

An overview of noncarbon support materials for membrane electrode assemblies in direct methanol fuel cells: Fundamental and applications



Yuzhi Ke^a, Wei Yuan^{a,*}, Qingsen Liu^a, Feikun Zhou^b, Wenwen Guo^c, Zi'ang Liu^a, Zhenhe Lin^a, Xinze Li^a, Jinguang Li^a, Shiwei Zhang^a, Yong Tang^a, Zhenghua Tang^d, Yu Chen^d, Bote Zhao^d

^a School of Mechanical and Automotive Engineering, South China University of Technology, Guangzhou 510640, China

^b Foshan Xianhu Laboratory of the Advanced Energy Science and Technology Guangdong Laboratory, Foshan 528000, China

^c GAC Automotive Research & Development Center, Guangzhou 511434, China

^d School of Environment and Energy, South China University of Technology, Guangzhou 510006, China

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ABSTRACT

Noncarbon support materials (NCSMs) used in the membrane electrode assemblies (MEAs) have received extensive attentions due to their better chemical stability, excellent corrosion resistance and high electrical conductivity. To develop high-quality MEA, great efforts have been devoted to improving the electrochemical performance and durability of MEAs through the surface engineering of NCSMs. With this context, the recent progress of the NCSMs as catalyst support and diffusion layer is summarized. The functional mechanisms and critical roles of NCSMs in MEAs are firstly discussed in terms of the structure-functions relationship. The design strategies and fabrication process based on different noncarbon materials (e.g., metal-based materials and carbides) as catalyst supports are summarized from the perspective of nanoscale structures like nanoparticles, nanofibers, and nanotubes. The structural design and surface modification of the noncarbon materials applied to the diffusion layer and stack-level MEA are also analyzed. Finally, the current limitations, prospective and future development tendency of NCSMs in MEA are proposed. This review is believed to provide an in-depth overview and promising research directions for the design of catalyst supports in fuel cells.

1. Introduction

As is well known, the direct methanol fuel cell (DMFC), which is based on the use of polymer electrolyte membrane (PEM), has been regarded as a hopeful power source due to its high energy density (pure methanol: 6000 Wh kg⁻¹), room-temperature operation, easy fuel storage and refueling, as well as good portability [1–4]. The DMFC has shown more competence over the conventional internal combustion engines and batteries in developing future sustainable energy conversion devices [5–7]. Moreover, compared with the methanol steam reforming system to supply the hydrogen source for proton exchange membrane fuel cells (PEMFCs), a DMFC directly converts the chemical energy into electricity by eliminating the methanol reformer and hydrogen purifier, which reduces the cost of electricity generation and infrastructure construction [8–11]. Currently, DMFCs have been widely used as power suppliers in many fields. For instance, the Smart Fuel Cell company has developed the DMFC (EFOY Pro 12,000 Duo) products with a power of 500 W, which are used for the typical applications as off-

grid power supplies for monitoring traffic and online power supplies for telecommunication systems [12]. The Suzhou Okhua New Energy company and the National Engineering Laboratory of Logistics Information led by Yuantong jointly developed a DMFC logistic vehicle in 2019 with a maximum driving mileage of near 500 km, and a filling time of 1 min [13].

Although many DMFC devices have been developed for practical applications, the low methanol tolerance, poor durability, CO poisoning and high-amount usage of Pt-based noble metal catalysts hinder its large-scale applications [14–16]. This explains why the DMFC is still not widely used for commercial purposes. The core of the above two issues is primarily related to the MEA that comprises two catalyst-supports, two diffusion layers (DLs) and a PEM. A qualified MEA is supposed to maintain strong corrosion resistance, high catalytic activity, low Pt loading and long lifetime [17–19]. Currently, carbon-based materials have been widely used as the catalyst support or diffusion medium in the MEA, such as the XC-72 carbon black in the catalyst support, and carbon-paper or carbon woven cloth in the DL [20–23]. The commercial

* Corresponding author.

E-mail address: mewyuan@scut.edu.cn (W. Yuan).

Pt nanoparticles can be distributed on the carbon black surface via different techniques like the hydrothermal method and electrodeposition [24,25]. To achieve a higher output performance of the fuel cell, it is indispensable to realize a good combination between the Pt catalyst and the catalyst support to form a high-performance Pt-based catalyst. Nano-crystallization design of the catalysts has been proven effective in enhancing the reaction efficiency of fuel cells. Especially, previous studies have demonstrated that Pt nanoparticles with a diameter of 2–4 nm mostly show the best electrocatalytic activity including specific activity and mass activity [26,27]. Despite the easy preparation process of conventional catalysts based on Pt/C nanoparticles, there are three evident disadvantages for DMFCs [28–30]: i) corrosion issue: the conventional carbon supports tend to be easily corroded during the electrochemical reaction because of the oxidation of carbon-based materials; ii) durability issue: the CO intermediate species are very likely to poison the Pt active sites after the methanol oxidation due to CO adsorption on the surface of Pt metals. In this case, the mitigation effect of catalyst supports is important; iii) synergistic effect: the weak interaction between carbon supports and the Pt may easily lead to dissolution or sintering of Pt nanoparticles.

Therefore, it is of great significance to design novel catalyst support with modified catalyst surface and decreased adsorption energy of CO in order to overcome the aforementioned problems. According to the open literature, there have been two research directions to reach the goal of improving the catalyst support, including morphological engineering (e.g., one-dimensional (1D) nanowire, two-dimensional nanosheet) and surface engineering (e.g., zero-dimensional (0D) structures) [31–36]. Especially, 0D structures include the nanosphere, core-shell, polyhedral and hollow spheres. In the case of morphological engineering, the fabrication methods of these catalyst supports are critical for their physical and chemical performances. The popular preparation methods include the hydrothermal reaction and the solvothermal method [37,38]. From the perspective of surface engineering, the noncarbon support materials usually design the surface morphology based on the 0D structures. With this context, the ideal catalyst supports for DMFCs should have the following features [39–41]: i) high electrical conductivity; ii) strong interaction between the catalysts and catalyst supports; iii) large electrochemical active surface area (ECSA) when it combines with Pt-based catalyst; iv) good ability in corrosion resistance; v) high durability with small CO adsorption energy; and vi) high structural stability. Particularly, the novel support materials for DMFCs even play a special role in the electrochemical reaction process. For instance, when Cu is used as a catalyst support, it helps facilitate the affinity in methanol molecules and improve the CO tolerance to maintain the activity of Pt/Cu catalyst [42]. In addition to the carbon-type supports, the noncarbon support materials (NCSMs) including the metal-based materials, silicon-based materials, perovskites, carbides, conducting polymers and supportless materials have been developed for the applications of DMFCs, as shown in Fig. 1.

In a DMFC, the methanol, liquid water and air need to diffuse to the catalyst layer (CL) through the DL to start the electrochemical reactions. In this context, a DL needs to facilitate reactant diffusion, conduction of heat and electricity, water transport and mechanical support for the electrode in the fuel cell. The traditional DL is mostly made of carbon paper or carbon cloth. Besides, other noncarbon materials have been also applied to the DL for DMFCs due to their low flow resistance and structural flexibility, which can enhance the multiphase mass transfer [43,44]. For example, Arisetty's group proposed a porous metal foam with a controllable porosity to construct the flow field and DL, improving the mass transfer in a DMFC due to the enhancement of electrode stiffness and CO₂ removal [45]. In order to enhance the performance, the as-prepared noncarbon materials (e.g., Ni mesh or metal foam) mostly need to be further treated by surface modification to regulate the surface properties (e.g., super-hydrophobic or super-hydrophilicity). This helps improve the functions of DL in fuel delivery, product removal, thermal management and even reaction

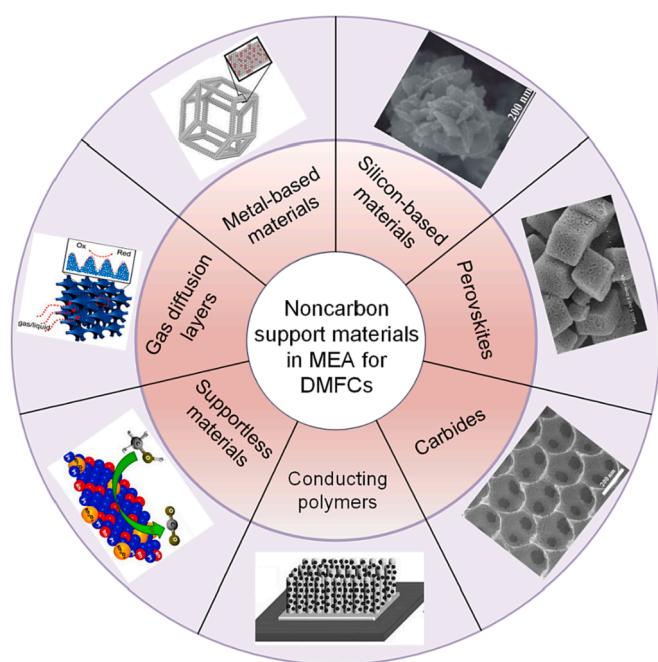


Fig. 1. Various different noncarbon support materials in MEA for DMFC applications. “Metal-based materials” (adapted from Ref. [39]. © 2020 American Chemical Society). “Silicon-based materials” (adapted from Ref. [40]. © 2013 The Royal Society of Chemistry). “Perovskites” (adapted from Ref. [41]. © 2012 The Royal Society of Chemistry). “Carbides” (adapted from Ref. [34]. © 2007 The Royal Society of Chemistry). “Conducting polymers” (adapted from Ref. [35]. © 2013 The Royal Society of Chemistry). “Supportless materials” (adapted from Ref. [36]. © 2014 American Chemical Society). “Gas diffusion layers” (adapted from Ref. [43]. © 2018 Elsevier).

enhancement [46]. For the future study, it is urgent to explore efficient methods for the design and manufacture of functional DLs which help realize the multiple and balanced control of mass transfer processes in the fuel cell.

Considering the drawbacks of traditional carbon-based support materials in MEA, many researchers are devoted to designing new support materials to gain more optimal performances. There have been several reviews focusing on the support materials (e.g., carbon type materials) for catalysts in PEMFC or DMFCs, which mainly encompass the carbon-based modified materials (e.g., carbon nanotubes or mixed carbon materials) [47]. Regrettfully, there is scarcely a dedicated review toward the surface engineering or compositional engineering for NCSMs oriented to DMFCs, from design principles to applications. Hence, this review comprehensively summarizes the design mechanisms, preparation methods, structural and functional properties and applications of NCSMs for DMFCs. The first subsection describes the roles of NCSMs in MEAs, especially their effects on the catalytic activity, durability, mechanical support and mass transport are discussed in detail. Secondly, the applications of various NCSMs for DMFCs are presented. For each type of material, the preparation processes, structural properties, and the performances of DMFCs are all included. Finally, the challenges and prospects of NCSMs in the MEAs for DMFCs are presented to provide a reasonable guide for future researches.

2. Critical roles of NCSMs in MEA for DMFCs

Compared to the carbon-based materials, NCSMs have attracted increasing attentions because of their higher durability performance, methanol tolerance, corrosion resistance and mechanical robustness. It is generally recognized that the catalyst support materials impact strongly on the reactivity of the catalytic sites, durability and mass transfer between the support materials and nanoparticle catalysts. For

instance, transition metal nitrides can restrain the aggregation or detachment of nanoparticle catalysts and possibly change their surface properties [48]. Moreover, the use of NCSMs can prevent strong adsorption of CO during the electrochemical reaction. In this section, the reviewed NCSMs in MEAs mainly include two types: one is for the catalyst support and the other is used as a DL component. In this field, the critical issue is to gain a deeper understanding of their effects on the internal working mechanisms of the DMFC.

2.1. Effects of NCSMs in catalytic layer

The catalyst support plays an important role in controlling the fuel distribution, electron transfer, electrocatalytic activity and active sites of nanoparticle catalyst. It is worth noting that many previous studies suggest that the traditional carbon-based supports like carbon black and carbon nanotube may cause instability of the material system so as to deteriorate the ECSA of Pt metals, and thereby reduce the cell performance. The degradation mechanisms of Pt/C catalyst for fuel cells include the following aspects such as Pt dissolution, carbon corrosion, particle detachment, agglomeration and Ostwald ripening, as shown in Fig. 2(a) [49]. Typically, different degradation pathways of Pt/C catalyst can be clearly shown in Fig. 2(b)-(c) [50]. Among these factors, carbon corrosion is regarded as a common issue leading to Pt catalyst degradation during the electrochemical reaction. On the other hand, the effective ECSA of Pt tends to decrease after the long-time operation of the fuel cell due to the agglomeration or dissolution of Pt nanoparticles. To overcome the aforementioned issues for the carbon-based materials, NCSMs, such as the metal alloys or metal oxides, have been developed to enhance the material stability, durability, electrocatalytic activity, as well as alleviate the adsorption of CO. Specifically, the metal-based support materials can offer additional functions to accelerate the methanol oxidation and the conversion of CO^* to CO_2 when used together with Pt. This is because the synergistic effects of metal-based supports and Pt can regulate the binding strength between the Pt atoms and the adsorbed oxygen-containing carbon species [51,52]. Pt is known as the best monometallic catalyst for methanol oxidation reaction (MOR), which can oxidize methanol to CO^* easily but combine with CO^* so strongly that makes it difficult to remove CO^* , while metal-based materials (e.g., Ru and Co) can activate H_2O (OH^*) readily in a lower potential. Therefore, the combination of Pt and metal supports provides synergistic effects, also known as the bifunctional mechanism, to enhance both CO^* removal and MOR activity [53,54].

The effects of catalyst support on the Pt catalyst can be also explained by the reaction formula. The catalytic reaction of Pt-based catalyst in an acidic environment for MOR includes the methanol dehydrogenation, CO oxidation and water adsorption, which can be expressed as follows

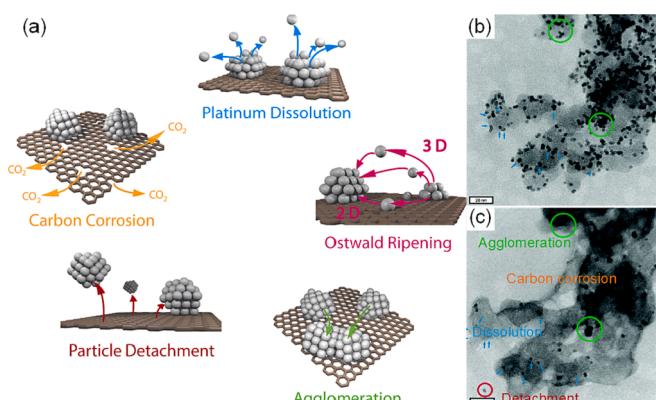
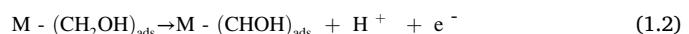


Fig. 2. Schematic illustration of (a) degradation behavior of Pt catalyst and carbon support (adapted from Ref. [49]. © 2014 Meier et al.). (b) TEM images of initial Pt/C catalyst, and (c) Pt/C catalyst after degradation (adapted from Ref. [50]. © 2012 American Chemical Society).

[55,56]:

Methanol dehydrogenation:



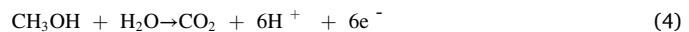
Water adsorption:



CO oxidation:



Overall reaction:



where the M and M' can be a different or an identical metal catalyst.

Methanol is successively dissociated into the protons (H^+) and CO species under the effect of metal catalysts like Pt ("M") nanoparticles (see Eq. (1.1)–(1.4)). In this process, the CO species may poison the Pt active sites. When the catalyst support accompanies a functional metal support made from Cu, Ni, Cr, Ti, Sn, Mo ("M'"), it is easier to oxidize CO into the CO_2 species according to the bifunctional mechanism (Eq. (3)) [57]. This is because the weaker adsorption energy of CO can be obtained under the electronic effect. On the other hand, the metallic supports help promote the water activation to provide more –OH group to oxidize the CO– intermediate species [58]. The detailed synergistic mechanism has been described above. Meanwhile, the use of metallic supports can realize strong connection with the pristine catalyst to prevent the oxidization corrosion for long-term operation. These effects also explain the superiority of NCSMs with respect to its outstanding durability, stability and catalytic activity. Based on this mechanism, the phenomenon of agglomeration of catalyst particles causing the reduced catalyst utilization and poor cell performance can be avoided. This explains why the DMFC mostly uses a binary catalyst on the anode side. More potential metallic supports with high conductivity, corrosion resistance and catalytic activity can be used as a supplementary catalyst. Owing to the above-mentioned advantages, the NCSMs based DMFC shows a much higher methanol tolerance and catalytic activity than the traditional one, and the output performance of DMFC can be further improved by using the Pt alloy catalyst [50]. Meanwhile, the strong corrosion resistance of NCSMs makes the catalyst possible to maintain high ECSA after the accelerated durability test, thus improving the lifetime of fuel cells [56].

In this context, the ECSA represents the effective active area of nanocatalysts (e.g., Pt) involved in the electrochemical reactions, which is usually used to investigate the reaction mechanism of the electrode surface and the performance evaluation of electrode materials [49]. Moreover, the ECSA is also an important parameter to evaluate the other aspects of the catalyst activity. For instance, the specific activity and charge transfer resistance need to be normalized by ECSA and ultimately used as an evaluation criterion for catalyst performance. The specific calculation formula of ECSA is as follows [33]:

$$\text{ECSA} = \frac{Q_H}{0.21 \times [\text{metal}]} \quad (5)$$

where Q_H (mC cm^{-2}) is the coulombic charge for H_2 adsorption, $[\text{metal}]$ (mg cm^{-2}) is the metal catalyst (e.g., Pt) coated on the electrode surface, 0.21 mC cm^{-2} is the charge required for oxidizing a H_2 monolayer.

2.2. Effects of NCSMs in diffusion layer

Unlike the high temperature PEMFC, a DMFC typically operates at a low temperature or even ambient temperature. In this context, the DL, used as a physical support for CL inside the fuel cell, plays a crucial role in mass and heat transfer, as well as electron transport, as depicted in Fig. 3. During the operation of a DMFC, the methanol and water solution are distributed on the DL surface by the anodic and cathodic flow fields, and then diffused into the CLs. Meanwhile, the produced heat and electricity also transport through the DL [59,60]. Since a DMFC mostly works at a lower temperature, it has relatively inertia diffusion kinetics. Especially during the high-current discharging, the fuel cell may encounter fuel starvation and water flooding at the interface between the DL and CL. In this case, the output performance of cell depends highly on the diffusion balance of multiphase species in the DL of a DMFC. It can be inferred that the structural and morphological properties of the DL may greatly influence the methanol and water delivery to the catalytic reaction area. In particular, the structural stability of a DL has a great effect on the cell performance. Therefore, it is quite essential to optimize the surface structure of the diffusion medium to improve the mass transfer process. In this regard, the porous metal-based materials, including metal foam, metal mesh and micro-fabricated metals, exhibit great potential to be used as the DL for DMFCs. Unlike the conventional carbon-based nanofiber materials, such metallic NCSMs are likely to promote a higher cell performance due to their advantageous mechanical and physiochemical properties [61].

3. Applications of NCSMs in MEA for DMFCs

To overcome the shortcomings of traditional carbon support, the NCSM as a new alternative support material has been widely used in the community of fuel cells. Tailored design and structural strategies of NCSMs have been investigated according to the different preparation processes. Particularly, the metal-based catalyst support can be made from various nanowires, nanotubes and core-shell structures with high surface area. These structurally synthesized materials are endowed with strong durability and catalytic activity. In this section, the applications of NCSMs for DMFCs can be classified into the catalytic layer, DL and stack-level DMFCs.

3.1. Applications of NCSMs in catalytic layer for DMFCs

The NCSMs with different structures can be used as a substitute to the conventional carbon-based materials for DMFCs. According to the open literature in this field, the NCSMs based different structures and materials can be classified into monometal materials [62–64], multimetal-based materials [65,66], silicon-based materials [67], perovskites [68], carbides [34,69], conducting polymers [55,70] and supportless materials [36]. Table 1 summarizes the advantages and properties of representative noncarbon materials used as the catalyst supports for DMFCs. Generally, the nonmetal-based materials have light weight and synergistic effect with metal catalysts. However, the relatively low electrical conductivity of the nonmetal materials usually leads to a higher resistance, compared with the metal-based materials [71].

For practical use, composite metallic materials (e.g., bimetallic support) have been explored to support the catalysts in order to achieve higher catalytic activity. There are a variety of nanostructured architectures of such materials which can be synthesized by different processes, including core-shell structure, single layer of metal, nanoframe and nanowire. According to their synthetic process, the synergistic effect between the metallic support and catalyst can be regarded as a positive aspect to enhance the catalytic activity and durability for MOR and oxygen reduction reaction (ORR). In addition, the noncarbon materials also have better toughness under the fuel cell environment compared with the conventional carbon black. The typical electrochemical properties of MOR and ORR are shown in Table 2. In this section, the preparation process, structural design, functional properties and applications of each type of noncarbon materials as the catalyst support are reviewed in detail.

3.1.1. Metal-based materials

Metal-based materials are regarded as the most promising catalyst support to substitute the conventional carbon support materials due to their excellent corrosion and oxidation resistance in the DMFC environment. Specifically, metal-based materials have excellent electrical conductivity and robustness when they are used as catalyst supports. The strong connection between the metal-based supports and Pt-based catalysts helps stabilize the electrode structure and thus improves the cell performance [82]. Currently, the metal materials usually used as the catalyst supports include Ru [83], Fe [84], Co [85], Au [86], Ni [87], Pd

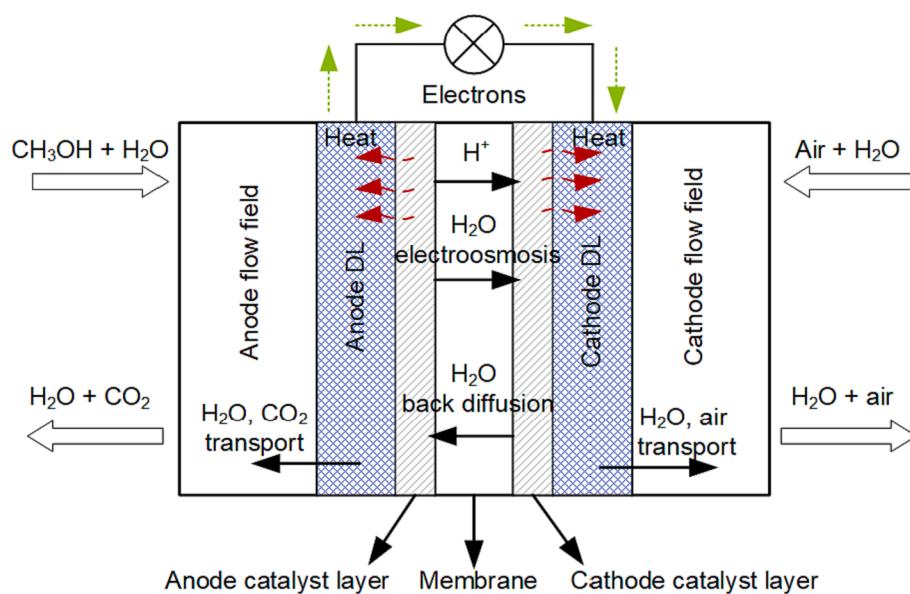


Fig. 3. Schematic of effects of the DLs inside the DMFC.

Table 1

Properties of noncarbon materials in catalyst support for DMFCs.

Types of noncarbon materials	Preparation process	Advantages	Drawbacks	Research activity ^b	Cost ^a	Ref.
Monometal catalyst support	Seed-mediated growth method/ template-based method	High electrical conductivity, strong metal-support interaction, high ECSA	Insert surface, high-weight	4	M	[62–64]
Multimetal-based catalyst support	Hydrothermal method/ chemical reduction method	High ORR catalytic activity, high surface area	Limitation of preparation method, relative high cost	5	H	[65,66]
Silicon-based materials	Surfactant template-assisted method	Large surface area, reusable, providing –OH in acidic environment	Low conductivity	1	L	[67]
Perovskites	Chemical reduction method	Excellent ionic conductivity, good proton-transport properties	Low stability	3	H	[68]
Carbides	Chemical synthetic process	Better oxidative stability, good corrosion resistance, low cost	High ohmic resistance	4	L	[34,69]
Conducting polymers	Chemical/ electrochemical synthesis	High electrocatalytic activity, light weight, easy chemical synthesis	Relatively low conductivity	2	L	[55,70]
Supportless materials	–	High mass activity: 1392.5 mA mg ⁻¹ , high conductivity	Worse CO tolerance	2	L	[36]

^a H: High; M: Moderate; L: Low.^b 1: Lowest research activity; 5: highest research activity.

[88], Ti [89], Cu [90], Sn [91], Ag [92], W [93], Cr [94] and Mg [95]. The surface morphology of metal-based materials includes nanoparticles, nanotubes, nanofibers and nanoporous thin films. The nanoparticle structures are typically in the form of nanoporous structure, core–shell structure, polyhedral structure and nanoframe structure. The fabrication methods, structural and functional properties for constructing the metallic support materials are respectively discussed in this subsection.

Core-shell structures.

Different nanostructures have different effects on the catalysts for DMFCs. Generally, the metal catalyst support based on core–shell structures plays a crucial effect on the enhancement of the mass activity and specific activity of Pt-based catalysts so as to improve the electrochemical performance of DMFCs. The reason for this enhancement can be ascribed to the following two aspects [96,97]: (i) The nano core–shell structures facilitate constructing the lattice mismatch of the Pt-based catalyst, thus causing the lattice strain to weaken the interaction between the adsorbed species and Pt catalyst, as well as produce more active sites on the Pt surface; (ii) The presence of Pt-skin based on core–shell structures can accelerate the electrons transport of the catalyst surface. As a result, the novel structures improve DMFC performances by modifying the catalyst–catalyst support interface based on core–shell structures to enhance the active sites and catalyst utilization. Tan et al. proposed a simple strategy to prepare Au@Pt core–shell nanoparticles as the anodic catalyst in a DMFC [98]. The process of chemical growth and an element-replacement reaction were used to prepare spiny Au nanoparticles, which are further used as seeds to synthesize the Au@Pt nanoparticles (Fig. 4(a)). In this process, the Au nanoparticles provide a nucleation core, while the Pt atoms are reduced from the chloroplatinic acid (H_2PtCl_6) and uniformly coated on the surface of Au nanoparticles. The TEM images demonstrate the elemental distribution of Au and Pt in

the Au@Pt nanoparticles, which further indicate the formation of the novel core–shell structure of the $Au_{90}@Pt_{10}$ nanoparticles (Fig. 4(b)). The catalytic performances of the catalysts with various kinds of Au@Pt nanoparticles show that the Au@Pt nanoparticles have a better specific activity compared to the commercial Pt/C catalyst, as shown in Fig. 4(c). Additionally, the durability tests of different catalysts are conducted at a stable voltage of 0.6 V for 4000 s (Fig. 4(d)). This rationale is of great significance in evaluating the design and functional realization of stabilized metal catalyst support. However, it is noted that some studies also found that the Au@Pt nanoparticles may exhibit a lower ECSA than the commercial Pt/C catalyst [71,98].

Another important strategy for designing the novel Pt-based catalyst based on core–shell structures is to use multimetal catalyst support, such as indium tin oxide (ITO) [99], $Ti_{0.7}Ir_{0.3}O_2$ [100], CuNi [101], Ag_2WO_4 [102] and AuCu [103]. Compared to the monometallic catalyst support, these multimetal-based support materials have shown excellent performances in methanol tolerance and catalytic activity [104,105]. Furthermore, the corrosion and aggregation of the multimetal-based catalyst support can be effectively alleviated by changing the electronic structure of Pt with titanium alloy materials [106,107]. Specifically, Wu's group proposed a simple one-step strategy to fabricate the CuNi nanoparticles, which was used as a catalyst support for Pt metal toward MOR [101]. The prepared catalyst morphology is shown in Fig. 5 (a) and (b). During this preparation, the different Pt metal contents can be controlled by impeding the reaction kinetics of Pt. To better understand the MOR catalysis mechanism, the DFT calculations for Pt/CuNi catalyst were implemented (Fig. 5(c)–(f)). The results demonstrated that the addition of Ni improves the catalytic activity of the Pt_5Cu_3 . In this process, the adsorption of OH^* can be strengthened with more metal doping. More importantly, it is noted that the specific activity of the Pt/CuNi catalyst is ~ 5 folds better than the conventional Pt/C catalyst

Table 2

Several typical electrochemical properties of different MOR and ORR electrocatalysts.

Types of electrochemical reaction	Catalyst and catalyst support	Electrolyte	Mass activity (mA mg ⁻¹)	Specific activity (mA cm ⁻²)	ECSA ^a (m ² g ⁻¹)	Ref.
MOR	PtRu nanowire	0.5 M H_2SO_4 , 1 M CH_3OH	820	1.2	71.3	[72]
	PtCu nanotube	0.5 M H_2SO_4 , 1 M CH_3OH	2252	6.1	37.0	[73]
	PtNiCo nanopolyhedron	0.5 M H_2SO_4 , 1 M CH_3OH	1500	4.9	30.5	[74]
	Pt nanowire	0.1 M $HClO_4$, 1 M CH_3OH	1312	5.8	22.6	[75]
	Pt nanotube	1 M KOH, 1 M CH_3OH	2330	4.94	47.2	[76]
ORR	PtRu/Cu nanowire	0.1 M $HClO_4$, 1 M CH_3OH	464	1.6	29	[77]
	Pd/Fe ₂ O ₃ nanoparticle	0.5 M NaOH	331.2	–	69.4	[78]
	Pt/Ti _{0.5} Nb _{0.5} N nanoparticle	0.1 M KOH	–	–	48	[79]
	Pt/IrNi core shell	0.1 M $HClO_4$	1350	0.6	–	[80]
	Pt/Ti _{0.7} Ru _{0.3} O nanowire	0.5 M H_2SO_4	–	–	21.05	[81]

^a A higher ECSA value indicates more active sites involved in the electrochemical reactions and better catalytic performance of the catalyst materials.

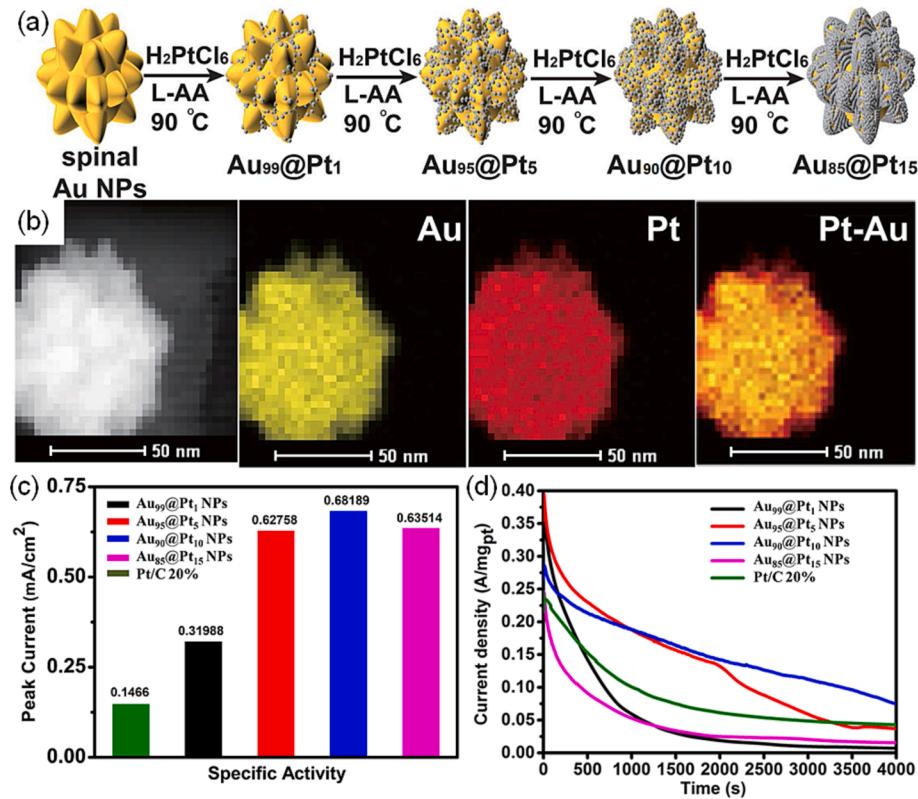


Fig. 4. Operation principle of (a) the formation process of morphology for Au@Pt nanoparticles including different Pt content. (b) TEM images and elemental mappings of Au₉₀@Pt₁₀ nanoparticles. (c) Specific activity of Pt/C and Au@Pt nanoparticles with different Pt content. (d) Durability test of conventional Pt/C catalyst and various types of Au@Pt nanoparticle catalyst (adapted from Ref. [98]. © 2017 Tan et al).

(Fig. 5(g)). The durability of Pt/CuNi is also higher than the conventional one (Fig. 5(h)).

Nanoframe structures.

Designing the nanoframe (or hollow) structures for Pt-based catalysts offers a good opportunity to further improve the utilization of Pt and catalytic activity toward the acid or alkaline environment in DMFCs. The representative fabrication methods include the chemical etching, sacrificial templates, Kirkendall effect and one-pot method [108,109]. In this case, the twinned defects in the nanoframe structure between the Pt and metal support can modulate their electronic structures and surface

activity, thus improving the catalytic performance. Considering the practical applications of DMFCs, various Pt-coated M (M = Ni, Co, Cu) nanoframes with tunable elemental compositions have been developed, as shown in Fig. 6. In this regard, a critical issue is how to realize the precise operation at the atomic level. To address this issue, the Pt₃Ni nanoframes with polyhedral structures have been prepared (Fig. 6a) [108]. It can be seen that the PtNi₃ polyhedra transforms into Pt₃Ni nanoframes with maintained symmetry and edge size during this process because the Ni atoms are dissolved and the Pt atoms are exfoliated in the polyhedral faces. In addition, Zhang et al. proposed a simple method to

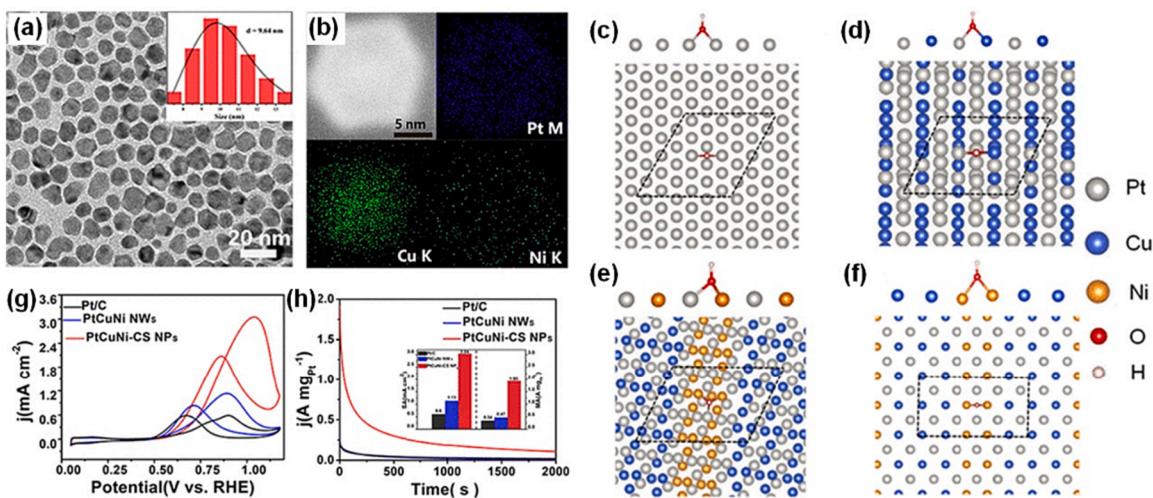


Fig. 5. Schematic illustration of (a) TEM images of Pt/CuNi core–shell nanoparticles. (b) HADDF-STEM image and the element mapping images of Pt/CuNi. Illustration of OH* adsorption on (c) Pt(111), (d) Pt₅Cu₃, (e) Pt₅Cu₃Ni₂(111), and (f) Pt₅Cu₃Ni₂(200). (g) CV curves of different catalyst at a scan rate of 50 mV/s. (h) Performance test of different catalyst at 0.75 V vs Ag/AgCl (adapted from Ref. [101]. © 2022 American Chemical Society).

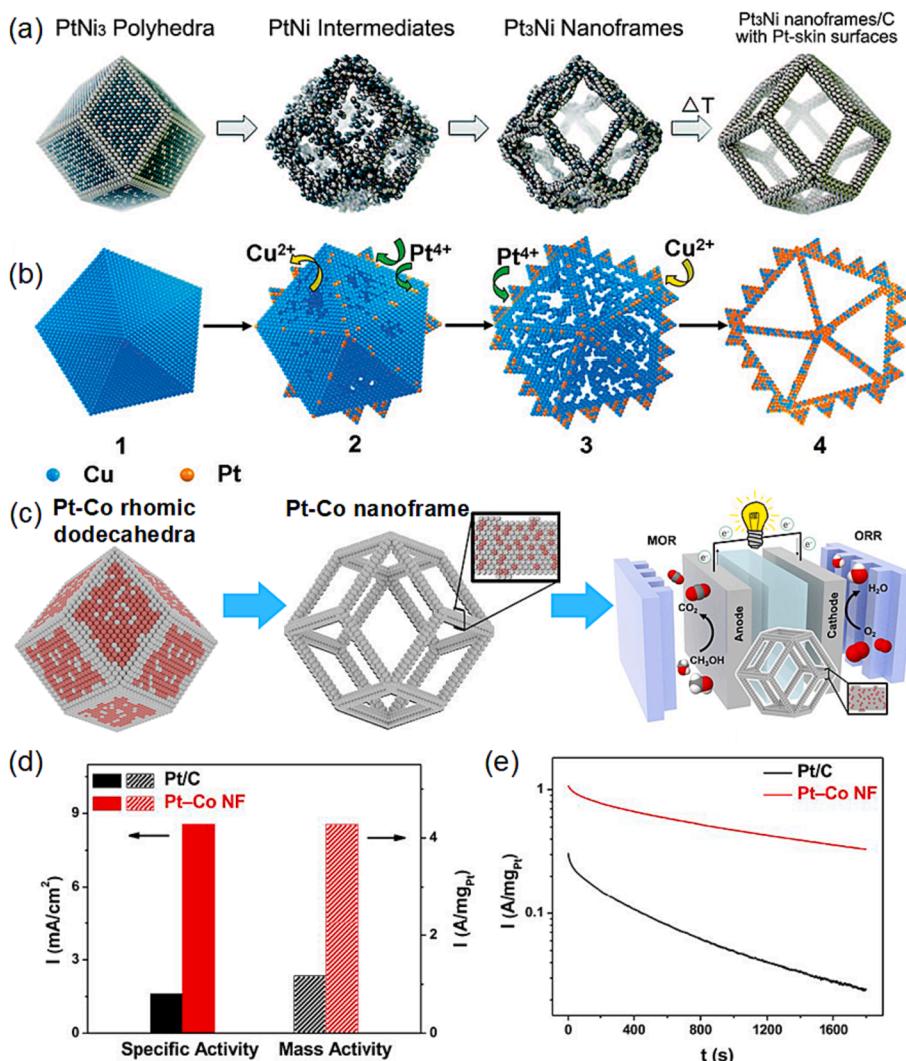


Fig. 6. Schematic illustration of a preparation strategy for (a) PtNi nanoframes (adapted from Ref. [108]. © 2014 American Association for the Advancement of Science), (b) Pt/Cu nanoframes (adapted from Ref. [109]. © 2016 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim). (c) The fabrication of Pt-Co nanoframes and used for DMFC. (d) MOR performance of Pt-Co nanoframes and (e) stability performance of Pt-Co nanoframes (adapted from Ref. [39]. © 2020 American Chemical Society).

prepare the Pt/Cu nanoframes catalyst for DMFCs via the hydrothermal treatment in a teflon lined stainless steel [109]. The formation mechanism of Pt/Cu nanoframes is shown in Fig. 6(b). The glycine, poly-(vinylpyrrolidone) (PVP), NaI and deionized water were used as a precursor solution, while H₂PtCl₆·6H₂O, CuCl₂·2H₂O and ethanolamine were used to prepare the Pt/Cu nanoframes. In this process, different lengths of as-synthesized nanothorns may be achieved by controlling the reaction kinetics. It is found that the Pt/Cu nanoframes exhibit the excellent performance for ORR due to its twinned defects, highly anti-isotropic structure and the coupled effects by Pt and Cu elements [110,111]. For the applications of MOR, a typical method to synthesize the nanoframe structure is to use chemical etching [39]. The Pt-Co nanoframes, as catalysts for MOR, can be produced by etching away the Co-rich phase in the Pt-Co rhombic dodecahedra, as seen in Fig. 6(c). In this process, to better analyze the evolution mechanism of as-prepared Pt-Co nanoframes, carbon black is mostly used to disperse the nanoframes. Results also indicate that the specific activity and the mass activity of Pt-Co nanoframes are 8.56 mA cm⁻² and 4.28 A mg_{Pt}⁻¹, respectively, which are 5- and 4-fold enhanced compared to the conventional Pt/C catalyst (see Fig. 6(d)). The reason for the enhanced catalytic activity can be attributed to the following major points: (i) the Pt-based nanoframes can substantially facilitate the oxidation removal of CO and reduce the carbonaceous poisoning from the Pt surface; (ii) the hollow structure in the Pt-based nanoframes helps enlarge the catalytic active sites [112]. Additionally, it is seen that the stability of Pt-Co

nanoframes merely exhibits a milder degradation after 1600 s. In contrast, the activity of the conventional Pt/C catalyst drops rapidly, as Fig. 6(e) suggests. With this context, it can be concluded that the durability of Pt-Co catalyst is superior to the Pt/C catalyst. On the other hand, the Pt-based nanoframe structure can precisely operate at the atom level to rationally design the Pt-based catalyst and catalyst support structures, aiming at improving the electrochemical performance of the electrode for DMFCs.

One-dimensional nanowires.

In addition to the metal nanoparticle and nanoframe structures, the 1D nanostructures, namely nanowire, nanotube and nanorod, have also been explored to compose the catalyst support materials [113–115]. It is commonly known that the use of 1D nanostructures can facilitate the electron transport and slow down the dissolution and aggregation issues of Pt-based metal, which improves the reaction kinetics and catalyst stability [116,117]. Compared to the 0D structures (e.g., nanoparticle) of a catalyst support, the 1D nanowires with special polyhedron-wire-polyhedron nanostructures are endowed with many special properties, such as non-grain boundary, direct electrical pathways for electrons and strong Pt-support interaction.

Fig. 7(a) compares the TiN nanotubes as a support material toward the Pt nanoparticles. During the ORR reaction, the nanoparticles may lose its original electrical conductivity due to its grain boundary which acts as electron reservoirs and traps. On the other hand, the TiN nanotube can offer direct electrical pathways to minimize

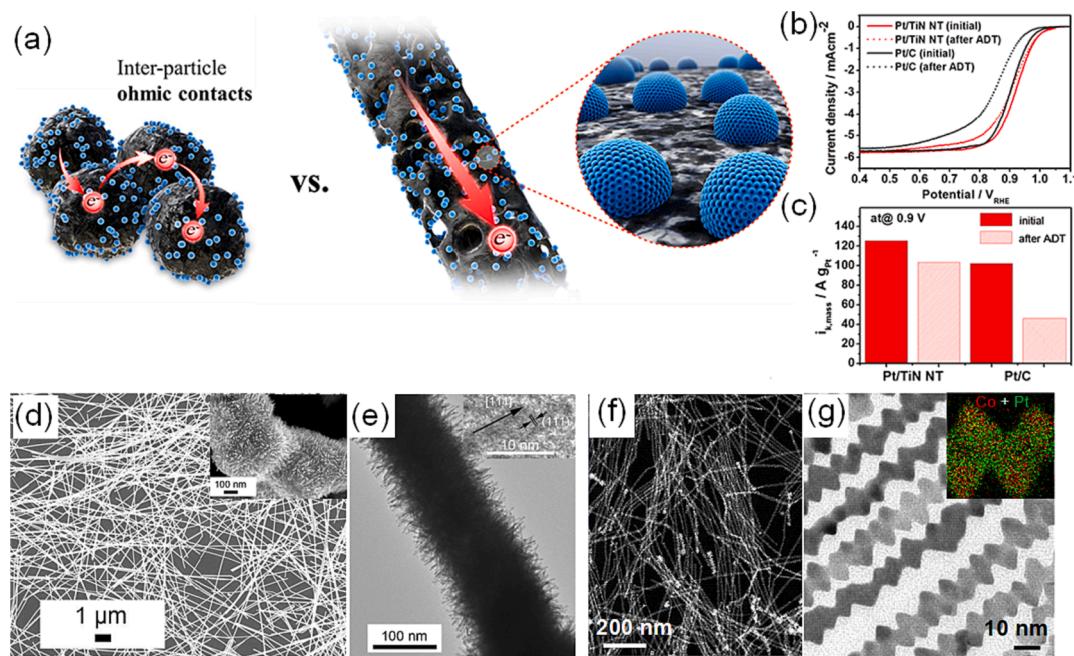


Fig. 7. Schematic illustration of (a) spherical TiN nanoparticles and TiN nanotubes as a catalyst supports for the Pt catalyst. (b-c) the performance comparison of Pt/TiN and Pt/C before and after the accelerated durability test (ADT) (adapted from Ref. [37]. © 2016 American Chemical Society). SEM images of (d) Ag nanowires and (e) Ag@Pt nanorod (adapted from Ref. [114]. © 2018 Elsevier). (f-g) TEM images of the Pt-Co nanowires at different magnification (adapted from Ref. [115]. © 2016, The Author(s)).

the interparticle ohmic resistance inside of the porous structure, which increases the transport rate of electrons. Moreover, results also indicate that the Pt/TiN nanotubes can maintain better catalyst durability after the accelerated durability test at 0.9 V, as shown in Fig. 7(b). Particularly, the mass activity of Pt/TiN nanotube shows a degradation rate of approximately 16.1%, which is much lower than the commercial Pt/C catalyst with an activity degradation rate of approximately 59.3% (Fig. 7(c)). As an excellent substitute to the traditional catalyst support for fuel cells, the nanotube- or nanowire-based samples provide special surface structures closely related to the electrochemical performance [118,119]. The influential factors of their surface properties include roughness, pore size distribution and connectivity, which have evident effects on the ion diffusion distance and transport resistance. To further understand the effects of surface structures on the durability and activity of a catalyst in a nanoscale level, the Ag nanowires were prepared by means of the hydrothermal method at 160 °C for 7 h, as shown in Fig. 7(d). The formed Ag nanowires were approximately 40–100 nm in diameter. Fig. 7(e) shows that the surface structures of Ag nanowires grow densely and vertically. This structure is beneficial to forming the Ag@Pt nanorods with a core–shell structure, which endows the catalyst of ORR with a higher ECSA. To precisely control the core–shell nanowires, some researchers proposed a facile method to synthesize the hierarchical Pt@Co nanowires (Fig. 7(f) and (g)) [115]. The precisely controlled amount of cetyltrimethylammonium chloride is a critical factor affecting the preparation of the hierarchical Pt@Co nanowires. Results suggest that the surface structure of Pt@Co nanowires with a core–shell structure can significantly enhance the durability and activity of the catalyst. More importantly, the usage of Pt catalyst can be largely cut down. This method provides a viable guideline for large-scale production of high-performance Pt-based catalysts for applications in DMFCs.

In addition, Xia's group investigated the effects of the surface structure of PtNi polyhedral nanowires catalyst for MOR (Fig. 8(a)-(c)) [113]. It is found that the alloy nanochain structure of PtNi catalyst facilitates mass and electron transfer during the catalytic process. The MOR testing results of the PtNi catalyst exhibit an excellent mass activity and specific activity, compared to the traditional Pt/C catalyst (Fig. 8(d))

and (e)). In addition, to design the hollow structures, the Ti_{0.95}Co_{0.05}N nanotubes with a large surface area were prepared by a feasible strategy (Fig. 8(f) and (g)) [120]. The presence of Co in the Pt/Ti_{0.95}Co_{0.05}N catalyst significantly improves the capability of removing the CO-absorbed intermediates. Typically, the Pt/Ti_{0.95}Co_{0.05}N catalyst delivers a higher current density in a steady state after the durability test at 0.4 V for 10000 s, compared to the Pt/TiN and commercial Pt/C catalyst (Fig. 8(h)). This indicates that the Pt/Ti_{0.95}Co_{0.05}N catalyst has better durability performance than the other Pt-based catalyst [121].

3.1.2. Silicon-based materials

Silicon-based materials with a unique nanoparticle structure are regarded as an important noncarbon catalyst support to improve methanol resistance during electrochemical reactions. Specifically, silicon dioxide (SiO₂) as a non-metal support material for Pt-based catalysts has been explored since this material can reduce the CO poisoning effect. In addition, the use of SiO₂ can provide the hydroxyl groups (–OH) for the CO oxidation in the acidic environment, which is also called bifunctional mechanism [67,122]. It is acknowledged that providing more –OH for the reaction can significantly boost the electrochemical reaction for MOR. Unfortunately, detailed structural design method for silicon-based support has been barely reported. The nanoparticle structures of SiO₂ as a catalyst support have been made to improve DMFC performances [123]. The reason for this improvement is associated to the reduction of methanol crossover and activation loss, as well as improvement of fuel feeding, when the Pt catalyst is modified by the SiO₂ materials. Moreover, the catalytic mechanism of Pt/SiO₂ catalyst for MOR highlights the superiority of using SiO₂ nanoparticles to support the Pt catalyst. It is inferred that the SiO₂-based support material can provide more –OH to enhance the removal of CO species after the reaction. Specific testing results for the CO oxidation on the Pt surface show that the absorbed CO tends to react with the –OH species provided by the SiO₂, which is called Langmuir-Hinshelwood mechanism [124,125]. More importantly, the presence of –OH, even in the acidic environment, can also facilitate the oxidation of CO into CO₂. Experimental results show that the as-prepared catalyst delivers a superior

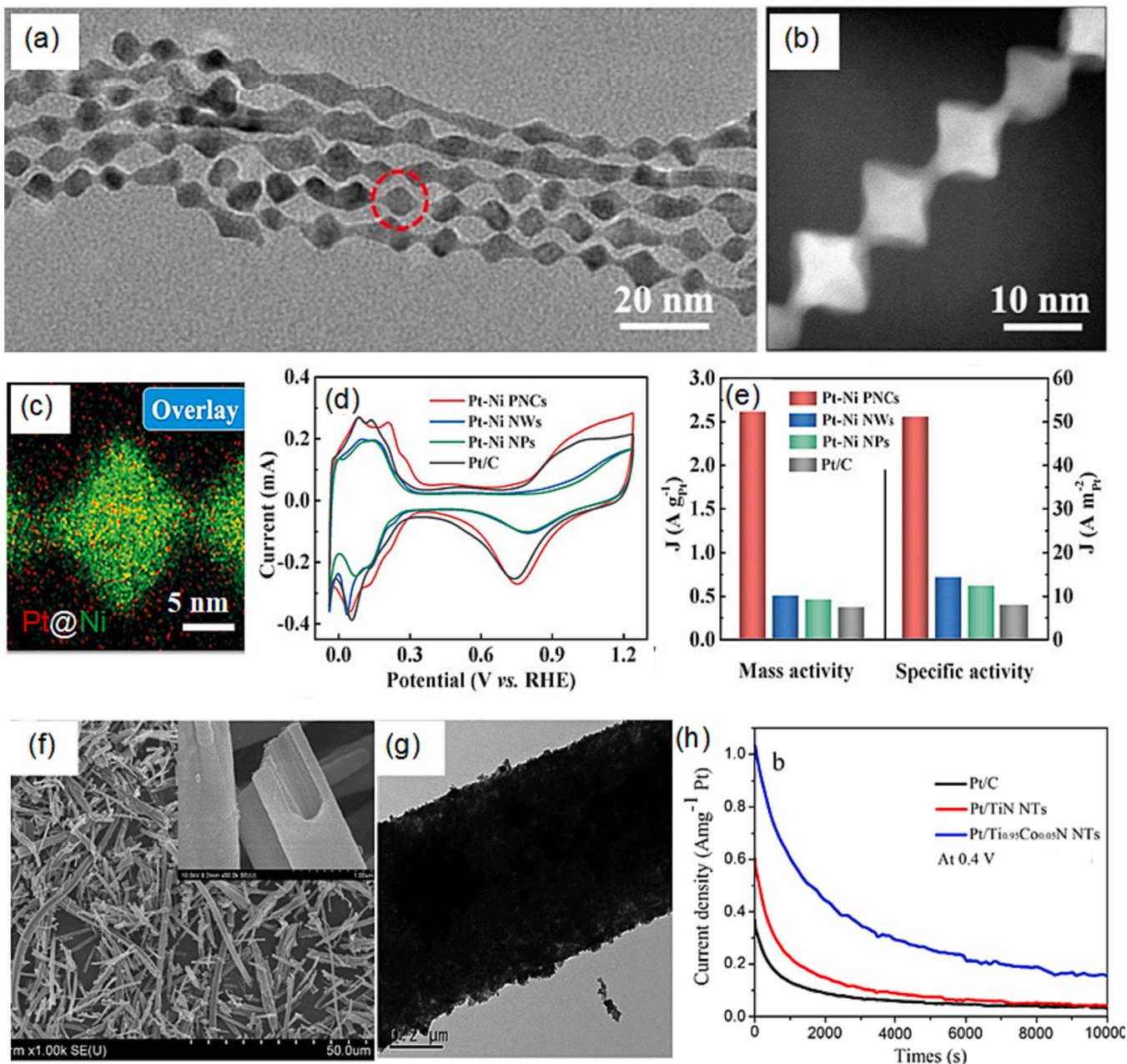


Fig. 8. (a) SEM images of Pt-Ni polyhedral nanochains, (b-c) HAADF-STEM image. (c) EDS elemental mapping. (d) CV curves of different catalysts for MOR. (e) The mass activity and specific activity (adapted from Ref. [113]. © 2022 Wiley-VCH). (f) SEM images of the Ti_{0.95}Co_{0.05}N nanotubes. (g) TEM images of the Pt nanoparticles supported on the Ti_{0.95}Co_{0.05}N nanotubes. (h) Stability test of Pt/Ti_{0.95}Co_{0.05}N nanotubes catalysts (adapted from Ref. [120]. © 2018 Elsevier).

output performance and excellent stability and durability after the accelerated durability test.

To better solve the problems of Pt utilization and catalyst loss, ordered Si nanocones were developed to uniformly distribute the Pt nanoparticles, which shows the enhanced electro-oxidation of methanol and improved CO tolerance [126]. Typically, results show that the catalyst made from Pt-silicon nanocones has a higher mass activity and a lower onset potential. Unfortunately, the inherent insulating nature of SiO₂ inevitably limits its practical use in DMFCs. To address this issue, one possible solution is to load Pt particles on the functionalized hollow-SiO₂ surface to enhance electron conduction. Hence, more efforts are still needed to improve the conductivity of Si-based materials before they are put into large-scale application.

3.1.3. Perovskites

Perovskites, as an emerging catalyst support, have also been widely investigated, which can be denoted by a basic formula of ABO₃ (A = rare-earth metal ions, alkaline-earth or alkaline and B = d-block transition metals) [127]. For DMFC applications, perovskites have shown many attractive advantages, which can be summarized as follows: i) the new nanostructured morphology of perovskites with a larger surface area helps enhance the efficiency of Pt utilization; ii) the novel catalyst support avoids generation of the carbon coking or agglomeration; iii) the perovskites can form the A or B site vacancies for the catalyst to maintain higher catalytic activity; iv) the synergistic effect between the perovskite and catalyst improves the durability and stability of the catalyst system [128]. As mentioned above, the interaction between the Pt nanoparticle and metal oxide support leads to increased

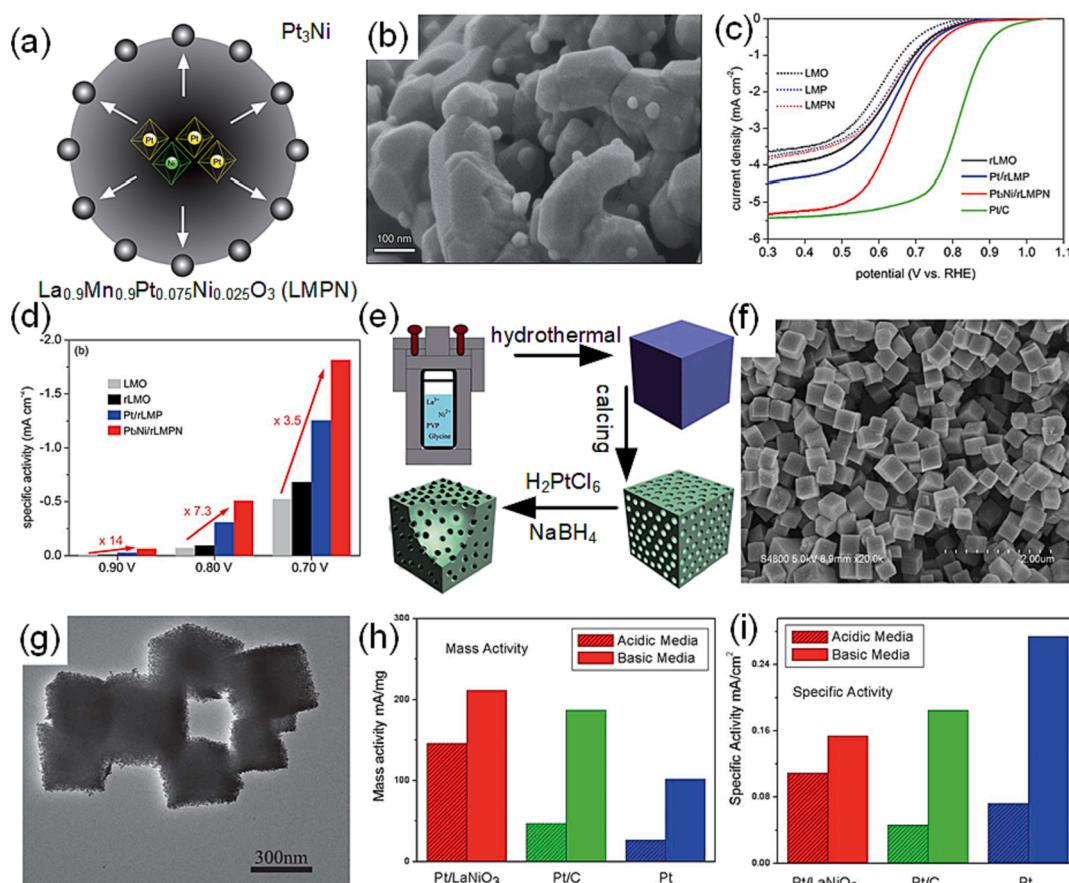


Fig. 9. (a) Schematic illustration of the exsolution process of $\text{La}_{0.9}\text{Mn}_{0.9}\text{Pt}_{0.075}\text{Ni}_{0.025}\text{O}_3$. (b) SEM image of the $\text{Pt}_3\text{Ni}/\text{rLa}_{0.9}\text{Mn}_{0.9}\text{Pt}_{0.075}\text{Ni}_{0.025}\text{O}_3$. (c) Current density of various catalyst-support at 1600 rpm in O_2 saturated 0.1 mol l^{-1} KOH solution. (d) Specific activity of various catalyst-support at 0.9, 0.8 and 0.7 V (adapted from Ref. [135]. © 2017 The Royal Society of Chemistry). (e) Schematic illustration of Pt supported on the porous LaNiO_3 nanocubes, (f-g) SEM images of the LaNiO_3 nanocubes and LaNiO_3 nanocubes loading Pt nanoparticles. (h-i) Mass activity and specific activity of Pt/LaNiO₃, Pt/C and Pt (adapted from Ref. [41]. © 2012 The Royal Society of Chemistry).

electrochemical stability due to their positive effect and ability in providing an external $-\text{OH}$ that can facilitate the removal of poisonous species. Especially, such an effect in ORR can be ascribed to the combined effects from both Pt catalyst and adjacent metal oxides [128].

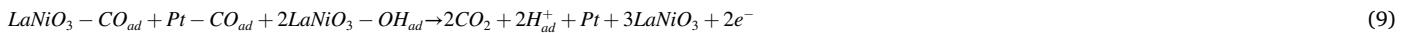
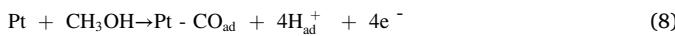
Specifically, in the case of ORR, Pt/CaMnO₃ composites have been prepared by a multistep process, including the preparation process of CaMnO₃ and Pt clusters loaded on the surface of porous CaMnO₃ nanoparticles [129]. The ORR catalytic activity of as-prepared catalyst has been evaluated in an alkaline solution. The testing results suggested that the Pt/CaMnO₃ catalyst exhibits better catalytic performance and durability. In this process, the improved performance of the Pt/CaMnO₃ catalyst can be ascribed to two aspects [130–132]: i) the coupling effects between the Pt metal and CaMnO₃ support help modify the surface structure of Pt, thereby improving the activity and durability of the electrocatalyst; ii) the highly uniform dispersion and nano-size of Pt clusters both benefit dissociation and activation of O_2 . Additionally, compared to the conventional carbon-based supports, the superiority of the CaMnO₃ from the structural properties is attributed to the following aspects [133,134]. i) the CaMnO₃ catalyst support inherently possesses excellent electrochemical stability because of the existence of crystal defect structure; ii) the confinement effect in porous-structured CaMnO₃ impedes the agglomeration of Pt clusters. In addition to depositing the Pt-based catalyst on the surface of perovskites, exsolving Pt-based alloy has also been regarded as an effective strategy to enhance the activity of ORR catalysts [135,136]. For instance, the preparation process of a Pt₃Ni supported LaMnO₃ substrate has been developed, which produces a composite of $\text{La}_{0.9}\text{Mn}_{0.9}\text{Pt}_{0.075}\text{Ni}_{0.025}\text{O}_3$ (LMPN). The exsolution

process of Pt₃Ni on the surface of LaMnO₃ and corresponding SEM image are seen in Fig. 9(a) and (b), respectively [135]. It can be seen that the ORR activity is significantly improved after exsolution (Fig. 9(c)). The limiting current density of Pt₃Ni/rLMPN is also enhanced. In addition, it is evident that the specific activity increases remarkably after exsolution (Fig. 9(d)). The experimental data shows that the Pt₃Ni/rLMPN is 14 and 3.5 times higher than the LMO-based samples at 0.9 and 0.7 V, respectively.

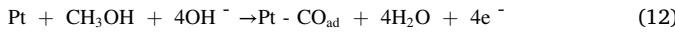
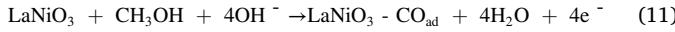
In the case of MOR, Yu et al. designed the Pt nanoparticles deposited on the porous LaNiO₃ nanocubes by ultrasonic irradiation [41]. The preparation procedure of porous Pt/LaNiO₃ nanocubes is illustrated in Fig. 9(e), including two steps: (i) the LaNiO₃ cubes with a nanoporous structure are prepared by the hydrothermal process and calcination treatment; (ii) the H_2PtCl_6 and NaBH_4 aqueous solution are added into the as-prepared LaNiO₃ solution and then treated by ultrasonic irradiation to synthesize the Pt/LaNiO₃. The prepared LaNiO₃ and Pt/LaNiO₃ can be seen in Fig. 9(f) and (g). It is found that the mass activity and specific activity of Pt/LaNiO₃ for methanol electro-oxidation can be simultaneously improved due to its better corrosion resistance in both acidic and alkaline media, compared to the Pt/C catalyst (Fig. 9(h) and (i)). To explain the above rationale, a reaction mechanism has been proposed, following the formula listed below [137,138]:

(a) Acidic media:





(b) Alkaline media:



3.1.4. Carbides

Currently, the high-surface-area carbon support materials (e.g., XC-72 carbon black) are the most widely used catalyst supports for practical applications of DMFCs. However, the oxidation, corrosion and agglomeration of carbon-based support materials are recognized as dominant factor responsible for performance degradation of DMFCs in the acidic or alkaline environments. Carbides, as electrocatalyst support materials, have been regarded as a promising candidate to substitute the conventional carbon materials due to its chemisorption capacity, platinum-like catalytic behavior toward unique chemical and electrochemical properties [139,140]. To this end, different carbides as catalyst supports including tungsten carbide (WC), molybdenum carbide (MoC), Niobium carbide (NbC) and boron carbide (B₄C), have been developed through various structural design methods [141–143]. In this process, these carbide materials with unique nanostructures were facilitated to construct the surface defects of the Pt-based catalyst, thus improving its chemisorption capacity. Nishanth et al. developed a feasible strategy to prepare the tungsten carbide (WC) and molybdenum carbide (MoC) to make the catalyst support for Pt-Ru catalysts by the carbonization method [142]. It is found that the Pt-Ru/MoC and Pt-Ru/WC catalysts

have better MOR activity and durability, compared to the Pt-Ru/C catalyst. Typically, the highest power density reaches 90.78, 79 and 65 mW cm⁻² for Pt-Ru/MoC, Pt-Ru/WC and Pt-Ru/C, respectively. After the stability test, the Pt-Ru catalysts combined with carbides show much smaller performance degradation due to its stronger metal robustness and corrosion-tolerance of carbide. This indicates that the carbides have a potential resistance to CO poisoning, which is beneficial to improving the methanol tolerance in high-methanol concentration reactions.

In addition, W₂C material as another catalyst support has been proposed due to its positive effects on Pt-based catalyst [143]. It is found that the Pt/W₂C microsphere catalyst outperforms the Pt/C catalyst even with a lower Pt loading. The advantages of W₂C as a support material can be ascribed to three aspects. (i) the W₂C has a higher ability to maintain the high dispersion of Pt than the carbon supports; (ii) the W₂C exerts a positive effect on the water activation and electrooxidation of methanol in the presence of Pt [144]; (iii) the W₂C has higher CO tolerance. Typically, the temperature of CO desorption for pure Pt is 187 °C, it can be decreased to 147 °C when the Pt/W₂C is adopted [145]. This helps reduce the loss of active sites and catalyst deactivation [143]. Compared with the traditional carbon-based nanoparticles, carbide nanowires have higher surface area, catalyst utilization, excellent oxidation resistance and better electron transport [146–148]. Qiu et al. proposed a preparation process of NbC nanowires as a catalyst support by using a bamboo-based carbon-thermal method [146]. The morphology of the prepared NbC nanowires and Pt/NbC catalysts are shown in Fig. 10(a) and (b), which demonstrates no obvious agglomeration of Pt nanoparticles. And the particle size distribution of Pt is within the range of 4.5–7 nm, as shown in Fig. 10(c). Results show that the maximum potential of Pt/NbC remains stable in the cycle voltammetry test, while the Pt/bamboo charcoal and conventional Pt-based

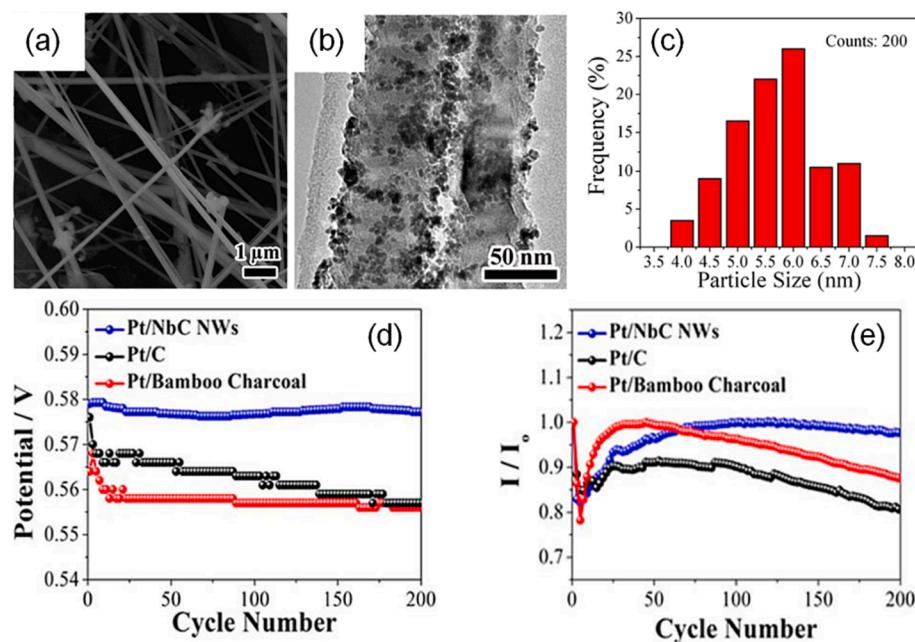


Fig. 10. (a) SEM image of NbC nanowires. (b) TEM image of Pt/NbC nanowires catalyst. (c) Nanoparticle size distribution of Pt coated on the NbC nanowires. (d) Peak potential of various catalyst after stability test. (e) Current density of various catalyst after stability test. (I_0 : maximum current density at the first cycle, I : maximum current density obtained from the subsequent cycles) (adapted from Ref. [146]. © 2013 American Chemical Society).

catalysts decrease gradually with the continuous scan (Fig. 10(d)). The maximum current density of Pt/NbC catalyst still maintains the original value of 97.6% after 200 cycles, which is significantly higher than the Pt/bamboo charcoal catalyst with 87.6%, as shown in Fig. 10(e).

Likewise, other carbides-based supports, like MXene [149], CN [150] and TiC [151], have been also developed to enhance the CO oxidation for MOR, which can be potentially used to replace the traditional carbon black. Particularly, MXene, as a new class of catalyst support, is attracting particular interest due to its unique mechanical, electrocatalytic, electrical and surface properties. Generally, the MXene can be denoted by a basic formula of $M_{n+1}X_nT_n$, where M refers to the transition metal, X represents the C/N, T is the functional groups on the surface of MXene, such as -F, -O and -OH [152]. In the presence of various surface functional groups, the layered MXene could adsorb the metal particles by electrostatic interactions, thus anchoring the active sites. Additionally, the MXene with large surface area also facilitates catalyst deposition. With this context, many researchers have developed a variety of novel MXenes as catalyst support for fuel cells. Specifically, the $Ti_3C_2T_x$ (MXene) as a catalyst carrier for MOR has been designed and fabricated by Elancheziyan et al. [153]. Results indicated that the use of $Ti_3C_2T_x$ improves the interface and surface properties of metal electrocatalyst. For the applications of ORR, Jiang et al. developed a new method to prepare the Fe-N-C/MXene heterostructure as the high-efficiency catalyst [154]. This functional structure indicated that the metal cluster can

be used to adjust the surface charge of the catalyst and with it catalyst support. Currently, most of experimental studies focus on the Ti based MXene, especially for $Ti_3C_2T_x$. Other MXenes based on transition metals (e.g., Mo and Nb) need to be further developed in the future. It is worth noting that carbides are mostly subject to thermodynamic instability on the cathode side of a DMFC. Although carbides are generally assumed to be stable, they also may be transformed to the unstable carbonaceous support under oxidative or reductive conditions. Hence, we believe that more efforts should be devoted to the development of stabilized carbides.

3.1.5. Conducting polymers

Conducting polymers (CPs) are promising materials as the catalyst support because of their unique electrical, mechanical, chemical and optical properties, so they can be potentially used for electrochemical reaction [155]. Several kinds of polymers, like polypyrrole [156], poly(brilliant cresyl blue) [157] and polyaniline [158], have been explored as catalyst supports to disperse the catalyst particles. Especially, the relatively high conductivity and surface area of these polymers make them possible to shuttle the electrons through polymer chains between the dispersed catalyst particles and electrode [159,160]. Therefore, using CPs as the catalyst support to enhance the charge transfer between the catalyst and support materials have been developed. For example, for DMFC applications, Kundu et al. proposed a useful method to

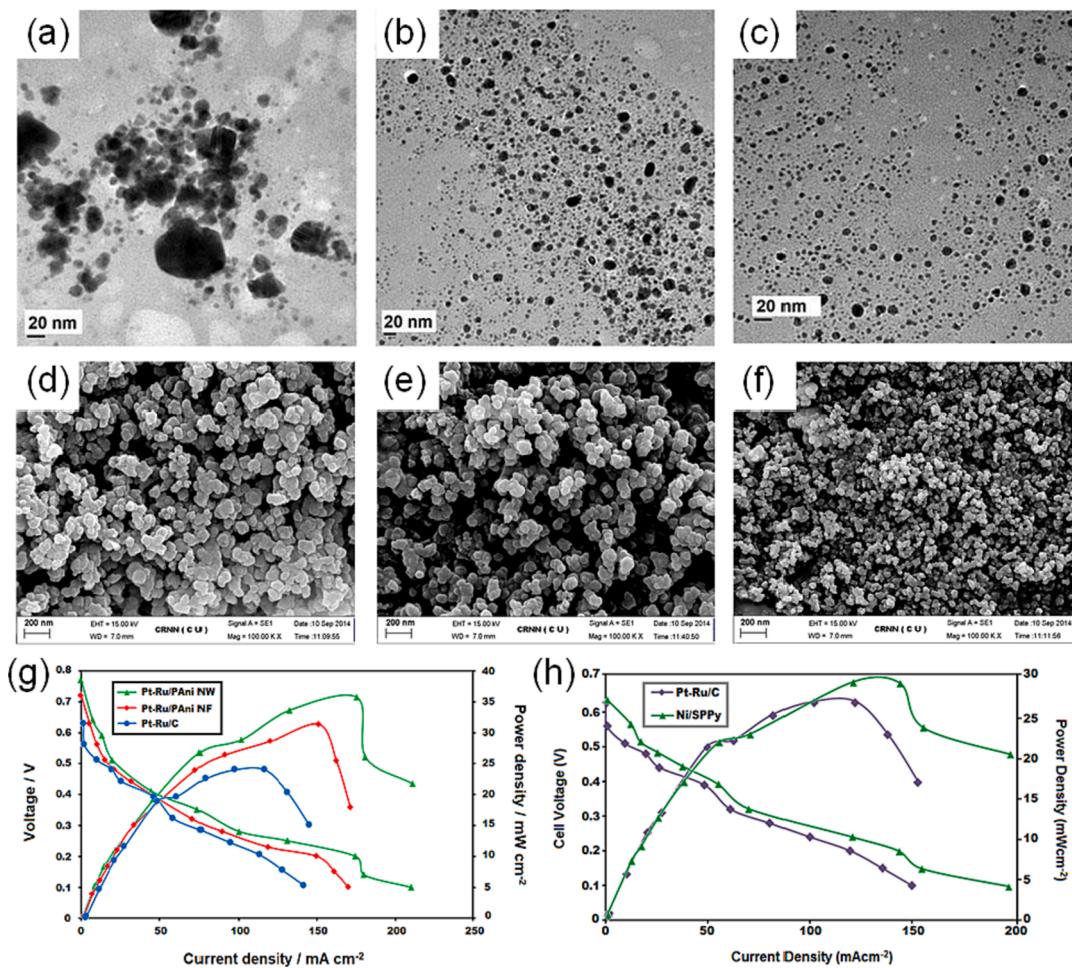


Fig. 11. TEM images of (a) PtRu/C, (b) PtRu/polyaniline nanofibers and (c) PtRu/polyaniline nanowhiskers catalyst (adapted from Ref. [55]. © 2018 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim). TEM images of (d) PtRu/C, (e) Ni/polypyrrole and (f) Ni/partially sulfonated polypyrrole catalyst (adapted from Ref. [161]. © 2016 Elsevier). (g) Performance of single DMFC using PtRu/C, PtRu/polyaniline nanofibers (PAni NFs) and PtRu/polyaniline nanowhiskers (PAni NWs) anode catalysts at 60 °C (adapted from Ref. [55]). (h) Performance of single DMFC using PtRu/C and Ni/partially sulfonated polypyrrole (Ni/SPPy) as anode catalysts at 60 °C (adapted from Ref. [161]).

enhance the charge transfer rate and electrocatalytic activity on the anode side by controlling and optimizing the morphology of polyaniline nanowiskers, which can achieve higher stability, durability and mitigant catalyst poisoning [55]. Importantly, the polyaniline nanowiskers or nanofibers are responsible for achieving uniform distribution and better dispersion of the Pt-Ru nanocatalysts (Fig. 11(a)-(c)). Results suggest that the catalysts based on Pt-Ru/polyaniline nanowiskers and Pt-Ru/polyaniline nanofibers exhibit better performances in a single DMFC test, compared with the Pt-based catalyst (Fig. 11(g)). Concretely, results show a peak power density of 35.09 mW cm^{-2} with the new catalyst.

Polypyrroles can be also practically used as the catalyst support for DMFCs, which can be prepared by many facile methods including oxidative, electrochemical and chemical polymerization [160]. Especially, the electrochemical route is mostly used to prepare the modified polypyrroles-based matrix with a high conductivity. For instance, the sulfonated polypyrroles can be prepared to support the Ni nanoparticles as the anode catalyst for DMFCs, which is demonstrated to be a special catalyst support material due to its high electrical conductivity, environmental stability and conjunctive effect of catalyst-support [161]. For this method, the chlorosulphonic acid can be used to provide the $\text{-SO}_3\text{H}$ matrices for the preparation of partially sulfonated polypyrrole during the experimental process. Results show that the Ni catalyst has better dispersity with a small particle size when the partially sulfonated polypyrrole is used as a support material, compared with the Ni/polypyrrole and Pt-Ru/C catalysts (Fig. 11(d)-(f)). More importantly, it is found that the Ni/partially sulfonated polypyrrole catalyst produces a peak power density of 28.9 mW cm^{-2} at 0.2 V , slightly higher than that of the Pt-Ru/C catalyst with a peak power density of 23.9 mW cm^{-2} at 0.2 V (Fig. 11(h)). The significant performance improvement of the DMFCs with Ni/partially sulfonated polypyrrole catalyst is related closely to the lower impedance and higher I_F/I_B ratio (I_F : forward peak current, I_B : backward peak current). Importantly, this embodiment

stimulates a good idea of employing the cost-effective Ni-based catalyst to substitute the Pt-based catalyst. For the future research, it is essential to develop the noble-metal catalyst with a lower loading or even non-noble metal catalyst for DMFCs.

3.1.6. Supportless materials

The noble metal catalysts (e.g., Pt-based and Pd catalyst) and low-cost metal catalysts (e.g., Ni-based and Ag catalyst) can be used in a supportless form, which are named as supportless materials for DMFC applications. In general, using catalysts based on nonsupport materials can significantly simplify the preparation process since it fully gets rid of catalyst supports or conducting substrates. Composite metal catalysts have been widely investigated to enhance the intrinsic activity and alleviate CO poisoning. In this field, there are two main directions for the metal-based catalyst, including the Co alloy and Pt alloy [162]. To achieve a high performance of the Co alloy, using mesoporous architecture is a major strategy to reach the goal of the high-quality MEA [3]. Liu et al. proposed a strategy to prepare $\text{Mn}_2\text{O}_3@\text{Co}_{1.2}\text{Ni}_{1.8}\text{O}_4$ as the catalyst for ORR [3]. For this work, the preparation process of composite metal catalyst mainly includes two steps: i) the $\text{Mn}(\text{CO}_3)_2$ and $(\text{NH}_2)_2\text{CO}$ was used to synthesize the Mn_2O_3 cubes by a hydrothermal method; ii) the $\text{Co}_{1.2}\text{Ni}_{1.8}\text{O}_4$ nanosheets was coated on the surface of Mn_2O_3 via a series of thermal annealing processes. The detailed fabrication process can be seen in Ref. [3]. The as-prepared $\text{Mn}_2\text{O}_3@\text{Co}_{1.2}\text{Ni}_{1.8}\text{O}_4$ catalyst exhibits the high-efficiency electron transfer and oxygen transport during the ORR process, as shown in Fig. 12(a) and (b). Moreover, it is found that the power density and cell voltage of fuel cell with the $\text{Mn}_2\text{O}_3@\text{Co}_{1.2}\text{Ni}_{1.8}\text{O}_4$ cathode can be significantly enhanced, compared to the cell with the Mn_2O_3 cathode (Fig. 12(c) and (d)). Regarding applications of Pt alloy, most studies focus on the design of catalyst structure and preparation of alloys based on Pt metal. For instance, the Rh and Ru metals are usually used to combine with the Pt catalyst to prepare the bimetallic catalyst, which can greatly improve the activity,

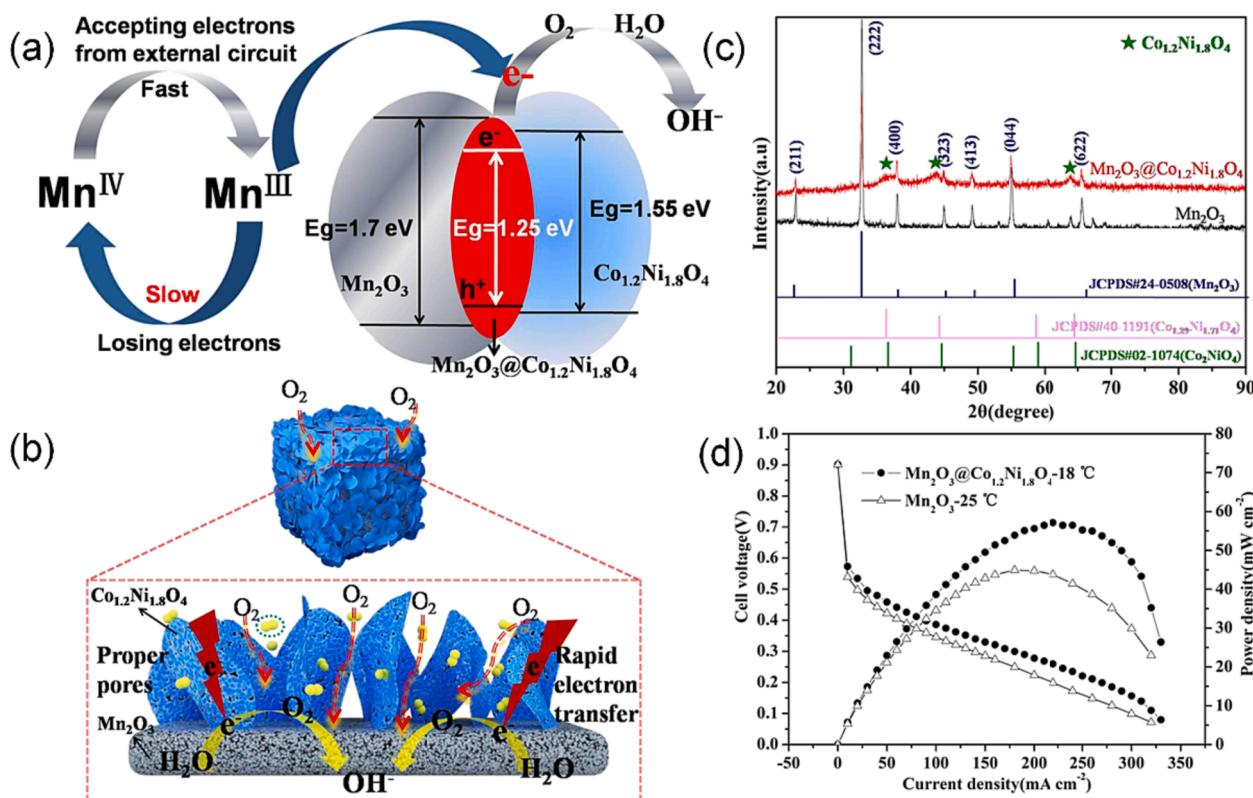


Fig. 12. Schematic illustration of (a) the valence changes of electron transfer. (b) ORR mechanism of the $\text{Mn}_2\text{O}_3@\text{Co}_{1.2}\text{Ni}_{1.8}\text{O}_4$ Composite. (c) XRD patterns of Mn_2O_3 and $\text{Mn}_2\text{O}_3@\text{Co}_{1.2}\text{Ni}_{1.8}\text{O}_4$. (d) Cell performance of the Mn_2O_3 - and $\text{Mn}_2\text{O}_3@\text{Co}_{1.2}\text{Ni}_{1.8}\text{O}_4$ -based DMFCs (adapted from Ref. [3]. © 2018 American Chemical Society).

durability, as well as poisoning resistance for methanol [72]. However, the high cost of the bimetallic catalysts has become the main reason limiting their large-scale applications.

In the case of MOR, the Ni-based catalysts (e.g., metallic nickel, nickel oxides and nickel alloys) have been applied to substitute the costly metal catalysts, especially on the anode side of the acidic DMFCs because of their low cost and electrocatalytic properties. To achieve the high catalytic activity of Ni-based catalysts, it is important to facilitate the formation of rational crystalline structure by use of appropriate synthetic techniques. A variety of structured Ni-based catalysts have been synthesized by different routes, such as sol-gel [163], hydrothermal process [164], atomic layer deposition [165], electro-deposition [166], chemical deposition [167] and anodization [168]. Using feasible anodization method to construct nanostructured Ni-based catalyst is regarded as a direction to gain different catalyst morphology that promotes an outstanding cell performance. Although many methods have been developed to achieve higher catalytic performances, most of the involved catalysts are very likely to cause evident agglomeration and great loss of catalytic active sites with a smaller surface area during practical operation. Furthermore, the Ni-based catalysts usually face the challenge of poor long-term durability in the acidic environment, which may cause unexpected material loss and structure change. As a result, the decline of electrocatalytic activity leads to a poor cell performance. In summary, there is still plenty of scope to solve the above problems of the catalyst with supportless materials for DMFCs.

3.2. Applications of NCSMs in diffusion layer for DMFCs

Traditional carbon-based materials, such as carbon paper and carbon cloth, mostly suffer from a great risk of corrosion and large mass transport resistance. Based on the special 3D structures, good corrosion resistance and fast multiphase mass transfer, it has been demonstrated that the porous metal materials (e.g., Ti foam [169], Ni mesh [170], Ni-Cr alloy foam [171]) can be used as the DL in MEA for DMFCs. It is worth mentioning that the common metal porous materials have a large surface area with a relatively high conductivity, which can be also used as current collectors. Currently, the structural design and surface modification of DLs are two major development directions. It is a favorable way to integrate the porous metal materials as a key component, e.g., DL and current collector, because of their excellent conductivity and mechanical characteristics. For example, Yin et al. prepared a Ni mesh with an Au layer as a DL/current collector at the cathode [170]. Results show that the Au-coated Ni mesh can achieve a reduced air transfer resistance, compared to that of the traditional carbon-based materials. Zhao's group proposed an alloyed metal foam as a DL instead of the traditional carbon-based materials and current collector [171]. It is found that the new DL structure helps enhance the mass transfer during the electrochemical process. Concretely, the transport resistance of oxygen on the cathode side can be reduced under the condition of high concentration operation, so as to alleviate the degree of water flooding on the catalyst layer. As a result, a higher cell performance can be achieved. On the other hand, some studies are mainly focused on special mechanical and material properties of metal fiber sintered felt [172–174]. For example, Yi et al. explored the feasibility of using a porous stainless-steel fiber sintered felt as the DL for fuel cells [175]. It is found that the porous stainless-steel fiber sintered felt delivers a higher tensile modulus and ductility. This effect also shows the superiority of the metal fiber sintered felt with a strong transport ability under assembly compression. Li et al. developed a stainless-steel fiber felt as the cathodic DL (or backing layer) and current collector [176]. Compared to the conventional carbon fiber material, the metal fiber felt has a higher material density, mechanical strength and lower porosity. They found that the power density of DMFC could be improved, especially in the case of a high methanol concentration. This can be ascribed to the reduced methanol crossover and improved water management. However, it is worth noting that the

metal-based DL is mostly subject to a higher resistance of interfacial contact inside the cell. This needs to be considered when designing the DL.

In addition to developing a new DL structure, the multiphase transport modeling (e.g., air, water, methanol and electrons) inside the DL still deserves more in-depth investigation. Specifically, the gas–water transport modeling is related closely to the porosity, surface roughness and wettability of DLs. Molecule diffusion is a major mechanism for two-phase transport in the DL. In practical operation, the methanol and air diffuse into the catalyst layer through the DL, simultaneously the smaller water droplets are produced in the cathode electrode with the electrochemical reaction. With this context, some studies have investigated the transport process by means of experimental and simulation methods. For instance, Tanaka et al. constructed a model of perforated metal plate as the DL, by coupling with mechanical, electrical and electrochemical factors [177]. Results showed that the large flooding effect could be eliminated when the DL and microporous layer were combined, and the assembly pressure has a strong impact on the contact resistance of a DL. Although many strategies have been used to investigate the transport process of reactant (e.g., gas, water and methanol) in DLs, the mechanism of multiphase transport between the reactant and DL material has not been absolutely comprehended, specifically for the NCSMs [178,179]. Furthermore, the fabrication techniques of NCSMs with controllable porosity and surface properties usually call for complicated and costly machines and equipment. Therefore, more efforts should be contributed to the design and low-cost manufacturing of noncarbon DLs for DMFC in the future work.

3.3. Applications of NCSMs in MEA for stack-level DMFCs

For DMFC stack applications, the durability performance of NCSMs has received increasing attention during the past decades. Generally, the lifetime of a laboratory-scale DMFC stack is in the range of 3000 to 6000 h [180]. The performance drop of DMFC stack can be ascribed to many aspects, including corrosion of bipolar plates, degradation of PEM and catalyst. Among these factors, the degradation or corrosion of conventional carbon-based materials becomes an urgent issue [181]. Hence, some researchers have developed novel noncarbon materials for DMFC stacks [182]. Concretely, the Pt-Ag catalyst used in micro DMFC stacks has been designed and fabricated by Abrego et al. [182,183]. Experimental results showed that the device delivered excellent durability of 10 h. In other aspects, the structure and connection design of DMFC stack are also the main factors affecting the output performance of the stack-level DMFC. The DMFC stack requires complex design and engineering from the material level to the component level. The cost of a DMFC stack should be reduced when it is put into the market for real applications [184,185]. Ultralow Pt-based catalyst loading is a potential way to solve this issue. From the perspective of real engineering, higher overall performance and lower production cost must be both realized for a balanced consideration.

In addition to developing new NCSMs, more efforts should be made toward the structural design and numerical analysis of the DMFC stack to achieve uniform fuel distribution, low methanol permeation and high power density. Currently, the DMFC stack with small power (<2 KW) and small volume has attracted more attentions [7,11,186]. Therefore, ideal structural design of DMFC stack should achieve the smallest kinetic energy loss and maximal volume power density under the supply of methanol solution and air. In addition, some studies have adopted numerical method to investigate the relationship between dynamic operating characteristics and output performances of DMFC stack [186,187]. Specifically, Fang's group proposed a DMFC stack model to investigate the polarization properties by using the Debye-Hückel ionic atmosphere theory [188]. Results revealed that the polarization coupling efficiency improved the output power as the loading increases. On the other hand, some studies tried to optimize the design of a DMFC system to reduce the size of external components and enhance the system efficiency

[189,190]. However, there are still many issues that need to be addressed in the future, such as the degradation of DMFC stack after long-term operation, the management of CO₂ gas product inside the stack, and the thermal management of DMFC system.

4. Conclusions

In summary, the recent advances of the functionalized various NCSMs are reviewed in this study. Specifically, these NCSMs materials can significantly enhance catalytic activity and durability of catalysts in CLs and promote the transportation of heat, mass and electrons in DLs, thereby improving cell performance. Various NCSMs including the transition metal elements, silicon-based materials, perovskites, carbides and conducting polymers for catalyst supports and metal-based porous materials for DL have been developed to optimize the MEA design and with it DMFC performance [71,191]. As novel catalyst supports for DMFCs, noncarbon materials with different material- and structure-related properties are summarized from the perspective of surface engineering design. The electrocatalytic mechanism and interaction mechanism between the Pt-based metals and support materials are analyzed in detail. The strategies for designing new structures of non-carbon supports are summarized according to the categories of 0D structure and 1D structure [192,193]. In terms of metal-based supports, the commonly-used Pt-based catalysts coated on the surface of transition metals facilitate forming of the intermetallic structure, which is endowed with higher corrosion resistance and more stable structures of catalyst supports [194,195]. Another purpose to develop the NCSMs is to decrease the use of Pt-based noble metals [196]. The outstanding performance of the Pt/NCSMs usually depends on the structural design, preparation methods, operational parameters (such as pH and temperature), thermal treatment, activation processes and material composition ratios. In the case of DL applications, to decrease the flow resistance and enhance the electron transport between the DL and CL, novel non-carbon materials (e.g., metal-based porous materials) have been developed [197–199]. With this context, the design of new functional materials with high conductivity and low mass transport resistance is the important development direction for the next-generation advanced GDL.

5. Future challenges and perspectives

Although great advances in NCSMs have been achieved, there are still many technical challenges and knowledge gaps to be addressed in future work.

(i) Developing new cost-saving preparation methods is important for real commercialization, especially for the Pt catalyst [200]. Although some Pt/NCSMs exhibit high ECSA features, the durability and power density of these materials are often unsatisfactory after long-term operation in DMFC. Thus, much more efforts still need to be devoted to revealing the degradation mechanisms of the newly developed electrode.

(ii) Since the design of the catalyst support affects the utilization and reliability of the catalyst, future work should put more emphasis on the modification of NCSMs. For instance, the nanoframe structure of the catalyst-support is seen as a promising candidate due to its large surface area and precise atom-level operation [201,202]. However, it is still unclear about how the nanoframe structure affects the electron transfer during the electrochemical reaction. Besides, the relationship between the new structure and material durability needs to be investigated in a more in-depth manner.

(iii) The obstacles of using conducting polymers lie in their low chemical stability and mechanical strength. Incorporating functional groups (e.g., sulfonic acid group) is a better way to solve these issues and enhance the efficiency of proton transportation. In addition, exploring new hybrid materials to gain higher electrical conductivity is an important development direction in the future.

(iv) For DL applications, more attention should be given to the surface modification toward noncarbon materials. For instance, the metal-based porous materials with structural flexibility can be used to improve the multiphase mass transfer during the electrochemical reaction [203]. Furthermore, more in-situ techniques to characterize the structural property and transport capability of new DL materials should be explored and used to help more efficiently evaluate the applied performances.

In summary, conventional carbon support materials have been widely used in commercial products not only for their low cost, but also for their abundant availability. It is of great significance to develop the novel MEA architectures based on the NCSMs. We believe that the NCSMs have great prospects to be used in the field of fuel cells, especially the DMFC is expected to benefit substantially from the use of such materials to construct high-performance and cost-effective electrochemical devices and power generation systems.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

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