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Research progress of different fuel cells

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Abstract:

The rising global energy needs and increasing emphasis on environmental protection have directed attention toward sustainable energy solutions characterized by renewability, high energy density, and minimal carbon emissions. These requirements can be fully met by fuel cells, which can transfer the energy contained in the fuel in the form of electricity. The reson for this paper is to provide a comprehensive review of fuel cell technology, which will examine the operational principles, technical attributes, and current applications of proton exchange membrane cells, alkaline cells, and direct alcohol fuel cells. Protons exchange membrane fuel cells are widely utilized in the market due to their modularity, high energy density, efficient energy conversion, and significant power density, as per our analysis. Their dependence on costly precious metal catalysts and vulnerability to platinum carbon monoxide poisoning are significant drawbacks. Conversely, both alkaline batteries and direct alcohol fuel cells are exploring non-platinum catalysts, but their corrosive operational environments necessitate highly durable materials. In this article, phosphoric acid fuel cells, molten carbonate fuel cells, and solid oxide fuel cells are also discussed.

Keywords: Energy Environment, Fuel Cells, Catalysts, Membranes.

1. Introduction

All human endeavors necessitate varying levels of energy consumption. Currently, the global energy supply predominantly relies on fossil fuels. Nevertheless, fossil fuels are associated with several drawbacks, including their finite nature, severe environmental and health consequences during extraction and use, and inherent price volatility. Conventional Energy utilization methods, such as internal combustion engines and thermal cycles, are typically used to extract and convert chemical energy from diverse fuels. These processes are not only inefficient but also release substantial quantities of harmful gases into the atmosphere. Environmentally benign renewable fuels like biodiesel and bioethanol are progressively replacing fossil fuels to mitigate these adverse environmental impacts. However, since these fuels still contribute significantly to greenhouse gas emissions, developing efficient energy conversion and storage technologies is crucial to further minimize or eliminate environmental harm and achieve complete reli-

ance on renewable energy [1].
Amidst worsening environmental conditions and the urgent need for enhanced energy efficiency, electricity is becoming more central to daily life, increasing reliance on both electrical power and batteries. Fuel cell systems, with their renewable attributes, substantial energy density, and relatively low carbon emissions, can fulfill energy needs for both industrial production and daily living, aligning with sustainability and environmental protection objectives. As a result, fuel cell systems are attracting more attention. A fuel cell system's core concept involves directly converting chemical energy from hydrogen or other fuels into electrical energy. By eliminating the intermediate combustion or mechanical processes, the thermal efficiency of fuel cells can reach the maximum value of the theoretical Carnot cycle, and can utilize up to one quarter or even half of the energy wasted by traditional internal combustion engines. Given their environmental compatibility, high efficiency, minimal emissions, quiet operation, and adaptable uses, countries worldwide are vigorously advancing the development and deployment of fuel cell technologies. Despite the significant potential of fuel cells across diverse fields, their widespread adoption continues to face numerous technical and economic hurdles. Specifically, current fuel cells show clear deficiencies in key aspects like energy density, longevity, storage, and transport, which consequently restrict their broad deployment [2]. This document seeks to classify existing fuel cells and detail their structures, operational principles, and respective benefits and drawbacks, thus offering a useful reference for fuel cell studies.

2. Working Principles of Fuel Cells

2.1 How the fuel cell works

By reacting with oxygen, a fuel cell directly turns chemical energy stored in fuel into electrical energy. The anode receives fuel, while the cathode receives oxygen. These substances engage in electrochemical reactions, producing electricity, water, carbon dioxide, and a minimal amount of waste heat. By bypassing intermediate energy forms, fuel cells generate significantly less waste heat than conventional combustion processes. The power output and capacity of fuel cells can be adjusted by altering the fuel type and density, with operating power capabilities ranging from milliwatts to megawatts. This adaptability allows fuel cells to meet diverse energy density requirements. With the continuous efforts of scientists, fuel batteries can now use not only hydrogen but also other fuels such as methanol. The types of electrolytes are also becoming increasingly diverse.

2.2 Basic characteristics of fuel cells

2.2.1 High efficiency

Traditional internal combustion engines generate thermal energy through fuel combustion, leading to the rapid expansion of high-pressure gas, which is subsequently transformed into mechanical energy via mechanical transmission. The process causes significant heat dissipation because most of the thermal energy is not utilized and is discharged as waste heat, leading to overall efficiencies of 20% to 30%. This avoids energy loss associated with converting thermal energy to mechanical energy, making it more efficient in conversion, with overall efficiency potentially exceeding 60% [3].

2.2.2 Reduced Pollution

The electrochemical reaction mechanism of fuel cell systems and the choice of fuel contribute to their low pollution attributes. The reactions occurring in fuel cells are similar to simple combustion. Therefore, when hydrogen is used as the fuel, the reaction products are only water. Also, because fuel cells have high efficiency, the vast majority of the energy produced by the reaction is converted into the work done by electrons, while the waste heat generated is very little. This has a significant improvement effect on air pollution and greenhouse gas emissions. The amount of CO_2 produced from carbon-containing fuels like methane (CH_4) is significantly lower than that from fossil fuels.

2.2.3 Minimal Noise

In traditional internal combustion engines, the fuel is ignited in the engine. The explosive combustion generates high temperatures, causing the gases to expand rapidly and thereby creating high pressure, which in turn drives the mechanical movement of the pistons and the crankshaft. Electrochemical reactions transfer energy through electron transfer. This is a very quiet process. Additionally, fuel cell cooling systems, often liquid- or air-cooled, typically generate considerably less sound than the fans found in internal combustion engines.

2.2.4 Broad Applicability and Flexibility

Fuel cells commonly feature a modular construction, in which numerous basic units are combined to form a fuel cell stack, and several such stacks can be integrated to create a complete power generation module. This modularity enables flexible configurations to meet diverse requirements. Additionally, their longer operating range and reduced refueling duration render fuel cells more appropriate for uses like electric vehicles and public transit, particularly when contrasted with traditional lithium-ion battery-powered vehicles.

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3. Fuel Cell Categories

3.1 Proton exchange membrane fuel cell (PEMFC)

The membrane electrode assembly (MEA) is the site of electrochemical reactions in a PEMFC. Here, hydrogen undergoes oxidation at the anode to produce protons (H^+), while oxygen is reduced at the cathode, combining with H^+ to form water (H_2O). A typical PEMFC's fundamental component is the MEA, which consists of a proton exchange membrane (PEM) flanked by two catalyst layers (CL) and two gas diffusion layers (GDL). Fig. 1 displays the structure of a PEMFC [4].

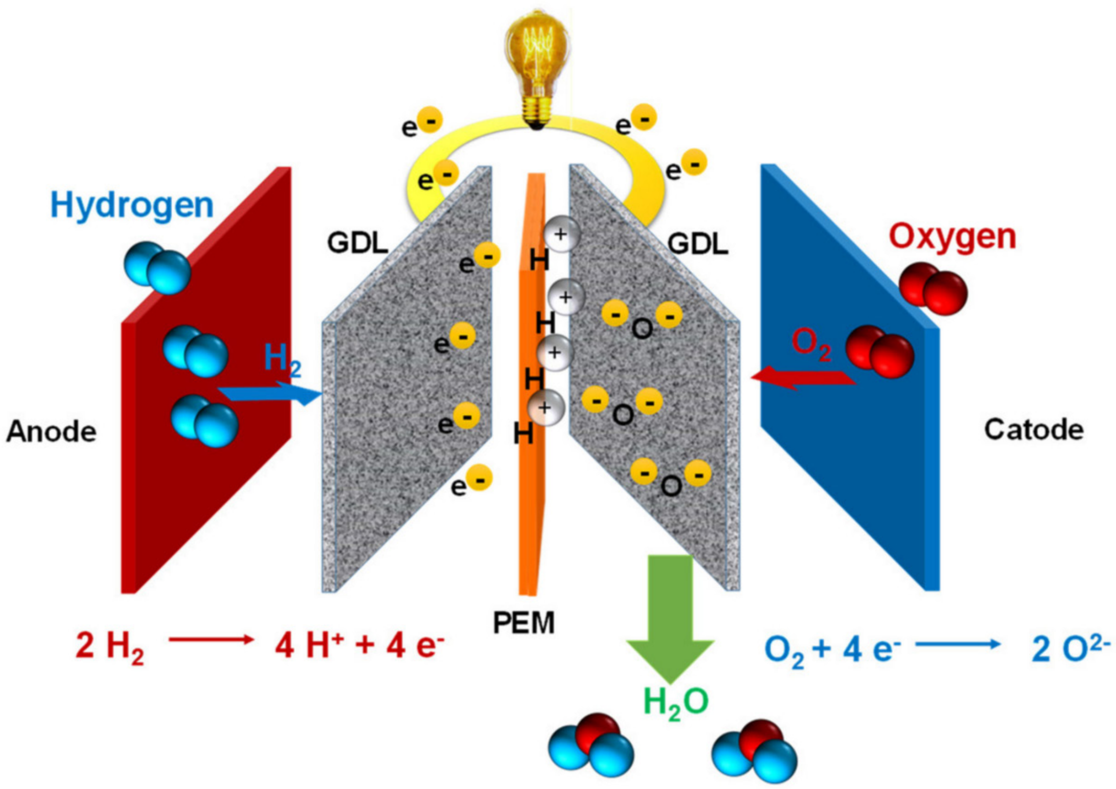

Fig. 1 The structure of proton exchange membrane fuel cell (PEMFC) [5]

The modular design of proton fuel cells allows for easy adjustment of power output, ranging from 1 watt to 500 kilowatts, by simply modifying the quantity of cells in the stack. This adaptability caters to diverse operational demands. PEMFCs also exhibit high energy density, efficient energy conversion, and high-power density. Furthermore, these electrical energy-generating cells offer quicker response times compared to internal combustion engines that rely on compressed gas expansion for mechanical work. Unlike lithium batteries, which experience energy loss with sudden temperature fluctuations, PEMFCs maintain stable operation in extreme weather conditions. Hydrogen fuel cells also boast faster refueling times than battery charging.

However, PEMFCs face several challenges. The oxygen reduction reaction (ORR), which takes 5-6 orders of magnitude longer than the hydrogen oxidation reaction (HOR), has a significant effect on platinum consumption at both anodes and cathodes, especially the latter. Additionally, platinum is susceptible to carbon monoxide poisoning at standard operating temperatures, where CO adsorption at platinum sites severely degrades performance, significantly impacting the overall cost of the fuel cell. Platinum-based catalysts alone account for approximately 40% of the cost of the PEMFC stack at an annual production scale of 500,000 units. Proton exchange membranes require specific hydration levels for optimal proton conductivity; however, excessive hydration can be detrimental and increase battery weight due to water accumulation. Moreover, dissipating waste heat from PEMFCs is more challenging than with internal combustion engines. Since PEMFCs operate at around 80°C, a temperature not significantly different from the ambient environment, they release heat to the surroundings at a slower rate. According to Newton's cooling law, a fuel cell vehicle's radiator needs a surface area 5 to 10 times larger to remove comparable waste heat compared to an internal combustion engine operating above 400 °C [5]. To address the issue of heat dissipation, people have equipped fuel cells with highly efficient heat diffusers, heat pipes, or active liquid/gas cooling systems to dissipate the heat. However, each method has some drawbacks. The heat spreader requires a large area, which has adverse effects on both the volume and weight of the battery. The heat pipe system needs to use working fluid/gas to transfer waste heat, and some of the working fluid/gas is toxic and has a potential leakage risk. Moreover, the active heat pipe requires an external power source for circulation, which consumes additional energy. Under the same volume, the cooling liquid has a significant impact on the weight of the battery, while the air cooling has an advantage in weight but lower efficiency. Additionally, high-purity hydrogen and oxygen are crucial for extending battery life, improving combustion efficiency, and reducing pollutant emissions.

3.2 Alkaline Fuel Cells (AFC)

Fig. 2 depicts the structure of an alkaline fuel cell. AFCs utilize alkaline solutions, such as NaOH or KOH, as electrolytes. Inside the battery, the anion exchange membrane (AEM) is a crucial component. It can control the main reaction to occur at the anode, thereby preventing the oxidant from directly contacting the fuel and causing non-electrochemical reactions.

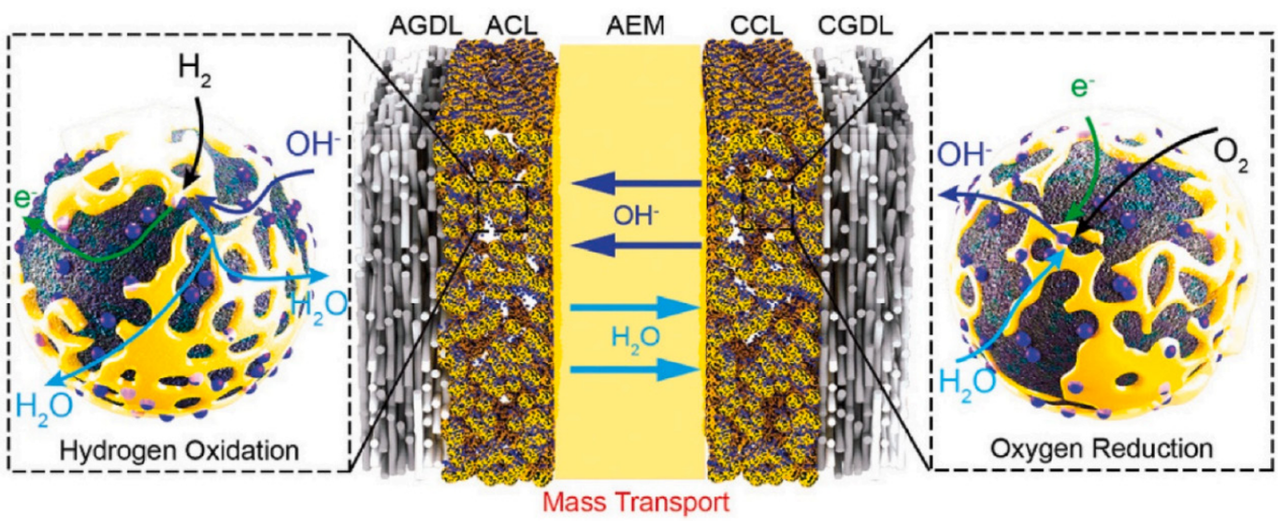

Fig. 2 Structure diagram of alkaline fuel cell [6]

AFCs exhibit higher power density and achieve peak efficiency at low operating temperatures, specifically between 60 °C and 80 °C [6]. As the electrolyte is a solution, minimal water removal is necessary. Researchers are actively seeking alternatives to expensive platinum group metals, such as nickel-based materials, to reduce battery costs.

HHowever, alkaline fuel cells demand high purity for both fuel and electrolytes. Moreover, due to the use of strong alkaline electrolyte solutions, the materials employed must possess exceptional corrosion resistance. Currently, AFCs largely depend on costly precious metals like palladium and platinum as catalysts because more affordable alternatives, such as nickel-based materials, iridium, and silver, lack sufficient activity, stability, and durability. Furthermore, prolonged exposure to an alkaline environment can degrade catalyst performance. The interaction between the catalyst and electrode also influences AFC performance. Impurities like CO and SO_2 can also lead to catalyst poisoning.

3.3 Direct Alcohol Fuel Cells (DAFC)

Fig. 3 shows the essential layout of a direct alcohol fuel cell (DAFC). DAFCs are typically used for portable power needs under 250 watts and function below 100°C. The open-circuit voltage (OCV) of DAFCs is higher than that of PEMFCs. Methanol and ethanol, which are the most basic alcohols and have energy densities of 6.1 and 8.2 kilowatt-hours per kilogram, have been extensively researched as fuels [7].

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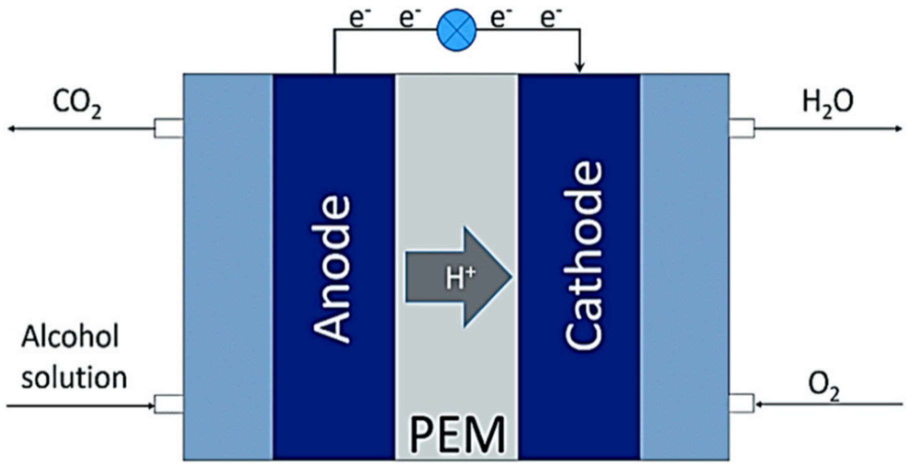

Fig. 3 Overview of the schematic diagram of electrocatalytic reaction in DAFCs [7]

Because the operating temperature of the direct alcohol fuel cell is not very high, it also has the advantages of higher energy density and faster startup speed. Moreover, both methanol and ethanol, when used as battery fuels, are more cost-effective and simpler to obtain and store than hydrogen. Nevertheless, the reliance on costly nickel and platinum catalysts keeps DAFC production expenses high. While researchers have investigated bimetallic modified platinum nanoparticles and the addition of metals like iridium and rhodium to boost AOR efficiency, the resulting overpotential reduction and mitigation of catalyst poisoning remain insufficient to make direct ammonia fuel cells commercially viable or competitive as an energy source [8]. Due to concentration gradients, fuel migrates from the anode to the cathode, where simultaneous oxygen reduction and alcohol oxidation generate a mixed potential at the cathode. This mixed potential negatively impacts the oxygen reduction reaction's efficiency, thereby reducing overall performance and leading to cathode poisoning. To counteract this, lower alcohol concentrations are often used, though this compromises energy density. Cathode reactions are characterized by a higher overpotential linked to the oxygen reduction reaction (ORR), and their kinetics are slow. Additionally, the oxygen reduction reaction can yield intermediate products. One of the main problems faced by DAFC using KOH as the alkaline medium is that the OH^- ions in the liquid electrolyte will undergo a side reaction with CO_2 in the air to form carbonates, which will reduce the concentration of OH^- and may clog the pores of the porous electrode by precipitating metal carbonates. At the same time, the precipitation of metal carbonates will block the pores of the porous electrode.

3.4 Other fuel cells

Other common fuel cell types include phosphoric acid fuel cells (PAFCs), molten carbonate fuel cells (MCFCs), and solid oxide fuel cells (SOFCs).

The electrolyte in a PAFC consists of concentrated phosphoric acid. MCFCs utilize molten carbonates, primarily lithium and potassium carbonates, as their electrolytes. Yttria-stabilized zirconia (YSZ) is a suitable material for making the solid electrolyte in SOFCs. PAFCs are classified as medium-temperature fuel cells because they operate at temperatures between 160 and 220 °C [9]. Both MCFCs and SOFCs are high-temperature fuel cells, operating between 600 and 900°C [10]. Their higher operating temperatures offer a broader selection of fuels. PAFCs can use hydrogen (H_2) and catalytically reformed natural gas. MCFCs can directly use carbon monoxide (CO) as fuel, or natural gas containing either oxygen or carbon dioxide as the oxidant, including CO_2. The ability to utilize CO and CO_2 makes them suitable for carbon capture and storage (CCS) applications. Furthermore, their high tolerance for impurities allows for the use of syngas derived from coal gasification and biomass gasification as fuels. A variety of oxygen-containing liquid hydrocarbon substances, such as simple oxygen-containing liquid hydrocarbon substances like acetic acid, ethylene glycol, ethanol and methanol, can be used directly; while more complex oxygen-containing liquid hydrocarbon substances, such as glycerol, can also be converted through internal reforming/part oxidation processes.

The elevated internal temperature of these batteries offers numerous advantages. Firstly, the high operating temperature accelerates reaction rates and minimizes polarization losses. Secondly, such high temperatures inevitably lead to outward heat radiation, prompting researchers to explore combining the waste heat from these batteries with gas turbines, steam turbines, etc., to create efficient combined cycle power generation systems. Moreover, for MCFCs and SOFCs, the high internal temperatures reduce their dependence on precious metals, leading to greater cost-effectiveness. Both the anode and cathode of MCFCs are constructed from nickel-based powder. For SOFCs, nickel-based ceramic-metal composites (Ni-based cermets) are the most common anode material, providing excellent stability and high electrochemical oxidation reactivity. Lanthanum strontium manganese oxide (LSM) is frequently employed as the cathode in SOFCs. As cathode materials, there have been reports of mixed materials including $La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-\delta}$ (LSCF), $Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-\delta}$ (BSCF), and solid solutions doped with $LaMnO_3$, $La_{1-x}Sr_xCuO_3$, $LaCrO_3$, and $LaCoO_3$ [11].

However, medium- and high-temperature fuel cells also present several challenges. Primarily, they require a significant heat-up period, resulting in prolonged start-up times. Secondly, material selection is limited. Due to the substantial difference between their operating temperatures and room temperature, the range of suitable materials for the battery structure is restricted. Selected materials must possess similar coefficients of thermal expansion to enhance structural stability. The melting point of the cathode material is not high, so the high-temperature environment within the molten salt fuel cell may cause the cathode material to dissolve in the electrolyte, thereby shortening the battery's lifespan. The highly corrosive nature of molten carbonate necessitates hardware with exceptional corrosion resistance. Furthermore, molten carbonates can decompose into basic oxides that form solid deposits with fuel or air impurities like sulfides, chlorides, and dust, leading to the blockage of electrode pores or coverage of active sites, making the management of molten carbonates particularly difficult.

4. Prospects

With advancements in computing technology, researchers are increasingly integrating AI-assisted methods into their work. This allows for predicting reaction feasibility by calculating the target product's structure in advance. As understanding of metal complexes deepens, the reliance of fuel cells on costly precious metals is expected to decline. Scientists have developed core-shell structures, nanowires, nanosheets, and nano frameworks by alloying platinum with transition metals. Notably, transition metal-nitrogen-carbon (M-N-C) catalysts have demonstrated exceptional activity as active sites for oxygen reduction reactions. Palladium-based anode electrocatalysts have also garnered academic interest due to their strong performance in alkaline fuel cells.

Simultaneously, researchers are actively developing improved polymer membrane materials. Based on reaction kinetics, it can be inferred that high temperature can enhance the operating efficiency of fuel cells. However, after numerous experiments, scientists have discovered that the perfluoro sulfonic acid (PFSA) series membranes (such as Nafion membranes) currently widely used in proton fuel cells can achieve the best proton conductivity only in low-temperature and high-humidity environments. In contrast, sulfonated hydrocarbon polymers, which are modified from conventional perfluoro sulfonic acid membranes, offer cost-effectiveness, excellent chemical and thermal stability across a broader temperature range, and do not require humidification. Future innovations are anticipated to yield more membrane materials suitable for a wide array of temperatures, particularly high-temperature applications.

Hydrogen production has been a contentious issue for PEMFC applications, primarily because current methods often involve fossil fuels and result in carbon dioxide emissions. To improve hydrogen utilization efficiency, efforts are underway to integrate PEMFCs with combined heat and power (CHP) systems that use renewable fuels like biogas. Battery miniaturization is another significant research area. However, challenges such as difficult charging, large size and weight, compromised safety, and high costs still need to be overcome. A novel battery type, the microbial fuel cell (MFC), has attracted considerable attention due to its low cost, minimal maintenance, extended operational life, and sustainable green power generation capabilities. Furthermore, MFCs have shown remarkable effectiveness in remediating pollutants by removing organic carbon compounds and phosphorus from fixed deposits.

5. Conclusion

This systematic review of fuel cells highlights the significant research focus on proton exchange membrane fuel cells. Microbial fuel cells and combined heat and power systems are also experiencing rapid advancement. Rapid start-up and suitability for everyday applications are advantages of PEMFCs, AFCs, and DAFCs due to their lower operating temperatures. Certain medium- and high-temperature fuel cells exhibit higher efficiency and reduced reliance on precious metal catalysts. However, the dependence of catalyst materials on precious metals and the stringent material requirements for high-temperature, highly corrosive environments continue to limit their industrialization due to material stability and manufacturing process challenges. The ongoing development of novel precious metal composite catalysts, advanced polymer membranes, microbial fuel cells, and combined cycle power generation systems aims to overcome these limitations.

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