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Compact solid oxide fuel cells and catalytic reformers based on microtubular membranes

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Graphical Abstract

Air CH4	C2-	products
Micr me	rotubular mbrane	

Highlights

- Compact catalytic reformers of methane have been successfully fabricated and tested.
- Proposed BSCFW2 perovskite is promising compound for a methane conversion.
- A crack-free dense electrolyte layer (20 µm) was prepared by co-firing method.
- Microtubular solid oxide fuel cell have been successfully fabricated and tested.

Abstract

AC heated oxygen-permeable microtubular membranes with the composition $Ba_{0.5}Sr_{0.5}Co_{0.78}W_{0.02}Fe_{0.2}O_{3-\delta}$ were used to provide catalytic reforming of methane into C₂-hydrocarbons. The methane conversion degree about 60% and acetylene yield about 27% at 1200°C was achieved. Microtubular solid oxide fuel cells based on gadolinium-doped ceria with perovskite-like cathode material composed of $Ba_{0.5}Sr_{0.5}Co_{0.75}Mo_{0.05}Fe_{0.2}O_{3-\delta}$ were prepared. The MT-SOFC demonstrates maximum power densities of 50, 100, 200 mW/cm² at 550, 600, 650 °C, respectively with humidified H₂ as fuel and ambient air as oxidant.

Keywords:

Microtubular Solid Oxide Fuel Cell (MT-SOFC); phase inversion; dip-coating; catalytic reforming; oxygen-permeable membranes.

1. Introduction

Recently, active efforts has been made to develop catalytic membrane reactors (CMR) in which separation of atmospheric oxygen with the help of oxygen-permeable (OP) membranes and catalytic conversion of hydrocarbons are combined in one reactor, which allows to significantly decrease in the prime cost of syngas [1]. In addition, OP membranes can also be used to produce pure oxygen for efficient fuel combustion in power engineering [2-4] and as cathodes for solid oxide fuel cells (SOFC) [5,6].

Recently, microtubular (MT) membranes manufactured by phase inversion method have been considered as the most promising among OP membranes. They provide not only high mechanical strength but also stability to thermocycling and electric load that ensures rapid initiation, and thin (20–50 μ m) gas-tight layer, which allows achieve high oxygen fluxes [7-11].

In this paper, we will discuss about two most promising applications of MT membranes (1) *MT catalytic reformers* based on perovskite-like Ba_{0.5}Sr_{0.5}Co_{0.78}W_{0.02}Fe_{0.2}O_{3- δ} (BSCFW2) oxide (2)MT SOFC with perovskite-like cathode material composed and of Ba_{0.5}Sr_{0.5}Co_{0.75}Mo_{0.05}Fe_{0.2}O_{3-δ} (BSCFM5) oxide. The above compounds were selected due to the following qualities. We demonstrated previously that partial substitution of cobalt in BSCF by high-valence cations (like tungsten [7,11] and molybdenum [12]) improves the functional properties of the material: causes an increase of its oxygen permeability, suppresses the polymorphous transition from cubic to hexagonal perovskite, increases the stability of the material in CO₂, which ensures the stable operation of the membrane in long-term tests.

Experimental

To obtain BSCFW2 and BSCFM5 materials [R2.1], ethanol was added into the stoichiometric mixture of the oxides (Co, Fe and W/Mo) and nitrates (Ba and Sr) in the amount of 1 ml of $C_2H_5OH / 1$ g of the mixture; then the mixture was treated in a planetary ball mill AGO-2 for 30 s. The resulting mixture was annealed at 900°C for 7 hours to remove gaseous products, then, after grinding in a mortar, the mixture was ground in the ball mill at the frequency of 1.5 r.p.s. for 48 hours. MT membranes (BSCFW2 and NiO/CGO : 60/40 [R2.3]) were obtained by means of phase inversion technique. Dried dispersed powder was mixed with the solvent (N-Methyl-2-pyrrolidone [R2.2]) and polymer binder (Polyethersulfone [R2.2]) at a ratio of 12:4:1 [6, 8]. The slurry was homogenized in a jar roller mill for 24 hours; the homogeneous mixture was subjected to several cycles of degassing. Then the resulting slurry was extruded through spinneret (Fig. 1a) to make the green bodies of OP membranes. The air-gap was in the range 5–10 mm.



Figure 1. Scheme of spinneret and dip-coater.

The resulting green bodies of MT membranes were annealed at 600°C [R2.4] in air for 2 hours, then heated at 1200°C [R2.4] in air for 6 hours. After such procedure BSCFW2 MT membranes were ready for measurements. Opposite, NiO/CGO tubes were dip-coated (Fig. 1b) in a slurry which is composed of CGO electrolyte powder; binder (Polyvinyl butyral [R2.2]), plasticizer (Dibutyl phthalate [R2.2]); dispersant (Dysperbyk-111 «BYK» [R2.2]) and solvents (Butyl glycol [R2.2]). The coatings were left to dry in air, then sintered at 1400°C for 6 h in air. After, the anode tubes with electrolyte were dip-coated in cathode slurry, which consists of BSCFM5/CGO:60/40 [R2.3] powder and organic components (similar with those of the electrolyte slurry). After dip-coated the cathode slurry, the tubes were dried in air and sintered at 1200°C for 2 h in air to complete a cell. The state of the surface was determined by the scanning electron microscope Hitachi TM–1000.

To carry out catalytic reforming of methane measurements, we used a reactor, described in detail in [11] (Fig. 2).



Figure 2. Scheme of reactor 2 for catalytic reforming measurements on AC heated MT membranes.

Pure CH₄ was used in experiment [R1.12] (F=100 ml/min). Ambient air was used as an oxygen source (F=150 ml/min). The reactor in which the BSCFW2 MT membrane (2) is fixed at the center has channels for gas input (1a, c) and output (1b, d). Channels 1a and 1b are connected with the MT membrane through polymer tubes; the connection sites are sealed by heat-shrink tubes. With the help of the deposited current-conducting (Ag) coating (3), a reliable contact between the MT membrane and the source of AC electric current (5) was provided. The temperature of the membrane was determined with the accuracy of 0.1° with the help of an IMPAC IGA 300 infrared pyrometer (4) through the window cut in the case. The window is sealed with a heat-resistant Kapton tape, which is able to transmit IR rays. AC current regulator (5) connected with the pyrometer allowed us to carry out controllable heating of the sample (heating rate was 60 °C/min, exposure time at each temperature was about ~ 15 min [R1.1]). Gas flows were controlled with a gas mixing unit UFPGS-4 (SoLO, Novosibirsk) (6). The concentrations of outgoing gases were determined by the quadrupole mass spectrometer QMS 200. The size of the membrane: inner/outer diameter = 0.55/1.75 mm [R2.6]; total length = 50 mm; active length = 35 mm; active area = 0.60 cm² [R2.6].

The scheme of single MT-SOFC measurements is shown in Fig. 3:



Figure 3. Scheme of single MT cell measurements.

A spiral of silver wire was placed in the inner side of tube (anode side) in such a way that it formed a good contact with a cermet support. The cell was heated with a furnace, while the entire cell was in the non-gradient zone of the furnace [R2.7]. Ambient air was used as an oxygen source (F=250 ml/min). Pure H₂ (humidified by bubbling water at 25°C) was used as a fuel (F=100 ml/min). Current collecting was obtained by Ag wire (d=0.3 mm). The size of the cell: inner/outer diameter = 1.0/2.0 mm; total length = 50 mm; cathode length = 15 mm; active area = 0.94 cm². Gas flows were controlled with a gas mixing unit UFPGS-4 (SoLO, Novosibirsk).

Results and discussion

According to the XRD data analysis, the BSCFW2 membrane material is a single phase and has a cubic Pm3m perovskite structure (Fig. 4, before). The cell parameter ($a = 3.989 \pm 0.001$ Å) agrees with the data for BSCFW2 obtained previously [11]. The micrographs of MT membranes obtained by phase inversion method are shown in Fig. 5a,b. Developed bulk finger-like porosity (Fig. 5b) and gas-tight layer (Fig. 5a) of the membranes are clearly seen. A crack-free dense electrolyte layer with a thickness of about 20 µm was prepared by co-firing method (Fig. 6). The thickness of cathode layer was ~ 10 µm [R1.7]. The thickness of the NiO/CGO tube was ~ 200 µm and the porosity of the anode determined to be ~ 36% (before reduction) and ~53% (after reduction) using helium pycnometer.



Figure 4. XRD pattern of BSCFW2 membrane material before (red line) and after (blue line) conversion of methane experiments. [R2.8]



Figure 5. SEM data of MT membranes composed of BSCFW2 (a) and NiO/CGO (b).



Figure 6. SEM data of NiO/CGO anode tube with co-fired CGO electrolyte: before (on the left side) and after (on the right side) reduction. [R2.11]



Figure 7. SEM data (on the left side) and photo (on the right side) of NiO/CGO anode tube with co-fired CGO electrolyte and cathode layer. [R2.7, 2.11]

Catalytic conversion of methane

The performance of catalytic converter of methane was studied and shown in Fig. 7. Temperature range of the experiment was 750–1200°C. The experiment was carried out for three hours, with no significant changes in the process indicators (Fig. 4, after).



Figure 8. Dependencies of conversion of methane (black line) and yield of C₂-hydrocarbons (red line) on temperature. [R1.4], [R2.12]

It can be seen from the Fig. 8 that the proposed compound BSCFW2 provides a yield of C_2 -hydrocarbons about ~ 27% and conversion of methane about ~ 60%. The obtained data indicate the promise of the proposed composition. Note that oxygen enters the reactor, diffusing through the walls of the catalyst tube. Thus, the formation of explosive mixtures is prevented. Moreover, the AC heating of the MT membrane generates high temperature gradients in the gas phase. This allows to not only reduce the requirements for structural materials and avoid additional heater, but to freeze metastable products and increase the selectivity of the oxidative conversion of methane.

Microtubular Solid Oxide Fuel Cell

The performance of the MT cell (Fig. 3) was studied and shown in Fig. 9. Temperature range of the experiment was 550–650°C. As can be seen from Fig. 9, the peak power density of 50, 125 and 200 mW/cm² were obtained respectively at 550, 600 and 650°C. Even though the peak power densities (N) are relatively high (in comparison with a similar cell which have peak power density 300 mW/cm² in [13]), the OCV value obtained in this work are not high enough. To solve this problem, according to the size and performance of the single tubular cell, a stack with 25 tube cells (5×5) in 1 cm³ can possibly be fabricated, which can be expected to generate 3.3 W/cm³ 650°C, respectively. Therefore, developing of stack fabrication method will be a key for realizing high volumetric power SOFC system, which is currently under investigation and will be reported separately.



Figure 9. V-I characterization data of the MT SOFC with BSCFM5/CGO [R2.3] cathode material.

Conclusion

Compact tubes based on oxide with mixed conductivity have been successfully fabricated and tested in terms of catalytic conversion of methane. It is shown, that BSCFW2 oxide is promising catalysis material and provides up to 60% conversion of methane and 27% yield of C_{2} hydtocarbons. At the same time, the stable operation time of the catalyst is 3 hours or more. An additional advantage of the proposed catalyst is the possibility of separating the streams of oxygencontaining gas and methane, which reduces the explosiveness of the process.

Microtubular solid oxide fuel cells with BSCFM5 cathode material have been successfully fabricated and tested in the intermediate temperature region. The cell consists of NiO/CGO as an anode (support tube), CGO as an electrolyte and BSCFM5/CGO as a cathode. The single cell generated 200 mW/cm² at 650°C operating temperature with H₂ fuel, which indicated a possibility of building cell stack with volumetric power density of 3.3 W/cm³ by stacking 25 tubes in 1 cm³.

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