



Short communication

A novel direct carbon fuel cell by approach of tubular solid oxide fuel cells

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ABSTRACT

A direct carbon fuel cell based on a conventional anode-supported tubular solid oxide fuel cell, which consisted of a NiO–YSZ anode support tube, a NiO–ScSZ anode functional layer, a ScSZ electrolyte film, and a LSM–ScSZ cathode, has been successfully achieved. It used the carbon black as fuel and oxygen as the oxidant, and a preliminary examination of the DCFC has been carried out. The cell generated an acceptable performance with the maximum power densities of 104, 75, and 47 mW cm⁻² at 850, 800, and 750 °C, respectively. These results demonstrate the feasibility for carbon directly converting to electricity in tubular solid oxide fuel cells.

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1. Introduction

Coal is the most abundant fossil fuel in China. In 1999, the coal output was near 1030 million metric tons (Mt) and it shared 68% in total primary energy output in China [1]. Nowadays, electric power from coal is achieved by coal-fired power plants, however, it is well-known that this method is not only a low-efficiency process, but also emits substantial amounts of greenhouse gases and pollutants, such as NO_x, SO_x, etc. On the other hand, the dependence upon coal as a fuel source continues to be widespread, as other natural resources remain in short supply. Therefore, it is logical to investigate a new and high-efficiency process for coal to be used for power generation.

The direct carbon fuel cell (DCFC) is a power generation device in which the chemical energy of carbon is directly converted into electrical energy by electrochemical oxidation, without the combustion or gasification process. DCFCs can use petroleum coke, coal coke, and gas carbon, as well as biomass carbon as fuel [2]. DCFCs offer comparative high efficiency of conversion, and can yield 2–3 times the amount of electrical energy as coal-fired power plants for a given amount of carbon (coal) [3], resulting in reduced carbon dioxide emissions per unit of generated electricity. For no combustion, they also typically do not emit pollutants, such as NO_x, SO_x, etc. [4].

In order to achieve high energy efficiency of DCFCs at current densities that could be acceptable for fuel cells applications, a high

temperature operation is needed. There are two high temperature approaches for DCFCs operation: (1) molten salt electrolyte approach with operating temperatures of 400–750 °C; (2) SOFCs approach operating at higher temperatures of 600–1000 °C.

The early attempts at DCFCs dated from the late 19th century [5,6]. By far, most DCFCs used molten carbonates or molten hydroxide as the electrolyte [7–15]. Recently, some researchers combined SOFCs and MCFCs technologies [3,16,17], using a solid oxide electrolyte to separate the cathode and anode compartments, whilst a molten carbonate electrolyte was utilized to extend the anode/electrolyte region. But all the fore-mentioned DCFCs contained molten salt electrolyte, accordingly, such cells would lead to some serious problems of degradation of the electrolyte and the risk of liquid leaking.

The SOFC is a completely solid energy conversion device. Due to their higher operating temperatures, SOFCs offer some significant advantages such as faster kinetics, better activity of electrodes, and higher efficiency, as well as more convenient fuel flexibility. Accordingly, SOFCs can utilize gas fuels, liquid fuels, as well as solid carbon fuel. SOFCs approach for DCFCs, which means direct carbon conversion in SOFCs, has no risk of liquid leaking and volatilization of the electrolyte. In this paper we describe a novel direct carbon fuel cell by the approach of conventional anode-supported tubular solid oxide fuel cell, and report the preliminary results of this proof-of-concept, which is not the optimized but an acceptable performance. Here “direct conversion” means converting chemical energy into electricity in a single process step or chamber, but does not infer or suggest that the conversion is achieved in a single elementary reaction step.

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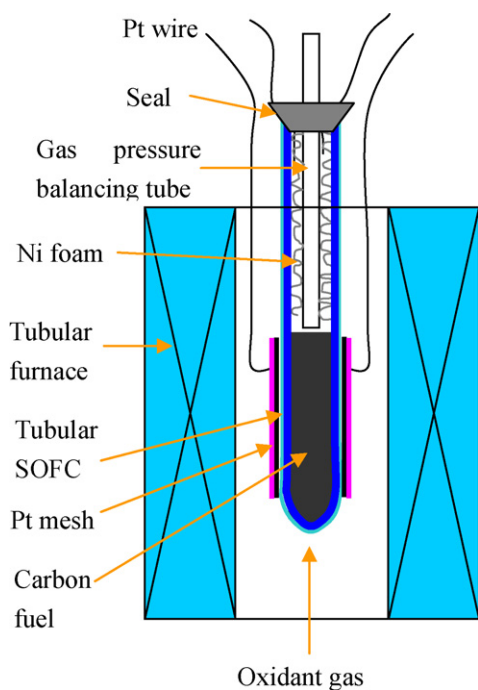


Fig. 1. Schematic design of the DCFC testing setup.

2. Experimental

The schematic design of the DCFCs testing setup is represented in Fig. 1. The conventional one-end closed anode-supported tubular SOFC single cell, consisted of a NiO–YSZ anode support tube, a NiO–ScSZ anode functional layer, a ScSZ electrolyte film, and a LSM–ScSZ cathode, was obtained by dip-coating and co-sintering techniques [18]. The length of the tubular cell was 10.8 cm (cathode length = 3.2 cm), the outside diameter of the tube was approx. 1.0 cm, the thickness of the tube was 0.5–0.6 mm, and the active area of the cell was approx. 10.0 cm².

Firstly, the anode of the tubular cell was reduced by hydrogen at high temperature; then the carbon black was dropped into the tubular cell used as fuel after the hydrogen was removed by nitrogen. The gas pressure balancing tube was subsequently connected with a sealed container. The particle size of the used commercial carbon black, which was supplied by ShaoXing Ren-Fei Carbon blacks CO., was in the range of 2–10 μm (0.633 m² g⁻¹). The oxygen with a flow rate of 40 mL min⁻¹ was introduced to the cathode from the bottom inlet. The current–voltage (*I*–*V*) curves and electrochemical impedance spectra (EIS) were obtained using an Electrochemical Workstation IM6ex (Zahner, GmbH, Germany) to evaluate the performance of the cell. The impedance spectra of the electrochemical cell were recorded under open circuit and under constant current densities of 50 and 100 mA cm⁻², with an amplitude of 20 mV, in the frequency range 0.03 Hz to 100 kHz. The measurements were carried out at 850–750 °C, in steps of 50 °C. The ohmic resistances (*R*_{ohm}) were estimated from the high frequency intercepts with the real axis and the overall electrode polarization resistances (*R*_E) were directly measured from the differences between the low and high frequency intercepts with the real axis.

3. Results and discussion

Fig. 2 shows typical curves of potential and power density versus the current density for the DCFC at different temperatures. As can be seen that the DCFC produced an acceptable performance, with maximum power densities of 104, 75 and 47 mW cm⁻² at 850, 800

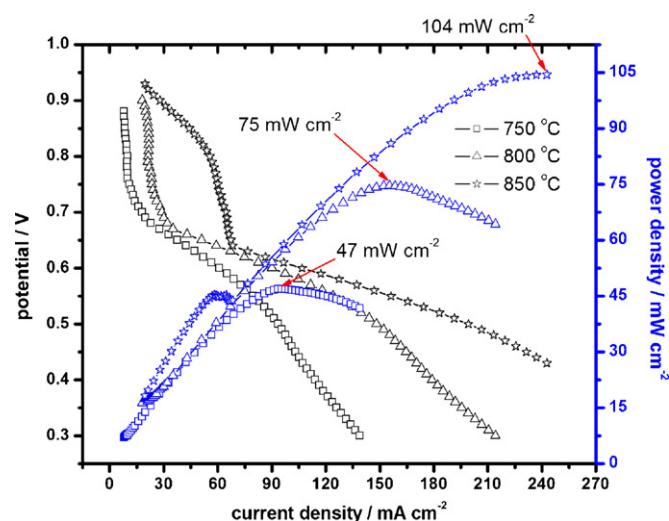


Fig. 2. The potential and power density versus the current density curves for the DCFC at different temperatures.

and 750 °C, respectively. The performance was better than that of DCFCs which used molten salt electrolyte [3,7,11–13] and that of DCFC by the approach of a solid oxide fuel cell based fluidized bed configuration [19]. There were obvious inflexions in the *I*–*V* curves, and it can be seen that the voltages decreased sharply before the inflexions as the currents increased slightly. The insufficient fuel gas may be the reason. The chemical and electrochemical reactions that occur in the DCFC when it was discharging were assumed to be as follow:



Eq. (1) is the reaction between oxygen and electrons that occurs at the cathode. The O²⁻ diffuses from the cathode can react with the carbon in intimate contact with anode surface at the anode, as shown in Eq. (2). The byproduct CO₂ then can be reformed with carbon within the fuel cell. As shown in Eq. (3), the well-known Boudouard reaction, has been thoroughly examined as a function of temperature and it is well established that the dominant gaseous species at a temperature above 750 °C is CO, whereas at lower temperatures the dominant gaseous species is CO₂ [2]. So after the inflexions, Eqs. (3) and (4) are the dominant anodic reactions. The large current, which means more CO₂ is being generated, can promote the reforming reaction, resulting in sufficient fuel gas CO.

Combining the anodic and cathodic reactions (Eqs. (1)–(4)), the overall DCFC cell reaction (considering only CO₂ and CO production) is



or



In practice both processes can occur, depending on the applied electrode potential, the temperature and the kinetics of reactions [7].

The AC impedance spectra for the DCFC under open circuit are shown in Fig. 3. The *R*_{ohm} and *R*_E increased as the temperature decreased. The *R*_{ohm} were 0.71, 0.74, and 0.82 Ω cm² at 850, 800, and 750 °C, while the *R*_E were 0.64, 1.12, and 2.23 Ω cm², respectively. It is well-known that the low frequency arc corresponds to

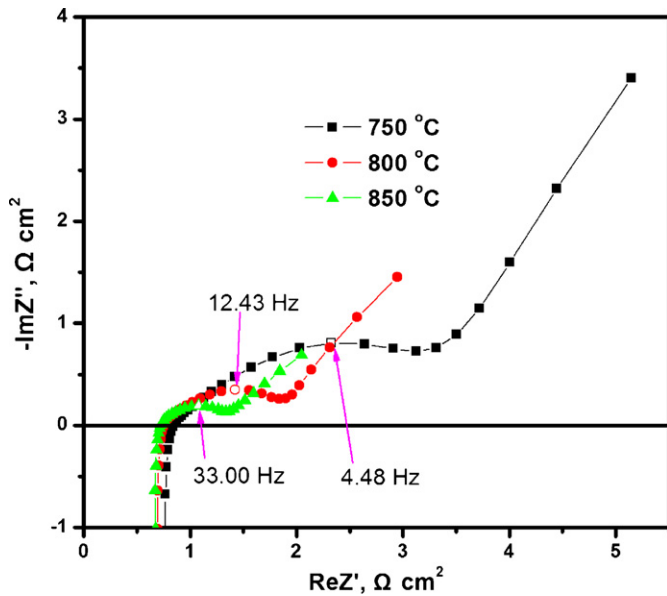


Fig. 3. The AC impedance spectra for the DCFC at different temperatures with O_2 as oxidant.

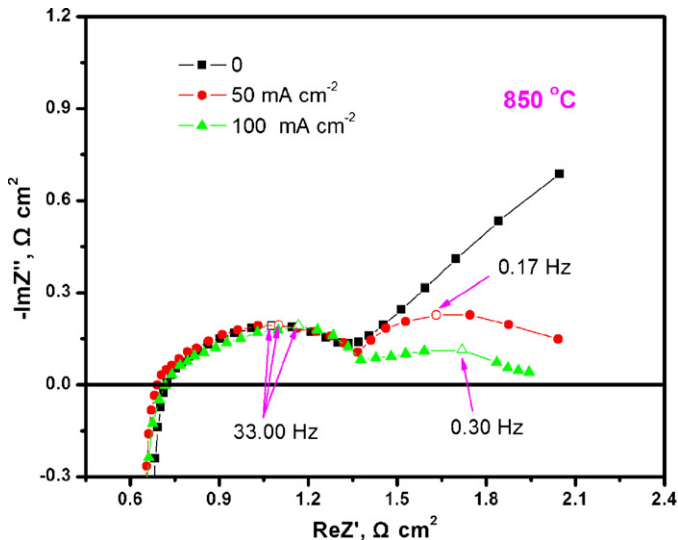


Fig. 4. The AC impedance spectra for the DCFC under different current densities at $850\text{ }^\circ\text{C}$ with O_2 as oxidant.

mass transport process, so the large arcs in the low-frequency zone in Fig. 3 may result because the fuel gas within the cell is insufficient. Fig. 4 shows the AC impedance spectra for the cell under different current densities at $850\text{ }^\circ\text{C}$. The ohmic resistances and

high-frequency arcs were almost constant under different current densities, but the low-frequency arcs, which correspond to mass transport process, decreased as the current density increased. This phenomenon not only means that the larger current, the more sufficient fuel gas, but also can explain the inflexions phenomenon in Fig. 2.

4. Conclusions

By approach of tubular SOFC, a novel DCFC which used carbon black as fuel has been successfully realized. A preliminary examination of the DCFC has been carried out, and an acceptable performance was obtained. The maximum power densities of the cell were 104 , 75 , and 47 mW cm^{-2} at 850 , 800 , and $750\text{ }^\circ\text{C}$, respectively. Further work, such as decreasing the ohmic resistance of the cell and improving carbon fuel within reforming process, is currently on-going in order to achieve a better performance.

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