Recent advances in high-loading catalysts for low-temperature fuel cells: From nanoparticle to single atom

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Abstract
Low-temperature fuel cells (LTFCs) are considered to be one of the most promising power sources for widespread application in sustainable and renewable energy conversion technologies. Although remarkable advances have been made in the mass activity of catalysts, mass transport impedance needs to be urgently addressed at a well-designed membrane electrode assembly (MEA) scale. Increasing the loading of electrocatalysts is conducive to prepare thinner and more efficient MEAs owing to the resulting enhanced reactant permeability, better proton diffusion, and lower electrical resistance. Herein, recent progress in high-loading (≥40 wt.%) Pt nanoparticle catalysts (NPCs) and high-loading (≥2 wt.%) single-atom catalysts (SACs) for LTFC applications are reviewed. A summary of various synthetic approaches and support materials for high-loading Pt NPCs and SACs is systematically presented. The influences of high surface area and appropriate surface functionalization for Pt NPCs, as well as coordination environment, spatial confinement effect, and strong metal-support interactions (SMSI) for SACs are highlighted. Additionally, this review presents some ideas regarding challenges and future opportunities of high-loading catalysts in the application of LTFCs.

KEYWORDS
high-loading catalysts, low-temperature fuel cells, membrane electrode assembly, nanoparticle catalysts, single-atom catalysts
1 | INTRODUCTION

Owing to the increase in global energy consumption and environmental pollution, developing promising renewable energy and conversion systems with excellent performance and stability is essential and urgent. Since the European Union and 65 countries declared their commitment to net-zero carbon dioxide emissions targets by 2050 at 2019 United Nations Climate Summit, reducing the dependence on fossil fuels and creating a renewable energy system have become a major issue for humanity today. In 2020, China also made the official announcement to peak carbon dioxide emissions before 2030 and achieve carbon neutrality before 2060. Nationwide actions have been taken to secure sustainable development for mankind.

As a promising next-generation energy system, low-temperature fuel cells (LTFCs), particularly proton exchange membrane fuel cells (PEMFCs) and direct methanol fuel cells (DMFCs), have outstanding advantages in high power density and energy conversion efficiency. Recently, the New Energy and Industrial Technology Development Organization in Japan have set the 2030 and 2040 targets of stack for PEMFC to be 6.0 and 9.0 kW/L, respectively. This means the potential in high-current-density region has to obtain a twofold increase in the single cell on the basis of the present level. Thus, designing efficient catalysts for slow kinetic electrocatalytic reactions like oxygen reduction reaction (ORR) and methanol oxidation reaction (MOR) is considered to be an attractive approach to promote the commercialization of LTFCs. Among them, Pt nanoparticle (Np) catalysts (NPCs, supported metal catalysts with metal crystallites close to the nanometer size) and emerging SACs (unique heterogeneous catalysts with a theoretical efficiency of 100%) are believed to be the most promising catalysts for LTFCs.

In the past few decades, remarkable advances have taken place in synthesizing NPCs, and they have become the most widely used catalysts for practical application due to their high activity, stability, and selectivity for electrocatalytic reactions like ORR and MOR. Tremendous amounts of research have concentrated on optimizing NP size, crystal facet, topography, and interface for enhancing intrinsic catalyst activity. In addition, different types of support materials with optimized surface area, surface properties, and precise structure also affect the adsorption, deposition, and formation of metal NPs. For example, Hao et al. carried out fundamental research on exploring the connection between adsorption equilibrium and NP synthesis on several support materials. They found that cationic Pt precursors are adsorbed over low- and mid-points of zero charge carbons in the high pH range, while anionic Pt precursors prefer high points of zero charge carbons in the low pH range. Pt NPs synthesized by strong electrostatic adsorption (SEA) are normally smaller and have narrower size distributions. Hence, NPCs, stemming from nanotechnology, have made an irreplaceable impact on facilitating the commercialization of LTFCs, owing to their outstanding level of intrinsic activity. Meanwhile, due to the inevitable use of expensive and scarce noble metals, NPCs are not suitable for further large-scale applications.

Therefore, enhancing the metal utilization efficiency is an option to minimize catalyst costs in power systems. Nowadays, although they are still at the laboratory scale, SACs have recently gained much attention in heterogeneous catalytic reactions and serve as promising alternatives for Pt NPCs. SACs have atomically dispersed active sites and theoretically possess a 100% utilization of metal atoms. Moreover, many SACs only use cost-effective non-noble metals like Fe, Co, and Mn as active sites but exhibit similar mass activity to Pt NPCs, thereby showing great potential for enabling reasonable utilization of Pt resources. Additionally, investigators have found that when the metal NPs are distributed evenly on the surfaces of support materials as single atoms, the active sites tend to exhibit identical spatial configuration and electronic structure. Thus, SACs exhibit excellent electrocatalytic performance and catalytic selectivity in various catalytic systems. Figure 1 illustrates the focus of this review and the respective features of NPCs and SACs.

Both Pt NPCs and SACs possess their own strengths, and have been widely investigated for their applications in LTFCs. However, despite the excellent mass activities of Pt NPCs and SACs, power density is also limited by inefficient charge transport and mass transfer in MEAs. To cope with internal electrical resistance, the electrocatalyst layers of MEA need to be reasonably thin. The catalyst layer (CL) thickness of conventional low-loading catalysts (catalyst loading: ~20 wt.%; CL thickness: ~20 μm) is approximately twofold higher than that based on high-loading catalysts (catalyst loading: ~50 wt.%; CL thickness: ~10 μm). This results in more impactful Knudsen resistance in micropores as well as molecular transport resistance in macro-mesopores in CL. For a well-designed MEA, the observed performance is confined by proton resistance and electrode mass transport properties in a high-current-density region (normally ≥1 A/cm²) rather than the intrinsic activity of a catalyst. As shown in Figure 2, the typical MEA prepared with low and high loadings of Pt NPCs are compared and the advantages of thinner MEAs are highlighted. As a result, increasing the mass loadings of catalysts is both essential and urgent. For the Pt NPCs, to achieve thin-layered MEAs, their loadings for commercially available LTFCs are nearly 50 wt.%. In particular for DMFC, owing to the poor kinetics of the anode reaction, metal loadings often have to be over 60 wt.%. 
FIGURE 1 The focus of this review and the respective features of NPCs and SACs.

FIGURE 2 Schematic cross-section of a typical PEMFC and the comparison of MEA with different thickness.
For SACs, their metal loadings seldom exceed 1.5 wt.%, but each individual metal atom is involved in the catalysis process. The high metal atom efficiency enables excellent mass activity with a relatively lower metal loading. However, an as-prepared CL of SACs is usually 10 times thicker than Pt NPCs, requiring higher metal loading to enhance mass transfer. Therefore, densely populated SACs have become a development trend of advanced electrocatalysts for LTFCs due to their enhanced mass activity and large active surface area.  

In the present review, we summarize the research progress of high-loading Pt NPCs and SACs in recent years in terms of unique synthesis methods and different support materials. Figure 3 presents Pt NPCs synthesized by various deposition methods or supported on different materials with a loading above 40 wt.%. For high-loading Pt NPCs, owing to the high surface energy of uniformly dispersed Pt NPs, the improved aqueous impregnation method, pulse-microwave-assisted polyol method, and multistep reduction strategy are highlighted to overcome the challenge of maintaining their high metal loading while avoiding metal migration and aggregation.  

Additionally, surface modifications, like acidic treatment, plasma treatment, and ozone treatment, have been developed to introduce a variety of functional groups containing heteroatoms on the inert surfaces of support materials to improve metal dispersion. In the following sections of this review, a series of synthetic strategies by utilizing the features of MOFs, heteroatom-doped carbon, and defective metal oxides are discussed to obtain versatile high-loading SACs. Figure 4 illustrates recent high-loading SACs prepared by the bottom-up strategy and top-down strategy with a loading above 2 wt.%. Increasing the intrinsic activity and density of active sites are keys to enhance their selectivity and catalytic activity.

## 2 | HIGH-LOADING Pt NPCs

Carbon-supported Pt NPCs constitute a significant class of heterogeneous catalysts in LTFCs owing to their size controllability, component tunability, structural diversity, and morphological variability. As mentioned above, to achieve better MEA performance, highly engineered electrodes require complex three-phase interfaces for efficient mass transfer and charge transport, and high-loading Pt NPCs are ideal candidates for the fabrication of relatively thinner electrodes. Thus, this section will be divided into two parts to systematically describe how high-loading Pt NPCs are obtained: (1) deposition methods and (2) electrocatalyst support materials. In general, with the assistance of well-designed support materials and advanced synthesis methods, the size, crystal structure, and morphology of Pt NPs can be precisely regulated and controlled. Table 1 summarized recent advances of Pt NPCs with metal loading ≥40 wt.%.

### 2.1 | Deposition methods for high-loading Pt NPCs

An appropriate synthesis approach is a vital factor in the preparation of high-loading catalysts, affects the isolation and separation of metal precursors, and prevents the as-formed Pt NPs from agglomerating. Therefore, it is necessary to cautiously select metal deposition methods for the synthesis of high-loading Pt NPCs. Many engaging
methods, such as seed-mediated growth method and metallic ion-containing reversed micelles approach, have been developed to prepare high-loading Pt NPCs. Xiong et al. synthesized a high-loading (40 wt.%) Pt₃Co/XC-72R with preferential crystal growth of Pt(111) facet by a novel seed-mediated growth approach with post-annealing treatment. It exhibited an $E_{1/2}$ of 0.943 V and $E_{\text{onset}}$ of 1.07 V for ORR in acidic medium. After 4000 cycles, only a decay of 25 mV in $E_{1/2}$ was observed (Figure 6(i) B and C), which was attributed to the ultradurability of Pt₃Co intermetallic core with two to three atomic layers thick Pt skin. Up to now, a variety of physical and chemical strategies have been developed to obtain carbon-supported catalysts. A physical strategy results in comparatively low metal loading, and is usually complicated and cost-ineffective for mass production. Thus, we focus on the chemical approach here. Impregnation and colloidal methods are two of the most likely candidates when it comes to chemical strategy for the large-scale production of high-loading Pt NPCs. Figure 5 illustrates the features of impregnation and colloidal methods.

### 2.1.1 Improved impregnation method

The impregnation method is the most cost-effective method since it is relatively simple (Figure 6(ii) B). Usually, for the impregnation method, metal precursors first impregnate the carbon support, and metal ions are then reduced to neutral atoms by using either an aqueous reducing agent or hydrogen. The simplicity and practicability of the impregnation method makes it the most popular method for large-scale industrial production of Pt NPCs. However, when increasing the metal loading from 20 to 60 wt.%, the metal NPs will migrate and agglomerate.

| Average Pt NP size | Loading [wt. %] | Support materials | Synthetic approaches | Refs. |
|--------------------|-----------------|-------------------|----------------------|-------|
| ~6.2 nm            | 80              | SiO₂-ZrO₂ (NCSs)  | Polyol + microwave   | 109   |
| ~3.6 nm            | 80              | SiO₂-SO₃H (NCSs)  | Impregnation (NaBH₄) | 110   |
| ~3.0 nm            | 80              | S-rGO (EGMs)      | Impregnation (NaBH₄) | 102   |
| ~3.2 nm            | 60              | 3D graphene aerogel (EGMs) | Polyol + Reflux | 105   |
| ~2.4 nm            | 60              | MWNT (CNTs)       | Polyol + microwave   | 92    |
| 5.6 nm             | 60              | MWNT (CNTs)       | Impregnation (NaBH₄) | 85    |
| ~2.5 nm            | 40              | HNO₃-CNT (CNTs)   | Polyol + Reflux      | 43    |
| ~3.0 nm            | 60              | SDS-MWCNT         | Polyol + Reflux      | 98    |
| ~2.2 nm            | 60              | SWCNT (CNTs)      | Surfactant-assisted   | 91    |
| ~3.3 nm            | 60              | OHNC (MCs)        | Polyol + microwave   | 79    |
| 2-3 nm             | 80              | POBPC (MCs)       | Impregnation (NaBH₄) | 80    |
| ~3.1 nm            | 40              | MC                | Impregnation (NaBH₄) | 72    |
| ~3.3 nm            | 60              | OMC (MCs)         | Impregnation (H₂)    | 76    |
| ~3.0 nm            | 60              | OMC (MCs)         | Impregnation (NaBH₄) | 78    |
| ~2.0 nm            | 60              | 3D-OMCS (MCs)     | Impregnation (H₂)    | 74    |
| ~3.0 nm            | 60              | OMC (MCs)         | Incipient            | 77    |
| ~2.8 nm            | 60              | HCMS (MCs)        | Impregnation (NaBH₄) | 82    |
| 2.2±0.5 nm         | 46.6            | Ketjen black 600J (CBs) | Polyol + Reflux   | 46    |
| ~3.3 nm            | 60              | carbon black 350G (CBs) | Impregnation (NaBH₄) | 29    |
| ~2.3 nm            | 40              | Vulcan XC-72R (CBs) | Impregnation (NaBH₄) | 42    |
| ~2.5 nm            | 40              | Vulcan XC-72R (CBs) | Polyol + pulse microwave | 25    |
| ~2.7 nm            | 50              | Vulcan XC-72R (CBs) | Polyol + pulse microwave | 48    |
| ~2.9 nm            | 40              | Vulcan XC-72R (CBs) | Polyol + Reflux      | 51    |
| ~4.2 nm            | 55              | Vulcan XC-72R (CBs) | Incipient            | 43    |
| ~5.0 nm            | 85              | Ketjen black 600J (CBs) | Multi-polyol + Reflux | 47    |
| ~2.3 nm            | 50              | Ketjen black 600J (CBs) | Impregnation (H₂)   | 44    |
| ~5.0 nm            | 50              | BP2000 (CBs)      | Impregnation (NaBH₄) | 55    |
The characteristics of impregnation and colloidal methods

Regulating the size and distribution of metal NPs is a major challenge for the impregnation method. Thus, several improved strategies need to be utilized during the impregnation process. For example, Joh et al.\textsuperscript{43} reported a unique strategy to obtain highly loaded (55 wt.\%) and dispersed Pt NPCs. The key point of this strategy is slowly adding a Pt precursor to a solution containing well-dispersed carbon supports and a high-concentration reducing agent, which instantaneously reduced the Pt precursors to granular NPs as soon as they were added. As a result, this improved impregnation method contributes to a relatively small Pt NP size of 4.2 nm. According to X-ray diffraction, this high-loading Pt NPC gives an electrochemically active surface area (ECSA) of 61.4 m\(^2\)/g\(_{\text{Pt}}\), while the ECSA of Pt NPC is prepared by traditional impregnation process with the same loading was only 47.7 m\(^2\)/g\(_{\text{Pt}}\). It also exhibited an increase by 15.0\% in power density according to the MEA tests. In another case, Pak et al.\textsuperscript{44} invented a multistep reduction strategy, in which Pt precursors were divided into several parts and

\begin{figure}[h]
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\caption{The characteristics of impregnation and colloidal methods}
\end{figure}

\begin{figure}[h]
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\includegraphics[width=\textwidth]{figure6.png}
\caption{(i) Schematic illustration of seed-mediated growth method (A) for preparing Pt\(_x\)Co/XC-72R; electrochemical performances (B-C), XRD (D), and SAED (E) patterns of Pt\(_x\)Co/XC-72R with preferential crystal growth of Pt (111) facet. Reproduced with permission from Ref. [39] Copyright 2018 American Chemical Society (ACS). (ii) Metallic ion-containing reversed micelles (A) Reproduced with permission from Ref. [40]. Copyright 2015 The Royal Society of Chemistry (RSC), impregnation (B) Reproduced with permission from Ref. [67]. Copyright 2010 Elsevier and multiple polyol method (C). Reproduced with permission from Ref. [67]. Copyright 2012 Elsevier for the synthesis of high-loading Pt NPCs}
\end{figure}
subsequently reduced via H₂ on the prepared Pt catalyst. Owing to this multistep reduction strategy, the externally exposed substrate surface was reutilized and the size of metal NPs remained small. The average NP size can be regulated in the range of 1 to 5 nm by controlling the number of multistep and the related reduction parameters, while the ECSA is still higher than 200 m²/gPt. Considerable efforts have been devoted to the improved impregnation method to fabricate high-loading Pt NPCs while maintaining a uniform NP dispersion and narrow size distribution. However, the improvement process itself inevitably increases the complexity of the whole impregnation procedure, leading to higher cost and lower efficiency. Therefore, efficient and low-cost synthesis methods are still desirable for the preparation of high-loading Pt NPCs.

2.1.2 Modified colloidal method

Compared with the impregnation method, the colloidal method can easily regulate and produce small, homogeneously distributed metal NPs. In the past decade, the modified polyol method which is a subset of the colloidal method has also been widely researched and applied to the preparation of ORR catalysts with a loading above 50 wt.%. For instance, Wang et al. reported a simple ethylene glycol/water strategy to synthesize highly dispersed Pt NPCs with a loading of 50 wt.%, in which the proportion of water must be carefully controlled. In their strategy, the carefully controlled EG diluted by water has two advantages: (1) helps to regulate the reduction rate of the Pt precursor in the reaction; (2) an appropriate amount of water contributes to the removal of EG during the purification process. This high-loading Pt NPC had an average NP size of 2.2 nm and showed a maximum ECSA value of 71 m²/gPt. In addition, accelerated degradation test (ADT) results exhibited that the stability of as-synthesized Pt NPC was comparable to commercial Pt/TKK. The ECSA of self-made Pt NPC decreased about 13% in comparison with 16% of the commercial one. Besides, mass activity was only slightly decreased from 151 to 121 mA/mgPt after ADT. Moreover, You et al. synthesized an ultra-high-loading Pt NPC (up to 85 wt.%) by a multiple polyol method (Figure 6(ii) C), which is similar to the multiple impregnation method mentioned in the former section. In this strategy, they continued deposition for the residual part of Pt precursors on the basis of a presynthesized Pt NPC with a loading of 76 wt.%, and kept the Pt NPs size to an average diameter of 4.60 nm by optimizing procedure parameters. In spite of the slight growth in size of the Pt NPs, their catalyst exhibited good Pt efficiency, high ORR activity, and power density. Additionally, to obtain a shorter crystallization time and attain a more homogeneous nucleation process, microwave irradiation is often used as an advanced technique to rapidly heat the precursor solutions. For example, Song et al. prepared 50 wt.% Pt NPCs by employing a pulse-microwave-assisted polyol synthesis strategy. By analyzing TEM images, the mean NP size of this Pt NPC was about 2.7 nm. Compared with continuous microwave activation, the pulse-microwave procedure does not have a rapid heating rate in the reduction process, avoiding agglomeration of the metal particles at high temperatures. Therefore, the modified colloidal method is also an excellent approach for the preparation of high-loading Pt NPCs. However, compared with the impregnation method, the modified colloidal method usually has a more complicated procedure. The polyol used in the colloidal method itself works as a kind of stabilizer and surfactant and is easily trapped in the support micropores because of its high viscosity, making it difficult to remove completely.

2.2 Electro catalyst support materials

Besides choosing an advanced synthesis method and regulating significant synthesis parameters, a well-engineered support material with optimal morphology, ideal surface area, a highly graphitized structure to resist corrosion, and favorable surface properties for metal-support interactions is also desired for high-loading Pt NPCs. More specifically, for an electrocatalyst with a loading above 50 wt.%, the proportion of mesopores should not be less than 80%, or the agglomeration of Pt NPs will rapidly increase and the active sites will be easily submerged in micropores. Here, appropriate support materials for high-loading Pt NPCs are divided into five parts: carbon blacks (CBs), mesoporous carbons (MCs), carbon nanotubes (CNTs), engineered graphene materials (EGMs), and noncarbon supports (NCSs). As presented in Figure 7, their respective unique strengths and characteristics are also systematically introduced. Surface functionalization and three-dimensional (3D) spatial configuration modification of these carbonaceous support materials need to be introduced before they are employed as favorable support materials for high metal loading.

2.2.1 Carbon blacks (CBs)

As a critical support material for LTFCs, CBs play a significant role in improving overall performance owing to a favorable balance of porosity and degree of graphitization. Vulcan XC-72R belonging to CBs manufactured
FIGURE 7 The characteristics of suitable support materials for high-loading Pt NPCs

by Cabot Corporation has become an advanced support material and global specialty chemical for Pt NPCs because of its advantages owing to low cost and excellent electronic conductivity. Recently, more CBs with high internal surface areas, such as Ketjen EC-300J (ca. 800 m²/g), Tanaka Kikinzoku Kogyo (ca. 800 m²/g), and Black Pearl 200055 (ca. 1200 m²/g) were also widely applied in the fabrication of high-loading Pt NPCs. In general, CBs are the most popular support materials for high-loading Pt NPCs with their advantages of high electrical conductivity and availability.56–59

To achieve higher metal loading as well as better dispersion of Pt NPs, support characteristics of CBs, such as surface heterogeneity and porous topology, are commonly enhanced. The most widely used surface activation methods are heat treatment and chemical modification. For example, Pinheiro et al.60 have found that high-loading Pt NPCs had an increase of approximately 50% in the active Pt area when the CBs were treated in Ar with a high temperature of 850°C followed by water vapor. The high temperature treatment is beneficial to the elimination of impurities in CBs, leading to an improved particle size or higher active surface area.

In addition, the dissolution-redeposition Ostwald ripening process61–63 inevitably occurs due to the acidic environment along with weak metal-support interaction on the surface of CBs. Thus, appropriate surface modifications are required to introduce a variety of functional groups on the inert surface of CBs to interact favorably with Pt NPs. For example, Wu et al.64 introduced a N-doped graphitic layer on a pristine CB particle, and then synthesized a Pt NPC with a loading of 60 wt.%. According to the CO stripping, the as-synthesized Pt NPC gives an ECSA of 68 m²/gPt, while the ECSA of commercial Pt/C catalyst with a loading of 60 wt.% is only 45 m²/gPt. Electrochemical impedance spectroscopy tests showed that N-doped Pt NPC (1065 Ω cm²) experienced a threefold lower charge-transfer resistance ($R_{ct}$) than nondoped one (2990 Ω cm²), confirming better performance of N-doped Pt NPC at high-current-density region in MEA. Activated carbon-supported Pt NPCs with tunable coordination environments and well-defined active sites display better mass activity and selectivity. The functional groups on the surface of CBs serve as anchoring sites and boost surface hydrophilicity, which leads to dispersion of metal atoms in a uniform manner.65,66 In particular, ether, hydroxyl, carbonyl or carboxylic groups can be introduced on the support materials by using acid or hydrogen peroxide treatment during a chemical activation process. These activated CBs will probably provide more anchoring sites for Pt NPs deposition than those without the requisite functional groups. However, as amorphous carbons, CBs lack surface homogeneity and the functional groups may have difficulty dispersing on the supports. Before the metal precursor ions can be reduced, they do not adsorb evenly on the supports resulting in serious aggregation during the reduction process. Thus, it is of great significance to emphasize that the functionalization process has to be regulated and controlled cautiously.67

2.2.2 Mesoporous carbons (MCs)

MCs belonging to porous carbonaceous materials are another type of ideal candidate to be electrocatalyst supports for LTFCs.68,69 They have received substantial attention due to their significant strengths in terms of surface area tunability, topology, stability, and conductivity. To date, the template method which contains procedures, such as infiltration of carbon precursors, carbonization, and template dissolution, has been proven to be appropriate for the preparation of ordered mesoporous carbons (OMCs) with monodispersed pores of well-defined size.70–72 Due to the tunability of pore size in the range of 2–50 nm, OMCs are an ideal support material for high-density deposition of Pt NPs. For example, Zhang et al.73 put forward a colloidal crystal templating strategy to prepare OMCs with large mesopores that had a diameter between 10 and 50 nm (Figure 8(ii) A and B). Then, OMCs were used as supports to load Pt NPs and the prepared Pt NPs on OMCs were uniformly distributed with an average size of 1.9 nm and a loading of up to 60 wt.%. In the same year, Zhang also synthesized a 60 wt.% Pt NPC supported on 3D-ordered MC sphere arrays (OMCS) with unique hierarchical nanostructures (Figure 8(i) B).74 With the benefits of specific ordered large mesopores and hierarchical nanostructures, mass transport was highly facilitated during the reactions. This homemade Pt/OMCS exhibited a MOR electrocatalytic activity of 0.69 mA/cm² (Figure 8(i) C And D) and possessed higher ECSA (73.5 m²/gPt)
than the commercial 60 wt.% Pt/C (43.5 m²/gPt), OMC (66.2 m²/gPt), and nitrogen-modified CB (68.0 m²/gPt). Figure 8(i) presents the synthetic procedures for Pt/OMCS.

To have a more comprehensive understanding of the influence of OMC properties on Pt deposition, research on carbon precursors and OMC particle sizes were highlighted. In 2001, Joo et al. first utilized CMK-5 MC as a carbon support for LTFCs. They used the ordered mesoporous silicas as templates, and successfully prepared a highly ordered graphitic framework with uniform nanopores and tunable diameters for Pt deposition. They found that the growth rate in the size of Pt NPs was much slower than conventional porous carbons, even though the Pt loading increased to 50 wt.%. On the basis of well-designed OMCs, they further developed a sequential impregnation-reduction method to increase the metal loading to 60 wt.%. Both the MA and SA of this high-loading Pt NPC for ORR and MOR reached maximum at the Pt NP size of 3.3 nm. For ORR, the highest MA and SA were 0.045 A/mgPt and 80 μA/cm². Furthermore, Joo and his coworkers conducted deep research into the effect of OMC carbon precursors and OMC particle sizes. By regulating and controlling the Na content of the silica source and synthesis pH, they synthesized three kinds of OMCs with different carbon particle sizes of 100, 300, and 700 nm. The as-formed three OMCs were used for the synthesis of Pt NPC with a loading of 60 wt.%. and they exhibited similar ORR activities and catalyst utilization efficiencies. Only the catalyst supported on 300 nm OMC displayed slightly higher activity than the other ones. In addition, by choosing sucrose and phenanthrene as carbon precursors, they prepared two kinds of OMCs named SOMC and POMC with similar large mesopore structures but different graphitic characters. SOMC showed a four-fold higher sheet resistance than POMC, indicating much lower electrical conductivity. Both Pt NPCs supported on SOMC and POMC exhibited similar ORR activity, electrochemically active surface area and high Pt NPs dispersion in spite of the high loading of 60 wt.%. However, in the MEA test, Pt NPC supported on POMC exhibits 50% higher power density than the one supported on SOMC, indicating that higher electrical conductivity is responsible for the enhanced performance. 78

Honeycomb-like OMCs have not only been successfully applied in LTFCs, but in many other high surface MCs with certain structures as well. These were also developed to
obtain high-loading catalysts. For example, Fang et al.\textsuperscript{79} first explored the possibility of applying an ordered hierarchical nanostructured carbon (OHNC) as a unique carbon support for PEMFC. They synthesized a novel periodically ordered bimodal porous carbon (POBPC) for the preparation of Pt NPCs with a loading of 60 wt.%\textsuperscript{80}. This POBPC has a framework with 3D interconnected, ordered, and uniform macropores surrounded by mesostructured walls (Figure 8(iii) A–C), leading to high loading, uniform Pt dispersion, and small particle size. In general, high metal loading will unavoidably result in the agglomeration of metal NPs. However, carbon materials with particular structures will constrain the growth of metal NPs to some extent via the spatial confinement effect. Hollow-core/mesoporous shell (HCMS)\textsuperscript{81,82} synthesized through solid core/mesoporous shell silica is another kind of MC with a well-designed interconnected void structure and high specific surface area. Joo et al.\textsuperscript{76} first synthesized several HCMS with different shell thickness and core size, and applied them to the preparation for Pt NPCs with a loading of 60 wt.%. In the same year, without adding of any commonly used reductant, they further invented a $\gamma$-ray irradiation method and successfully prepared a cathode catalyst supported on HCMS with a much higher loading of 80 wt.%. In this method, they were able to conveniently select appropriate $\gamma$-ray irradiation dose rate to control the reduction rate, which possessed an advantage of creating a mild reaction condition for uniform NP size distribution. XRD patterns and TEM images showed Pt NPC prepared by $\gamma$-ray irradiation had an average Pt NP size of about 3.0 nm in comparison with that of 3.6 nm of nonirradiation one. Pt NPC prepared by $\gamma$-ray irradiation also demonstrated an enhancement of 17% in power density than that of nonirradiation one in MEA tests.

2.2.3 Carbon nanotubes (CNTs)

CNTs were first discovered by Dr. Iijima from NEC Corporation in Japan in 1991. Since then, their unique nanoscale cylindrical tube structure in the form of a single carbon atomic layer has attracted the attention of investigators.\textsuperscript{83–86} Recently, CNTs were applied on LTFCs owing to their excellent properties such as high electrical and thermal conductivity, lighter weight, high surface area and mechanical strength.\textsuperscript{87–90} For example, Cao et al.\textsuperscript{91} prepared a uniformly dispersed high-loading Pt NPC supported on single-wall carbon nanotubes (SWCNTs) with the assistance of sodium dodecylbenzene sulfonate as a surfactant. The as-prepared Pt NPC had a loading of 60 wt.%, and the Pt NPs were deposited on the surface of SWCNTs with a high degree of uniformity and average diameter of 2.2 nm. With the benefits of specific 1D nature of SWCNTs, mass transport of reactants or products was highly improved in the diffusive electrodes. In comparison with the commercial 60 wt.% Pt/C, cyclic voltammograms (CVs) tests indicated that ECSA of this Pt/SWCNTs was about twofold larger than controllable sample, indicating a higher Pt utilization. In a similar case, Sakthivel et al.\textsuperscript{92} synthesized an outstanding Pt NPC supported on multiwall carbon nanotube (MWCNT) catalysts with an average Pt NP diameter of 1.8 nm and a loading of 60 wt.% through a microwave-assisted polyol reduction method. When applied on a MEA, this Pt/CNT achieved 2.5 times higher maximum power density than that of the commercial one. In addition, TEM images of this catalyst after 200 potential cycles exhibited no significant detachment and aggregation of Pt NPs, which indicates outstanding stability of NPs on the catalyst surface.

Since the pristine CNTs surface are usually inert, chemical modification processes are necessary before being applied as an ideal support for high metal dispersion. In general, the functionalization process of CNTs can be divided into doping treatments and surface modification. Doping treatment usually has similar changes to physical adsorption processes, such as doping nitrogen or boron atoms on the surface of CNTs.\textsuperscript{93–95} Doped heteroatoms possess superior electron donation properties and can act as active anchoring sites for Pt dispersion. Zhu et al.\textsuperscript{96} introduced N$^+$ group by grafting poly(diallyldimethylammonium chloride) on the surface of CNTs. Then they successfully prepared a high-loading (40 wt.%) Pt NPC with an ECSA of 68.68 m$^2$/gPt and a MA of 115.25 mA/mgPt (Figure 9(i) B and C). In addition, by virtue of a vacuum filtration method (Figure 9(i) A), they developed a double-layered CL with gradient distribution of pore size and Pt content. In MEA tests, this special structure of CL obtained a maximum power density of 520.7 mW/cm$^2$ at 1100 mA/cm$^2$ (Figure 9(i) D and E). Surface modification is a process of regulating the chemical state and morphology of CNT through the introduction of various functional groups on the CNT surface. The most intensively studied surface modification is acidic oxidation along with ultrasonic treatment, which introduces oxygen-containing functional groups to enhance interfacial interaction between CNT and the metal precursor and also increases reaction specificity. In addition, surface modifications, like introducing heteroatoms and phenyl rings containing polymers to the backbone of CNTs by $\pi$–$\pi$ bonding, also enhance the interaction between CNT walls and Pt NPs (Figure 9(ii) A–E). For example, Fang et al.\textsuperscript{98} successfully enhanced the hydrophilicity of the MWCNT through a surfactant-assisted approach to functionalize the MWCNT surface. Then, on the basis of a urea-assisted deposition method, the sodium dodecylsulfate (SDS)-modified MWCNT was further applied as a support for synthesizing Pt NPCs with a loading of 60 wt.% (Figure 9(iii) A). The metal precursors were
much more readily and uniformly anchored on the support with the assistance of SDS on the outer surface of MWCNT. SMSIs were responsible for the uniform deposition of Pt NPs and improvement of mass activity. The calculated ECSA of this high-loading Pt/SDS-MWCNT was 83 m²/gPt, which was about 1.5 times higher than that of commercial J.M. Pt/C (ca. 56 m²/gPt). In H₂-O₂ MEA tests, much lower potential loss was observed in the polarization measurement particularly at high-current-density region, indicating a higher MA and smoother mass transfer due to its one-dimensional nanostructure. In comparison with commercial Pt/C (276 mW/cm²), this high-loading Pt/SDS-MWCNT exhibited a maximum power density of 451 mW/cm² owing to high conductivity of unique 1D nature promoting fast electron transfer in the CL (Figure 9(iii) B-D).

2.2.4 Engineered graphene materials (EGMs)

Since Andre Geim and Konstantin Novoselov successfully separated graphene from graphite by micromechanical exfoliation, researchers have been exploring the application field of graphene due to its specific morphology, physical and chemical properties. Recently, EGMs, including reduced graphene oxide⁹⁹ (Figure 10(ii) A-G) and 3D graphene aerogels, have become widely used support materials and are integrated into LTFCs owing to their excellent properties in terms of high electrical conductivity, electron mobility, and good corrosion resistance.¹⁰⁰ Usually, specific intercalation or surface modification has to be tailored in advance, as graphene sheets are tightly stacked. Covalent or noncovalent engineering processes have been widely accepted as the most effective approaches to modify graphene surface characteristics. For example, Choi et al.¹⁰¹ innovatively developed a catalyst with a Pt loading of 40 to 80 wt.%, in which Pt NPs were deposited over surface-functionalized graphene nanosheets (GNSs). In particular, this GNS support material was prepared from pristine graphite through acid treatment and a subsequent thermal exfoliation process, introducing ether, hydroxyl, carbonyl or carboxylic groups on the support surface. Owing to significant amounts of oxygenated functional groups on GNSs, the catalyst can
maintain uniform, small, and highly concentrated Pt NPs in spite of high metal loading. The TEM images revealed that Pt/GNS with a loading of 40 and 60 wt. % possessed an average Pt NP size of about 1.8 and 2.0 nm, respectively. Even when the catalyst loading increases to 80 wt. %, the Pt NP size grew slightly to 2.9 nm. In another case, Lu et al. utilized a self-assembly route to synthesize Pt NPCs supported on sulfonic acid-grafted reduced graphene oxide (S-rGO). They synthesized Pt/S-rGO catalysts with loadings from 20 to 80 wt. %. TEM micrographs demonstrated that the average particle size only increases slightly with the increase of Pt loadings, and the size dispersion was still uniform and symmetrical even though the loading was up to 80 wt. %. The chronoamperometry measurement was conducted at a constant voltage of 0.6 V to evaluate the catalyst stability. Among four kinds of catalysts (Pt/C, Pt/GO, Pt/rGO, and Pt/S-rGO), this Pt/S-rGO exhibited the slowest current decay with the testing time. This was due to the strong metal-support interaction (SMSI) from the considerable number of grafted sulfonic acid groups.

Usually, a catalyst support material should not only possess a well-functionalized surface but also a 3D porous network structure over multiple length scales to increase specific surface area and reactant accessibility. Recently, methods, like light scribe patterning, organic sol-gel reaction, template-guided growth, and self-assembly technology have been utilized to synthesize 3D graphene aerogels. Chen and coworkers systematically introduced a self-assembly synthetic route for 3D graphene aerogels (Figure 10(i) A-E). With the assistance of sufficient hydrogen bonds, π–π stacking, and Van Der Waals forces, the strong cross-links in the 3D graphene network could be obtained by cautiously assembling fractionally reduced GO. The robust interconnection among graphene layers was expected to prevent the stacking and piling up of graphene, thus, generating abundant large mesopores for metal deposition and mass transport (Figure 10(i) F-I). For example, Huang et al. reported an easy and straightforward one-step coreduction method to prepare Pt NPCs with a loading of 60 wt. % and an average Pt NP size of 3.2 nm by virtue of the combination of excellent intrinsic properties and specific porous structures of 3D graphene aerogels (Figure 10(iii) A). According to the analysis of ORR activity in the Tafel region (0.9 V/RHE), this Pt/GA possessed a 3.7-fold higher MA than that of commercial J.M. Pt/C (Figure 10(iii) B-E). In addition, accelerated stress tests were conducted by potential cycling between 0 and 1.2 V to evaluate the durability of Pt/GA. After 3000 cycles, Pt/GA exhibited a positive shift of 96 mV in ORR overpotential in comparison with 125 mV of commercial
Pt/C, indicating better electrochemically stability within the electrode.

2.2.5 Non-carbon supports (NCSs)

Although carbon-based supports mentioned above have been broadly applied in LTFCs and appropriate graphitization process has been introduced to enhance durability, they are still deemed difficult to meet the critical demands for repeated start/stop cycles and long-term running on vehicles. In comparison with carbon-based supports, noncarbon supports, such as metal oxides (TiO₂, CeO₂, SiO₂), nitrides (TiN, MoN, CrN), carbides (WC, NbC, TiC), and recently emerged novel MXene materials are also appealing owing to their good oxidation resistance, SMSIs, and high corrosion-resistant. Among these materials, metal oxides have been considered the most suitable candidate for widespread application on the support of high-loading catalysts in LTFCs owing to their low cost and excellent electrochemical stability in harsh acidic environment. For example, Ko and coworkers prepared a high surface area HZrO₂ with novel hollow sphere structure as support material for high-loading Pt NPCs. Due to its hydrophilic surface property, the metal loading was able to rise up to 43 wt.%, while Pt NPs were still dispersed uniformly on the support. According to low relative humidity (RH) MEA tests, they obtained a power density of 0.5 and 0.4 W cm⁻² under 40 and 0% RH, respectively. The successful application of this catalyst under low RH was contributed to the excellent capacity of water retention owing to the hollow structure of support, which would spill over water to neighboring Pt NPs. However, metal oxides suffer from the obstacles of low surface area and poor electrical conductivity, thus, chemical surface modifications were considered to be essential for bare metal oxides. Roh and coworkers introduced -SO₃H on SiO₂ and synthesized a Pt/SiO₂-SO₃H catalysts with a loading of 80 wt.%. Owing to the extremely high Pt loading of this catalyst, the electrical conductivity of silica support was considered to be significantly enhanced. The activity of this catalyst was tested in PEMFC, and the authors found that the initial performance achieved 800 mA/cm² at 0.7 V, which was comparable to commercial Pt/C. The stability of this catalyst was also enhanced due to the SMSIs between SiO₂ and Pt NPs. After five cycles in PEMFC, it still exhibited a current density of 350 mA/cm² at 0.7 V.

3 HIGH-LOADING SACS

To overcome the drawbacks of high-loading Pt NPCs, such as high cost and low metal utilization efficiency, high-loading single-atom catalysts (SACs) have recently attracted extensive research attention in electrocatalysis as a new frontier for heterogeneous catalysts due to their high selectivity, stability, catalytic activity, and efficiency in metal atom utilization. The history of using isolated and individual atoms as active species can be traced back to 1995. Thomas and coworkers did pioneering studies on the synthesis of a titanium (Ti) single-site heterogeneous catalyst through grafting metallocene complexes onto mesoporous silica, which was considered to be the first case of isolated atoms being used as active species of heterogeneous catalysts. Since then, a variety of SACs have gradually become mainstream among researchers. By definition, SACs contain only isolated and individual atoms dispersed on the surface of an appropriate substrate. More broadly, SAC refers to atomically dispersed supported metal catalysts, including site-isolated heterogeneous catalysts and single-site heterogeneous catalysts. Figure 11 illustrates the different types of active sites from particle to SAC. Ideally, no spatial ordering or any other types of appreciable interactions will appear among the isolated individual atoms.

However, high atom utilization efficiency along with high surface energy leads to low metal loading of SACs. To enhance the performance of SACs, the common strategy is increasing the loading of SACs or enhancing their intrinsic activity. To accelerate the commercialization of SACs, synthesis of highly stable, atomically dispersed noble metal catalysts with tunable metal loading are in high demand. Herein, recent advances of high-loading SACs for LTFCs are summarized. We focus on universal synthesis strategies, appropriate substrates, and assembling principles for the preparation of SACs with a loading above 2 wt.%. Table 2 summarized recent advances of SACs with metal loading ≥ 2 wt.%.
TABLE 2  Recent advances of SACs with metal loading ≥ 2 wt.%

| Catalysts | Loading [wt.%] | Support materials | Synthetic approaches | Refs. |
|-----------|----------------|-------------------|----------------------|-------|
| Pt1/NPC   | 3.8            | N-doped porous carbon (NPC) | Bottom-up           | 134   |
| Pt/CeO2   | 3              | CeO2              | Bottom-up           | 128   |
| Pt1/HSC   | 5              | High S-content carbon (HSC) | Top-down            | 149   |
| Fe-N-C SA/HCF | 4.8         | Hyphae-derived carbon fibers (HCF) | Top-down            | 120   |
| FeSAs/PTF | 8.3            | Porous porphyrinic triazine-based frameworks (PTF) | Top-down           | 143   |
| Fe-SA-G   | 7.7            | 2D graphene       | Bottom-up           | 146   |
| Fe-LSAs/CN| 2.16           | N-doped porous carbon | Top-down            | 151   |
| Fe3–N-C   | 3.46           | SiO2@ N-doped porous carbon (SiO2@NPC) | Top-down            | 157   |
| Fe–N/C    | 5.86           | Fe-N codoped carbon | Top-down            | 156   |
| Fe–N/CAC  | 12.1           | carbon nitrogen species (CNx) | Top-down           | 121   |
| TimB–Fe5–C| 2.58           | 1,2,4,5-tetramidazolebenzene (TimB)-based frameworks | Top-down           | 155   |
| FeSAs/N–C| 3.5            | N-doped porous carbon nanosheet | Top-down          | 152   |
| Zn–N–C   | 9.33           | N-doped porous carbon | Top-down            | 142   |
| Co SAs/N–C| 4              | N-doped porous carbon | Top-down            | 138   |
| Mo1/OSG   | 10             | Porous oxygen, sulfur-doped graphene (OSG) | Top-down          | 150   |
| Cu–N–C   | 20.9           | Nitrogenated carbon nanosheet | Top-down         | 148   |

coordination or anchor sites and enhancing electrostatic adsorption.118,119 Recently, various approaches like the defect engineering strategy, coordination design strategy, and spatial confinement strategy have been developed to modify the skeleton frame or substrate surface followed by an increase in their loading capacity. For example, Lei et al.120 creatively combined a spatial confinement strategy and a bioconcentration process to prepare a high-loading Fe-N-C SAC. They introduced ferrous glycinate into a fungal structure and developed a Fe-rich hyphae. By pyrolyzing these bioconcentrated Fe-rich hyphae, they finally obtained a highly dispersed Fe-N-C SAC with a high metal loading of 4.8 wt.% and a half-wave potential (\(E_{1/2}\)) of 0.802 V for ORR, which is comparable to commercial Pt/C. In addition, according to durability tests (after 10 000 cycles), the ultimate diffusion current density of this high-loading Fe-N-C SAC only exhibited a decay of 5.6%, indicating its excellent stability. In another case, Zhao et al.121 successfully obtained densely populated Fe-N-C SACs with a loading above 12.1 wt.% via a coordination design strategy. During the synthesis process, they systematically investigated the coordination of metal ions, physical isolation of the chelate complex at high loading, and the binding with N-species at elevated temperature. Apart from excellent ORR activity (\(E_{1/2}: 0.9 \text{ V}; \ E_{\text{onset}}: 0.98 \text{ V}\)), this high-loading Fe-N-C SACs also exhibited negligible degradation for limiting current density and half-wave potential after 5000 cycles.

In 1978, Tauster and coworkers first proposed the concept of SMSI, and early researchers preferred to understand SMSI as an electronic effect, which means the activity, stability, and selectivity of catalysts are intensely impacted by the electron transfer between metal/alloy and support. They classified SMSI into two categories according to the nature and cause of the interaction: (1) surface structural defects and (2) electronic defects.122,123 The former type represents individual atoms are anchored by point defects, surface vacancies, surface steps, or effects like caging and configuring. The latter one highlights the chemisorption behavior, interfacial bonding (M1-M2 or M1-O-M2), and charge transfer between metal atom and support. With these concepts and essential aspects, SMSI has been frequently introduced on developing stable high-loading SACs. For instance, Wei et al.124 developed a NP-to-SA conversion method to obtain stable SAC, in which the SMSI caused by surface structural defects is more thermodynamically stable than the Pd-Pd metal bond. The mobile noble atoms can be captured by the defects of N-doped carbon and form a more stable Pd-N4 structure. Furthermore, to have a more comprehensive understanding of the relationship between material structure and property, renewed attention has been paid to the concept of electronic metal-support interactions (EMSI)125,126 coined by Campbell. Compared with the classic SMSI, an EMSI puts forward a more specific description of the underlying correlation or relationship for specific activity improvements of heterogeneous catalysts. Electronic perturbations, such as shifts in the energy of d-band center (\(\epsilon_d\)) have been proved to have intense impact on catalytic properties of heterogeneous catalysts.127 For example, Kunwar et al.128 reported a high-loading (3 wt.%) and thermally stable Pt single atoms supported on cerium oxide. The strong interaction of Pt precursors with undercoordinated Ce\(^{3+}\)
cations present at CeO$_2$ (111) step edges allows Pt to form a stable square planar configuration, which strengthens sinter resistance of individual Pt atoms. The individual and isolated Pt single atoms were tightly anchored onto the substrate, altering the charge state of Pt atoms by electron transfer from or to the substrate. The effect of EMSI can be interpreted as changes in the $\varepsilon_d$ connected with the Fermi level. The desirable upshift in $\varepsilon_d$ results in significant EMSI and by extension enhanced catalytic properties.\textsuperscript{129}

3.2 Synthesis strategies of high-loading SACs

Recently, strategies like the wet-chemistry method, mass-selected soft-landing (MSSL), atomic layer deposition (ALD),\textsuperscript{130,131} and the pyrolysis method have been applied to synthesizing SACs. Among them, MSSL, ALD, and wet-chemistry methods can be categorized as “bottom-up” strategies, and pyrolysis methods can be classified as “top-down” strategies. For “bottom-up” strategies, the focus is to obtain atomic dispersion of metal precursors and further stabilize the as-formed individual metal atoms on substrates against migration and aggregation.\textsuperscript{132} In contrast, the starting precursors of a “top-down” strategy are generally metal NPs or bulks. The challenge is to break the metal-metal bonds of metal NPs and establish new and stronger bonds between the anchoring sties of substrates and as-formed single metal atoms. Currently, the wet-chemical method (including coprecipitation, impregnation method, and photochemical strategy) and the pyrolysis method are considered the most promising routes owing to their ease of operation and possible production on a large scale. In addition, MSSL and ALD are two powerful deposition methods for synthesizing SACs owing to their ability to regulate the size of metal species with high precision. However, these two techniques typically involve expensive equipment and only afford low yields, which are only appropriate for very low metal loading and often used to provide excellent model SACs for fundamental studies. In this section, simple and low-cost bottom-up and top-down strategies for high-loading SACs are systematically summarized.

3.2.1 Bottom-up strategy

Recent achievements regarding high-loading SACs have heightened the significance of a bottom-up strategy because of its feasibility of commercial application and ease of operation. Commonly, a bottom-up strategy involves adsorption, reduction, and finally confinement by the vacancy defects of the substrates. For example, Liu et al.\textsuperscript{133} prepared a single-anchored pyridinic nitrogen atom, with a cost-effective and durable CB-supported Pt SAC for ORR. Although the catalyst loading is relatively low (0.4 wt.%), the MEA with such a catalyst as cathode delivers a power density above 680 mW/cm$^2$ at 80°C with a Pt CL loading of 0.09 mgPt/cm$^2$. The stability of this Pt SAC was also tested under a constant potential of 0.5 V for 200 h, and the current density only exhibited a decay of 26% at fuel cell temperature of 80°C. This study demonstrates the possibility of applying SACs for practical use, and also highlights the urgency of increasing their metal loading. To overcome this challenge mentioned above, Li and coworkers\textsuperscript{134} developed a modified photochemical solid-phase reduction method to obtain Pt SACs with a loading of 3.8 wt.%, which is anchored on a N-doped carbon (Figure 12(i) F). With the assistance of nitrogen atoms on the carbon surface, this synthesis strategy directly reduced the PtCl$_6^{2-}$ ions to Pt single atoms by ultraviolet irradiation, with no need for any further postphysical or chemical treatment process (Figure 12(i) A). Moreover, the stability of this catalyst was highly enhanced owing to the stable Pt-N$_4$ configuration. According to ADT (3000 CV cycles) results, this Pt SAC only showed a negative shift of 1 mV, which is negligible and much lower than commercial Pt/C (Figure 12(i) B-E). Typically, heteroatoms help ensure that active metal species are firmly adsorbed on the substrate surface, increasing the number of active sites and enhancing their intrinsic reactivity. In a similar case, Han et al.\textsuperscript{135} induced the formation of densely populated Cu single atoms (5.4 wt.%) on an engineered graphene matrix by a specific confined self-initiated dispersing protocol (Figure 12(ii) A). Dicyandiamide was used to create highly active Cu-containing gaseous intermediates, which avoid the sintering of Cu single atoms. Spherical aberration-corrected high-angle annular dark-field scanning transmission electron microscopy (Figure 12(ii) B) and extended X-ray absorption fine structure (EXAFS) measurements were conducted to prove the presence of Cu single atoms and explore their local electronic structure. No obvious Cu-Cu coordination peak was observed at 2.2 Å in the Fourier-transformed EXAFS, indicating that Cu atoms were atomically dispersed (Figure 12(ii) C). In addition, real space multiple scattering program of FEFF9 was applied to fit EXAFS spectroscopy, and they found that Cu atom coordinate with two N atoms (Figure 12(ii) D). Moreover, both chronoamperometry (10 h of constant potential at 0.65 V) and ADT (10 000 cycles between 0.6 and 1.0 V) were conducted to evaluate long-term durability of this Cu SAC. Only less than 7% of current drop was observed for Cu SAC in chronoamperometric test, which was much lower than that of commercial Pt/C (>25%). The $E_{1/2}$ of ORR polarization curve also decreased only 10 mV for Cu SAC, compared to 22 mV loss of commercial Pt/C.
Metal oxide-based substrates are also commonly used for stabilizing high-density single atoms in the wet-chemical method. For example, Liu et al. 136 demonstrated a SAC with Pt loading as high as 5 wt.%, which anchored Pt single atoms on Fe-modified spinel by an incipient wet impregnation method. In this process, the strong interaction between Pt and FeOx species made high loading and thermal stability possible. SMSI is the key issue for high loading and thermally stable SACs. Recently, Liu et al. 137 proposed a general strategy for producing high-loading SACs which started from a well-defined substrate with strong binding to the target metal. They found that for a sufficiently large electrochemical potential window, aggregates of the target metal on substrates leached away, leaving the strongly bound single atoms on the surface (Figure 12(iii) A-C). It revealed that surface properties, carbon divacancies, or unique confined configurations helped anchor mononuclear metal species on substrates due to the coordination between the ligands and surface groups.

### 3.2.2 Top-down strategy

To overcome the drawbacks of the bottom-up strategy, the top-down strategy has been widely applied to the synthesis of high-loading SACs due to its simplicity in controlling synthesis conditions. 138-141 A top-down strategy normally involves a pyrolysis procedure, and the interaction between metal single atoms and the pyrolysis products can be controlled by tuning the temperature cautiously. For example, Li et al. 142 demonstrated a Zn-N-CSAC with a metal loading of 9.33 wt.%. The key point of their strategy was utilizing an extremely low annealing rate of 1°/min, which unexpectedly limited the high volatility of Zn active sites during the high-temperature annealing procedure. The as-synthesized Zn-N-CSAC exhibited better ORR stability than the Fe-N-C SAC and comparable ORR activity in both acidic and alkaline media. According to ADT (1000 CV cycles between 0.6 and 1.1 V) results, this Zn-N-CSAC only showed an $E_{1/2}$ decay of 19.88 mV, much lower than that
of Fe-N-C catalyst prepared at the exactly same annealing rate (31.03 mV). In contrast, Yi et al. developed a highly reactive and stable single-atom Fe catalyst with high Fe loading of 8.3 wt.% via a rapid ionothermal annealing process. The as-synthesized SAC exhibited a half-wave potential $E_{\text{1/2}}$ (0.87V vs. RHE) and onset potential $E_{\text{onset}}$ (1.01V vs. RHE). Nowadays, Hai et al. introduced a universal approach to prepare high-loading SACs, which combined an impregnation method and a two-step annealing process (Figure 13(i) A). By cariously controlling the anchor of metal precursors and conducting a stepwise ligand removal process, their SACs reached an extremely high loading of 23 wt.%. These studies reveal that appropriate temperature control plays a significant role in a top-down strategy.

Coordination environment is remarkably significant when it comes to increasing the active metal density of SACs. Via chemical bonding (ionic and covalent bonding) with surrounding atoms, the electronic and geometric properties of active metal sites are modified and stabilized by the local coordination nature. Adjacent coordinative dopants with lone pairs of electrons, such as N, O, or S, on the substrate surface, are able to develop strong covalent interactions with metal single atoms and induce the variation of oxidation state at the active sites. The coordination number of metal-N is proved to be a significant descriptor of the catalytic activities and structure-performance relationship. For example, Li et al. obtained a Cu SAC with an ultrahigh loading of over 20.9 wt.% by introducing abundant N atoms to an ultrathin two-dimensional carbon matrix. N atoms on the carbon substrate anchored and stabilized the high-density Cu single atomic centers. This Cu-N-C exhibited an $E_{\text{1/2}}$ of 0.869 V in comparison with that of Pt/C (0.838 V), indicating superior activity for ORR. In addition, the author also tested the CO poison effect and chronoamperometry on the Cu-N-C SAC to evaluate its durability. They found that Cu single atoms exhibited no sensitivity to CO and only a current loss of 0.2% was
observed after 10,000 s, much lower than that of commercial Pt/C (53.1%).

Similarly, sulfur atoms on the structural framework could also stabilize the metal in the form of site isolated atoms. Choi et al.\(^\text{149}\) developed a zeolite-templated substrate with abundant sulfur atoms (17 wt.% S) to synthesize an atomically dispersed catalyst with a Pt loading of 5 wt.%. This high-loading Pt SAC exhibited a superb \(E_{\text{onset}}\) of 0.99 V, which is comparable to commercial Pt/C. Moreover, a top-down strategy containing oxygen and sulfur for dual coordination was also carried out to fabricate high-loading SACs. Tang et al.\(^\text{150}\) obtained a high-loading Mo SAC by tuning the local environments and isolation features. This was identified by advanced microscopy and spectroscopy techniques and achieved a metal loading over 10 wt.% because of synergistic dopant-chelating effects. This Mo SAC showed high limiting current density of -2.78 mA/cm\(^2\) at 0.30 V, as well as a high \(E_{\text{onset}}\) of 0.78 V. According to chronoamperometric test at 0.45 V for 8 h, only a current loss of less than 8% was observed.

Atomic dispersion of metal species can also be stabilized by the spatial confined effect (Figure 13(i) B and C), even if high metal loading is present.\(^\text{151,152}\) The metal precursors are commonly accommodated in support with well-defined limited spaces such as 0D nanospheres with micro-/nanopores on the surface, 1D nanotubes (CNTs), 2D nanolayers (montmorillonite and graphite), and 3D architectures with interconnected physical spaces (metal-organic frameworks). The limited spaces of these materials physically prevent the migration and aggregation of metal atoms, and enable the formation of uniform and stable active sites at the atomic level.\(^\text{153,154}\) For example, Lin et al.\(^\text{155}\) designed a novel steric tetra-imidazole structure that contained a benzene ring located in the center of each of the four imidazole groups. This functioned as a sharing side-chain substitution which controlled the distance between each metal rivet center. With the assistance of this unique structure, the migration and aggregation of Fe atoms were effectively impeded. The as-formed atomically dispersed Fe-N\(_4\) catalyst was identified to have a loading of up to 2.58 wt.%. In both acidic and alkaline medium, this high-loading Fe-N-C SAC exhibited comparable \(E_{1/2}\) of 0.78 and 0.89 V to that of commercial Pt/C (0.80 and 0.895 V) for ORR activity. Using a similar method, Ye et al.\(^\text{156}\) synthesized a Fe-N-C SAC with a loading of up to 5.86 wt.% by using ZIF-8 to adsorb and confine gas-phase ferrocene molecules with a cage-confinement synthesis strategy (Figure 13(ii)). This Fe-N-C SAC displayed an outstanding ORR activity with an \(E_{1/2}\) of 0.85 V. Moreover, according to ADT tests, a subtle current decay of 10 mV in \(E_{1/2}\) was observed after 10,000 CV cycles between 0.6 and 1.0 V.

Researchers also combined the spatial confined effect with strong interaction from surface heteroatoms. For example, Zhang et al.\(^\text{157}\) developed a unique hierarchical carbon nanocage with nitrogen dopants on its edges to support Pt single atoms. By the synergy of nitrogen anchoring and micropore trapping, they were able to construct a high Pt loading (2.92 wt.%) SAC even with a simple impregnation-adsorption strategy. Similarly, Jiao et al.\(^\text{158}\) developed a dual-protection pyrolysis method to synthesize a Fe SAC with a loading of 3.46 wt.%, in which the precursor was a SiO\(_2\)-@MOF composite (Figure 13(iii) A). During the pyrolysis process, N atoms in a porphyrin MOF anchored with the spatial isolated Fe atom acted as the first protective barrier to prevent Fe aggregation. Meanwhile, the SiO\(_2\) introduced in MOF pores developed a strong interaction with Fe atoms and helped to stabilize highly loaded SACs. The Fourier-transformed EXAFS of this Fe-N-C SAC exhibited a dominated Fe-N peak at 1.4 Å, indicating the strong interaction between Fe and N atoms. In addition, no obvious Fe-Fe bond at around 2.2 Å was observed, demonstrating that Fe atoms were atomically dispersed (Figure 13(iii) B). Moreover, according to RDE and MEA tests, this Fe-N-C SAC exhibited excellent performance with a high \(E_{1/2}\) of 0.80 V and considerable a peak power density of 0.68 W/cm\(^2\), respectively (Figure 13(iii) C-E). Durability tests indicated that a current density of 0.3 A/cm\(^2\) at 0.5 V was able to maintain about 20 h.

4 | CONCLUSIONS AND PERSPECTIVES

In this review, recent advances of high-loading Pt NPCs and SACs for LTFCs have been summarized and classified. In particular, efforts are concentrated on systematically reviewing support materials and synthesis strategies of Pt NPCs with a metal loading over 40 wt.% and SACs with a metal loading over 2 wt.%. For high-loading Pt NPCs, traditional impregnation and colloidal methods were modified or improved to increase metal loading as well as to keep metal atoms well-dispersed. The influences of high surface area and appropriate surface functionalization for support materials were also highlighted. For high-loading SACs, approaches, like anchoring at coordination sites, enhancing metal-support interactions, spatial confinement, and mitigating thermal motion of molecules, were applied to inhibit metal migration and agglomeration. Although support design and innovative methods of synthesizing high-loading Pt NPCs and SACs have seen great progress, many following challenges and opportunities still need to be settled in LTFCs:

1. **High-loading Pt NPCs**: Electrocatalytic activity and metal utilization efficiency of high-loading Pt NPCs need to be boosted further. The increased metal loading
cannot sacrifice catalytic mass activity, which means that the power density generated per μgPt should be optimized when applied in a MEA. In addition, the costs of Pt NPCs have to be further minimized. Developing well-designed approaches to reduce the use of noble metals is also urgent. To date, focus has been placed on exploring new approaches of constructing core-shell or hollow Pt-based nanostructures using cheaper and more durable transition metals. Furthermore, to meet the requirements for practical applications and fundamental research, the production of high-loading Pt NPCs at a gram-scale or even kilogram-scale is also currently a major challenge.

(2) High-loading SACs: The preparation strategies of high-loading SACs are still complex and difficult to scale up. Therefore, developing simple methods suitable for large-scale production is currently the major direction in the synthesis of SACs with high metal loading. Moreover, dual SACs and single-atom alloy catalysts have recently become new popular research thrusts in the field of SACs. The electrochemical properties of these catalysts have been tailored via alloy bonding. When the metal type is extended to transition metals or even rare earths, the coexistence of two metal species or metal dimers renders excellent performance due to the synergistic effect. Thus, it is expected that the number of applications of high-loading dual SACs and single-atom alloy catalysts will continue to expand so as to further encourage reduction in the thickness of MEAs prepared by SACs.

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CONFLICT OF INTEREST
The authors declare no conflict of interest.

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