Performance evaluation of solid oxide fuel cell with in-situ methane reforming

Tenglong Zhu [a], Zhibin Yang [a], Minfang Han [a,b,*]

[a] Union Research Center of Fuel Cell, School of Chemical and Environmental Engineering, China University of Mining and Technology, Beijing 100083, China
[b] State Key Laboratory of Power Systems, Department of Thermal Engineering, Tsinghua University, Beijing 100084, China

HIGHLIGHTS

- CO_2 in-situ reforming of CH_4 was successfully achieved on LSCFN based anode.
- Cell performance was dramatically promoted by CO_2 addition.
- LSCFN based anode possessed stable and wide operation range with CO_2–CH_4 fuel.
- A_2BO_4 with metal structure demonstrated good catalytic activity to DRM reaction.

ARTICLE INFO

ABSTRACT

Solid Oxide Fuel Cell (SOFC) is a promising power generation technology with a wide range of fuel flexibility. In this paper, performance evaluation of SOFC fuelled with carbon based fuels like CH_4 were carried out on $La_{0.8}Sr_{0.2}Ga_{0.83}Mg_{0.17}O_{3-\delta}$ (LSGM) electrolyte supported single cell with symmetrical electrodes consisted of $La_{0.4}Sr_{0.6}Co_{0.2}Fe_{0.7}Nb_{0.1}O_{3-\delta}$ (LSCFN)–$Gd_{0.1}Ce_{0.9}O_{1.95}$ (GDC) functional layers and LSCFN current collect layers. In-situ reforming of methane by carbon dioxide at the anode was successfully achieved on LSCFN based anode, which greatly enhanced the cell performance. The maximum power density of the single cell was dramatically increased from 280 to 455 mW/cm^2 when fuelled with 10% CO_2–90% CH_4 compared with pure methane at 850 °C with a fuel inlet rate of 50 mL/min. No obvious degradation was observed during the cell operation, demonstrating a stable and wide operation range with CO_2–CH_4 fuel on LSCFN based anode.

© 2015 Elsevier Ltd. All rights reserved.

1. Introduction

Conventional fuel utilization technologies are mostly based on the burning process, which are inefficiency and environmental unfriendly. Fuel cells can convert the chemical energy in fuels directly into electricity, in which Solid Oxide Fuel Cell (SOFC) is the most promising energy conversion technology with its high efficiency, low cost and fuel flexibility [1–3]. Despite the most commonly used H_2 in fuel cells, a wide range of fuels can be used in SOFC like gaseous fuels (hydrocarbon, syngas and coal gas), liquid fuels (methanol, gasoline and jet fuel) and even solid coal [4–6]. Plenty of studies have been conducted on the application of carbon based fuels in SOFC; however, running these fuels in SOFC was mainly restricted by the anode materials, during which,

carbon deposition was the primary issue in the traditional nickle-ceramic anode. Therefore, most commonly application method for the hydrocarbon based fuels like methane was firstly to be reformed externally or internally [7–10]. SOFC favorable hydrogen rich fuel could be obtained by the methane external reforming method, however part of the energy would be wasted during the reforming process which led to the decrease of the whole system efficiency.

The direct utilization of methane will get the energy in fuel being used as much as possible. Air, steam and CO_2 were most commonly used to reform methane. Barnett et al. studied the performance and stability of Ni–YSZ (yttria stabilized zirconia) anode supported single cell fuelled with CH_4 and different proportion of CO_2 or air with a barrier layers adjacent to the anode side [11,12]. However, the performance degradation could only be suppressed at certain operation conditions like high current density and lower temperature. Furthermore, the barrier layer would increase the complexity of the cell integration and lead to disadvantages on the gas flow and current collecting in the

practical application. Despite the Ni based anode in SOFC, several perovskite oxides were developed as promising anode materials for their stability in carbon based fuels, like $La_{0.75}Sr_{0.25}Cr_{0.5}Mn_{0.5}O_{3-\delta}$, $Sr_2MgMoO_{6-\delta}$ and $La_{0.3}Sr_{0.7}TiO_{3-\delta}$ [13–15]. However, their electrochemical catalytic activity toward fuels and conductivity under reducing atmosphere was not good enough which limited the output cell performance.

Guntae Kim et al. studied the performance and stability of single cell with $PrBaMn_2O_{5+\delta}$ scaffold and infiltrated Co–Fe catalyst anode [16]. However, the Co–Fe catalyst particles obtained by infiltration technique increased the fabrication complexity, and the uniformly distribution and coarsening of the infiltrated particles were still tough issues during high temperature operation in SOFC. In our prior work, coking-resistant and sulphur-tolerant anode composited of $Pr_{0.8}Sr_{1.2}(Co,Fe)_{0.8}Nb_{0.2}O_{4+\delta}$–CoFe (PSCFN-CFA) was developed through annealing perovskite $Pr_{0.4}Sr_{0.6}Co_{0.2}Fe_{0.7}Nb_{0.1}O_{3-\delta}$ oxide in reducing atmosphere. The in-situ precipitated Co–Fe alloy on ceramic scaffold exhibited good catalytic activity toward hydrocarbon fuels like CH_4 and C_3H_8 [17]. Thus, the anode structured of ceramic oxide scaffold with in-situ precipitated metal catalyst particles was promising in the direct application of the carbon based fuels, which has drew much attention.

Recently, $La_{0.4}Sr_{0.6}Co_{0.2}Fe_{0.7}Nb_{0.1}O_{3-\delta}$ (LSCFN) oxide material was studied as promising symmetrical electrode material [18,19]. B-site metal precipitation was also detected after annealing in reducing atmosphere which could made positive contribution to the catalytic activity in fuel oxidation when used as anode [16,17]. LSCFN anode was stable enough when operated with humidified methane, but with a relative low output power density. Herein, CO_2 was introduced to reform the methane at the anode layer in order to promote the cell performance. The catalytic activity and cell performance of LSCFN based anode were studied with CO_2 contained CH_4.

2. Experimental

2.1. Material synthesis and single cell preparation

$La_{0.4}Sr_{0.6}Co_{0.2}Fe_{0.7}Nb_{0.1}O_{3-\delta}$ (LSCFN) and $La_{0.8}Sr_{0.2}Ga_{0.83}Mg_{0.17}O_{3-\delta}$ (LSGM) powders were synthesized via solid-state reaction as we reported elsewhere [18], and $Gd_{0.1}Ce_{0.9}O_{1.95}$ (GDC) powder was purchased from commercially available products (Huatsing Power, China). LSGM powder was mixed with binders, solvents, plasticisers and additives by ball-milling and then tape-casted into green film on a tape caster. The green film was punched into disks with a diameter of 19 mm, followed being sintered at 1450 °C for 10 h yielding LSGM electrolyte ceramic pellets with a diameter of about 15.5 mm and thickness of about 280–300 μm. LSCFN–GDC (weight ratio 1:1) and LSCFN slurries were prepared by ball-milling for 48 h with a powder, binder (3% w.t. ethyl cellulose in terpineol) and pore former (methyl cellulose) weight ratio of 100:100:15. LSCFN–GDC (functional layer, ~10 μm) and LSCFN (current collect layer, ~30 μm) slurries were screen printed on the one whole side of LSGM pellet as anode, and an active working area of 0.3 cm² on the other side as cathode. The following calcination of the electrodes was conducted at 1100 °C for 2 h in air. Gold slurry and platinum slurry was coated on anode and cathode respectively followed being calcined at 900 °C for 1 h to help the current collection to the silver wires for testing.

2.2. Fuel cell evaluation description

The as-prepared symmetrical single cell with a structure of LSCFN|LSCFN–GDC||LSGM||LSCFN–GDC|LSCFN was sealed on top of the alumina tube as shown in Fig. 1(a). H_2, CH_4 and CO_2 were applied to the anode side as fuel, and the ambient air was used as oxidant at the cathode side, while the N_2 was used as the anode side sweeping gas. The single cell was heated up to 850 °C, firstly the N_2 was applied as sweeping gas at a flow rate of 50 mL/min for 20 min to remove any excess air in the pipes, mixing tank and anode side, then the H_2 was applied to the anode side to reduce the anode for 1 h at the same flow rate prior to any tests.

The electrochemical performance characterization was carried out using Metrohm Autolab Electrochemical Workstations. The electrochemical impedance spectra (EIS) tests were conducted in the frequency range between 0.1 Hz and 1 MHz with potential amplitude of 20 mV. All the gas flows were controlled using mass flow controller (MFC, Alicat), and the temperature was monitored using K-type thermal couple. Outlet gas composition was detected by gas chromatography (Angilent 7890A GC).

2.3. LSCFN catalyst characterization description

The as-prepared LSCFN powder was firstly dry pressed into pellet under a uniaxial pressure of 220 MPa for 1 min. Then the pellet was crushed and sieved into particles with diameter of 250–380 μm. Then the LSCFN particles were loaded on the top of the porous quartz support as catalyst inside the quartz tube of which the inner diameter was 1 cm as displayed in Fig. 1(b). The total LSCFN catalyst volume loaded in was 0.3 mL, the inlet gas flow rate was 60 mL/min, which meant that the catalysis test was conducted with a space velocity of 12,000 h^{-1}. The LSCFN catalyst was firstly reduced by H_2 at 850 °C for 1 h before the catalysis test. Outlet products were examined by GC with a time interval of 20 min.

3. Results and discussion

3.1. Cell performance baseline

Fig. 2 shows the electrochemical performance of the symmetrical single cell under different fuels. All results were measured at 850 °C with a fuel flow rate of 50 mL/min. The open circuit voltage of the cell was 1.07 and 0.95 V at 850 °C when fuelled with humidified H_2 and dry CH_4, respectively. The maximum power density under humidified H_2 reached 817 mW/cm². The higher peak power density compared with 500 mW/cm² of what we reported before was mainly due to the thinner LSGM electrolyte prepared by tape casting and introduction of LSCFN–GDC functional layer at both anode and cathode side [18]. However, the performance of dry methane was not that promising with a maximum power density of 280 mW/cm².

3.2. Effect of CO_2 addition in CH_4: in-situ reforming

Different contents of CO_2 were mixed into CH_4 as fuel of the single cell, and the reaction in Eq. (1) (dry CO_2 reforming of methane, DRM) was expected to happen at the anode:

$$CO_2 + CH_4 \rightarrow 2CO + 2H_2 \tag{1}$$

Fig. 3(a)–(c) presents the outlet gas composition from the anode side measured by GC when fuelled by CH_4 with different contents of CO_2 at 850 °C and OCV condition. H_2 was firstly introduced in for 1 h to reduce the anode, and then the inlet gas was changed to the corresponding gas compositions. GC tests were done after 1 h of the gas switch in order to get the whole set-up working at a steady state.

CH_4, CO_2, CO and H_2 were detected in the outlet gas according to the GC results. As displayed in Fig. 3(b) and (c), negligible CO and H_2 were generated with dry CH_4. When small portion of CO_2 was