Journal of Power Sources 185 (2008) 188–192

Contents lists available at ScienceDirect

Journal of Power Sources

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

Short communication

Direct liquid methanol-fueled solid oxide fuel cell

Mingfei Liu[a], Ranran Peng[a], Dehua Dong[b], Jianfeng Gao[a], Xingqin Liu[a], Guangyao Meng[a,*]

[a] Department of Materials Science and Engineering, University of Science and Technology of China, Hefei, 230026 Anhui, China
[b] Department of Chemical Engineering, Monash University, Clayton, Vic. 3800, Australia

ARTICLE INFO

Article history:
Received 16 May 2008
Received in revised form 26 June 2008
Accepted 27 June 2008
Available online 6 July 2008

Keywords:
Methanol
SOFC
SDC
Liquid fuels
Ammonia

ABSTRACT

Anode coking problem of solid oxide fuel cell (SOFC) when using hydrocarbon fuels has been the major barrier for the practice and commercialization of well-developed high performance SOFC. In this work, based on fuels consideration, we chose liquid methanol as the candidate fuel for SOFC with the configuration of NiO/SDC–SDC–SSC/SDC. For comparison, traditional fuels, hydrogen and ammonia, were tested. With methanol as fuel, the maximum power densities were 698, 430 and 223 mW cm^{-2} at 650, 600 and 550 °C, respectively, which were higher than that with ammonia and lower than that of hydrogen. The electrochemical properties of the cells with the three fuels were investigated by AC impedance spectroscopy. The long-term stability of the cell with methanol, methane and ethanol were also studied at a constant output voltage of 0.5 V.

© 2008 Elsevier B.V. All rights reserved.

1. Introduction

Solid oxide fuel cell (SOFC), with outstanding advantages of fuel flexibility and module integrity, has been expected to be an excellent green energy sources that be used as portable applications [1]. As countries develop, the exponential increase in the demand for energy has brought SOFC to a commercial stage.

Nowadays the crucial issue for the developments of SOFC is to explore proper fuels. Though hydrogen is the most optimal fuel for being directly used in SOFC, the requirement of storage and transportation for hydrogen is not only too expensive but also very severe. The intrinsic advantage of SOFC is that hydrocarbon fuels can be utilized directly with little or minimal fuel processing. However, the conventional Ni-based anodes suffers a number of drawbacks while using hydrocarbon fuels due to the propensity of Ni to catalyze carbon formation, resulting in the rapid degradation of the cell performance, which hindered SOFC from its commercialization. In order to overcome the carbon deposition problem at the anode, several solutions have been investigated: (1) using SDC coated Ni anode [2] or making anode protection with a composite layer of Ru–SDC [3] to block hydrocarbon from approaching the Ni; (2) exploring other appropriate active anodes, such as copper anodes [4], single phase redox-stable $La_{0.75}Sr_{0.25}Cr_{0.5}Mn_{0.5}O_3$ (LSCM) anodes [5], and Cu, Cu–Pd or GDC-impregnated $La_{0.75}Sr_{0.25}Cr_{0.5}Mn_{0.5}O_3$ (LSCM) anodes [6,7], to supersede the traditional Ni-based anode. Though coking problems were suppressed effectively and positive results were obtained partially in all these cases, neither was the right solution due to their shortcomings, such as insufficient catalysis activity or high cost. In addition, even if the new anodes are applied in SOFC, they are difficult to achieve a universal fuel cell to satisfy all the fuels. Therefore, from the viewpoint of practical considerations, the well-developed Ni-based anodes would be the best choice. The problem is how to overcome the coking problems.

In the authors' lab, we have focused mostly on the fuel consideration to solve the carbon deposition in recent years. Firstly, industrial liquid ammonia was taken as the right source of H_2 fuel as it can decomposes into H_2 and N_2 under the operation temperature and Ni-based anode condition of SOFC. And the experimental results have well met the expectation [8–12]. Tough ammonia has demonstrated as an excellent green fuel for SOFC. However, we cannot evade carbon-containing fuels as hydrocarbons spread everywhere and are the major energy carriers in the nature. Among the various fuels, methanol might be an ideal alternative green fuel for the following reasons. Firstly, methanol is the simplest hydrocarbon fuel except methane, and the liquid state of methanol at ambient conditions makes it ease of handling, transportation and storage. Secondly, methanol has a volumetric energy density of 15,800 kJ m^{-3} [13], which is even higher than that of liquid hydrogen. Thirdly, methanol is a clear and renewable source (say "it is a way of storing energy" maybe more exactly) that can be derived from all fossil resource, agricultural byproducts and biomass [14]. Fourthly, methanol can be also easily reformed back to CO and

* Corresponding author. Tel.: +86 551 3603234; fax: +86 551 3607627.
E-mail addresses: mfliu@mail.ustc.edu.cn (M. Liu), mgym@ustc.edu.cn (G. Meng).

0378-7753/$ – see front matter © 2008 Elsevier B.V. All rights reserved.
doi:10.1016/j.jpowsour.2008.06.076

H_2 at relatively mild temperatures [15,16]. All of above imply that methanol could be an optimal candidate for a liquid fuel for SOFC. And methanol is much different from other hydrocarbon fuels, which carries sufficient oxygen to avoid entering into the thermodynamically unstable, carbon-forming regime [17,18]. Hence, methanol has been extensively researched in SOFC [14,19–22], even with Ni-based anodes, but there were some arguments on the long-term stability. Saunders et al. [20] found that carbon formed on Ni anodes when operated on methanol and the amount of carbon deposition was increased with decreasing temperature over the range of 700–850 °C. In contrast, Jiang and Virkar [14] reported that there was no carbon deposition when SOFC operated on direct methanol at temperatures as low as 550 °C. Another investigation, reported by Bi et al. [21], has also achieved pretty good results by using Ni-GDC anodes, but there was no evidence of the long-term stability to check whether the coking appeared or not on the anodes. Hence, it is necessary for us to study the stability of direct methanol-fueled SOFC.

In the present work, we tried to feed SOFC with liquid methanol at 550–650 °C. The cell is consisted of conventional Ni/SDC anode, SDC electrolyte and $Sm_{0.5}Sr_{0.5}CoO_3$ (SSC)/SDC cathode. The cell performance of the cell with methanol as fuel was investigated, and the characteristics of the cell with methane, ethanol, hydrogen and ammonia as the fuels were studied.

2. Experimental

2.1. Fabrication of NiO/SDC anode support

Commercial NiO and SDC powders prepared by citric acid–nitric auto ignition process were mixed in a weight ratio of 6:4, and the mixture with a proper amount of starch was ball-milled in an ethanol medium for 24 h and dried subsequently. Starch was used as a pore former to enhance the porosity of anode. NiO/SDC anode supports were made by uniaxially pressing the mixed powders under a pressure of 250 MPa and then pre-calcined at 600 °C for 2 h.

2.2. Fabricating SDC membrane on anode substrates

Thin electrolyte membrane of SDC was processed by a refined particles suspension coating technique [23,24]. SDC powders, synthesized via carbonate co-precipitation process [25], were employed to make a suspension. The suspension was drop-coated on the porous NiO/SDC anode supports surface to make SDC layers. Finally, the anode supports with SDC coats were co-sintered at 1400 °C for 5 h.

2.3. Preparation of cathode

$Sm_{0.5}Sr_{0.5}CoO_3$ (SSC)/SDC was applied as the cathode. The SSC and SDC powders were synthesized by glycine–nitrate process (GNP) [26]. The preparing process of cathode was similar to the previous studies [23,27]. The cells coated with cathode layer were finally sintered at 950 °C for 2 h in air.

2.4. Evaluation of cell performance

To avoid the possible catalysis decomposition of methanol to form carbon, the cell support and the gas tubing in our home-developed-cell-testing systems (see Fig. 1) are all made of alumina instead of stainless. The single cell was sealed on alumina tube with silver paste and tested at 500–650 °C. Liquid methanol in a glass was directly injected into the anode compartment at a feeding rate of 0.013 ml min^{-1} (roughly calculated from the result, about 120 ml of methanol has been used up in 160 h) by a peristaltic pump and then vaporized into gas at anode side. NiO in anode was directly reduced to form metal Ni in situ by methanol gas at 650 °C before the electrochemical measuring. The cell voltages and output currents of the cell were measured and recorded using an electronic load (IT8500, ITECH Electronic Co., Ltd.). AC impedance of the cells was conducted via a two-probe impedance spectroscopy (Chenhua Chi604c, Shanghai) under open circuit conditions in the frequency range of 0.01 Hz to 100 kHz with 10 mV as the excitation ac amplitude. The microstructure and the morphology of the tested cell was observed using scanning electron microscopy (SEM, model KYKY 1010).

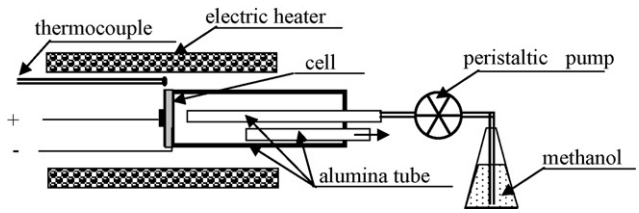

Fig. 1. A schematic diagram of the home-developed-cell-testing system.

3. Results and discussion

Fig. 2 shows the SEM image of the fractured Ni/SDC–SDC–SSC/SDC fuel cell after electrochemical testing. It can be seen that the SDC membrane about 24 m seems uniformly continuous and is well adhered to both the porous Ni/SDC anode substrate and the cathode, almost without any cracks or noticeable pores.

Fig. 3 presents current–voltage (*I–V*) and current–power density (*I–P*) curves of the as-fabricated cell using liquid methanol and ambient air as fuel and oxidant, respectively. The maximum power density of 698 mW cm^{-2} is obtained at 650 °C, which is much higher than the highest record at 650 °C known to date (about 560 mW cm^{-2}) reported by Jiang and Virkar [14] for a cell with Ni/YSZ anode support, Ni/YSZ anode interlayer, 10- m thick YSZ electrolyte, LSM/YSZ cathode interlayer and LSM cathode. The higher performance achieved in our case may result from the higher conductivity of SDC than that of YSZ at intermediate temperatures. As the temperature reduced to 600 and 550 °C, the maximum power

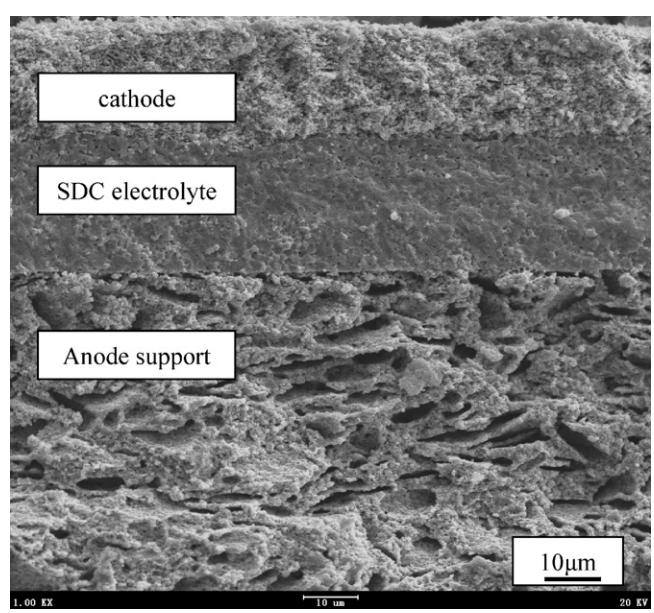

Fig. 2. Cross-sectional image of the tested cell with Ni/SDC, SDC and SSC/SDC.

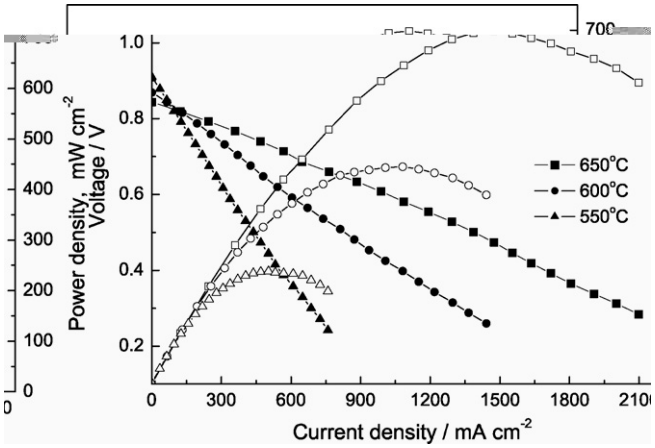

Fig. 3. Cell performance with methanol at various temperatures. The solid symbols correspond to the cell voltage and open symbols to power density.

densities are 430 and 223 mW cm^{-2}, respectively. Although there is a significant decrease in cell performance at lower temperatures, power densities of practical interest can be realized at temperatures as low as 550 °C.

To investigate the endurance of the cell with methanol as fuel, the cell was operated at a voltage of 0.5 V at 550 and 650 °C for several days. As can be seen from Fig. 4, no detectable decay in the cell current is observed within the operating duration. The fluctuation in the current densities of the cell was due to that the liquid methanol was directly injected into the anode compartment by a peristaltic pump which works in a disconnected way and the evaporation of the methanol needs time. Though the current fluctuated around 200 mA cm^{-2}, the highest and the average current values are always kept almost constant at a certain temperature. This result surely demonstrates no degradation of the cell performance, indicating no coking on anode. After running about 160 h, the methanol in the glass was exhaust, so the current density attenuated to zero, as well as the voltage.

As a comparison, the long-term stability of the cell with methane and ethanol as fuels at 650 °C are shown in Fig. 5. However, the current densities of the cell with methane and ethanol as fuels exhibit severe degradation at a voltage of 0.5 V. The very encouraged results from methanol-fueled SOFC compared with that fueled with other hydrocarbons can be surely attributed to methanol itself. Originally, we tried to explain this nice expected result from the thermodynamic viewpoint. The so-called Gibbs free energy minimization method [28] is used to calculate the equilibrium compositions. In order to simplify the calculation, we assume that methanol decomposes completely at anode side and the species of H_2, CO_2, H_2O, CO, CH_4 [22], as well as solid carbon in the form of graphite are considered in the equilibrium composition. As shown in Fig. 6, the thermodynamic equilibrium analysis of methanol vapor in the temperature range of 500–1000 °C indicates a rather high carbon formation at below 900 °C, even assuming existence of a quite high O^{2-} current come from cathode side. Brett et al. [29] also reported a similar conclusion. This means that the behavior of methanol at anode surface is not controlled by thermodynamic. Hence, we have to consider it based on the kinetic factors. The molecule structures of these three substances possess quite different characteristics as shown in Fig. 7. The C–O bond in methanol

Fig. 5. Long-term stability of the cell *t* with methanol, methane and ethanol as fuel tested at 650 °C.

Fig. 6. The equilibrium partial pressures of the chemical species from methanol gas in the temperature range of 500–1000 °C.

Fig. 4. Long-term stability of the cell tested at 550–650 °C with methanol as fuel.

Fig. 7. The chemical bonds in methanol, methane and ethanol.