Study of 10kW molten carbonate fuel cell power generation system and its performance test

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Abstract

High-temperature fuel cells are a power technology that can improve the efficiency of electricity generation and achieve near-zero emissions of carbon dioxide. The present work explores the performance of the 10kW high-temperature molten carbonate fuel cell (MCFC). The key materials of the molten carbonate fuel cell single cell were characterized and analyzed by X-ray diffraction(XRD) and scanning electron microscope (SEM). The results show that the pore size of key electrode material was 6.5 μm and the matrix material is α-$LiAlO_2$.The open circuit voltage of the single cell is 1.23 V in experiment. The current density is greater than 100 mA / cm^2 when the operating voltage is 0.7 V. The 10 kW fuel cell stack was constitutive of 80 pieces single fuel cells with area of 2000 cm^2. The open circuit voltage of the stack reaches above 85 V. The fuel cell stack power and current density can reach 11.7 kW and 104.5 mA/cm^2 when the operating voltage is 56 V. The influence and long-term stable operation of the stack were also analyzed and discussed. The successful operation of 10kW high temperature fuel cell promotes the scale of domestic fuel cell and provides the research basis of fuel cell capacity enhancement and distributed generation in the next step.

1 Introduction

In recent years, with the restriction of carbon emissions in the world, more countries have changed their coal utilization technologies. China currently mainly uses coal resources and has a certain degree of dependence on oil and gas. It is particularly critical to improve the efficiency of coal power generation and reduce carbon dioxide and pollutant emissions in the period of energy transformation (Xu et al, 2019; Zhang, 2018; Mehrpooya et al, 2017). Fuel cell power generation technology (Mcphail et al, 2015; Mastropasqua et al, 2019) has entered people's vision and has been continuously developed by various countries in the world. Fuel cell power stations were demonstrated in Europe, America and other countries (Carapellucci et al, 2019;). However, there is not a stationary high temperature fuel cell power station in China due to the certain technological gap with foreign countries. Many scholars have started the research of fuel cell technology, such as proton exchange membrane fuel cell (PEMFC), solid oxide fuel cell (SOFC), molten carbonate fuel cell (MCFC) and so on.

The integrated gasification fuel cell (IGFC) power generation technology, based on Integrated gasification combined cycle (IGCC) power generation, can greatly improve coal power efficiency and carbon dioxide capture (Torabi et al, 2016; Duan et al, 2015; Dong et al, 2019; Wang et al, 2020), and achieve near zero emissions of carbon dioxide and pollutants. IGFC remains a conceptual approach in China (Ku et al, 2018). But it may be possible to move towards a IGFC demonstration in the next decade with the progress of the fuel cell technology. The IGFC systems were demonstrated based on MCFC and SOFC(Mu et al, 2018; Slater et al,2018; Samanta et al, 2017; Wolfersdorf et al, 2017; Campanari et al, 2016) and the fuel cell integrated CO_2 capture process is a promising route and more effective if fuel cell technology can be commercialized (Wang et al, 2020). Fuel cell as its key power generation device has the advantages of high efficiency and environmentally friendly. It can directly convert chemical energy into electrical energy, refrigeration and heat by system coupling (Wu et al, 2016; Ghorbani et al, 2019; Marefati et al, 2019) . The theory of energy conversion efficiency can reach over 85% without emissions of nitrogen oxides and sulfur oxides. As a high-temperature fuel cell, molten carbonate fuel cell (MCFC) has a wide range of fuel sources that does not rely on precious metals as electrode catalysts. It can be combined with gas turbines and steam turbines to achieve jointed heat and power, which improved energy utilization and conversion effectiveness (Tano et al, 2017).

Molten carbonate fuel cells are mainly used as large-scale power generation, distributed power generation and fixed power systems. It is still the largest single-unit installed capacity among different types of fuel cells (Makino et al, 2018; Mastropasqua et al, 2017; Samanta et al, 2016;). It also has attached great importance and developed by the United States, Germany, Italy, South Korea, Japan and other countries (More et al, 2020; Haghghi et al, 2019; Mehmeti et al, 2018). Fuel Cell Energy (FCE) of the United States continues to research and develop fuel cell-gas turbine power generation systems with the natural gas fuel. FCE has owned three commercial products of 300 kW to 2.8 MW MCFC, named DFC300MA, DFC1500 and DFC3000. The maximum effective area of a single cell can reach $1m^2$ and the current density of the stack is 80-120 mA/cm^2. The power generation efficiency is greater than 47 %. In 1995, Japan built a 1MW power station composed of four 250KW fuel cell modules (Da Silva et al, 2019; Discepoli et al, 2016). It would integrate coal gasification combined cycle power generation and coal gasification fuel cell combined cycle power generation (IGFC) with the 55% power efficiency in the future goals. The MCFC power station (58.8 MW (2.8 MWx21 fuel cell module)) was established by South Korea's POSCO in Gyeonggi Province, which can provide power for 140,000 households.

In 2017, the Ministry of Science and Technology set up a major special project "CO_2 near-zero emission coal gasification power generation technology" to conduct research and demonstration of MW-level thermal power integrated gasification fuel cell power generation system. The core of the project is to develop the first domestic 500kW high temperature fuel cell power generation. The goal of this research project is to develop domestic high temperature fuel cell technology, accelerate the demonstration application of fuel cell power generation technology, and narrow the technological gap with foreign countries. The 500 kW high temperature fuel cell consists of solid oxide fuel cell(SOFC) and molten carbonate fuel cell(MCFC). The 10kW fuel cell in this study will be used as the module unit of molten carbonate fuel cell.

In this paper, the 10kW MCFC stack was designed and built, which was the domestic leading fuel cell technology. We studied the operation and performance of fuel cell stack. The problems existing in the operation process of the stack were analyzed discussing the results in terms of operation power and time. The operation of 10kW MCFC promotes the power and scale generation of domestic fuel cell and provides the research basis of fuel cell capacity enhancement in the next step.

2 Experimental

2.1 Materials of fuel cell

Molten carbonate fuel cells are mainly composed of electrodes, separators, metal bipolar plates, and electrolytes as shown in Fig.1(a).The flow channel of fuel cell in stack is illustrated in Fig.1(b).

The anode material is porous metal nickel (Antolini, 2011; Kulkarni et al, 2012) and the cathode is porous nickel oxide (generally obtained by oxidizing pure nickel during fuel cell heat treatment). The electrode is prepared by carbonyl nickel powder as the raw material, adding sodium carboxymethyl cellulose solution as a binder, The slurry is casted on a flat surface by mixing and stirring, and the electrode blank is dried after dried. The electrode blank is placed in a high-temperature furnace for heat treatment. During the sintering process, it is controlled by controlling the temperature and pore-forming agent. The size and distribution of the pore size.

The matrix material is α-$LiAlO_2$ (Kim et al, 2019; Zhang et al, 2017) in molten carbonate fuel cells. The α-$LiAlO_2$ powder is prepared by high-temperature roasting method. The process is as follows: Li_2CO_3 and basic alumina are mixed in an equimolar ratio. In order to complete the reaction, the added amount of Li_2CO_3 is excessive (2 wt.%). Distilled water is used as the ball milling medium. After ball milling, drying and roasting, α-$LiAlO_2$ can be obtained. The preparation process of the matrix is as follows: the solvent (n-butanol), binder (polyvinyl butyral), dispersant (fish oil), plasticizer (dioctyl phthalate), defoamer (silicone oil)). The $LiAlO_2$ powder are ball milled according to a certain proportion, and the ball mill rotates to form a uniform slurry. After the obtained slurry was subjected to vacuum defoaming, a film casting method was used to form a film. The bipolar plate material is 316L stainless steel, and the processing method is a combination of stamping and welding. The electrolyte is Li_2CO_3-K_2CO_3 (mol 62mol% / 38mol%).

2.2 Fuel cell stack

The fuel cell stack and the single cell are assembled manually. The single cell is based on the anode and the cathode on both sides of the bipolar plate respectively. The single cell is separated by a matrix. The 10kW molten carbonate fuel cell stack is shown in Fig.2 and Table 1 is the fuel cell parameter data.

Table 1 Molten Carbonate Fuel cell parameters

Molten Carbonate Fuel Cell Item	Parameters
Anode	Porous Ni
Cathode	Porous NiO
Electrode area	2000 cm^2
Matrix	α-$LiAlO_2$
Electrolyte	Li_2CO_3/K_2CO_3
Bipolar plate	316L
Sealing method	Wet seal
Numbers of single cell	80

2.3 MCFC power generation system test

The molten carbonate fuel cell stack test system is shown in Fig.3. During the test, the fuel gas is pure hydrogen, carbon dioxide and nitrogen. The oxygen comes from the air. The hydrogen and nitrogen are mixed and passed to the anode inlet of the fuel cell. Carbon dioxide mixed with air enter the cathode air inlet. The gas flow equipment is the D07 mass flow controller. The upper and lower end plates of the fuel cell are connected to the electronic load FT6800 series (Faith) . The discharge test of the stack is performed by controlling the computer end connected to the load. Fig. 4 shows the gas flow control equipment, electronic load and stack heating furnace in Huaneng Clean Energy Institue(HNCERI).

3 Results And Discussion

3.1 Characteristics of fuel cell materials

Fig. 5 is the morphology of the molten carbonate fuel cell electrode. Fig. 5a is the nickel electrode after casting. The morphology is a loose porous structure. The nickel powder is connected by a binder, and the pore of the porous structure is less than 10 μm. Fig. 5 (b) and (c) are the morphology of the anode and cathode electrodes after firing. The morphologies are all loose and porous structures, and the distribution of different pores is relatively uniform. The average pore size tested is 6.5 μm.

Fig. 6 shows the XRD curve of the powder prepared from the separator. From the curve, the main $\alpha\text{-}LiAlO_2$ can be analyzed, and there is a small amount of Li_2CO_3 that did not participate in the reaction.

3.2 Test of 10kW fuel cell power generation

The high-temperature fuel cell stack is an important part of the IGFC with nearly zero CO_2 emissions. As shown in Figure 7, the fuel gas enters the high-temperature fuel cell and reacts to convert it into electricity and heat. The gas that participates in the reaction is discharged with the anode exhaust of the fuel cell To enter the next link of waste heat and waste gas utilization.

The fuel cell power generation system is mainly composed of molten carbonate fuel cells and solid oxide fuel cells. Our research team is mainly working on the molten carbonate fuel cell power generation module and will provide a 100kW molten carbonate fuel cell stack and system for the IGFC power generation system. The 10kW molten carbonate fuel cell power generation unit is the smallest module in the fuel stack, which provide research foundation of 20 kW, 50 kW and 100kW.

The voltage-current performance test of the single cell was carried out before experiment of the 10 kW MCFC stack. The curve of voltage and current density is shown in Fig. 8. It can be seen that the open circuit voltage of the stack is 1.23 V. The voltage continues to decrease with the increase of current density. Current density is greater than 100 mA/cm^2, when the discharge voltage is 0.7 V. However, the current density dropped below the 100 mA/cm^2, closed to the 90 mA/cm^2 with the increase of operation time.

Table 2 is the gas flow value of the experimental stack. The power curve of MCFC is shown in Fig.9. The working voltage is 56 V (0.7 V, 80 single cells). It can be illustrated that the max power of MCFC can reach 11.7 kW. The operating time of over 10 kW can reach 140min. However, the power decreased with the operating time. It also found that the experimental gas flow values exceed the theory value. The preliminary reason is the gas flow ratio and the wet seal method (Koh, et al, 2000). It is found that we adopt the combined bipolar plate, which the sealing material is achieved through the matrix and electrolyte by the analysis of our fuel cell module. However, it is found that leakage phenomenon occurs between the combined bipolar plates after temperature cooling process. Compared with the structure diagram of foreign fuel cell bipolar plates, It is found that the cathode and anode flow field are separated by welding bipolar plates. This welding method can effectively reduce the possibility of fuel leakage, which is technological gap with us and also our next experimental plan. In addition, the ratio of fuel gas has a certain influence on the performance of the fuel cell. Concerning on the difference of reaction speed and concentration polarization of anode and cathode gases in the fuel cell, the theoretical ratio of fuel gas may not reach the theoretical power value. It is especially necessary to consider the proportion of fuel gas.

The molar ratios of gases are H_2:N_2(0.84:0.16) and O_2:CO_2(0.33:0.67). The value of H_2 fuel utilization can be calculated by the equation (1) [Yi, 2003]

$$\eta_{\text{fuel}} = \frac{Pt}{UeN_A\rho V_{H_2}} \quad (1)$$

P: fuel cell power, W; t: unit time, min; U: operate voltage, V; ρ: density of hydrogen, g/L;

V_{H2}: hydrogen flow, L/min; *e*: electronic, C.

The η_{fuel} of H_2 fuel is 73%.

Table 2 Gas flow of the experimental fuel cell

Gas flow	Theory value	Experimental value
H_2	110 L/min	160 L/min
CO_2	110 L/min	165 L/min
O_2, Air	55 L/min, 275 L/min	80 L/min, 400 L/min
N_2	30 L/min	30 L/min

3.3 Question and challenge

In this study, the power of molten carbonate fuel cell reached 10kW required by the project. The cause of the problem is that the fuel leak occurred during the reaction of the stack, and the sealing state of the stack was not enough. The stack inlet was analyzed. Because the gas flow increased, the salt between the single cells was lost, resulting in the wet seal strength of the fuel cell decline. In addition, the matching of the electrode separator used needs to be further improved, the thickness of the electrode needs to be further reduced, the gas diffusion distance is reduced, and the reaction rate is increased. In this study, the anode and cathode materials used the same thickness and porosity, which has a certain gap with foreign fuel cell electrode technology. It is necessary to continue the experimental work to reduce the thickness of the cathode electrode and increase the porosity. From the analysis of current density results (> 100 mA/cm^2), the total number of designed fuel cell stacks can reach 20 kW at the theoretical output power, but the actual output cannot reach 20 kW in next experiment. During the experiment, the peak power reached 16.7 kW, but the stability is not ideal, which is also related to the above problems. The long-life operation of the stack is an important factor for successful fuel cell demonstration, and experiments and tests for long-term operation of fuel cells should be increased.

The key material technology of the fuel cell in this research process has been consistent with foreign technology. The gap mainly lies in the mutual matching of the internal materials of the single cells and the assembly matching between the single cells, as well as the gas flow rate and flow control during the operation. In overcoming the current technical problems, It is believed that it will gradually narrow the gap with foreign technologies and accelerate the demonstration of the application of molten carbonate fuel cells in China.

4 Conclusion

In the present study, the 10kW fuel cell stack was established based on the previous research. The effects of the materials and operating conditions on the system 10 kW MCFC was analyzed. The pore size of key molten carbonate fuel cell electrode material was 6.5 μm and the matrix material is α-$LiAlO_2$.The open circuit voltage of the single cell is 1.23 V in experiment. The current density is greater than 100 mA /cm^2 when the operating voltage is 0.7 V. The 10kW fuel cell stack was constitutive of 80 pieces single fuel cells with area of 2000 cm^2. The fuel cell stack power and current density can reach 11.7 kW when the operating voltage is 56 V. The experiment results can effectively reflect the current technology of the MCFC key materials and the technical level of fuel cell stack operation. The successful development of the 10 kW stack has promoted the progress of domestic molten carbonate fuel cell technology. However, the paper focuses on engineering application and ignores the theoretical analysis of the experimental process and results. Additional tests are needed to ensure the integrity of the results. Furthermore, there are certain problems existed in the long-term operation of the fuel stack, such as the material stability and the wet seal of the fuel cell stack.

Declarations

Acknowledgment

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Figures

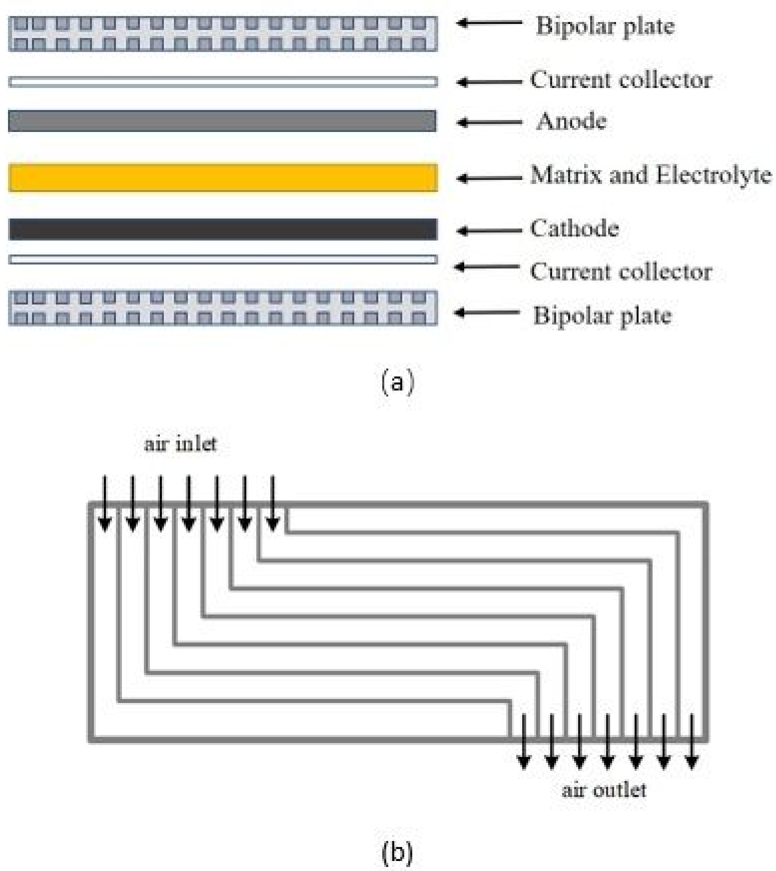

Figure 1

(a) Structure diagram of molten carbonate fuel cell (b) flow channel

Figure 2

molten carbonate fuel cell stack

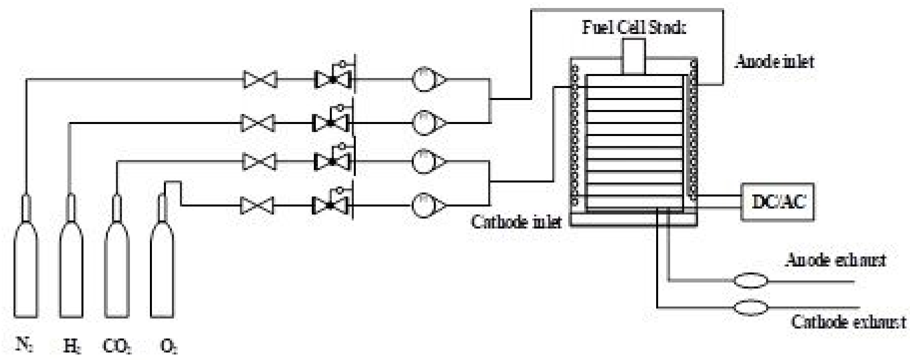

Figure 3

Schematic diagram of the fuel cell test device

Figure 4

Fuel cell test equipment (a) gas flow control (b) electronic load (c) fuel cell stack heating furnace

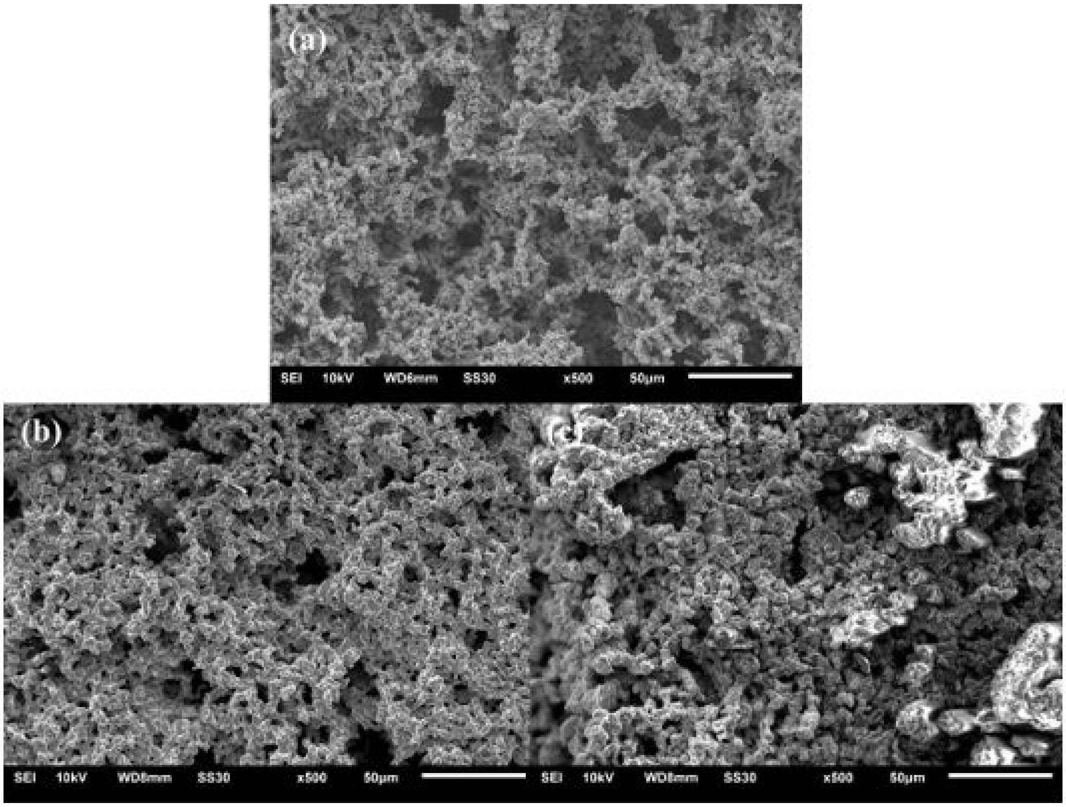

Figure 5

(a) Electrode before firing (b) Anode morphology after firing (c) Cathode morphology after firing

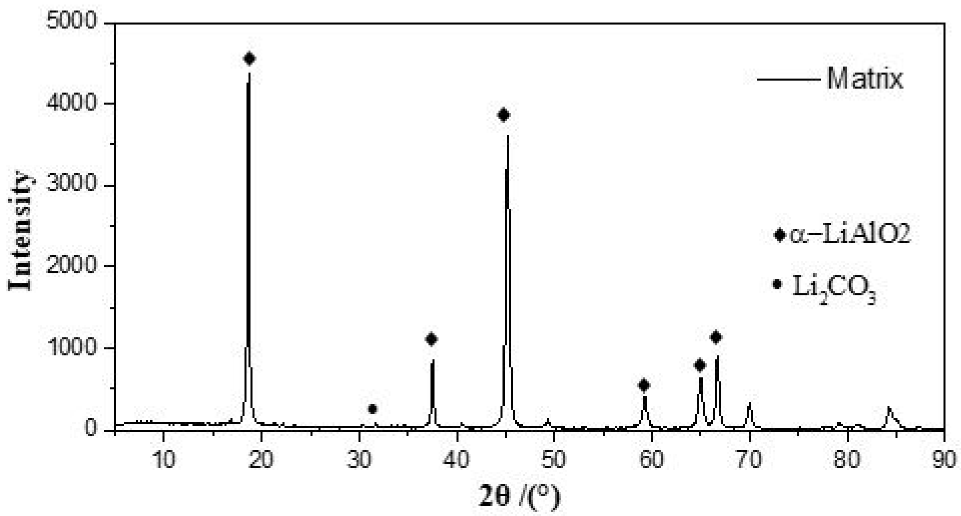

Figure 6

XRD diagram of matrix powder

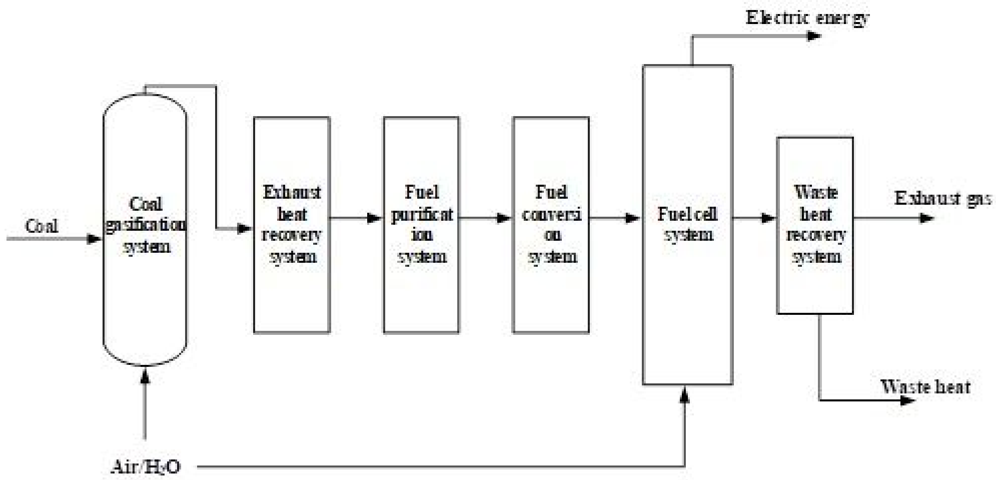

Figure 7

Schematic diagram of IGFC power generation

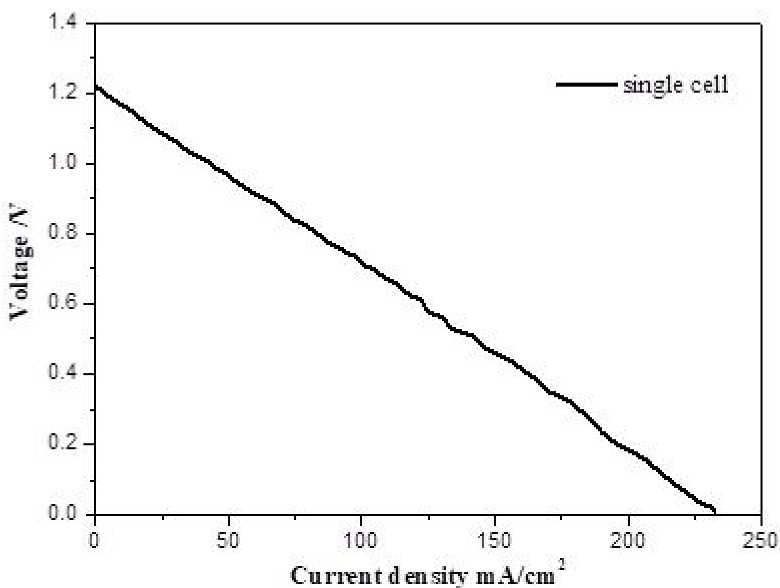

Figure 8

Voltage-current density (V-I) curve of a single cell

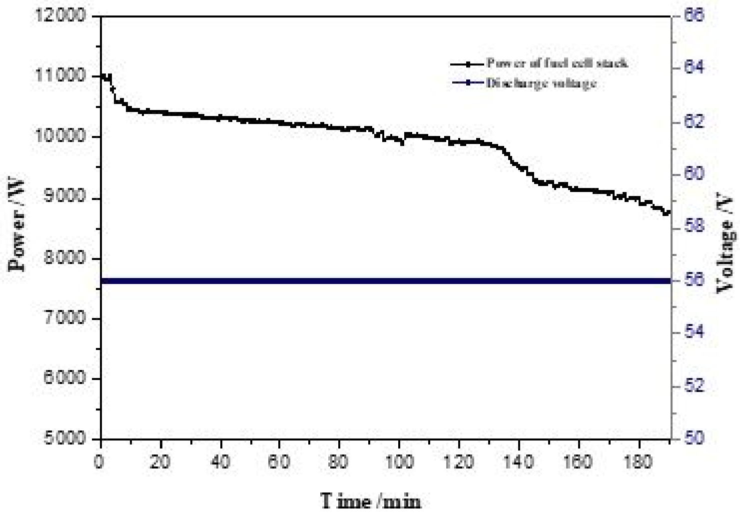

Figure 9

The curve of fuel cell stack operating voltage and power