SOFC and MCFC: New Energy Technologies of The Future

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Abstract. The new energy technology is the hot spot and key point to solving the current environmental problems. In this paper, two types of fuel cells, SOFC and MCFC, were introduced in order to show their contributions to the energy transition. The two kinds of fuel cells were described in detail from the aspects of working principle, power generation mechanism, engineering application, current research and future prospect. Finally, the two fuel cells were compared in terms of electrochemical reaction and outstanding advantages.

Keywords: Energy transition; Fuel cell; SOFC; MCFC; Electrochemical reaction.

1. Introduction

Nowadays, climate change such as the EINino effect [1] or other natural disasters caused by global warming have been affecting people around the world, which is a shared problem that the whole world needs to face. Energy, as the heart of the climate challenge, is the key to our efforts to address it. Scientists are committed to researching various new energy technologies [2], eager to help mankind achieve energy transformation through the crystallization of wisdom and experimentation. The energy transition [2] means reducing greenhouse gas emissions through new technologies, especially CO2 generated by conventional energy sources such as oil and gas.

Carbon capture and storage (CCS) technology [3] is one of the main paths able to mitigate the risks associated with CO2 emissions. Then, CCS represents a bridge technology in the transition from the current/near-term fossil fuel energy and industrial systems and a future sustainable system based on renewable as well as zero-emission energy sources.

Among those new technologies, the fuel cell [4] is the fourth power generation technology after hydropower, thermal power generation and atomic power generation. The fuel cell is an energy conversion device, which is based on the principle of electrochemistry, that is, the working principle of galvanic batteries. The chemical energy stored in fuel is oxidized, isothermally, to directly form electrical energy, so the actual process is a redox reaction.

Fuel cells [4] can be divided into various types according to different classification methods, such as fuel type or reaction mechanism. Among the different fuel types we have the hydrogen type, carbon type, nitrogen type, and organic type fuel cells.

This article will introduce several representative fuel cells, analyze their decarbonization process, and discuss their potential to contribute to the energy transition.

2. Solid Oxide Fuel Cell (SOFC)

The highest energy density and the most potential for development in high-temperature fuel cells is the Solid Oxide Fuel Cell (SOFC)[5−8], which has made rapid technological progress in recent years and has entered a rapid decline in cost.

2.1. Working principle

The main part of a single SOFC consists of an anode, a cathode, and a solid oxide electrolyte.[5] SOFCs can be divided into two categories proton conductor SOFCs and oxygen ion conductor SOFCs according to the type of ions conducted by the electrolyte, among which oxygen ion conductor SOFCs are widely studied and applied. Among all fuel cells, SOFCs operate at the highest temperature and belong to high-temperature fuel cells.[5]

Reaction mechanism

The SOFC anode catalyzes the electrochemical reaction of oxidizing the fuel and conducts the released electrons to the external circuit.[6] The anode passes fuel gas, such as hydrogen, natural gas, methane, gas and so on in a reducing atmosphere. Hydrogen-rich compounds have abundant reserves, low cost and easy storage and transportation.[7] They are the most used fuel of SOFCs at present, and are the most likely fuel to realize industrialization. The main function of SOFC cathodes is to catalyze the reduction of oxygen into oxygen ions and transfer them to the electrolyte. The cathode is fed with oxygen or air and is in an oxidizing atmosphere. For a schematic of atypical SOFC see Figure 1.

SOFCs work as the ‘reverse’ process of hydrolysis. Electrons from the external circuit are used to convert O2 to 2O2- at the SOFC cathode and then, driven by a chemical potential, enter the solid electrolyte, where they migrate to the anode side of the electrolyte under ionic conduction.[8] The external circuit obtains O2- and oxidizes with the reducing gas at the anode to release electrons, thus forming a closed-circuit DC circuit cycle.

The reaction products of SOFCs are only CO2 and H2O. Because water vapor can be used to trap CO2 gas, it is a great way to achieve almost zero CO2 emissions.[9]

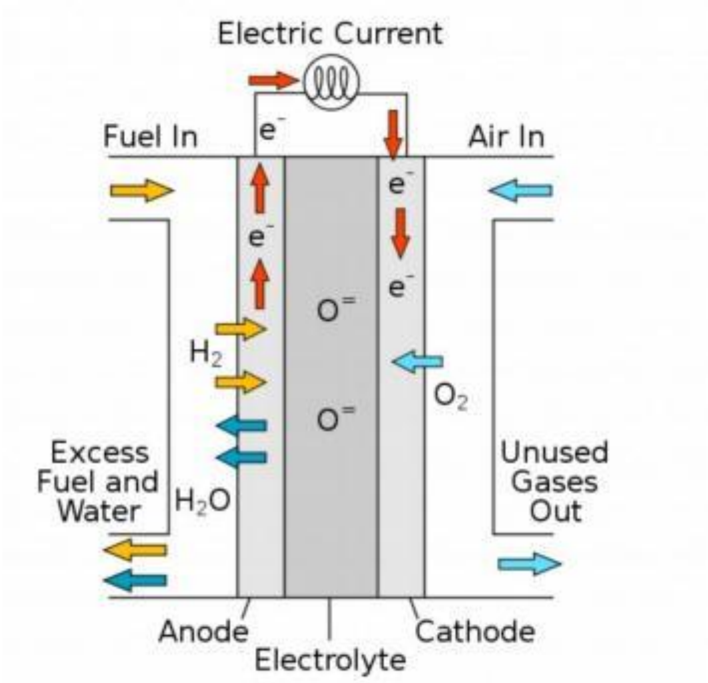

Fig 1. Working principle of SOFC [10]

2.2. Engineering application

Sewage treatment plant

In order to reduce energy consumption and carbon emissions in sewage treatment plants, existing studies[11−12] have innovatively applied SOFCs, which have challenging manufacturing costs, to the combined cooling and thermal power supply system composed of sewage treatment plants.

In the implementation process of the sewage plant, anaerobic fermentation technology is used to ferment sludge to produce biogas, which provides fuel for the SOFC. This work uses a cost-optimal unit commitment model for the techno-economic appraisal of the retrofitting of the sub-MW Collegno WWTP managed by SMAT in Turin.[12] Because these parameters in the actual operation will affect the battery capacity. Then the biogas data from the sewage treatment plant is used to analyze the thermal and power requirements of the system and the battery performance to evaluate the feasibility of SOFC technology in the actual system operation. In Figure 2, the overall power generation efficiency was increased to 60%.

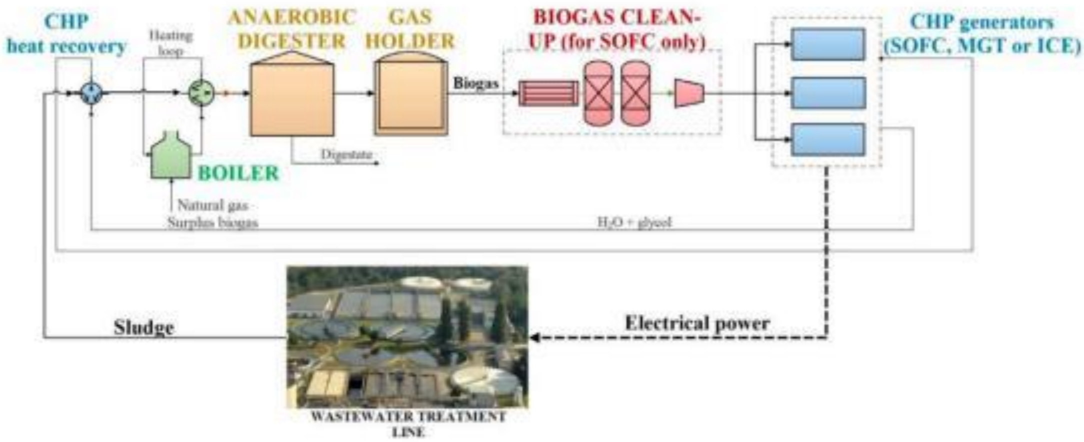

Fig 2. Integrated WWTP CHP plant configurations [11]

Anaerobic fermentation type sewage treatment plants use SOFC cogeneration technology, which is an efficient energy flow conversion technology. From the perspective of end users, this technology is no longer simply burning excess biogas. At the same time, biogas fuel is used in the sewage treatment plant for cogeneration. Through this process, the self-sufficiency rate of heat energy can reach 25% and the self-sufficiency rate of electricity could be 26%. The operating cost and the emission of CH_4 to the atmosphere could also be reduced to varying degrees. [12] In addition, the battery can process fuel gas mixtures such as biogas and methane to reduce seasonal constraints on biogas supply.

Ship power

Northwestern University proposed a new technology [13] to reduce CO_2 emissions from ships. With this technology, SOFCs can be used to achieve carbon neutral or even negative emissions from ships simply by replacing the fuel tanks with two-cavity storage tanks and introducing CO_2 compressors. In Figure 3, the application of SOFCs in shipping power is shown.

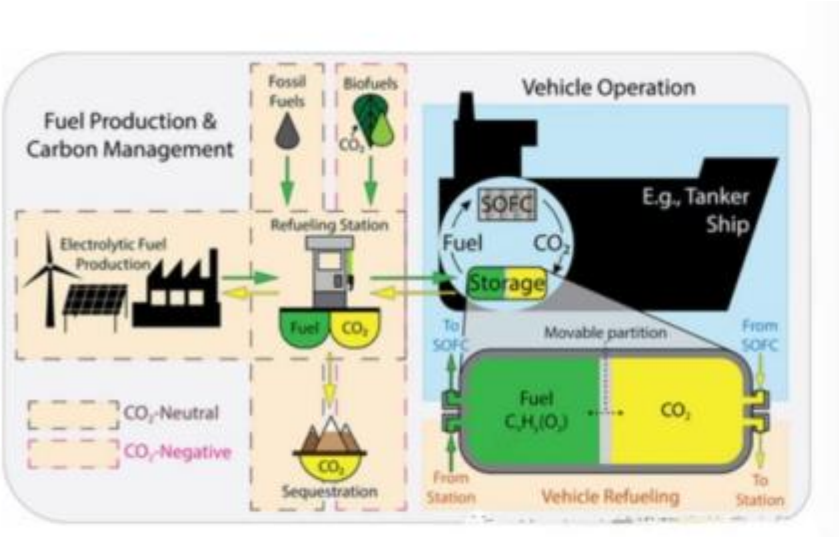

Fig 3. Decarbonization application of SOFC in shipping power [14]

After the SOFC generates energy from carbon-based fuel stored in the first chamber of the two-chamber tank, CO_2 is compressed and stored in the second chamber. The stored CO_2 can be sequestered underground or processed into other renewable hydrocarbon fuels for reuse. The bulkhead separating the two chambers is mobile and the CO_2 storage space in the second chamber increases as the fuel is reduced.

SOFCs use pure oxygen to burn fuel and emit concentrated CO_2 that can be stored. When air burns, it produces nitrogen, which increases the volume of the gas and makes it difficult to store. Compressed and concentrated CO_2 can be stored in a smaller space than the fuel.

The technology uses carbon-based fuels, so its contribution to global warming is questionable, but the electricity from EVs and hydrogen from fuel cells also emit large amounts of CO_2 during manufacturing.

The use of battery packs instead of carbon-based fuels on long-haul tankers requires more space than the ship can carry. In addition, hydrogen tanks are very large, so using carbon-based fuels and capturing CO_2 onboard is the best way to achieve carbon neutrality in long-haul ships. The new technology can also be used for range extenders in EV and fuel cell vehicles.

2.3. Status quo of technological development

International SOFC application is relatively mature. Because SOFC projects consume huge talents and financial resources, there are not many enterprises that can truly realize large-scale commercial supply. Notable enterprises involved in SOFC development[15] include Bloom Energy, Ceres Power, Elcogen, Mitsubishi Heavy Industries and Kyocera, and KCERACELL, KOREA SOFC FORUM, HNPOWER and so on. There are no more than 10 SOFCs globally capable of generating megawatts of electricity per year.

SOFC market application in China has not really started. In the absence of policy support, the industrial chain supporting development is very immature. As a result, the market has not created the environment and enterprises needed to invest in research and development production needs, support, and encouragement. At present, very few companies have invested in research and mass production of SOFCs in China.

2.4. Future prospects

The operating temperature of early-developed SOFCs is higher, generally 800 ~ 1000℃. Scientists have developed medium-temperature SOFCs, which typically operate at about 800 ℃. Nowadays, scientists in several countries are also working to develop cryogenic SOFCs, which can operate at temperatures as low as 650 to 700 °C. The further reduction of operating temperature makes the practical application of SOFCs possible.[16]

SOFCs are best suited to clean natural gas as raw material, and can achieve good synergy and integration with the natural gas industry.[17] SOFCs with natural gas as

raw material can make full use of the mature infrastructure advantages of the Liquefied Natural Gas (LNG)/natural gas industry, such as storage, transportation, distribution, pipeline, and refueling. At the same time, it has been deeply rolled out to the end users, which are more efficient and environmentally friendly than the traditional centralized power generation and heating mode and natural gas distribution. Therefore, it is an important direction for the future integration and development of the natural gas industry and SOFC commercialization.[18]

In addition, the CO_2 separation unit may be the spark unit for ignition, making the SOFC a critical component in a closed and renewable energy cycle. Over time, SOFCs can generate heat and electricity. For example, in facilities used in large greenhouses, CO_2 produced by SOFC devices can be used to accelerate plant growth. And any leftover organic matter from harvested crops can be converted into gas to fuel SOFCs

3. Molten Carbonate Fuel Cell (MCFC)

3.1. Working principle

The structure of the Molten Carbonate Fuel Cell (MCFC)[19-21] mainly includes a cathode, anode, electrolyte, and separator, of which the anode generally uses Ni-Al, Ni-Cr as a catalyst, and the cathode adopts lithiated NiO ($Li_xNi_{1-x}O$) as a catalyst and the electrolyte is molten carbonate

(Li_2CO_3 . Na_2CO_3 . K_2CO_3), the diaphragm uses a porous $LiAlO_2$ membrane to carry molten carbonate.

High conductivity of electrolytes

Molten carbonate is a liquid obtained by melting the carbonate of ionic crystals at high temperatures above the melting point.[21] It is composed of cations such as alkali metal ions and anions of carbonate ions. Molten carbonates used as MCFC electrolytes are ionic liquids above 500℃, pure solute electrolytes without solvents, and have higher ionic conductivity than other electrolyte systems. It can be said that the high conductivity of molten carbonate is due to the high operating temperature, which can reduce the internal resistance and inhibit the resistance polarization.

Reaction mechanism

The oxygen reduction reaction of MCFCs is carried out in molten carbonate electrolyte at 650℃, so the catalytic effect related to electrode materials is not high.[20]

When working, air and CO_2 are introduced into the cathode, and an electrochemical reaction:

$$O_2+2CO_2+4e^-=2CO_3^{2-} \tag{1}$$

The carbonate ions pass through the electrolyte and reach the anode; at the anode H_2 and the carbonate ion react to generate H_2O and CO_2 :

$$H_2 + CO_3^{2-} = H_2O + CO_2 \tag{2}$$

At the same time, electrons from the anode pass through the external circuit to the cathode, and do electrical work externally. For a schematic of a typical MCFC see Figure 4.

At present, MCFC single cells adopt a flat plate structure, the power density of the single cell is over 160 mW/cm (working voltage 0.8V, pressure 0.1MPa, fuel utilization rate 20%), and the maximum area is 1 m^2.[19]

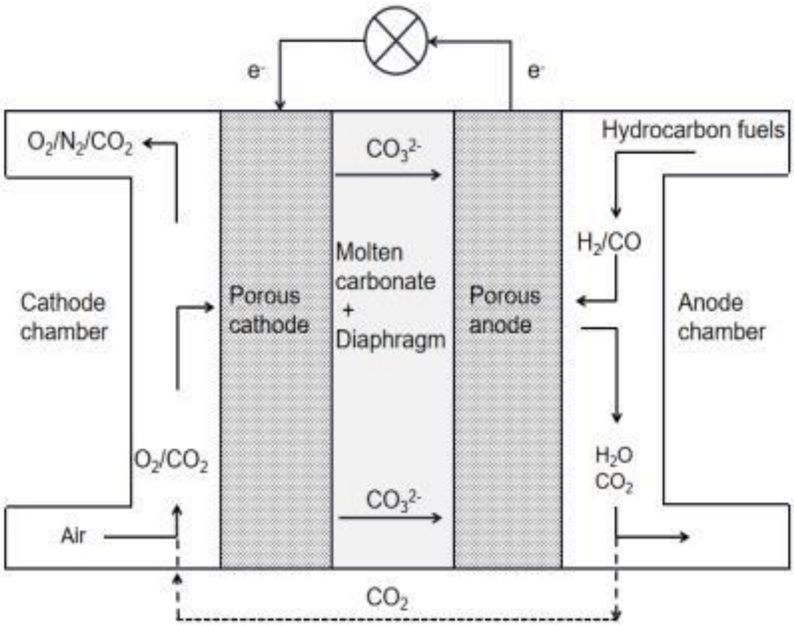

Fig 4. Working principle of MCFC [19]

3.2. MCFC for CO2 separation

MCFCs are an innovative and flexible way to reduce CO_2 emissions and provide energy more efficiently, fueled by fossil and renewable energy sources. MCFCs can operate as CO_2 separators and concentrators when generating electricity and are therefore a valuable candidate for carbon capture systems in fossil-burning plants.

CO2 Capture

When the MCFC works, it uses CO2 and oxygen in the air as oxidants. CO2 migrates from the cathode to the anode through an electrochemical reaction, which can enrich CO2 and capture it.[22] Specifically, the separation of CO2 is due to an electrochemical reaction that occurs within the cell: $CO3^{2-}$ ions pass through the electrolyte and are converted, moving CO2 directly from the cathode to the anode side. The flue gas sent to the cathode inlet will leave the cathode outlet at a significantly reduced CO2 concentration, reducing CO2 by up to 85%. CO2 is transferred to the anode exhaust system. If no inert gas is mixed with the main fuel, water is the only other product of the anode reaction and can therefore be easily isolated or reused in fuel production. Additional power is generated during CO2 concentrations, as the MCFC will add H2 gas-rich fuel produced during the process to the anode side. The path of CO2 during the reaction of MCFCs is shown in Figure 5.

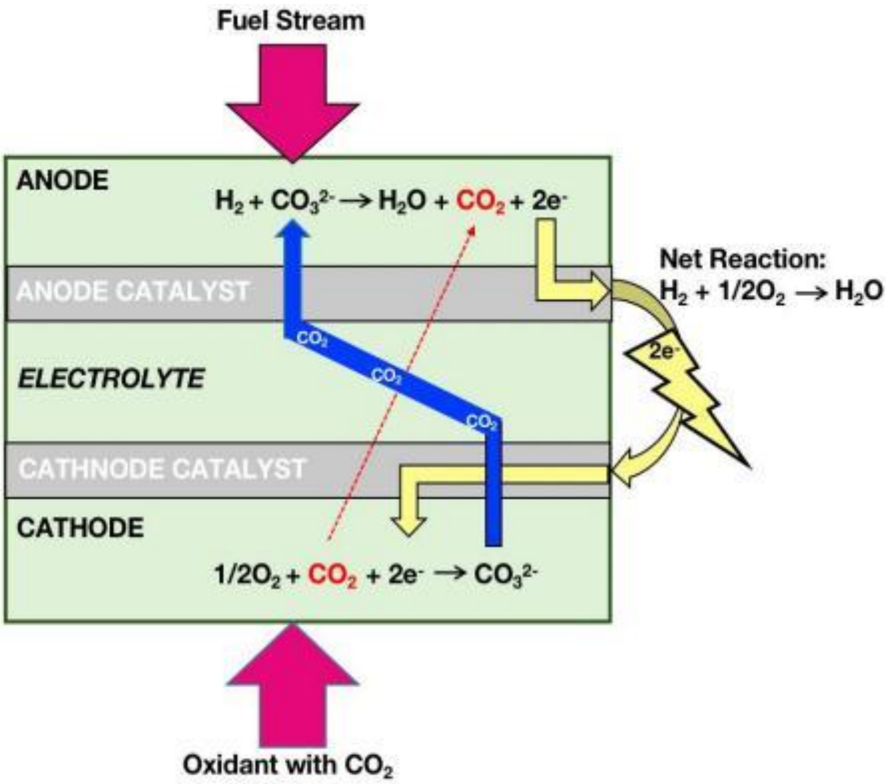

Fig 5. The path of CO2 during the reaction of MCFCs [22]

Engineering application

The modular nature of the MCFC system allows the capture equipment to be progressively increased in size and customized to meet actual capture needs. The use of MCFCs as a CO2 concentrator has been proposed by Fuel Cell Energy Corporation (FCE), which developed the combined Power and Carbon Dioxide Separation (CEPACS) system concept. [23]

A simplified diagram of the CEPACS system concept is shown in Figure 6. This contribution is part of a comprehensive effort to evaluate the MCFC-integrated process of decarbonizing wastewater that generates electricity (and heat) during industrial symbiosis.

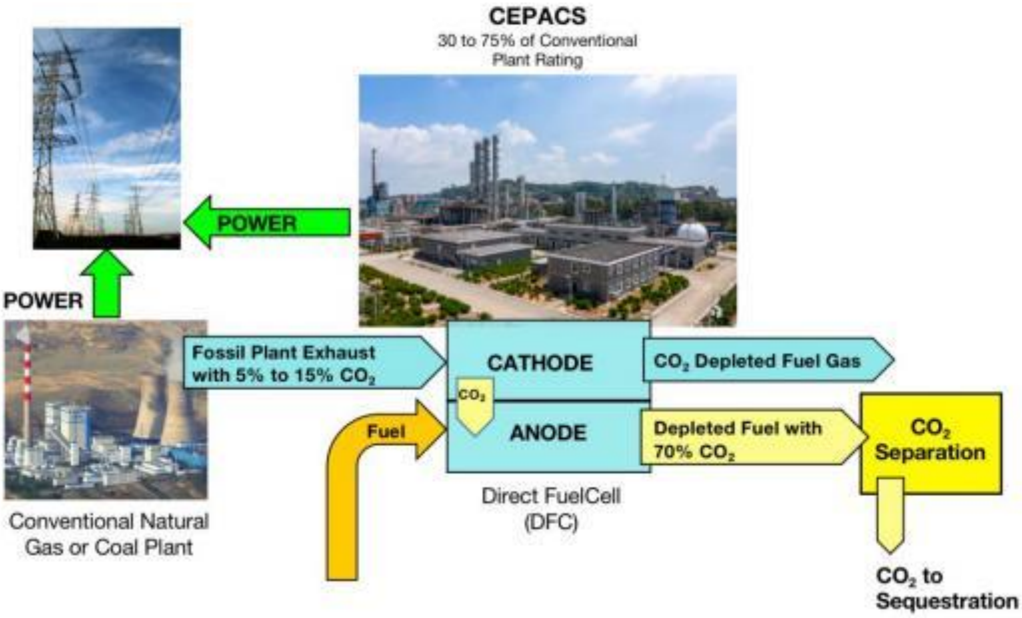

Fig 6. CEPACS CO2 separation and power system concept [23]

Take powerplants for an example

MCFC decarbonization can be widely used in large factories and power plants. When factories use MCFC technology to decarbonize, they can effectively decrease the emission of polluting gases and improve the utilization rate of substances. As a CO2 separator, MCFCs can be effectively integrated with traditional thermal power plants to form a thermal power plant -- Molten carbonate fuel cell system (PP-MCFCs)[24] .

The PP-MCFC system directly pretreats the exhaust gas discharged from the thermal power plant, mixes it with air /O2, and then passes it to the MCFC cathode. After the electrochemical reaction, the volume fraction of CO2 in the exhaust gas was reduced to less than 1%, and then put into the atmosphere. At the MCFC anode, the natural gas reformed *syn*-gas is passed through. After an electrochemical reaction, the unreacted gas is fully reacted in a catalytic burner and then passed through a CO2 capture device to separate the high concentration of CO2.

3.3. Research and development

In the early 1950s, MCFCs came into the limelight with the prospect of large-scale civilian power generation and attracted worldwide attention.[25] The early MCFC developed very fast, and the battery materials, process, structure, and other aspects were improved through technological development, but in fact, the working life of the battery was not ideal.[25]

By the 1980s, it was regarded as the second generation of fuel cells and became the main research target to realize the commercial fuel cell power station megawatt level in the near future. It also means that MCFCs would witness rapid developments. At present, the main researchers of MCFCs are concentrated in the United States, Japan, Western Europe, and other countries, and was commercialized in 2002.

In fact, there are not many MCFC research units in China.[25] The Harbin Institute of Power Supply Complete Equipment studied MCFCs in the late 1980s and stopped the research in the early 1990s. In 1993, Dalian Institute of Chemical Physics, Chinese Academy of Sciences started the research of MCFCs under the support of the Chinese Academy of Sciences. By making LiAlO2 micro-powder, the diaphragm for MCFCs was prepared by cold rolling method and strip casting method, and the single battery was assembled. The performance reached the international level in the early 1980s.

3.4. Future prospects

The MCFC is a kind of high-temperature fuel cell operating at 650℃. It has the advantages of a wide array of fuel sources (no pure H_2 can be used as fuel), small footprint, less pollutant emission, and high power generation efficiency. The service life can reach more than 40,000 hours.[26] The greenhouse gas emissions have been greatly reduced, which is especially suitable for distributed power stations to realize cogeneration of heat and power, which has great practical significance for energy saving and emission reduction, improving energy utilization efficiency.

In terms of market competitiveness, MCFCs can launch modular products ranging from a household kilowatt scale products to a 100-megawatt scale molten carbonate fuel cell plant. A single MCFC module can output a maximum of 300KW, which can meet the needs of dozens of homes. In addition, MCFCs have a wide range of raw materials, including gas, natural gas and biogas, and can be used as the main power supply for residential areas, hospitals, base stations and border guards. It has a very wide application market and certain social and economic benefits.

From 1981 to 2005, MCFCs made great strides during the development of energy saving technology in the Moonlight Project and the New Daylight Project[27], and became the mainstream in the development of fuel cells for automotive use and household cogeneration. In the process of development, MCFCs continue to expand their development purpose and scope of application. Combined with the current research on global warming countermeasures, further developments and improvements of MCFCs has become more urgent. MCFCs, with their advantages, are considered an essential technology for the future.

4. Comparison between two fuel cells

4.1. Similarities

As fuel cells, SOFCs and MCFCs have the same essence and similar characteristics. Due to the advantages of high power generation rate and low environmental pollution, these fuel cells have made a significant contribution to the energy transition.[4] They not only produce exclusively the carbon-free substance (H_2O) as the product, but also help different industries to save energy and reduce emissions in practical applications.

4.2. Differences

In practice, however, SOFCs and MCFCs have their own advantages and disadvantages due to differences in electrolytes and power generation principles.

Electrochemical reaction

The main features of the MCFCs and SOFCs [27,28] are tied to their operating temperature. In the former case, a minimum temperature level of 600 °C has to be maintained to guarantee the liquid state of the carbonate electrolyte and thus the mobility of the carbonate ions. In the latter, oxygen ions are transferred from the cathode to the anode through an oxygen conducting solid electrolyte. SOFCs can be operated between 600 and 1000 °C[16]. In other words, the charge carriers that are used to close the electrical circuit are different for SOFC and MCFC: ionized oxygen in the case of the SOFC, carbonate ions in the MCFC. For the latter, this requires an additional feed of CO_2 at the cathode side. For the former, this means that if pure hydrogen is introduced at the anode, no carbon is involved in SOFC operation.

Electrochemical reactions at the anode and cathode of the MCFC and SOFC are set out schematically in Figure 7.

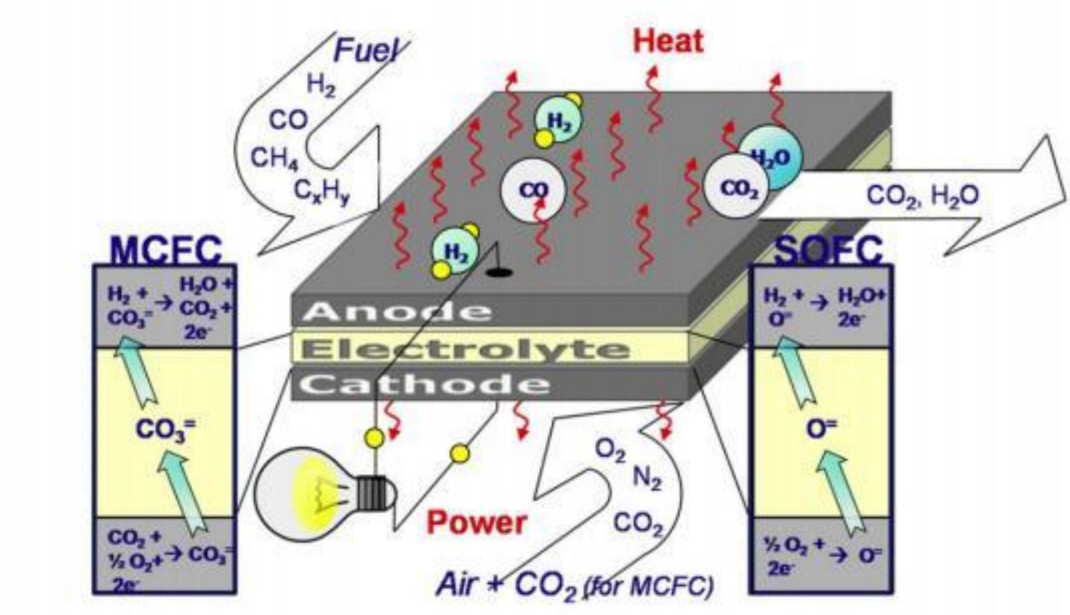

Fig 7. Differences about electrochemical reactions of MCFC and SOFC[30]

Outstanding advantage

SOFCs widely use ceramic materials as electrolytes, cathodes, and anodes. It has an all-solid structure, and there is no management problem of leakage and corrosion. SOFCs have power densities of up to 1MW/m3, with the possibility of up to 3MW/m3 for block designs.[31] In fact, SOFCs can be used in power generation, thermoelectric reuse, transportation, space aerospace, and many other fields, which is called the green energy of the 21st century.

MCFCs can use non-precious metals as catalysts, which reduces operating costs. At the same time, they can tolerate the effects of CO and CO2, and can use hydrogen-rich fuels. Since the working temperature of MCFCs is 600 ~ 700℃ [16], the discharged gas can be used for heating, and also can be combined with the turbine for power generation. The efficiency can be increased to 80% if the heat and electricity are combined.

5. Conclusions

With increasing greenhouse gas emissions, an energy transition is necessary and of great significance. Among them, fuel cells play an irreplaceable role as a new energy technology. Fuel cells are electrochemical power generation devices that convert chemical energy directly into electricity without going through a thermal engine process. It is not restricted by the Carnot cycle, so the energy conversion efficiency is high. Coupled with its pollution-free characteristics, it is becoming an ideal way to use energy.

There are many kinds of fuel cells. This paper mainly introduces SOFCs and MCFCs, and compares them.

SOFCs are third-generation fuel cells. A SOFC is a newtype of power generation device. Its high efficiency, no pollution, solid-state structure and wide adaptability to a variety of fuel gases are the basis of its wide application. Of the several fuel cells, the theoretical energy density is the highest. At present, there have been studies combining the use of SOFC with sewage treatment and ship power to save energy and reduce emissions, which would make great contributions to the realization of decarbonization. It is widely believed to be one of the most popular fuel cells in the future.

MCFCs use molten carbonate as an electrolyte and work at high temperatures during the reaction at a fast speed. MCFCs work well as a decarbonization technology to capture CO2. On the practical side, MCFCs generally work with factories and power plants to capture and separate CO2 emissions. In the process of development, MCFCs continues to expand its development purpose and scope of application. MCFCs, with its advantages, is considered as an essential technology in the future.

Fuel cell research is slowly gaining popularity around the world. Admittedly, the key technologies related to fuel cells have not been extensively studied in China, nor have they fully entered the public's vision and life. As a result, this is also something that needs attention. China needs to actively learn from other countries technology and learn from their experience. More importantly, we should encourage the ability of independent innovation, and constantly explore the unknown fields for continuous harvest.

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