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Proton exchange membrane fuel cells: application for value-added chemical productions

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Abstract

Proton exchange membrane fuel cells (PEMFCs) can be used as reactors to produce chemicals and co-generate electricity and chemicals. Their mild reaction conditions, high product selectivity, and energy utilization have profoundly impacted gas separation, water treatment, and energy utilization fields. Given the lack of systematic reports on the current research status of utilizing PEMFCs for chemical production and the co-production of electricity and chemicals, this article summarizes the types of reactions and catalyst usage involved in this multifaceted application. It analyzes how to improve the production and performance of the system from four aspects: electrolyte membranes, catalysts, assembly methods, and reaction processes. Finally, the article analyzes the current research shortcomings in utilizing PEMFCs for these applications and provides prospects for future development.

Keywords: PEMFCs, chemical production, co-generation of electricity, chemicals



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INTRODUCTION

Fuel cells are green and efficient power generation devices, representing the fourth generation of power generation technology after hydropower, thermal, and nuclear power. Many developed countries and developing nations worldwide have elevated fuel cell development to a national strategic level, particularly in the field of transportation applications^[1]. Among them, the proton exchange membrane fuel cells (PEMFCs) have been widely used in portable power sources, transportation sectors, *etc.* Moreover, research and development of hydrogen fuel PEMFCs for automobiles have become even more vigorous than before^[1,2]. With the development of science and technology, researchers have expanded fuel cell reactors to produce high-value-added chemicals. Using fuel cell methods to create chemicals with fuel cells offers several advantages over traditional catalytic methods. For instance, the isolation of different reactants enhances system safety; continuous circulation of reactants at the electrodes improves catalytic performance and the ease of product separation from reactants. Furthermore, the integration of fuel cells for the simultaneous production of chemicals and electrical energy has shown strong potential for various applications. Their capability to simultaneously generate power, produce chemicals, and contribute to environmental protection profoundly influences energy utilization^[3,4]. Solid oxide fuel cells (SOFCs) have garnered significant research attention due to their high operating temperature, which enables reduced impurity presence and the utilization of non-precious metal catalysts with superior catalytic performance. Numerous studies have reported the simultaneous production of electrical energy and chemicals using SOFCs^[5,6]. However, it is challenging to use them at operating temperatures < 600 °C. The cost and stability issues of catalysts hinder the application of SOFCs for chemical production and the co-production of electricity and chemicals. On the other hand, the PEMFCs can operate at relatively low temperatures (low temperature ~70-95 °C, high temperature ~120-250 °C), with lower operational costs and faster response times, providing the possibility to achieve chemical production and the co-production of electricity and chemicals at lower operating costs. Currently, researchers have summarized their applications in the production of chemicals and the co-generation of electricity and chemicals^[7-9]. However, existing review articles either focus on fuel cell reactions with a specific fuel or provide a general overview of the production of chemicals or the co-generation of electricity and chemicals using PEMFCs. Therefore, it is necessary to publish a comprehensive review article to summarize the current research status in this field. This article attempts to collect and summarize previous research on utilizing PEMFCs to obtain chemicals or simultaneously produce electrical energy and chemicals. It analyzes the types of feasible reactions and the catalysts involved, summarizes the ways to enhance the capacity and performance of PEMFCs, and provides a future outlook on the development of PEMFCs in co-generation energy and chemical products.

FUNDAMENTAL OF PEMFCs FOR CHEMICAL PRODUCTIONS

PEMFCs, a commonly used form of fuel cells, offer advantages such as high power density, low operating temperature, and minimal noise. Reactors also possess the benefits of mild reaction conditions and high product selectivity. Based on different operating temperatures, PEMFCs can be classified into low-temperature (~70-95 °C) PEMFCs (recorded as LT-PEMFCs) and high-temperature (~120-250 °C) PEMFCs (recorded as HT-PEMFCs). Compared to LT-PEMFCs, HT-PEMFCs have attracted increasing attention due to their improved reaction kinetics on the electrodes, enhanced tolerance to fuel/air impurities, simplified stack design, and better thermal and water management^[1]. Generally, a single cell of PEMFCs consists of an anode gas diffusion layer, an anode catalyst layer, a proton exchange membrane, a cathode catalyst layer, a cathode gas diffusion layer, and bipolar plates [Figure 1]. The proton exchange membrane separates the two electrodes. Hydrogen gas undergoes an oxidation reaction to produce protons in the anode catalyst layer. It reacts with oxygen in the cathode catalyst layer through the proton exchange membrane, generating internal current. The electron flow isolated by the proton exchange membrane passes through the external circuit to produce electricity. Utilizing PEMFCs as reactors for synthesizing

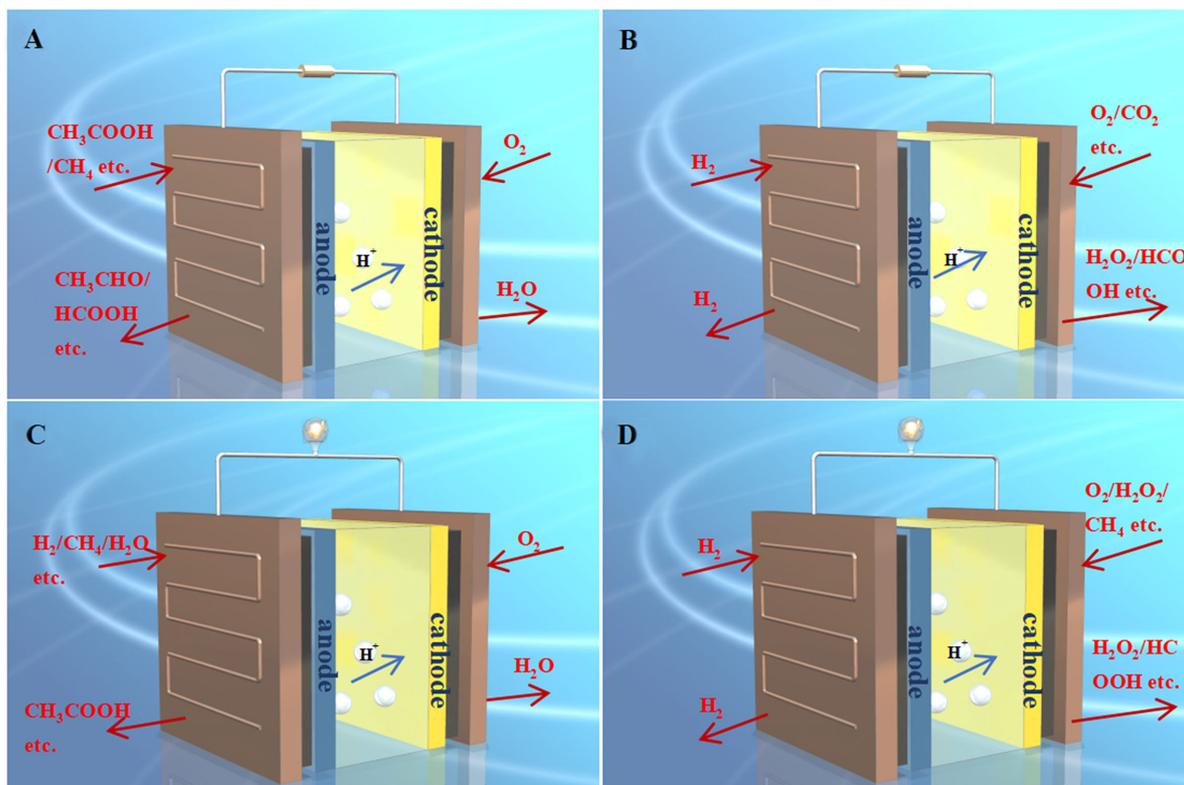


Figure 1. Schematic diagram of (A and B) chemical products, and (C and D) co-generation of electricity and chemicals using PEMFCs. PEMFCs: Proton exchange membrane fuel cells.

value-added chemicals, dehydrogenation reactions (partial oxidation) can occur at the anode, and gases that can be oxidized, such as hydrogen, methanol, and methane, can be used as fuel gases. Hydrogenation reactions can occur at the cathode, and substances with oxidation ability, such as oxygen, carbon dioxide, and cyclic ketones, can be used at the cathode. If the overall fuel cell has a positive standard free enthalpies change, the partial external voltage is required to drive the reactions [Figure 1A and B]. If the standard free enthalpies change is negative, co-generation of electricity and chemicals can be achieved [Figure 1C and D].

REACTION TYPES AND CATALYSTS OF PEMFCs FOR CHEMICAL PRODUCTIONS

Considering the operating temperature of PEMFCs, the chemical reactions that can be achieved on PEMFCs mainly involve reactions that can be carried out at relatively low temperatures (below 250 °C). Currently, the responses that can be realized at the anode as reactors include methanol/ethanol oxidation, methane oxidation, and propene epoxidation. In contrast, the reactions achieved at the cathode mainly include CO₂ reduction, H₂O₂ production, and hydrogenation of some alkynes or cyclic ketones. However, to the best of our knowledge, there is no report of producing high value-added chemicals in the cathode and anode simultaneously. Table 1 summarizes the current research on chemical production using PEMFCs and shows that both the cathode and anode reactions predominantly utilize precious metal catalysts (Pt or Pd) with carbon materials as the support. The selectivity of the product is high, but the yield is low.

REACTION TYPES AND CATALYSTS OF PEMFCs FOR POWER AND CHEMICALS CO-GENERATION

There are few reports on using PEMFCs for the co-generation of electricity and chemicals. The reactions

Table 1. Selected research on the utilization of PEMFCs for chemical production

Section	Reactions	Catalyst	Conv.	Current density	Main product	Ref.	
Anode	$2\text{CH}_3\text{OH} \rightarrow \text{HCOOCH}_3 + 4\text{H}^+ + 4\text{e}^-$	Pt-Ru/C	-	50 mA/cm ² at 1.7 V (vs. SHE)	HCOOCH ₃ [7-9 μmol/(min·cm ²)] FE (80%)	[10]	
	$\text{CH}_2\text{CH}_2\text{OH} + \text{H}_2\text{O} \rightarrow \text{CH}_3\text{COOH} + 4\text{H}^+ + 4\text{e}^-$	PtRu/C 2:1	-	740 mA/cm ²	CH ₃ COOH FE (15%)	[11]	
	$3\text{CH}_3\text{CH}_2\text{OH} \rightarrow \text{CH}_3\text{CH}(\text{OCH}_2\text{CH}_3)_2 + \text{H}_2 + \text{H}_2\text{O}$	Pt/C	-	-20 mA/cm ² at 2.0 V (vs. SHE)	CH ₃ CH(OCH ₂ CH ₃) ₂ FE (78%)	[12]	
	$\text{CH}_3\text{CH}_2\text{OH} \rightarrow \text{CH}_3\text{CHO} + 2\text{H}^+ + 2\text{e}^-$	PtRu/C	1%	0.2 A	CH ₃ CHO FE (100%)	[13]	
	$\text{CH}_4 + \text{H}_2\text{O} \rightarrow \text{CH}_3\text{OH} + 2\text{H}^+ + 2\text{e}^-$	V ₂ O ₅ /SnO ₂	-	-	CH ₃ OH (0.03) FE (88.4%)	[14]	
	$\text{C}_3\text{H}_6 + \text{H}_2\text{O} \rightarrow \text{C}_3\text{H}_6\text{O (PO)} + 2\text{H}^+ + 2\text{e}^-$	PtO _x (O ₂)	0.4%	13.4 mA/cm ² at 1.6 V (vs. SHE)	C ₃ H ₆ O [37 μmol/(h·cm ²)] FE (7.4%)	[15]	
	$\text{O}_2 + \text{H}_2 \rightarrow \text{H}_2\text{O}_2$ $\text{C}_3\text{H}_8 + \text{H}_2\text{O}_2 \rightarrow \text{C}_2\text{H}_8\text{O} + \text{C}_3\text{H}_6\text{O} + 7\text{C}_3\text{H}_6\text{O}_2$	MIL-53 (Al, Fe)/C acid	-	-35 mA/cm ² at -0.2 V (vs. RHE)	C ₃ [2.65 μmol/(h·cm ²)]	[16]	
	$\text{CH}_3\text{OH} \rightarrow \text{HCHO} + 2\text{H}^+ + 2\text{e}^-$	Pd/C	-	-50 mA/cm ² at 2.0 V	HCHO [682 mmol/(h·g _{cat})] FE (-45%)	[17]	
	$\text{CH}_3\text{CH}_2\text{OH} \rightarrow \text{CH}_3\text{CHO} + 2\text{H}^+ + 2\text{e}^-$	Pt-Ni/GNPs	-	590 mA/cm ² at 1.4 V	CH ₃ CHO	[18]	
	$\text{C}_3\text{H}_7\text{OH} \rightarrow \text{C}_2\text{H}_5\text{CHO} + 2\text{e}^- + 2\text{H}^+$ $\text{C}_2\text{H}_5\text{CHO} + 2\text{C}_3\text{H}_7\text{OH} \rightleftharpoons \text{C}_3\text{H}_6(\text{OC}_3\text{H}_7)_2 + \text{H}_2\text{O}$	Pt/C	-	-10 mA/cm ² at 2 V	1,1-dipropoxypropane FE (78%)	[19]	
	$\text{PhCH}_2\text{OH} \rightarrow \text{PhCHO} + 2\text{e}^- + 2\text{H}^+$	Nafion ionomer	-	8.3 mA/cm ² at 2.5 V	PhCHO FE (80%-90%)	[20]	
	Cathode	$\text{O}_2 + 2\text{H}^+ + 2\text{e}^- \rightarrow \text{H}_2\text{O}_2$	VGCF-XC72	-	-	H ₂ O ₂ (7%) FE (95%)	[21]
		$x\text{CO}_2 + 2(2x - z + y/2)\text{H}^+ + 2(2x - z + y/2)\text{e}^- \rightarrow \text{C}_x\text{H}_y\text{O}_z + (2x - z)\text{H}_2\text{O}$ (CO ₂ reduction)	Cu-CNF	< 2%	0.8 mA/cm ²	Acetaldehyde (85%)	[22]
Sn nanoparticles (60-80 nm) + 5% CNT			-	140 mA/cm ² at 3.5 V	HCOOH (5-20 wt%) FE (94%)	[23]	
2.5%Cu complex/carbon Vulcan			-	0.021 pA at -1.2 V	CH ₃ OH [4 mol/(h·L)] FE (22%)	[24]	
$\text{CH}_3\text{-C}_6\text{H}_5 + 6\text{H}^+ + 6\text{e}^- \rightarrow \text{CH}_3\text{-C}_6\text{H}_{11}$		Ru/BP3500	-	50 mA/cm ² at -0.255 V (vs. SHE)	Methylcyclohexane FE (91%)	[25]	
		Ru(5)-Ir(5)/KB	-	200 mA/cm ² at -0.183 V (vs. SHE)	Methylcyclohexane FE (86%)	[26]	
$\text{C}_{14}\text{H}_{10} + 2\text{H}^+ + 2\text{e}^- \rightarrow \text{C}_{14}\text{H}_{12}$		Pt1Pd99	-	20 mA/cm ² at 0.05 V (vs. RHE)	C ₁₄ H ₁₂	[27]	
		Pt1Pd99	-	15 mA/cm ² at 0 V (vs. RHE)	C ₁₄ H ₁₂ FE (40%)	[28]	
$\text{C}_7\text{H}_6\text{O}_2 + 6\text{H}^+ + 6\text{e}^- \rightarrow \text{C}_7\text{H}_{12}\text{O}_2$		Pt ₁ Ru _{1.5}	-	3.0 mA/cm ²	C ₇ H ₁₂ O ₂ FE (93%)	[29]	

$C_6H_8O + 2H^+ + 2e^- \rightarrow C_6H_{10}O$	Pd/C	82%	50 mA/cm ²	C ₆ H ₁₀ O (64%) FE (97%)	[30]
cyclohexanone + 2H ⁺ + 2e ⁻ → cyclohexanol	Rh/C		24 mA/cm ²	Cis-cyclohexanol FE (96%)	[31]

CNF: Carbon nanofiber; CNT: carbon nanotube; FE: Faraday efficiency; GNPs: graphene nanoplatelets; MIL-53: materials of Institut Lavoisier frameworks-53; PEMFCs: proton exchange membrane fuel cells; RHE: reversible hydrogen electrode; SHE: standard hydrogen electrode.

involved mainly include the reduction of nitrobenzene, oxidation of phenol to benzoquinone, and production of H₂O₂. [Table 2](#) summarizes the research status of utilizing PEMFCs for co-generating electricity and chemicals. [Table 2](#) shows that the current reaction temperatures are relatively low (below 100 °C), the catalysts used are mostly carbon-supported noble metal-based catalysts, the generated electrical power is low, and the chemical yields are not high.

STRATEGIES TO IMPROVE PRODUCTIVITY PERFORMANCE IN PEMFCs

The components involved in PEMFCs and the reaction processes affect chemical production and electricity generation. Moreover, although the conversion rate is an important parameter for chemical production, our research has found that there are few reports mentioning conversion rates in the use of PEMFCs for chemical preparation [[Table 1](#)]. This may be related to the frequently lower conversion rates of electrochemical production of chemicals. It is well known that conversion rates are related to reaction conditions such as gas velocity, pressure, *etc.* However, except for one report proposing that continuous operation modes can improve the conversion rate of raw materials^[30], no other research has been found on enhancing this aspect. Therefore, this section summarizes strategies to enhance the capacity and performance (mainly selectivity) of PEMFCs based on four aspects: electrolyte membranes, catalysts, assembly modes, and reaction processes.

ELECTROLYTE MEMBRANE

Polymer electrolyte membranes (PEM) are essential components of PEMFCs, which require characteristics such as high proton conductivity, mechanical stability, *etc.*^[37] [[Figure 2](#)]. Most commercialized naphthol membranes, such as Nafion 117, are used at low temperatures (< 120 °C), while polybenzimidazole (PBI)-based membranes are preferred at higher operating temperatures. Compared to low-temperature membranes, developing membrane materials that can be used at higher temperatures can enhance the system's tolerance to pollutants, reduce the use of precious metal catalysts, and simplify the system by eliminating the need for liquid water operation. The types of high-temperature membranes currently developed and their proton conductivities are shown in [Table 3](#)^[38]. Currently, the PEMs used in the production of chemicals using PEMFCs and in chemical production and chemicals and electricity co-generation systems are mostly commercial Nafion membranes; research on the involved membrane materials and their modification are relatively lacking. In addition, recent studies have found that ionomer content in Naphthol membranes in PEMFCs affects catalytic activity. Abdelnasser *et al.* reported that adding Nafion ionomer could expand the electrochemical active site, accelerating the electrochemical reaction in the proton transfer process^[20]. In addition to the amount, the type and properties of ionomer binders can also affect the performance of PEMFCs in electricity generation^[39,40], but no related reports have been found in the production of chemicals and the co-generation of chemicals and electricity using PEMFCs.

Table 2. Selected research on the utilization of PEMFCs for co-generation of electrical energy and chemicals

Anode (catalyst)	Cathode (catalyst)	T (°C)	Chemicals	Power (mW/cm ²)	Ref.
H ₂ (Pt/C)	H ₂ O ₂ + CH ₄ (Pt/C)	80	Methanol, formic acid and formaldehyde	70	[32]
H ₂ O + CH ₄ (Pd ₅₀ Ni ₅₀ /Sb ₂ O ₅ -SnO ₂)	O ₂ + H ₂ O (Pt/C)	85	CH ₃ COOH [-6.3 μmol/(h·L)]	-0.375	[33]
H ₂ (Pt/C)	O ₂ + H ₂ O (Pt/Co-C)	60	H ₂ O ₂ [8 μmol/(h·cm ²)]	133	[34]
H ₂ (Pt/C)	Nitrobenzene (Pt/C)	70	Aniline FE (28.2%)	1.5	[35]
Phenol (PtRu/C)	O ₂ (Pt/C)	80	Hydroquinone FE (80%)	-	[36]

FE: Faraday efficiency; PEMFCs: proton exchange membrane fuel cells.

Table 3. Membrane proton conductivity for HT-PEMs

Membrane type	Proton conductivity/(mS·cm ⁻¹)
Cesium dihydrogen phosphate solid acid	410
Ionic liquid-doped membrane composites	59-148
Pyridine-based PBI	200
Sn _{0.9} In _{0.1} P ₂ O ₇	195
Nanocomposite membranes (based on PBI and porous SiO ₂ NPs)	244
Lonically cross-linked PBI-blend membranes mixed with PBI and sulfonated or phosphonated acidic polymers	100
3,5-Pyridine-PBI	279.38
Protic ionic liquid-modified silica	238.17
Functionalized PBI	152.41
H ₃ PO ₄ -PBI (20.4 mol per repeating unit)	200
H ₃ PO ₄ -PTFE/PBI (300% mol)	300
PBI-OO	98
c-PBI-30	198
AA-MCM-41	356
PES-PVP/PTFE	260
PA/PBI/SiO ₂	41

This table is quoted with permission from Meyer *et al.*^[38] published in *Electrochem Energy Rev.* A-MCM-41: Anhydrous m-PBI composite membrane using Al-substituted mesoporous silica; HT-PEMs: high-temperature polymer electrolyte membranes; NPs: nanoparticles; PBI: polybenzimidazole; PBI-OO: polybenzimidazole; PA: phosphoric acid; PES: poly(ethersulfone); PTFE: polytetrafluoroethylene; PVP: poly(vinyl pyrrolidone).

CATALYST

In catalyst design, because high-value-added chemicals are in a semi-stable state, controlling the degree of oxidation-reduction catalysis is necessary to produce high-value-added chemicals. As the fuel cannot be completely oxidized or reduced, some power will be lost when electricity is produced in co-generation with fuel. The current research on catalysts mainly focuses on the rational design of supports and active sites. The catalysts used mainly consist of noble metals. Researchers such as Rodríguez-Gómez *et al.*, Kuramochi *et al.*, Serrano-Jiménez *et al.*, Inami *et al.*, Nogami *et al.*, and Fukazawa *et al.* have made significant contributions in the field of catalyst design and mechanism exploration^[11,13,17,18,25,26,28,29]. The catalytic performance can be improved by constructing the alloy structure, changing the electronegativity of the original active atoms, and dispersing the active centers [Figure 3]^[28,29]. Adequate combinations of non-precious metal oxides can also achieve good catalytic performance. Lee *et al.* used V₂O₅/SnO₂ as the anode catalyst to convert methane to methanol (selectivity 88.4%)^[14]. Different methods of noble metal treatment

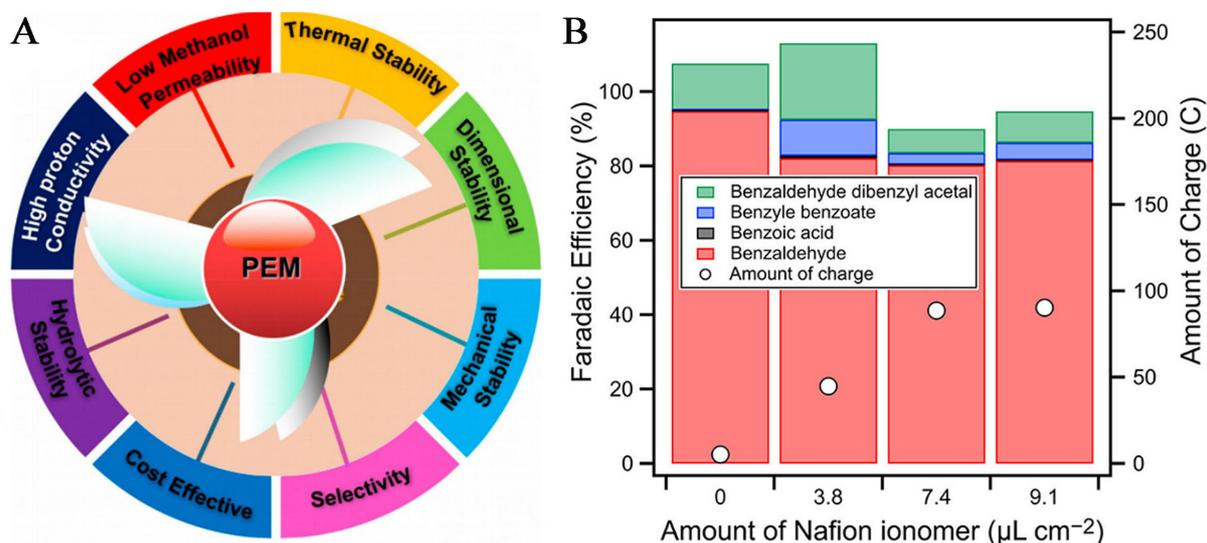


Figure 2. (A) Characteristics of PEM. This figure is quoted with permission from Ahmed *et al.*^[37]; (B) Effect of Nafion ionomer content on catalytic performance. This figure is reproduced with permission from Abdelnasser *et al.*^[20]. PEM: Polymer electrolyte membranes.

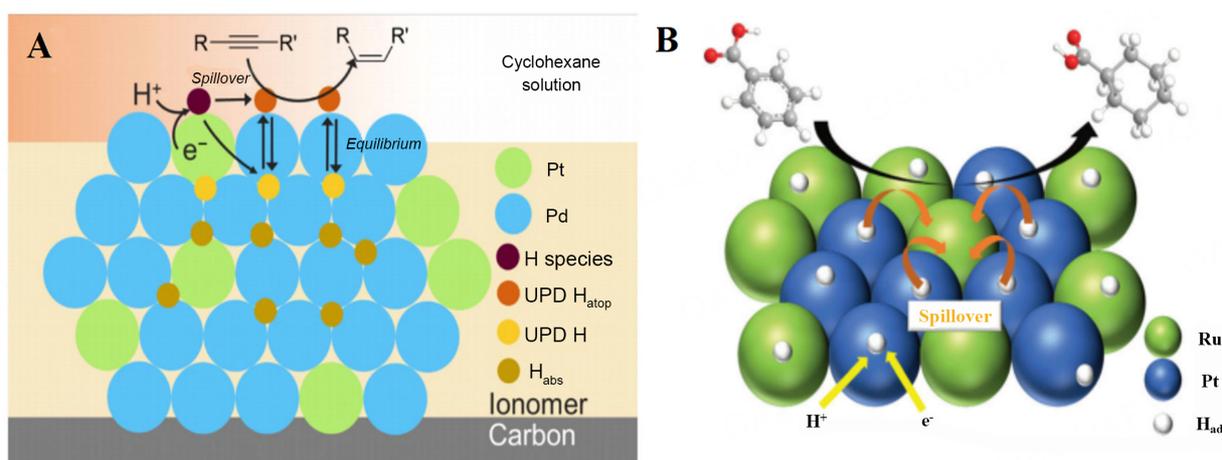


Figure 3. (A) Conceptual diagram of the reaction model for the electrocatalytic semihydrogenation of alkyne to (Z)-alkene on a Pt-Pd electrocatalyst. This figure is quoted with permission from Nogami *et al.*^[28]; (B) Proposed mechanism for the electrocatalytic hydrogenation of BA using a PtRu catalyst in a PEM reactor. This figure is quoted with permission from Fukazawa *et al.*^[29]. BA: Benzoic acids; PEM: polymer electrolyte membranes.

may also lead to excellent catalytic performance^[41]. In addition, suitable supports need to possess a large specific surface area, excellent electronic conductivity, better durability, reliable interfacial adhesion, and appropriate porosity^[42]. Therefore, the current focus is on improving catalytic performance through modification of carbon supports and selecting appropriate carbon supports (such as biochar)^[25,43].

ASSEMBLY METHOD

Currently, there are three main methods for assembling membrane electrodes: the catalyst layer loaded on the gas diffusion layer (CCS), the catalyst layer loaded on the proton exchange membrane (CCM), and the catalyst layer loaded on the proton exchange membrane through transfer (DTM) [Figure 4]. The advantages and disadvantages of these three assembly methods are shown in Table 4^[44]. Compared to the demanding

Table 4. Advantages and disadvantages of assembly methods

Assembly method	Advantages	Disadvantages
CCS	Easy implementation	Catalyst inks easily penetrate GDLs
CCM	Excellent interfacial properties between the catalyst layer and membrane	Solvent easily causes membrane expansion, and the manufacturing system is more complex than CCS
DTM	Excellent interfacial properties between the catalyst layer and membrane, reduced membrane expansion, multilayer catalyst stack	High-cost manufacturing system, limitations on the amount of catalyst

CCM: The catalyst layer loaded on the proton exchange membrane; CCS: the catalyst layer loaded on the gas diffusion layer; DTM: the catalyst layer loaded on the proton exchange membrane through transfer; GDLs: gas diffusion layers.

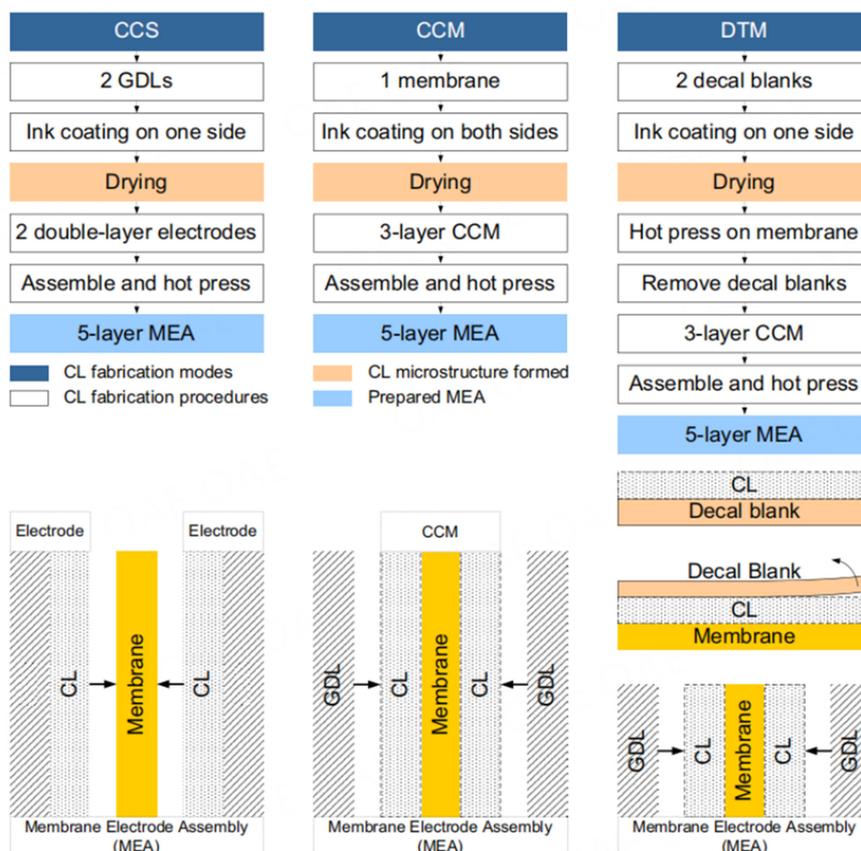


Figure 4. Three major approaches for the catalyst layer fabrication. This figure is quoted with permission from Zhao *et al.*^[44]. CCM: The catalyst layer loaded on the proton exchange membrane; CCS: the catalyst layer loaded on the gas diffusion layer; CL: catalyst layer; DTM: the catalyst layer loaded on the proton exchange membrane through transfer; GDL: gas diffusion layer; MEA: membrane electrode assembly.

technical requirements of the DMT method and the significant mass transfer resistance caused by the CCS approach, the CCM method can achieve excellent catalytic performance at a higher cost-effectiveness^[44]. Rodriguez-Gómez *et al.* achieved higher catalytic performance in ethanol oxidation for acetic acid production by loading the catalyst layer on the proton exchange membrane and using carbon paper as the gas diffusion layer.^[45] The assembly method can improve mass transfer and other issues in the reaction system, thus affecting catalytic performance. However, currently, there is insufficient research on the impact of assembly methods on the production of chemicals and chemical-electro-thermal co-generation systems using PEMFCs, alongside a lack of studies on the kinetics aspect.

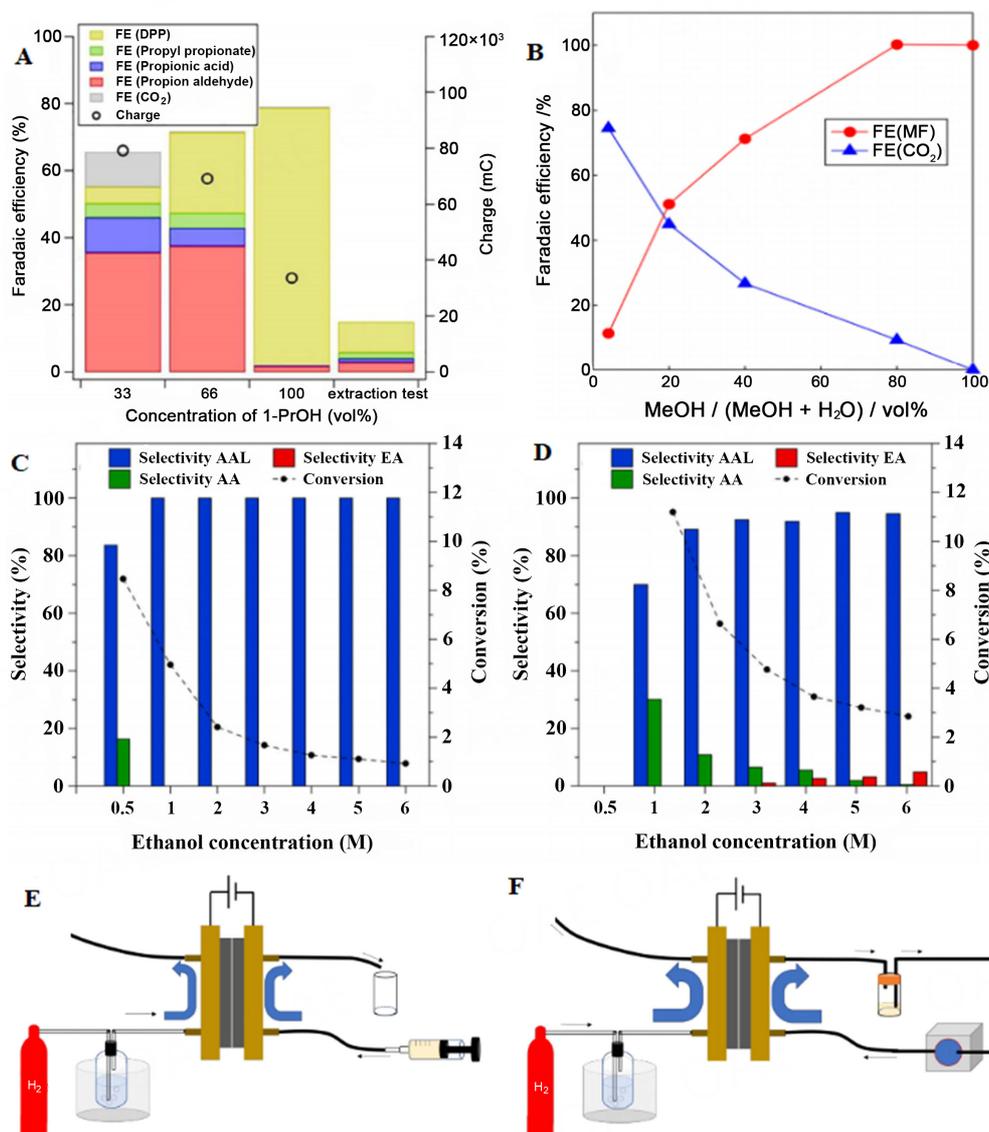


Figure 5. (A) Effect of 1-PrOH content on catalytic performance. This figure is quoted with permission from Abdelnasser *et al.*^[19]; (B) Effect of MeOH content on catalytic performance. This figure is quoted with permission from Kishi *et al.*^[10]; (C and D) Effect of EtOH content on catalytic performance. This figure is quoted with permission from Rodríguez-Gómez *et al.*^[48]; (E and F) The operational mode of the system. This figure is quoted with permission from Mitsudo *et al.*^[30]. AA: Acetic acid; AAL: acetaldehyde; DPP: 1,1-dipropoxypropane; EA: ethyl acetate; FE: faradaic efficiency; MF: methyl formate.

REACTION PROCESS

Exploration of reaction conditions, such as reaction medium, reactant concentration, and reaction temperature, can lead to efficient catalytic performance. Currently, research in the production of chemicals and chemical-electrical co-generation systems using PEMFCs mainly focuses on the influence of reactant concentration. Kishi *et al.* investigated the influence of water on electrolysis of reactants in multiple reaction types^[10,12,17,19,25]. However, there remains a gap in understanding regarding the influence of other reaction conditions, especially the electrolyte. Although the impact of the type of electrolyte has been preliminarily explored^[46], parameters such as pH, which have a significant impact on electrocatalytic performance^[47], have not been fully investigated. In the oxidation reaction of alcohols, researchers have found that increasing the concentration of alcohols favors the production of high-value chemicals; adjusting the concentration can

also modulate the selectivity of products [Figure 5]^[10,19,48]. As shown in Table 2, the preferred temperature for co-production of chemicals and electricity is around 80 °C, indicating that an appropriate operating temperature can enhance gas diffusion capability and maintain high ionic conductivity, thereby improving performance. Furthermore, in terms of the operational mode of the system, continuous operation modes, compared to batch mode, can not only reduce the consumption of raw materials but also improve the conversion rate of raw materials^[30].

CONCLUSION AND OUTLOOK

Currently, PEMFCs can be used to produce chemicals, such as ethanol, epoxypropane, formate acid, *etc.*, and achieve co-production of hydrogen peroxide (or formate acid, ethanol, *etc.*) and electricity. The catalysts used during this process are mainly carbon-supported noble metal-based catalysts, with limited reports on non-noble metal-related catalysts. Additionally, improvements in production and performance can be achieved by modifying the membrane properties and monomer usage, constructing catalyst alloy structures, utilizing the MCC membrane electrode assembly method, and studying suitable process conditions. Although significant progress has been made in utilizing PEMFCs for the production of chemicals or co-production of chemicals and electricity, the following issues still exist: (1) a restricted range of catalytic reactions involved; (2) a limited variety of catalysts and high cost, primarily focused on precious metal catalysts; (3) lower conversion rates, yields, selectivity towards single products, and current densities; (4) insufficient research on reaction intermediates and reaction pathways; (5) a lack of standardization of reaction devices and studies on the impact of the reaction process. Therefore, addressing the aforementioned issues, developing more reaction types, reducing the usage of precious metals in catalysts or exploring non-noble metal catalysts with higher cost-effectiveness, conducting comprehensive and in-depth studies on improving productivity performance, and utilizing density functional theory (DFT) and *Operando* characterization techniques to study reaction mechanisms are the main directions for future research.

DECLARATIONS

Authors' contribution

Prepared and revised the manuscript: Jiang X, Chen R

Designed and revised the manuscript: Chen YX, Lu CZ

All authors contributed to the discussion and preparation of the manuscript.

Availability of data and materials

Not applicable.

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Conflicts of interest

All authors declared that there are no conflicts of interest.

Ethical approval and consent to participate

Not applicable.

Consent for publication

Not applicable.

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