An Electricity and Value-added Gases Co-generation via Solid Oxide Fuel Cells

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In this study, an electricity and value-added chemicals co-generation system using methane-fueled single chamber solid oxide fuel cells (SC-SOFCs) was successfully developed and investigated. The SC-SOFCs, which operated on methane/oxygen gas mixture with a ratio of 2:1, achieved an open-circuit voltage of 1.0 V and a maximum peak power density of ~ 840 mW.cm\(^{-2}\) at 700 °C. By passing the exhaust gas of the fuel cell through a Ru/Al\(_2\)O\(_3\) catalyst at 700 °C, the synthesis gas is obtained with a methane conversion of higher than 95%, while CO and H\(_2\) selectivity is higher than 92%. This study provides a novel strategy for energy conversion which is one of the major concerns in energy field and a new frontier for improving the energy efficiency of SOFCs.

1. Introduction

Solid-oxide fuel cells (SOFCs) are all-solid electrochemical devices that convert the chemical energy stored in fuels to electricity directly [1, 2]. Due to a couple of advantages such as high fuel flexibility, non-noble electrodes, SOFCs have received considerable attentions [3]. Among many fuel cell configurations, the development of single-chamber SOFCs (SC-SOFCs) (Fig. 1) has generated widespread interest [4,5] due to its simple configuration which both the anode and cathode of these cells are exposed to the same fuel-oxidant gas mixture. In this simple, one-chamber configuration, no sealant is necessary and the cell can be rapidly heated and cooled. The operation of this kind of fuel cell is based on the different catalytic selectivity of the anode and cathode. Under ideal conditions the cathode reacts only on the oxygen activation, while the anode reacts only on the partial oxidation of fuel. The different catalytic selectivity of anode and cathode leads to an oxygen partial pressure gradient which drives continuous power output. Extensive studies have been conducted to improve the power output and systematic configurations of SOFCs [6-8] and high power output which is comparable to dual chamber SOFCs (DCSOFCs) has been achieved [6]. However, one disadvantage of SC-SOFCs prohibits its applications; SC-SOFCs require fuel rich conditions for operation. In other words, excessive fuel will be supplied and wasted which lowers system efficiency. Also, whether through thermal power or conventional fuel cells, power generation and the chemical energy conversion...
The process of hydrocarbon fuels involves the emissions of CO$_2$ greenhouse gases. If the excessive hydrocarbon fuels could be simultaneously converted into value-added chemical products (like syngas) during electricity generation instead of CO$_2$, higher energy conversion efficiency could be expected meaning zero emissions of environmental pollutants. Some researchers have shown generating electricity while simultaneously converting the fuel into value-added chemical products through a fuel cell reactor [9]. However, using a DC-SOFC for gas co-generation is confronted with a common problem: the product selectivity and yield is restricted by the fuel cell’s operating conditions. Changes in the polarization current lead to significant changes in product composition and yield. Also, the direct exposure of the anode to pure hydrocarbons presents a serious coking problem.

In this study, a SC-SOFC combined with a downstream Ru/Al$_2$O$_3$ catalyst was investigated towards the co-generation of electricity and syngas. Synthesis gas is an important raw chemical material, for example it is used to synthesize synthetic methanol, hydrogen and dimethyl ether as well as other chemical products. The methane was selected as the fuel for fuel cell operation because methane can be found in a variety of raw materials as well as considered to be a clean energy source. When methane is used as fuel, the byproduct is simultaneously converted into value-added chemical during the power generation process, leading to zero emissions from chemical energy conversion.

2. Experimental

2.1 Fuel cell fabrication & Catalyst

Anode-supported complete cells were prepared using a tape casting with wet spraying technique [10]. YSZ (NexTech materials), SDC, NiO + YSZ (60:40 w/w, NexTech materials) and BSCF + SDC (70:30 w/w) were used as the electrolyte, interlayer, anode and cathode materials, respectively. NiO–YSZ anode-supported substrates with YSZ thin film electrolyte were fabricated by a tape-casting and lamination process [10]. The green tape was cut into discs, sintered at 1200 °C for 2 h. The sintered substrate (15 mm in diameter) consisted of two layers: anode and electrolyte. A SDC interlayer was deposited on top of the YSZ electrolyte by using wet spraying method. Then, the substrate with SDC layer was sintered at 1350 °C for 4 h to compact the electrolyte layer. The sintered pallet was reduced using hydrogen at 700 for 5 h to convert NiO into Ni. Following the deposition of cathode (0.51cm$^2$) on the top of SDC layer, the complete cells were sintered at 1000 °C for 5 h in the N$_2$ atmosphere. Fig.2 shows the completed fuel cell. The YSZ layer is about 10μ and has a pin hole free structure. The SDC inter-layer is about 3μ and shows a good attachment with YSZ layer.

The Ru (5wt. %)/Al$_2$O$_3$ catalyst powders was obtained from Alfa Aesar. About 0.5 g of catalyst particles in the size range of 40-60 mesh was used during the testing.

2.2 Characterization

The IV method was used to measure the fuel cell performance such as power density, open circuit voltage (OCV), and overpotential by using a digital sourcemeter (Keithley 2420) interfaced with computer for data acquisition. An SRI
Instruments 8610C gas chromatograph (GC) was used to measure exhaust compositions. The temperature was monitored using K-type thermocouples. The surface morphologies of the fuel cells were observed by a scanning electron microscope (SEM).

2.3 Testing setup

Fig. 3 is a schematic of co-generation testing system. Silver wire, net and paste were applied as current collectors to either side of the fuel cells. The fuel cell was placed under the catalyst (0.5g) with a distance of 2 cm. Some quartz sands were filled into the quartz tube to avoid flashback. Two mass flow controllers were employed to provide oxygen/methane mixtures. The water from exhaust was removed before it went into GC. A tubular furnace was employed to heat up the system to the target temperature at a rate of 5°C/min.

3. Results and Discussion

At first, the current–voltage /power polarization curves of SC-SOFC were measured at the furnace temperatures of between 600 and 700°C. The molar ratio of methane-oxygen gas mixture was set to 2:1 because this is the ideal condition to obtain the syngas. The total flow of methane-oxygen was 150 mL/min. As shown in the Fig. 4, the cell voltage of 1.02–1.04 V was achieved which is much higher compare to the SDC based SC-SOFC (typically 0.70-0.78V) [7]. This is mainly because the combination of SDC-YSZ bilayer can effectively prevent electron diffusion which is a typical problem of SC-SOFC with a pure SDC layer. Another contribution for the high OCV is the high partial oxygen pressure. Conventional SC-SOFC applied air as the oxidant during the test which has lower partial oxygen pressure. At a furnace temperature of 700°C, a peak power density of about 840 mW/cm² was achieved, which is comparable to the DCSOFC. Also, as shown in the Fig. 4, the performance was improved when temperature increase which indicate that the temperature mainly determines the fuel cell power output. However, the real fuel cell temperature is much higher that of furnace temperature. As shown in the Fig. 5, the fuel cell temperature is about 170 °C higher compare to the furnace temperature. The increase of fuel cell
temperature is due to the oxidation of methane which can release a lot of heat near the anode. As we know, the fuel cell anode contains Ni which is widely used as the catalyst for partial oxidation and steam reforming reactions. These reactions produces a low oxygen potential near the anode surface, thus increase the oxygen potential differential across the two electrodes. Also they can electrochemically generate H₂ and CO which is the direct fuels for power generation. However, because of the poor activity of the BSCF+SDC cathode for methane partial oxidation [7], a considerable amount of methane is unreacted in the effluent gas of the fuel cell which need to be converted into syngas.

The Fig. 6 shows the CH₄/O₂ conversion and CO/CO₂ selectivity as a function of temperature for the methane oxidation reaction under a regular single-chamber operation conditions with total flow rate of 150 mL/min. The conversion of methane is around 20 -25% which indicated a large amount of unreacted fuels. At the same time, there is also a part of unreacted oxygen existing in the exhaust. As indicated by the selectivity of CO₂ and CO, the reacted methane are mostly converted the undesired CO₂ which indicated the deep oxidation happens. To convert these unreacted methane and achieve high CO selectivity, a Ru/Al₂O₃ was placed in the upstream of SCSOFC. The Fig. 7 shows the CH₄/O₂ conversion and CO/H₂ selectivity of combined SCSOFC and Ru/Al₂O₃ catalyst system.

4. Conclusions

An electricity and value-added chemicals co-generation system using methane-fueled single chamber solid oxide fuel cells (SC-SOFCs) was successfully demonstrated and investigated. The SC-SOFCs, which operated on methane/oxygen gas mixture with a ratio of 2:1, achieved an open-circuit voltage of 1.04 V and a maximum peak power density of ~ 840 mW.cm⁻² at 700 °C. By passing the exhaust gas of the fuel cell through a Ru/Al₂O₃ catalyst at 700 °C, the synthesis gas is obtained with a methane conversion of higher than 95%, while CO and H₂ selectivity is higher than 92%. This study
provides a novel strategy for energy conversion which is one of the major concerns in energy field and a new frontier for improving the energy efficiency of SOFCs.

References