Electrochemistry Communications 86 (2018) 126–129

Contents lists available at ScienceDirect

Electrochemistry Communications

journal homepage: www.elsevier.com/locate/elecom

Molybdenum dioxide as an alternative catalyst for direct utilization of methane in tubular solid oxide fuel cells

Xin Yang[a,b,c], Dhruba Panthi[b], Nader Hedayat[b], Tianmin He[a], Fanglin Chen[c], Wanbing Guan[d], Yanhai Du[b,*]

[a] Key Laboratory of Physics and Technology for Advanced Batteries, Ministry of Education, College of Physics, Jilin University, Changchun 130012, PR China
[b] College of Aeronautics and Engineering, Kent State University, 1400 Lefton Esplanade, Kent, OH 44242, USA
[c] Department of Mechanical Engineering, University of South Carolina, 300 Main Street, Columbia, SC 29208, USA
[d] Ningbo Institute of Material Technology and Engineering, Chinese Academy of Sciences, Ningbo 315201, PR China

ARTICLE INFO

Keywords:
Tubular SOFC
Molybdenum dioxide catalyst
Catalytic partial oxidation
Direct methane
Stability

ABSTRACT

Direct utilization of methane in conventional tubular solid oxide fuel cells (SOFCs) with a Ni-YSZ anode support was proposed using MoO_2 as a partial oxidation catalyst for methane reforming at the cell inlet. A promising stability was achieved for a continuous operation in a mixture of methane and air (1, 1.5) for > 150 h under a load voltage of 0.7 V at 750 °C. The addition of the MoO_2 catalyst at the anode inlet made tubular SOFCs with the conventional Ni-YSZ anode an efficient and practically promising candidate for direct hydrocarbon utilization.

1. Introduction

Among different types of fuel cells, solid oxide fuel cells (SOFCs) with a ceramic oxide electrolyte offer high flexibility in fuel choices such as natural gas, coal gas, methanol, and biogases [1]. Internal reforming technology brings decreased mechanical complexity and eliminates the need for fuel processing apparatus over reformer-based designs. Unlike direct internal reforming, indirect internal reforming designed the catalysts for fuel reforming and electrochemical oxidation separately, whereby the reforming section was adjacent and in close thermal contact to the anode [2]. Catalytic partial oxidation (CPOX), which usually takes place at a relatively low temperature and pressure, was reported to be a simple technology to convert hydrocarbon fuels into synthesis gas [3]. In the case of methane, the reaction follows the formula below:

$$\text{Partial Oxidation:} CH_4 + {}^{1}\!/_{2}O_2 \rightarrow CO + 2H_2,\ \Delta H^0_{298} = -36\ \text{kJ/mol}$$

where $\Delta H_{298}{}^0$ refers to standard enthalpy change of reaction at 298 K and a pressure of 1 bar.

Methane has a tendency to be pyrolysed at high temperatures, especially when catalysts are involved. The reforming process usually accompanies severe carbon deposition on the anode that covers the active anodic sites and blocks the gas channels, ultimately causing severe deactivation in cell performance and reliability [4–6]. Unlike the strongly endothermic steam and dry reforming processes, the partial oxidation is much milder ($\Delta H \approx 0$), requiring no additional water and does not involve side reactions. Currently, the partial oxidation approach has been used in portable SOFC power source development with the desired thermally self-sustained hot-zone (a stack incorporated with a CPOX unit) [7].

The conventional Ni–yttria-stabilized zirconia (YSZ) anode is most commonly used owing to its reasonable electrocatalytic activity and relatively low cost. However, nickel also promotes hydrocarbon cracking [8]. A great deal of effort has been devoted to the modification of the Ni-based anode either by introducing a barrier layer or by impregnating metal catalysts. However, either the additional complexity or the high cost limits its use [9–11]. In searching for non-noble transition metallic catalysts for partial oxidation of hydrocarbon fuels, molybdenum dioxide (MoO_2) has been reported to be used as an anode for SOFCs due to its promising cost and high catalytic activity [12]. However, a thin MoO_2 seed layer was necessary between the bulk anode and electrolyte, which added complexity to the cell fabrication process.

In this communication, we report direct utilization of methane with MoO_2 at the cell inlet as a partial oxidation catalyst for methane reforming on a conventional tubular SOFC with Ni-YSZ as the anode. A design with a catalyst on the cell inlet eliminated the need for a barrier layer, which adversely affects the power output. In addition, no modification in the cell fabrication process and sintering process for the catalyst preparation were required.

* Corresponding author.
E-mail address: ydu@kent.edu (Y. Du).

https://doi.org/10.1016/j.elecom.2017.12.004
Received 28 October 2017; Accepted 4 December 2017
Available online 06 December 2017
1388-2481/

2. Experimental

The compositions of the tubular SOFCs used in this study were Ni-YSZ/YSZ/strontium-doped lanthanum manganite (LSM)-YSZ. All specimens were fabricated by the extrusion process and co-sintering using the technique described elsewhere [13]. The dimensions of the tubes were as follows: outer diameter 10.3 mm, length 40 mm, and wall thickness 1.6 mm. Copper foam inserted inside the cell and connected to a silver wire was used as the anode current collector. Silver conductor paste (Heraeus C8728) was used to improve the contact between the electrodes and current collectors.

Molybdenum (IV) oxide powder (48117, 99%, metals basis, Alfa Aesar) was used as the partial oxidation catalyst. 4 g MoO_2 powder and 0.5 g dispersant (Hypermer KD-1, Tape Casting Warehouse) were mixed in a solvent mixture of 18 g ethanol and 18 g toluene. The suspension was ball milled for 2 h. Then, 0.5 g polyvinyl butyral (B-98, Tape Casting Warehouse) and 0.5 g dioctyl phthalate (D201154, ≥ 99.5%, Sigma Aldrich) were added into the suspension. After ball milling for 12 h, the catalyst slurry was vacuum coated onto highly porous alumina support (CAS #: 43855, 3.2 mm pellets, Alfa Aesar), which offered a supporting bed for the reforming catalyst. Al_2O_3-supported MoO_2 formed an in-situ catalyst network allowing the gases to pass through and improving the contact between the gases and the reforming catalyst. Thus, methane was converted into syngas before it reached the cell. Then, the catalyst-coated alumina pellets were loaded into an alumina tube, which was connected and sealed to the fuel cell.

All cell samples were heated to 750 °C in H_2/N_2 (1:1) at a flow rate of 100 mL/min. Subsequently, the fuel was switched to a mixture of methane and air. The flow rate of methane was 100 mL/min and the flow rate of air was varied to achieve the desired methane–air ratio. An electrochemical workstation (PGSTAT 302N, Metrohm Autolab) was used for the electrochemical performance tests. The microstructure of the tested cell and the catalyst was characterized by a scanning electron microscope (SEM, FEI Sirion 200) with an Oxford energy dispersive X-ray spectrometer (EDS). The exhaust gas compositions were examined with a gas chromatograph (GC-7820).

3. Results and discussion

The phase instability of MoO_2 and the explosive limits of methane were considered when setting the ratio of fuel and oxygen. Air containing 79% nitrogen was used as the oxidant to dilute the fuel to maintain the MoO_2 phase and to improve the cell performance compared with oxygen [14]. The 1:2.4 stoichiometric ratio of CH_4 and air appears to be the most reasonable set (O/C = 1). However, not all of the fuel can be reformed, and the excess air might oxidize nickel, ultimately damaging the cell. Fang et al. found that 10% of reformed methane can effectively prolong a SOFC's lifetime and apparently prevent carbon deposition on the anode [15]. In addition, it was reported that the 1:1 ratio of the fuel and air can yield sufficient synthesis gas and prevent coke build-up [16]. The ratio of methane and air was then set to 1:1 (O/C = 0.42) and 1:1.5 (O/C = 0.63).

Fig. 1(a) shows the initial I–V characteristic plots for the cell under different fuels at 750 °C. The maximum power density of 853 mW cm^{-2} was achieved at 750 °C in hydrogen. The presence of MoO_2 on the cell inlet did not affect the performance. Decreased maximum powder density values and OCV were obtained after the fuel was switched from hydrogen to a mixture of methane and air, which were attributed to the reforming process. The maximum power density values of 562 and 522 mW cm^{-2} were observed for the methane-air ratios of 1:1.5 and 1:1. Therefore, the 1:1.5 stoichiometric ratio appeared to give the optimum performance from the single cell tests. In fact, a combination of

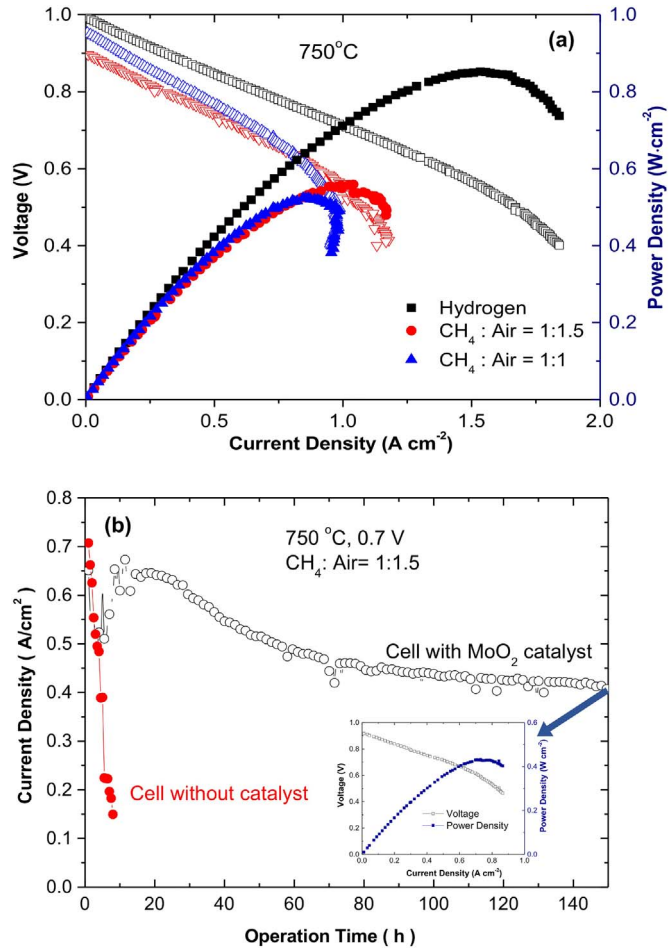

Fig. 1. a. Initial I–V curves comparison fed with different fuels b. Short-term stability of single cell with and without the reforming catalyst fed with methane and air (1:1.5) under a load voltage of 0.7 V at 750 °C.

electrochemical reactions was ongoing apart from partial oxidation, which affected the initial cell voltage and power output.

Fig. 1(b) shows the current density of the cell as a function of time under a potentiostatic mode with a load voltage of 0.7 V at 750 °C on 1:1.5 methane–air mixture with and without MoO_2 at the cell inlet. The cell without the reforming catalyst underwent a severe carbon deposition within the 8 h of operation. Conversely, the cell with catalyst was successfully operated with CH_4 and air as the fuel for over 150 h and there was no damage on the cell after the test. The current density was first improved in the first 20 h, then decreased in the following 40 h reaching nearly a stable value, corresponding to the syngas yield during reforming process (shown in Fig. 2). After the stability test for 150 h, the maximum power density was recorded to be 434 mW cm^{-2} (shown in the I–V plot embedded in Fig. 1(b)). Although there was a slight decrease in the cell performance, the reasonably stable operation indicated the effectiveness of the MoO_2 catalyst bed for direct hydrocarbon utilization in the Ni-based SOFCs.

The effluent gas compositions was characterized by gas chromatography. Without the reforming catalyst at the cell inlet, the main active catalyst turned to be metallic Ni. As depicted in Fig. 2(a), a high H_2 yield was observed, paralled by a relatively low CO yield and negligible CO_2 yield, implying that methane cracking was significant at the initial state. In contrast, an initial carbon convertion of 92% and reasonable