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 $6.5\text{ }\mu\text{m}$ and the matrix material is $\alpha\text{-LiAlO}_2$. 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). Fuel cell power generation technology (Mcphail et al, 2015) 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 (Bischoff et al, 2002).

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 (Duan et al, 2015), and achieve near zero emissions of carbon dioxide and pollutants. 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. 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. From the perspective of the application of fuel cells, the installed capacity of molten carbonate fuel cells in 2014 exceeded 70 MW, which was used in the fixed station power market. In 2015, the installed capacity of molten carbonate fuel cells reached 180 MW. In 2016, the number of MCFC power stations reached 100, and the installed capacity exceeded 200 MW.

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 (Bischoff, 2006; Dicks et al, 2000). It also has attached great importance and vigorously developed by the United States, Germany, Italy, South Korea, Japan and other countries (Plomp et al, 1992; Tanimoto et al, 1998). 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 1 m² and the discharge current density of the stack is 80–120 mA/cm². The power generation efficiency is greater than 47%, mainly used in hospitals, food freezing plants, sewage treatment plants, universities and mechanical processing plants. In 1995, Japan built a 1 MW power station and worked continuously for 6 years, composed of four 250KW fuel cell sets (Grillo et al, 2003). It will realize 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. Europe and South Korea mainly develop internal reforming systems and cogeneration systems based on Fuel Cell energy's products. They installed and operated large-scale power plants from 100 kilowatts to megawatts in Europe. The MCFC power station (58.8 MW (2.8 MWx21 hydrogen fuel cell)) was established by South Korea's POSCO in Gyeonggi Province, which can provide power for 140,000 households, and completed the construction of 20 MW in Seoul.

In 2017, the Ministry of Science and Technology set up a major special project "CO₂ 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 500 kW high temperature fuel cell power generation.

In this paper, the author studied the operation of the domestic 10kWMCFC fuel cell stack, and analyzed the problems existing in the operation of the stack and the next step in the development of technical development plans.

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.

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 $\alpha\text{-LiAlO}_2$ (Terada et al, 1998) in molten carbonate fuel cells. The $\alpha\text{-LiAlO}_2$ 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, $\alpha\text{-LiAlO}_2$ 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 $\text{Li}_2\text{CO}_3\text{-K}_2\text{CO}_3$ (mol 62 mol% / 38 mol%).

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 10 kW 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	$\alpha\text{-LiAlO}_2$
Electrolyte	$\text{Li}_2\text{CO}_3/\text{K}_2\text{CO}_3$
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 upper and lower end plates of the fuel cell are connected to the electronic load. The discharge

test of the stack is performed by controlling the computer end connected to the load. Figure 4 shows the gas flow control equipment, electronic load and stack heating furnace.

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 $10\mu\text{m}$. 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 $6.5\mu\text{m}$.

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 10 kW 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 Fig. 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 battery 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 100 kW molten carbonate fuel cell stack and system for the IGFC power generation system. The 10 kW 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 100 kW.

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 1.23V. 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 0.7V.

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 56V (0.7V, 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 140 min. 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 (Koh, et al, 2000).

Table 2
Gas flow of the experimental fuel cell

Gas flow	Theory value	Experimental value
H ₂	110 L/min	130 L/min
CO ₂	110 L/min	145 L/min
O ₂ , Air	55 L/min, 275 L/min	75 L/min, 375 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 10 kW required by the project. From the analysis of current density results ($> 100 \text{ mA/cm}^2$), the total number of designed battery stacks can reach 20 kW at the theoretical output power, but the actual output cannot reach 20 kW. 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 good. 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 battery. 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. 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

The pore size of key molten carbonate fuel cell electrode material was $6.5 \mu\text{m}$ and the matrix material is $\alpha\text{-LiAlO}_2$. The open circuit voltage of the single cell is 1.23V in experiment. The current density is greater than 100 mA/cm^2 when the operating voltage is 0.7V.

The 10 kW fuel cell stack was constitutive of 80 pieces single fuel cells with area of 2000 cm². The open circuit voltage of the stack reaches above 85V. The fuel cell stack power and current density can reach 11.7 kW and 104.5 mA / cm² when the operating voltage is 56V.

The successful development of the 10 kW stack has promoted the progress of domestic molten carbonate fuel cell technology. However, there are certain problems in the long-term operation of the stack, preliminary because of the gas flow control and the wet seal between the stack.

Declarations

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Figures

Figure 1

Schematic diagram of the fuel cell test device

Figure 2

XRD diagram of matrix powder

Figure 3

Schematic diagram of IGFC power generation

Figure 4

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

Figure 5

The curve of fuel cell stack operating voltage and power