Performance of an anode-supported tubular solid oxide fuel cell (SOFC) under pressurized conditions

Li Zhou *, Mojie Cheng, Baolian Yi, Yonglai Dong, You Cong, Weishen Yang

Dalian Institute of Chemical Physics, Chinese Academy of Sciences, Dalian 116023, China

Received 26 November 2007; received in revised form 28 January 2008; accepted 2 February 2008
Available online 17 February 2008

Abstract

An anode-supported tubular solid oxide fuel cell (SOFC) with a 15-μm thick YSZ electrolyte and an active area of 100 cm² was successfully fabricated by co-firing process, and the cell performance was measured under both atmospheric and pressurized conditions. The experimental results showed that the cell performance was significantly improved under the pressurized condition. When the pressure was increased from 1 to 6 atm, the maximum power density increased from 135.0 to 159.0 mW cm⁻² at 650 °C, and from 266.7 to 306.0 mW cm⁻² at 800 °C. The maximum power density at 800 °C and 4 atm was decreased from 334.8 to 273.9 mW cm⁻² when increasing the fuel utilization from 10% to 90%. Under the test condition of 70% fuel utilization, 800 °C and 4 atm, the cell could run stably at 0.7 V and 350 mA cm⁻² for 50 h, almost without any performance loss.

© 2008 Elsevier Ltd. All rights reserved.

Keywords: Solid oxide fuel cell (SOFC); Anode supported; Tubular; Pressurized operation

1. Introduction

Solid oxide fuel cells (SOFCs) are one of the promising technologies for highly efficient and environmentally friendly power generation. Tubular SOFCs have many advantages with the ease of sealing, the ability to cope with higher thermal stresses, rapid response to load variation, and tolerance to fuel feed variation and to load interruption [1]. Particularly, the ratio of the seal length to the active area is lower in the tubular SOFCs than that in planar SOFCs, thus providing an option of easy assembly and operation [2].

Performance and efficiency are two important parameters for SOFCs, and both of them can be improved by elevating the operating pressure. In the pressurized operation, SOFC can be used as the replacement for combustors in gas turbines [3], and the pressurized hybrid SOFC/gas turbine power systems in multi-megawatt sizes are expected to approach an efficiency of 70%, resulting in less fuel consumption and less capital cost per unit power output. However, there are some technical issues of the pressurized operation, and few researches have been reported.

Siemens Westinghouse Power Corporation (SWPC), in conjunction with Ontario Hydro Technologies, has tested air electrode supported (AES) cells at pressures up to 15 atm with both hydrogen and natural gas [3]. When hydrogen was used as the fuel and the operating pressure was increased from 1 to 5 atm at 1000 °C, the cell output power was significantly enhanced by 9%. However, the cell output power had only a 6% increase when the operating pressure was further increased from 5 to 15 atm [4,5]. The operating pressure increase becomes less effective for further improving the output power when the operating pressure is high, therefore, the pressure should be in a suitable range of 3–10 atm.

Recently, much attention has been paid to anode-supported SOFCs due to their high power density, low manufacturing cost and low operating temperature [6–9], and rapid progresses [10–17] have been made on the anode-supported tubular SOFCs. Accordingly, it is of significance to develop hybrid SOFC/gas turbine power systems for studying the performance of anode-supported tubular SOFCs under pressurized operation conditions.
In this study, an anode-supported tubular SOFC has been fabricated using a wet ceramic process. A dense YSZ film was obtained by a co-firing process. Under pressurized condition, the cell performance has been investigated at temperatures from 650 to 800 °C, pressures from 1 to 6 atm, and fuel utilizations from 10% to 90%.

2. Experimental

2.1. Fabrication of anode-supported tubular SOFC

A green NiO–YSZ tubular support was prepared by an extrusion method. An equal weight of NiO (commercial nickel oxide from J. T. Baker Corporation) and YSZ (commercial YSZ from Tosoh Corporation, 8 mol% Y₂O₃ stabilized ZrO₂) were used. After the extruded tube was dried, a thin film of the YSZ electrolyte was coated on the tube. The anode support/electrolyte assembly was then co-fired at 1450 °C for 4 h. A LSM–YSZ (LSM: YSZ = 60:40 wt.%) cathode was slurry-coated on the YSZ film, and then fired at 1250 °C for 2 h. The thicknesses of the anode, cathode and electrolyte were 1000, 40 and 15 μm, respectively. The cell tube was 50 cm in length, 8 mm in diameter and the electrode active area was 100 cm². Nickel mesh was used as the anode current collector and silver mesh was used as the cathode current collector. The specifications of the anode-supported tubular SOFC are listed in Table 1.

2.2. Assembly and operation of the cell

Fig. 1 shows the schematic of the pressurized reactor of the tubular cell. The reactor was heated at 5 °C min⁻¹ by an electric furnace, while nitrogen and air were introduced into the anode and the cathode chambers, respectively, both at a flowing rate of 100 ml min⁻¹. At 800 °C, the nitrogen gas was switched to a hydrogen gas (H₂), and then the NiO–YSZ substrate was gradually reduced into a porous Ni–YSZ anode. The H₂ was saturated with water and all the gases were preheated before entering the reactor. The performance of the tubular cell was measured after the open circuit voltage (OCV) of the cell reached at 1.0 V.

During the measurement, H₂ and air were the fuel gas and the oxidant gas, respectively. All the gases flowed out of the reactor without cycling. In this study, the air flow was kept at six times of the air consumption in the electrochemical reaction. The gas flows were controlled by mass flow controllers and pressure valves and adjusted according to the fuel utilization.

Fig. 1. Schematic of the pressurized reactor for the tubular cell: (1) reactor; (2) tubular SOFC; (3) H₂ mass flow controller; (4) air mass flow controller; (5) H₂ valve; (6) air valve; (7) sealing.

3. Results and discussion

3.1. Effect of pressure

The effect of pressure on the single tubular cell performance was investigated at the temperature range of 650–800 °C when the H₂ utilization was kept at 70%. Fig. 2A–D shows that all the measured OCVs were more than 1.0 V even when the cell was operated at 6 atm, thus demonstrating that the electrolyte film was dense and the cell was adhered with the sealant very well. They also show that the OCV increased with the temperature decrease or the pressure increase. The voltage was decreased with the increase of the current density at the same operational temperature and pressure. However, the effect of temperature on the cell performance was greater than that of the pressure. The maximum power density was increased from 135.0 to 159.0 mW cm⁻² at 650 °C when the pressure was raised from 1 to 6 atm, and from 266.7 to 306.0 mW cm⁻² when the temperature was 800 °C. Thus, the maximum power density increased with the pressure by 17.78% and 14.71% at 650 and 800 °C, respectively. It suggested that the effect of the pressure on the cell performance was more significant under low temperatures than at high temperatures. On the other hand, the maximum power density increase was 97.56% and 92.45% when the temperature was elevated from 650 to 800 °C at 1 and 6 atm, respectively, indicating that the effect of the temperature on the cell performance was greater under lower pressures than at higher pressures.

The variations of OCVs with the temperature and pressure can be expressed according to the Nernst equation as
follows:

\[ E = E_0 - \frac{RT}{n_e F} \ln \left( \frac{P_{\text{H}_2\text{O}}}{P_{\text{H}_2} P_{\text{O}_2}^{1/2}} \right) \]  

(1)

where \( E_0 = -\Delta G^\circ/n_e F \) is the Nernst potential at standard conditions (\( P_0 = 1 \text{ atm} \)), \( \Delta G^\circ \) is the change of Gibbs free energy in standard state between the products and the reactants of the total electrochemical reaction (\( \text{H}_2 + 0.5\text{O}_2 \rightarrow \text{H}_2\text{O} \)) in the cell, \( F = 96485.309 \text{ C mol}^{-1} \), which is the Faraday’s constant, \( n_e = 2 \), which is the mole number of electron transfer in the reaction when producing 1 mol of water, \( R = 8.314 \text{ J (mol K)}^{-1} \), which is the universal gas constant, \( T \) is the absolute temperature, and \( P_{\text{H}_2\text{O}}, P_{\text{H}_2} \) and \( P_{\text{O}_2} \) are the partial pressures of \( \text{H}_2\text{O}, \text{H}_2 \) and \( \text{O}_2 \), respectively, in the system.

The relationship between the voltage and the current density at various operating temperatures and pressures could be evaluated by combining thermodynamics with polarization kinetics together. The effect of temperature on the performance was thermodynamically negative and kinetically positive, while the effect of pressure of the fuel gas or oxidant gas was positive both thermodynamically and kinetically.

Fig. 3 shows the changes in the cell area specific resistances (ASRs), \( R_{\text{cell}} \), calculated by the slope of the linear region from Fig. 2. It was apparent that the ASRs were decreased with pressure increase in the investigated temperature range. The total activation energy of the cell reaction, \( Q_{\text{cell}} \), can be obtained from the slope of the plot of \( \ln(R_{\text{cell}}/T) \) vs. \( 1/T \), where \( T \) is the temperature in (K). At different pressures, \( Q_{\text{cell}} \) remained at \( 54.5 \pm 1 \text{ kJ mol}^{-1} \). The results indicated that the increase in pressure did not change the rate-determining step of the total cell reaction, although the raising of the pressure could improve the cell output. Kim et al. have reported that \( Q_{\text{cell}} \) was \( 50 \text{ kJ mol}^{-1} \) in a planar cell at ambient pressure [18], which was very close to our results in the tubular cell.

3.2. Effect of fuel utilization

Fuel utilization is one of the most important operating parameters for fuel cells and has a significant impact on the cell output voltage and system efficiency. Fuel utilization usually can be evaluated by the ratio of the fuel consumed in the electrochemical reaction to the total fuel feeding flow. Fig. 4 shows the impact of the fuel utilization on the cell performance at 800 °C and 4 atm. The terminal voltages at any current densities decreased with increasing the fuel utilization. The decreases were more pronounced at higher utilizations than that at lower ones. The maximum power density was decreased from 334.8 to 273.9 mW cm\(^{-2}\) when the fuel utilization was increased from...
10% to 90%. The high cell performance at low fuel utilization was due to the low concentration overpotential, i.e. at a higher fuel flow rate. However, it would be a great waste under such a low fuel utilization for a high performance of the cell when there was no cycling of the anode gas flow. So, it is a necessity to balance the cell performance and the fuel utilization.

3.3. Stability

Fig. 5 shows the variation of the cell output voltage with the operating time at 350 mA cm$^{-2}$, 800°C, 4 atm and 70% fuel utilization. It can be seen that the voltage is increased slightly after operating for 15 h, and then showed little decrease from 15th to 50th h. The output power was increased from 24.34 to 25.89 W in the first 15 h, and then remained at about 24.75 W. The stable running of the cell implied that the contact between the metal collectors and the cell tube was in a good state, the material and structure of the tubular cell was stable and the operation was feasible.

4. Conclusions

An anode-supported tubular SOFC was successfully fabricated by a wet process and the cell was operated under a pressurized condition. Raising the operation pressure could improve the cell performance significantly. The effect of the pressure on the cell performance was more significant at low temperatures than at high temperatures. The output voltage was dropped significantly with an increase in the fuel utilization. The output power of 25 W was reached at 0.7 V and 800°C for a cell with an effective area of 100 cm$^2$, and the cell had run for 50 h without any loss in cell performance at 350 mA cm$^{-2}$, 800°C and 4 atm when the fuel utilization was kept at 70%.

Acknowledgements

The authors are thankful for the financial supports from Chinese Ministry of Science and Technology and Chinese Academy of Sciences.

References