and more attention due to their merits, such as high efficiency (60%) compared with the traditional gas turbine power plants (30%–40%) and little pollution[2,3]. Although SOFCs can operate with any fuel in theory, the present SOFCs operate with pure hydrogen as fuel. However, hydrogen is obtained by steam reforming of methane[4,5] and water electrolysis. Compared with the hydrogen price[6], the price of sulfur[7] is cheap. If S/O$_2$-SOFC is developed, it can convert sulfur into sulfur trioxide directly and transform the combustion heat of sulfur into electricity energy. If 1 t of sulfur is used as the fuel, about 53000 kWh of electricity energy can be generated by S/O$_2$-SOFC in theory and the resultant sulfur trioxide can be used for producing sulfuric acid.

The structure of S/O$_2$-SOFC is anode/SDC/LSM-SDC. The main difference between the S/O$_2$-SOFC and the other kinds of SOFCs is the anode materials. Cowin et al.[8] reported that it is necessary for anode materials to have good performance in fuel at working temperature, such as good stability, catalytic activity for fuel oxidation, high ion conductivity, good electronic conductivity, chemical stability to contacting components and matched thermal expansion coefficient (TEC) to contacting components. Although the SOFCs have been developed for a long time, as far as we known, the SOFCs using sulfur as the fuel and its anode materials with good performance are rarely reported. Zhu et al.[9,10] studied preliminarily the performance of sulfur/oxygen SOFC using Ca or Mg doped LaCrO$_3$ as the anode material. Joseph et al.[11] reported that Fe-substituted LaCrO$_3$ could be used as the anode material for methane SOFC. Marti et al.[12] reported that AMnO$_{3+x}$ and AFeO$_{3+x}$ (A=La, Pr, Nd and Cd) perovskite-type oxides have catalytic activity for methane combustion and AFeO$_{3+x}$ perovskite are more stable than the manganites thermally. In our present work, the performance of

S/O₂-SOFCs using $NdFeO_3$ as anode catalyst was studied preliminarily.

1 Experimental

1.1 Preparation of anode $NdFeO_3$ powder and electrolyte $Ce_{0.8}Sm_{0.2}O_{1.9}$ (SDC) ceramic

The $NdFeO_3$ powder was prepared via sol-gel method according to the literatures[13,14]. Stoichiometric $Fe(NO_3)_3 \cdot 9H_2O$ and Nd_2O_3 were weighed and dissolved in nitric acid solution. Citric acid ($n_{nitric\ acid} : n_{metal\ ion} = 1:1$) was added under stirring. Ammonium hydroxide was used to adjust the pH to 7. The resulting solution was heated slowly to evaporate water until the viscous gel formed; the gel was then milled and heated at 700 ºC for 2 h.

The SDC powder was prepared via co-precipitation method[15]. The powder was dry-pressed at 200 MPa into a cylinder of 25 mm diameter to form 1 mm thick SDC pellets, and sintered at 1200 ºC for 6 h with a heating rate of 3 ºC/min[15]. The density of the sintered SDC pellet was measured by the Archimedes method.

1.2 Characterization of anode material

The difference thermal analysis (DTA) and thermal thermogravimetry (TG) of as-prepared gel were conducted in air at a heating rate of 5 ºC/min. The $NdFeO_3$ powder was characterized by an X-ray diffractometer (XRD) (D/max-rA, Rigaku) with Cu Kα radiation in the range of 20º–80º. The chemical stability between $NdFeO_3$ and SDC was tested by calcining the mixture of $NdFeO_3$ and SDC at 800 ºC for 4 h and analyzing the phase composition of the mixture. The microstructure of $NdFeO_3$ powder was observed with a transmission electron microscope (TEM) (JEM-100CX II). The $NdFeO_3$ powder was exposed to sulfur vapor or SO_2 at 800 ºC for 2 h to study the stability of $NdFeO_3$ anode material in sulfur vapor or SO_2.

1.3 Fabrication and testing of single cell

The electrode slurries were prepared according to the following procedure: the mixture of SDC powder, electrode material and absolute ethanol was ball-milled for 3 h until ethanol volatized. The electrode slurries was continually ground for 2 h after ethyl cellulose terpineol solution ($w=6\%$) was added. The anode and cathode slurries were printed on both sides of SDC electrolyte, respectively. Then the cells were calcined at 1200 ºC for 2 h. The cathode area (1 cm⁻²) was used to calculate power density. The composition of the electrode slurries is listed in Table 1.

The home-built equipment for testing the performances of single cell is shown in Fig. 1. The temperature of tube furnace I must be higher than the boiling point of sulfur (444 ºC) if sulfur is used as fuel. N_2 is the carrier gas of sulfur vapor. SO_2 gas could be introduced into the cell directly at a flow rate of 100 ml/min. The temperature of tube furnace II is the working temperature of cells.

Table 1 Composition of electrode slurries

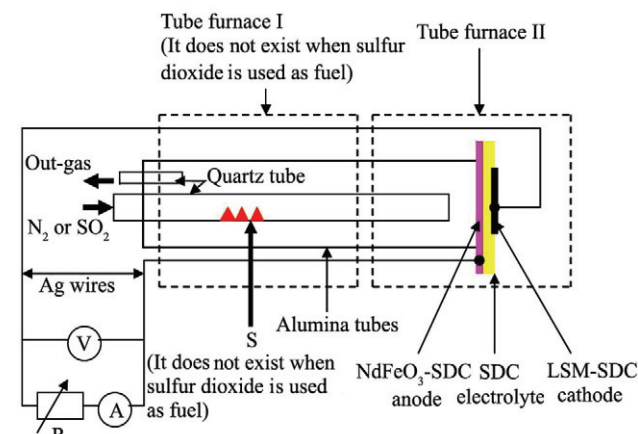| Slurry component	Anode slurry	Cathode slurry
SDC	1 g	1 g
$NdFeO_3$	1 g	–
$La_{0.8}Sr_{0.2}MnO_3$ (LSM)	–	1 g
6% ethyl cellulose+94% terpineol	3 g	3 g
Ethanol	20 ml	20 ml

Fig. 1 Home-built equipment of single cell

2 Results and discussion

2.1 Thermoanalysis of dry gel

Fig. 2 presents the TG curve and DTA curve of the gel. The mass loss occurring between 90 and 132 ºC results from the release of adsorbed water and hydrated water, and two endothermic peaks appear in DTA curve at 90 and 132 ºC. A sharp exothermic peak exists between 132 and 163 ºC, which is due to the decomposition of citric acid ($C_6H_8O_7 \rightarrow H_2O + CO_2$). As shown in Fig. 2, the mass of the sample decreases sharply between 132 and 163 ºC. A small exothermic peak at 320 ºC is attributed to the decomposition of nitrate[16]. A tiny mass loss occurring between 640 and 660 ºC is due to the phase-crystallization step. No more mass loss was observed in the temperature range from 660 to 700 ºC corresponding to crystallization of $NdFeO_3$.

2.2 Phase stability and microstructure of anode powder

The XRD patterns of the samples are shown in Fig. 3. The XRD pattern of $NdFeO_3$ before exposure to sulfur vapor or SO_2 (shown in Fig. 3 (1)) suggests that $NdFeO_3$ was well
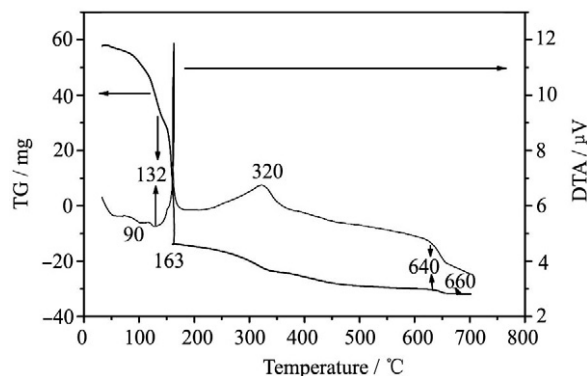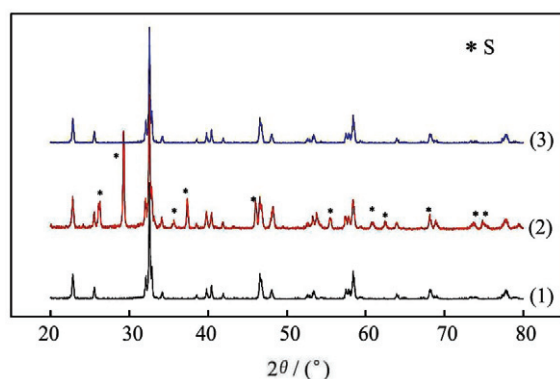

Fig. 2 TG and DTA curves for the gel

Fig. 3 XRD patterns of NdFeO₃ before exposure to S(g) or SO₂ (1),
after exposure to S(g) at 800 ºC for 2 h (2) and after exposure
to SO₂ at 800 ºC for 2 h (3)

crystallized. The chemical stability to fuel is of great impor-
tance for SOFC anode materials[17]. Fig. 3 (2) and (3) show
the patterns of NdFeO₃ powder after exposure to sulfur va-
por or SO₂ at 800 ºC for 2 h, respectively. Compared with
the XRD pattern in Fig. 3 (1), there are no additional diffrac-
tion peaks besides the peaks of sulfur (shown in Fig. 3 (2)).
It indicates that the stability of NdFeO₃ powder in sulfur va-
por or SO₂ at 800 ºC is good. As shown in Fig. 4, the XRD
pattern of the mixture of NdFeO₃ and SDC have hardly
changed after calcining at 800 ºC for 4 h. It reveals that there
is no chemical reaction between NdFeO₃ and SDC at 800 ºC.
It can be observed from the TEM photographs of NdFeO₃
powder (shown in Fig. 5) that the average grain size of
NdFeO₃ powder is about 80 nm. The aggregation of grains
may be attributed to the high temperature of calcining[18].

2.3 Performance of a single cell

Fig. 6 shows the temperature dependence of the OCVs for
a single cell with sulfur vapor or SO₂ as fuel. It is clear that
the OCVs increase with the increase of temperature and
reach the maximum value of 409 mV at 620 ºC and 474 mV
at 650 ºC using sulfur vapor or SO₂ as fuel, respectively. The
OCVs decrease when the working temperature is higher than
the optimum temperature. When the operating temperature is
low, the OCVs are low because of low mobility of oxygen
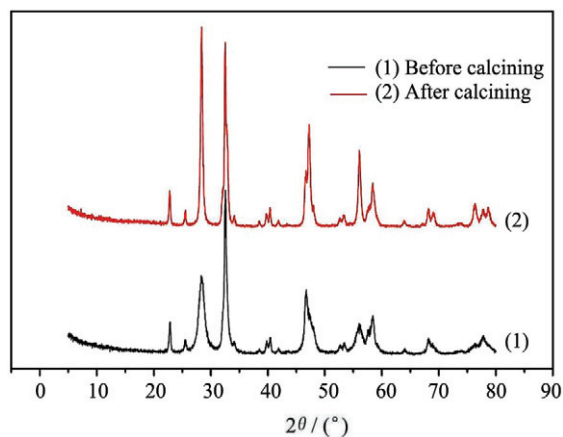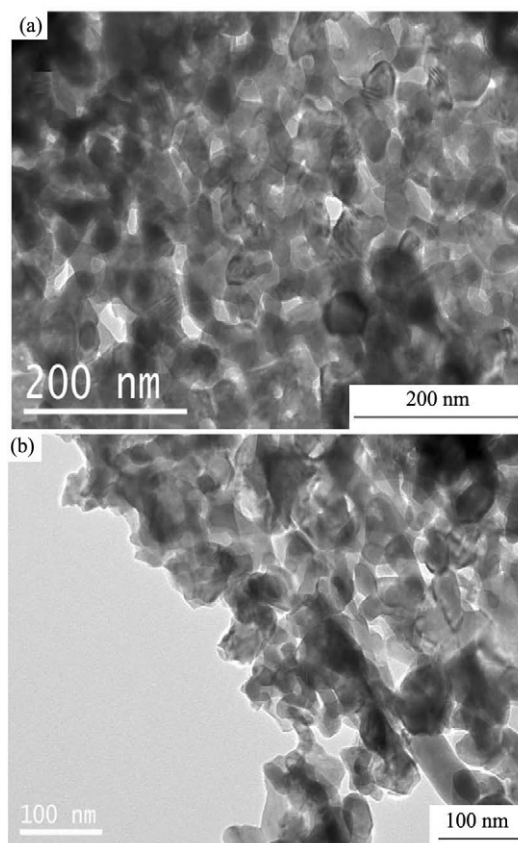ion in SDC electrolyte and low vapor pressure of sulfur va-
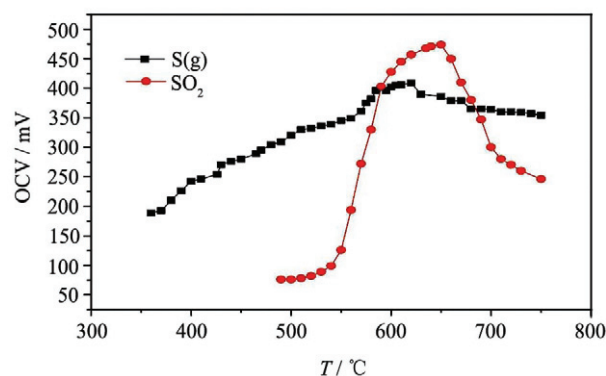

Fig. 5 TEM micrographs of NdFeO₃ powder

Fig. 6 Temperature dependence of the OCVs for single cells

por (sulfur as fuel)[19,20]. The fall of OCVs at high tempera-
ture (higher than 650 ºC) may result from the following two
reasons: (1) Instability of Ag current collector in sulfur vapor
or SO₂; (2) Theoretical reversible potential ($E_{(t)}$) of the cell is
not determined by Nernst equation, but by entropy change
($E_{(t)} = E_o + \Delta S * (T - T_o)$). Hence, current collectors with good
stability for S/O₂ SOFC are being studied in our group.

The performance of the single cell using sulfur vapor or
SO₂ as fuel is shown in Fig. 7. The maximum power densi-
ties of the single cell using sulfur vapor or SO₂ are 0.154
mW/cm² at 620 ºC and 0.265 mW/cm² at 650 ºC, respec-
tively. The low power density, which impedes application of
S/O₂ or SO₂/O₂-SOFC, could be attributed to high ohm re-
sistance of electrolyte, low electrical conductivity (most of
electric energy is lost on the internal resistance of cell) and
non-porous microstructure of NdFeO₃ (the sulfur vapor or
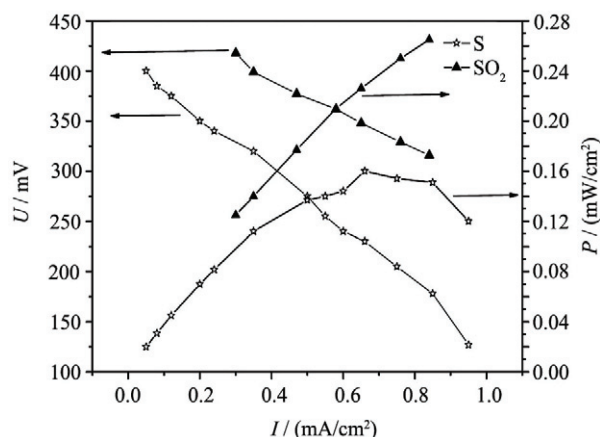SO₂ molecule is hard to diffuse into non-porous anode mate-

Fig. 4 XRD patterns of the mixture of NdFeO₃ and SDC before cal-
cining (1) and after calcining at 800 ºC for 4 h (2)

Fig. 7 Cell performance of a single cell (NdFeO₃-SDC/SDC/LSM-SDC)

rial)[8]. However, if anode material $NdFeO_3$ is doped with some other elements in A-site or B-site, porous anode material is prepared and anode-supported single cell using doped-$NdFeO_3$ as anode is assembled, the performance of cell could be improved[21]. Hence, $NdFeO_3$ will be a promising candidate for S/O₂-SOFC and SO₂/O₂-SOFC anode and further investigation on this subject is now being done by our group.

3   Conclusions

$NdFeO_3$ powder was prepared via sol-gel method at 700 ºC for 2 h. A drastic decomposition reaction of citric acid around 160 ºC could be seen from the TG/DTA curves. The pure phase was formed at the temperature of 660 ºC. The average grain size of $NdFeO_3$ powder was about 80 nm. The $NdFeO_3$ anode material exhibited good stability in sulfur vapor or SO₂ at 800 ºC. There was no chemical interaction between $NdFeO_3$ and SDC at 800 ºC. With sulfur vapor or SO₂ as fuel, the maximum open circuit voltages of single cell were 409 mV at 620 ºC and 474 mV at 650 ºC, respectively; the maximum power densities of single cell were 0.154 mW/cm² at 620 ºC and 0.265 mW/cm² at 650 ºC, respectively. Although the power densities were not ideal, further studies are in progress, and the power density of the single cell can be further improved. $NdFeO_3$ is a possible candidate for S/O₂ and SO₂/O₂-SOFCs anode.

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