Pt-Based Catalysts in Proton Exchange Membrane Fuel Cells

Subjects: Electrochemistry

Contributor: Hongda Li , Hao Zhao , Boran Tao , Guoxiao Xu , Shaonan Gu , Guofu Wang , Haixin Chang

Proton exchange membrane fuel cells (PEMFCs) have attracted extensive attention because of their high efficiency, environmental friendliness, and lack of noise pollution. However, PEMFCs still face many difficulties in practical application, such as insufficient power density, high cost, and poor durability. The main reason for these difficulties is the slow oxygen reduction reaction (ORR) on the cathode due to the insufficient stability and catalytic activity of the catalyst. It is very important to develop advanced platinum (Pt)-based catalysts to realize low Pt loads and long-term operation of membrane electrode assembly (MEA) modules to improve the performance of PEMFC. By designing the structure of a Pt-based catalyst, it can be generated on a special surface structure, so as to boost the stability and activity of Pt-based catalysts, such as low-dimensional nanostructures (e.g., two-dimensional nanoplates and one-dimensional nanowires). These structures not only have high conductivity, but can also make sure the nanocrystals are fully in contact with the support and effectively inhibit Ostwald ripening, with excellent stability.

Pt-based catalysts
oxygen reduction reaction (ORR)
catalytic layer
proton exchange membrane fuel cell (PEMFC)

1. Introduction

Fossil fuels and massive energy consumption, as well as the consequent serious climate and environmental issues, pose a serious threat to the sustainable development of human society. In this regard, the utilization and development of clean energy has gradually spread across the globe. In addition to the common photovoltaic power stations and solar thermal power stations, researchers are slowly turning their attention to fuel cells [1][2][3][4]. Fuel cells can be divided into alkaline fuel cells (AFCs) [5][6][7], phosphoric acid fuel cells (PAFCs) [8][9][10], solid oxide fuel cells (SOFCs) [11][12][13], molten carbonate fuel cells (MCFCs) [14][15][16] and proton exchange membrane fuel cells (PEMFCs) [17][18][19] according to different electrolytes. In addition to the general characteristics of fuel cells, PEMFCs also have the outstanding advantages of fast response, low operating temperature, high energy conversion efficiency and high power density. A PEMFC is an energy conversion device that converts hydrogen energy into electric energy effectively through electrochemical reactions, and which can effectively alleviate the problems of global warming and fossil energy shortage. However, all the commercial PEMFC catalysts used are Pt-based catalysts, which are expensive; the stability and activity of the catalysts need to be improved, and the hydrophobic/hydrophilic balance in the catalytic layer (CL) greatly limits their application. It is of great significance to improve the overall performance of PEMFCs by improving the stability and activity of catalysts, minimizing the Pt load, optimizing the structure of each functional layer, and reducing the transmission resistance between the CL and the proton exchange membrane (PEM).

2. Design Principle of Pt-Based Catalysts

The ORR on the cathode of a PEMFC is a complex reaction process involving multiple elemental reactions. In the whole reaction process, there are multiple reaction pathways (such as direct reaction pathway and continuous reaction pathway) and reactions of various intermediates (such as O_2^{2-}, O^{2-}, H_2O_2, surface Pt-O and Pt-OH). The specific reaction mechanisms are still unclear. However, through many researchers' theoretical and experimental studies on ORR, a practical and significant theoretical basis has been obtained for the mechanism of ORR. At present, researchers generally believe that ORR mainly takes two paths [20][21]. One is a direct four-electron pathway, in which O_2 reacts directly into H_2O under the action of catalyst; the reaction mechanism equation is as follows: [$O_2 + 4H^+ + 4e^- \rightarrow 2H_2O$, $E^0 = 1.229$ V]. The other is the indirect two-electron pathway; under the action of the catalyst, O_2 is first converted into the intermediate product H_2O_2, and then continues to obtain the electron reaction to generate H_2O; the reaction mechanism equation is as follows: [$O_2 + 2H^+ + 2e^- \rightarrow H_2O$, $E^0 = 0.67$ V], [$H_2O_2 + 2H^+ + 2e^- \rightarrow H_2O$, $E^0 = 1.77$ V].

Theoretical and experimental studies have found that in either four- or two-electronic pathways, the chemical bond of oxygen in the initial reaction will be broken. As a result, the reduction potential of the four-electronic pathway is higher than the two-electronic pathway, and the dissociation of the O-O bonds in O_2 is higher than that in H_2O_2, thus the two-electron pathway with low catalytic activity tends to occur. However, the actual reaction is much more complicated, and the oxidation reaction at the cathode may be a mixture of two and four electrons. For PEMFC, the operation of the electric potential and current efficiency are higher when the electrode reaction is carried out in a four-electron pathway, which can avoid the influence of H_2O_2 produced by the indirect two-electron pathway on the proton membrane. Therefore, the four-electron pathway is also considered to be a more effective ORR process [20].

In PEMFC, the main obstacle limiting its discharge performance is the slow ORR on the cathode. The reaction cannot meet the discharge requirements of PEMFC without external force, but can be carried out with the ORR smoothly under the action of appropriate catalysts. Pt has been used as an electrocatalyst for PEMFC for decades due to its unique properties of accelerating ORR reactions [22]. Compared with other single-element catalysts (Ag, Pd, Au, Cu, Co and Ni, etc.), Pt has special electronic properties and has moderate interactions with oxygen-containing substances, so it is more favorable to catalyze ORR [23]. The ORR activity can also be reflected according to the binding capacity of single element catalyst with O or OH.

In practical applications, strain effect and ligand effect often act synergically on Pt-based catalysts. Strain effect enhances the performance of Pt-based catalysts by adjusting the distance between Pt atoms to change their electronic structure. In addition, the ligand effect can effectively reduce the difference of electronegativity and mean the whole catalyst is in the lowest energy state, thus developing a novel approach to boost the catalytic performance [24]. Synergistic effects often occur in the interface construction between Pt-based nanomaterials and other components, such as Pt and metal, Pt and support, and Pt and other compounds [25].

3. Controllable Preparation of Pt-Based ORR Catalysts

So far, the studies on the stability and activity of Pt-based catalysts have mainly looked at the following four aspects:

(1) The development and design of novel Pt-based nanocatalysts with more stable structure and more efficient performance, such as porous nanowires [26], hollow nanostructures [27] and highly open nanoframes [28].

(2) The activity of a Pt-based catalyst is closely related to the crystal face structure. The crystal face exposed by the Pt-based catalyst determines the atomic arrangement and electronic structure of the surface, which directly affects the electrochemical adsorption and decomposition of reactant molecules in the catalytic reaction process [29].

(3) To enhance the intrinsic activity of Pt (increase the unit activity of Pt), the way to change the intrinsic activity of Pt itself is usually alloying, by introducing another or more transition metal elements, such as Cu, Cr, Co, Ni, Fe and other metal elements, to build a Pt-based alloy, heterogeneous structure or core-shell type [30][31].

(4) More and more new support materials have attracted the attention of researchers, such as composite materials or ceramic materials with better stability than carbon materials. The physicochemical properties and structure of the surface of such support materials play an important role in the stability and activity of the final catalyst. Moreover, the interactions between the Pt-based NPs and the supports help to regulate the electronic structure of Pt, thus further enhancing the catalytic performance of Pt-based NPs [32].

3.1. Structural Control of Pt-Based Catalysts

In commercial applications, Pt/C catalysts are commonly used in the cathodes of PEMFCs, as they have 2–3-times more catalytic activity than that of pure Pt, but this is far from expected. The Pt/C catalyst still has obvious disadvantages [33], such as high cost, easy CO poisoning, poor stability and other problems. In order to further enhance the stability and catalytic activity of Pt-based catalysts, researchers have developed Pt-based NPs with special structures, which typically have more than 10-times higher ORR mass activity than Pt [34]. At present, Pt-based catalysts can be divided into one-dimensional (1D) nanowires/nanotubes, two-dimensional (2D) nanoplates, three-dimensional (3D) polyhedrons, nanoframes and other special structures according to their different structures [35].

Low-dimensional Pt-based nanomaterials (e.g., nanowires and nanoplates) have been widely used in electrocatalysis and energy conversion due to their special atomic arrangement and electronic structure as well as good solubility and aggregation [36]. Results show that the combination of the porous metal structure and one-dimensional nanostructure is an effective method to enhance the stability and activity of Pt-based catalysts [37][38]. A porous metal structure is a very efficient structure which can provide high specific surface area and abundant catalytic active sites. The porous structure not only enhances the efficiency of Pt, but also inherits the high conductivity of the Pt, thus maximizing the electron transfer rate in the porous nanostructures [39][40]. However, the porous metal structures tend to be less stable, often in the form of NPs, which can easily agglomerate or detach from the supports [41][42][43]. The anisotropic structure of 1D nanowires can ensure sufficient contact with nanocrystals and support, which is conducive to inhibiting the agglomeration, separation and Ostwald ripening of the nanocrystals in the reaction process, thus improving the stability [44].

3.2. Morphology Control of Pt-Based Catalysts

For Pt-based ORR catalysts, the preparation of different morphologies is mainly to expose more highly active sites and thus improve the catalytic activity. In addition, Pt atoms on the surface of Pt nanocrystals of different morphologies are also arranged in different ways. For example, a Pt octahedron is dominated by Pt (111), a Pt cube is dominated by Pt (100), and a Pt concave cube is dominated by Pt (110). Common pure Pt polyhedral NPs [45]. Due to the different catalytic activity of Pt atoms on different crystal faces, the order of ORR activity of Pt atoms on different crystal faces is Pt (110) > Pt (111) > Pt (100) in non-adsorbent electrolytes (0.1 M $HClO_4$ electrolyte), but the order of ORR activity of Pt atoms on polyhedral Pt-based catalysts is not the same, such as Pt_3Ni catalysts.

Based on Pt crystal nucleation growth theory, the control experiment in the process of experimental conditions such as reactant concentration, reaction time and reaction temperature, etc., can effectively affect the growth of crystal nucleation thermodynamics and dynamic factors in the process of crystal nucleus to control the initial topography and Pt-accumulated growth process, and end up with a different morphology of Pt NPs.

3.3. Composition Control of Pt-Based Catalysts

Although Pt is an ideal material for electrocatalysis, its high cost and scarcity limit the commercial application of PEMFC [46][47]. In order to improve the stability and activity of ORR, the electronic structure of Pt needs to be adjusted to solve the key problems of the surface adsorption of various oxygen-containing intermediates in the ORR process. Researchers have developed a series of Pt-based alloy catalysts for PEMFCs, which were alloyed with transition metals (e.g., Zn, Cu, Ni, Co, Fe, Mn, etc.) to change the atomic arrangement of the d-band center of Pt and the catalyst surface, thus changing the chemisorption state of oxygen-containing species on the surface of catalysts [48]. The introduction of transition metals not only effectively reduces the cost of Pt-based catalysts, but also makes their catalytic activity much higher than Pt/C catalysts due to the interaction of strain effect and ligand effect [24][31][49][50].

Pt-based alloys are usually disordered structures with Pt and transition metals randomly distributed in NPs. However, acidic environments ($pH < 1$) and high chemical potentials ($>0.7\ V_{RHE}$) can lead to the dissolution and oxidation of transition metals, thus reducing the overall activity of the catalyst [51][52]. Therefore, the ordered Pt-based alloy catalysts, such as Pt_3Co [53][54], Pt_3Fe [55][56], Pt_3Cu [57][58], etc., have attracted more and more attention. Compared to the disordered structure, the ordered Pt-based alloy catalyst has a high degree of alloying, definite composition and structure, and electronic properties, so this type of Pt alloy generally has higher electrochemical stability.

In addition to the ordering process, researchers have also developed a new type of catalyst—Pt-based core-shell catalyst [59][60][61]. This catalyst can solve the previous problems effectively, requiring only a tiny amount of Pt to cover the NP surface and protect the transition metals that are easily soluble on the NP surface. The core-shell type catalyst design is very effective, because the electrochemical reaction occurs only on the surface layer of the NPs [51].

3.4. Optimization of Pt-Based Catalyst Supports

It is well known that the catalyst support plays a key role in regulating the activity and durability of catalysts [62][63][64]. At present, carbon black materials (such as Ketjen Black and Vulcan XC-72, etc.) have been widely used as PEMFC catalyst supports due to their advantages of high conductivity, high active area, porous structure, good stability in acidic and alkaline media, and relatively low price [50][65][66]. However, in the case of PEMFCs running for a long time, the charcoal supports easily form oxygen-containing groups on the catalyst support surface, which will reduce the conductivity of the catalyst and lead to serious sintering of catalyst NPs. In addition, the oxygen-containing groups also improve the hydrophilicity of the supports, thereby affecting the air permeability and drainage performance [67].

4. Effect of CL Structure on the Performance of MEA

The MEA modules of PEMFC are composed of catalytic layers (CLs), polymer electrolyte membranes (PEMs) and gas diffusion layers (GDLs) on both sides of the membrane [68]. The electrochemical reaction of the PEMFC occurs in the MEA. Specifically, the reaction gases H_2 and O_2 are transferred to the CLs at the anode and cathode through the diffusion layers, respectively. H_2 is oxidized to protons on the anode, while O_2 will be reduced to oxygen ions on the cathode, and combine with protons transferred from the anode side to form water molecules [69]. Although the operation of PEMFC requires water to ensure adequate electrical conductivity, the reaction can be hampered if excess liquid water is not properly treated. Therefore, researchers have attempted to improve the performance of the membrane electrode by constructing a cathodic catalytic layer (CCL) with a special structure to achieve a hydrophilic/hydrophobic balance or adding hydrophobic materials to improve its hydrophobicity [70].

The electrochemical reaction on the MEA of PEMFC is a multiphase reaction, which is carried out on the three-phase boundary (TPB) formed by electrolytes, reaction gas (oxygen/air and hydrogen) and catalysts. Because PEMFC adopts solid electrolytes, its sulfonate radical is fixed on the resin of PEM and will not invade the electrode; the TPB of the reaction is limited to the part where the reaction layer contacts the PEM. Only the surface of CL and PEM can effectively conduct protons. Therefore, in order to ensure that the reaction takes place in the electrode CL, it is necessary to establish ion channels in the CL. Moreover, since the reaction requires gas reactants to reach the catalyst surface and the generated water to leave the surface quickly, it also requires that the CL has hydrophobic channels. In addition, the ionomers in the CLs will occupy part of the pores, so it is necessary to adjust the content and distribution structure of ionomers in the CL to meet the needs of proton conduction and prevent too many ionomers from reducing the porosity of the CL and affecting the transmission of O_2. The ideal catalytic layer should have an excellent electrochemical three-phase interfacial reaction region, allowing good transfer and transport of electrons, protons, oxygen, and water [71]. Thus, it is necessary to improve the CL structure, among which the gradient structure and the ordered structure design are very effective approaches.

4.1. Gradient Catalyst Layer Structure

In the CL, poly tetra fluoroethylene (PTFE) and ionic conductive polymers (such as Nafion) are commonly used as binders. The content of the binder affects the gas permeability, catalytic activity and ionic conductivity of the CL [72]. If the Nafion content is too low, the ionic conductivity of CL will be insufficient, resulting in low Pt utilization and high impedance. In contrast, too much Nafion will fill the pores in the layer, affecting the gas transport and electron conduction of the CL [73]. Therefore, Nafion content in the CL should be controllable within a reasonable range, and its distribution should be gradient design.

4.2. Ordered Catalyst Layer Structure

At present, the effects of the catalyst-coated membrane (CCM) [74][75][76][77], gradient catalyst layer structure [78][79] and ordered catalyst layer structure on the performance of MEA have been studied, and some achievements have been made. CCM directly coats the catalyst ink on both sides of the PEM to form CLs, which can effectively improve the catalyst utilization rate and greatly reduce the proton transfer resistance between PEM and CL. The gradient concentration CL was designed to better balance the relationship between operating conditions and electrode structures, electrode performance and precious metal load. However, both the catalyst-coating catalytic layer and the gradient concentration design catalytic layer have shortcomings. The disorder of multiphase transport channels of electrons, protons, water, gas and others will increase the mass transfer resistance and greatly reduce the utilization efficiency of catalysts [80]. Therefore, it is of great significance to study the structure of ordered catalytic layers in order to reduce the amount of Pt, enhance the utilization efficiency of catalysts and increase the three-phase interfaces of reactions.

The concept of ordered membrane electrodes was first proposed by Middelman et al. [81]. In the process of CLs preparation, porous ordered structure and nanoarray structure were introduced to achieve the separation and ordering of mass transfer channels, protons and electrons. The three-phase reaction interface of the electrodes was utilized to the maximum extent, the content of precious metal Pt was effectively reduced, and the stability of the electrode structure was improved. In recent years, with the deepening of research, other ordered membrane electrodes have appeared, such as carbon nanotubes/nanowires arrays, metal oxide arrays, conductive polymer arrays as the support or Pt nanostructure arrays directly as the electrode, which have different characteristics and disadvantages.

References

1. Staffell, I.; Scamman, D.; Velazquez Abad, A.; Balcombe, P.; Dodds, P.E.; Ekins, P.; Shah, N.; Ward, K.R. The role of hydrogen and fuel cells in the global energy system. Energy Environ. Sci.

2019, 12, 463–491.

2. Zhao, J.; Dong, K.; Dong, X.; Shahbaz, M. How renewable energy alleviate energy poverty? A global analysis. Renew. Energy 2022, 186, 299–311.
3. Yuan, X.; Su, C.-W.; Umar, M.; Shao, X.; Lobonţ, O.-R. The race to zero emissions: Can renewable energy be the path to carbon neutrality? J. Environ. Manag. 2022, 308, 114648.
4. Abdelkareem, M.A.; Elsaid, K.; Wilberforce, T.; Kamil, M.; Sayed, E.T.; Olabi, A. Environmental aspects of fuel cells: A review. Sci. Total. Environ. 2020, 752, 141803.
5. Ferriday, T.; Middleton, P.H. Alkaline fuel cell technology—A review. Int. J. Hydrog. Energy 2021, 46, 18489–18510.
6. Wang, Z.; Zhang, X.; Rezazadeh, A. Hydrogen fuel and electricity generation from a new hybrid energy system based on wind and solar energies and alkaline fuel cell. Energy Rep. 2021, 7, 2594–2604.
7. Firouzjaie, H.A.; Mustain, W.E. Catalytic Advantages, Challenges, and Priorities in Alkaline Membrane Fuel Cells. ACS Catal. 2019, 10, 225–234.
8. Park, C.; Jung, Y.; Lim, K.; Kim, B.; Kang, Y.; Ju, H. Analysis of a phosphoric acid fuel cell-based multi-energy hub system for heat, power, and hydrogen generation. Appl. Therm. Eng. 2021, 189, 116715.
9. Cheng, S.; Zhao, G.; Gao, M.; Shi, Y.; Huang, M.; Marefati, M. A new hybrid solar photovoltaic/phosphoric acid fuel cell and energy storage system; Energy and Exergy performance. Int. J. Hydrog. Energy 2020, 46, 8048–8066.
10. Wu, M.; Zhang, H.; Zhao, J.; Wang, F.; Yuan, J. Performance analyzes of an integrated phosphoric acid fuel cell and thermoelectric device system for power and cooling cogeneration. Int. J. Refrig. 2018, 89, 61–69.
11. Peng, J.; Huang, J.; Wu, X.-L.; Xu, Y.-W.; Chen, H.; Li, X. Solid oxide fuel cell (SOFC) performance evaluation, fault diagnosis and health control: A review. J. Power Sources 2021, 505, 230058.
12. Golkhatmi, S.Z.; Asghar, M.I.; Lund, P.D. A review on solid oxide fuel cell durability: Latest progress, mechanisms, and study tools. Renew. Sustain. Energy Rev. 2022, 161, 112339.
13. Singh, M.; Zappa, D.; Comini, E. Solid oxide fuel cell: Decade of progress, future perspectives and challenges. Int. J. Hydrog. Energy 2021, 46, 27643–27674.
14. Wejrzanowski, T.; Cwieka, K.; Skibinski, J.; Lysik, A.; Ibrahim, S.H.; Milewski, J.; Xing, W.; Lee, C.G. Microstructure driven design of porous electrodes for molten carbonate fuel cell application: Recent progress. Int. J. Hydrog. Energy 2020, 45, 25719–25732.

15. Haghghi, M.A.; Shamsaiee, M.; Holagh, S.G.; Chitsaz, A.; Rosen, M.A. Thermodynamic, exergoeconomic, and environmental evaluation of a new multi-generation system driven by a molten carbonate fuel cell for production of cooling, heating, electricity, and freshwater. Energy Convers. Manag. 2019, 199, 112040.
16. Mehmeti, A.; Pérez-Trujillo, J.P.; Elizalde-Blancas, F.; Angelis-Dimakis, A.; McPhail, S.J. Exergetic, environmental and economic sustainability assessment of stationary Molten Carbonate Fuel Cells. Energy Convers. Manag. 2018, 168, 276–287.
17. Jiao, K.; Xuan, J.; Du, Q.; Bao, Z.; Xie, B.; Wang, B.; Zhao, Y.; Fan, L.; Wang, H.; Hou, Z.; et al. Designing the next generation of proton-exchange membrane fuel cells. Nature 2021, 595, 361–369.
18. Xiao, F.; Wang, Y.; Wu, Z.; Chen, G.; Yang, F.; Zhu, S.; Siddharth, K.; Kong, Z.; Lu, A.; Li, J.; et al. Recent Advances in Electrocatalysts for Proton Exchange Membrane Fuel Cells and Alkaline Membrane Fuel Cells. Adv. Mater. 2021, 33, e2006292.
19. Wang, X.X.; Swihart, M.T.; Wu, G. Achievements, challenges and perspectives on cathode catalysts in proton exchange membrane fuel cells for transportation. Nat. Catal. 2019, 2, 578–589.
20. Sui, S.; Wang, X.; Zhou, X.; Su, Y.; Riffat, S.; Liu, C.-J. A comprehensive review of Pt electrocatalysts for the oxygen reduction reaction: Nanostructure, activity, mechanism and carbon support in PEM fuel cells. J. Mater. Chem. A 2016, 5, 1808–1825.
21. Wang, Y.-J.; Zhao, N.; Fang, B.; Li, H.; Bi, X.T.; Wang, H. Carbon-Supported Pt-Based Alloy Electrocatalysts for the Oxygen Reduction Reaction in Polymer Electrolyte Membrane Fuel Cells: Particle Size, Shape, and Composition Manipulation and Their Impact to Activity. Chem. Rev. 2015, 115, 3433–3467.
22. Cruz-Martínez, H.; Rojas-Chávez, H.; Matadamas-Ortiz, P.T.; Ortiz-Herrera, J.C.; López-Chávez, E.; Solorza-Feria, O.; Medina, D.I. Current progress of Pt-based ORR electrocatalysts for PEMFCs: An integrated view combining theory and experiment. Mater. Today Phys. 2021, 19, 100406.
23. Lima, F.H.B.; Zhang, J.; Shao, M.H.; Sasaki, K.; Vukmirovic, M.B.; Ticianelli, E.A.; Adzic, R.R. Catalytic Activity—d-Band Center Correlation for the O2 Reduction Reaction on Platinum in Alkaline Solutions. J. Phys. Chem. C 2006, 111, 404–410.
24. Wang, Y.; Wang, D.; Li, Y. A fundamental comprehension and recent progress in advanced Pt-based ORR nanocatalysts. SmartMat 2021, 2, 56–75.
25. Shao, Q.; Wang, P.; Huang, X. Opportunities and Challenges of Interface Engineering in Bimetallic Nanostructure for Enhanced Electrocatalysis. Adv. Funct. Mater. 2019, 29, 1806419.

26. Mi, S.; Cheng, N.; Jiang, H.; Li, C. Porous Pt3Ni with enhanced activity and durability towards oxygen reduction reaction. RSC Adv. 2018, 8, 15344–15351.
27. Asset, T.; Chattot, R.; Fontana, M.; Mercier-Guyon, B.; Job, N.; Dubau, L.; Maillard, F. A Review on Recent Developments and Prospects for the Oxygen Reduction Reaction on Hollow Pt-alloy Nanoparticles. ChemPhysChem 2018, 19, 1552–1567.
28. Chen, S.; Li, M.; Gao, M.; Jin, J.; van Spronsen, M.; Salmeron, M.B.; Yang, P. High-Performance Pt–Co Nanoframes for Fuel-Cell Electrocatalysis. Nano Lett. 2020, 20, 1974–1979.
29. Nakamoto, T.; Seki, R.; Motomiya, K.-I.; Yokoyama, S.; Tohji, K.; Takahashi, H. Morphological control of carbon-supported Pt-based nanoparticles via one-step synthesis. Nano-Struct. Nano-Objects 2020, 22, 100443.
30. Kim, M.; Lee, C.; Ko, S.M.; Nam, J.-M. Metal alloy hybrid nanoparticles with enhanced catalytic activities in fuel cell applications. J. Solid State Chem. 2019, 270, 295–303.
31. Zhao, Z.; Chen, C.; Liu, Z.; Huang, J.; Wu, M.; Liu, H.; Li, Y.; Huang, Y. Pt-Based Nanocrystal for Electrocatalytic Oxygen Reduction. Adv. Mater. 2019, 31, 1808115.
32. Lori, O.; Elbaz, L. Recent Advances in Synthesis and Utilization of Ultra-low Loading of Precious Metal-based Catalysts for Fuel Cells. ChemCatChem 2020, 12, 3434–3446.
33. Ren, X.; Wang, Y.; Liu, A.; Zhang, Z.; Lv, Q.; Liu, B. Current progress and performance improvement of Pt/C catalysts for fuel cells. J. Mater. Chem. A 2020, 8, 24284–24306.
34. Lin, R.; Cai, X.; Zeng, H.; Yu, Z. Stability of High-Performance Pt-Based Catalysts for Oxygen Reduction Reactions. Adv. Mater. 2018, 30, e1705332.
35. Huang, L.; Zaman, S.; Tian, X.; Wang, Z.; Fang, W.; Xia, B.Y. Advanced Platinum-Based Oxygen Reduction Electrocatalysts for Fuel Cells. Accounts Chem. Res. 2021, 54, 311–322.
36. Li, X.; Wang, J. One-dimensional and two-dimensional synergized nanostructures for high-performing energy storage and conversion. InfoMat 2019, 2, 3–32.
37. Li, M.; Zhao, Z.; Cheng, T.; Fortunelli, A.; Chen, C.-Y.; Yu, R.; Zhang, Q.; Gu, L.; Boris, V.M.; Lin, Z.; et al. Ultrafine jagged platinum nanowires enable ultrahigh mass activity for the oxygen reduction reaction. Science 2016, 354, 1414–1419.
38. Niu, H.; Xia, C.; Huang, L.; Zaman, S.; Maiyalagan, T.; Guo, W.; You, B.; Xia, B.Y. Rational design and synthesis of one-dimensional platinum-based nanostructures for oxygen-reduction electrocatalysis. Chin. J. Catal. 2022, 43, 1459–1472.
39. Li, C.; Tan, H.; Lin, J.; Luo, X.; Wang, S.; You, J.; Kang, Y.-M.; Bando, Y.; Yamauchi, Y.; Kim, J. Emerging Pt-based electrocatalysts with highly open nanoarchitectures for boosting oxygen reduction reaction. Nano Today 2018, 21, 91–105.

40. Cao, H.; Cao, J.; Wang, F.; Di, S.; Zhu, H.; Pu, M.; Bulanova, A. Composition-tunable PtCu porous nanowires as highly active and durable catalyst for oxygen reduction reaction. Int. J. Hydrog. Energy 2021, 46, 18284–18293.
41. He, D.S.; He, D.; Wang, J.; Lin, Y.; Yin, P.; Hong, X.; Wu, Y.; Li, Y. Ultrathin Icosahedral Pt-Enriched Nanocage with Excellent Oxygen Reduction Reaction Activity. J. Am. Chem. Soc. 2016, 138, 1494–1497.
42. Zhang, L.; Roling, L.T.; Wang, X.; Vara, M.; Chi, M.; Liu, J.; Choi, S.-I.; Park, J.; Herron, J.A.; Xie, Z.; et al. Platinum-based nanocages with subnanometer-thick walls and well-defined, controllable facets. Science 2015, 349, 412–416.
43. Wang, L.; Yamauchi, Y. Metallic Nanocages: Synthesis of Bimetallic Pt–Pd Hollow Nanoparticles with Dendritic Shells by Selective Chemical Etching. J. Am. Chem. Soc. 2013, 135, 16762–16765.
44. Zeng, Z.; Xu, R.; Zhao, H.; Zhang, H.; Liu, L.; Xu, S.; Lei, Y. Exploration of nanowire- and nanotube-based electrocatalysts for oxygen reduction and oxygen evolution reaction. Mater. Today Nano 2018, 3, 54–68.
45. Kang, Y.; Li, M.; Cai, Y.; Cargnello, M.; Diaz, R.E.; Gordon, T.R.; Wieder, N.L.; Adzic, R.R.; Gorte, R.J.; Stach, E.A.; et al. Heterogeneous Catalysts Need Not Be so “Heterogeneous”: Monodisperse Pt Nanocrystals by Combining Shape-Controlled Synthesis and Purification by Colloidal Recrystallization. J. Am. Chem. Soc. 2013, 135, 2741–2747.
46. Yi, S.; Jiang, H.; Bao, X.; Zou, S.; Liao, J.; Zhang, Z. Recent progress of Pt-based catalysts for oxygen reduction reaction in preparation strategies and catalytic mechanism. J. Electroanal. Chem. 2019, 848, 113279.
47. Zhang, X.; Li, H.; Yang, J.; Lei, Y.; Wang, C.; Wang, J.; Tang, Y.; Mao, Z. Recent advances in Pt-based electrocatalysts for PEMFCs. RSC Adv. 2021, 11, 13316–13328.
48. Wang, X.X.; Sokolowski, J.; Liu, H.; Wu, G. Pt alloy oxygen-reduction electrocatalysts: Synthesis, structure, and property. Chin. J. Catal. 2020, 41, 739–755.
49. Han, X.F.; Batool, N.; Wang, W.T.; Teng, H.T.; Zhang, L.; Yang, R.; Tian, J.H. Templated-Assisted Synthesis of Structurally Ordered Intermetallic Pt3Co with Ultralow Loading Supported on 3D Porous Carbon for Oxygen Reduction Reaction. ACS Appl Mater Interfaces 2021, 13, 37133–37141.
50. Hou, J.; Yang, M.; Ke, C.; Wei, G.; Priest, C.; Qiao, Z.; Wu, G.; Zhang, J. Platinum-group-metal catalysts for proton exchange membrane fuel cells: From catalyst design to electrode structure optimization. EnergyChem 2019, 2, 100023.
51. Jung, N.; Chung, D.Y.; Ryu, J.; Yoo, S.J.; Sung, Y.-E. Pt-based nanoarchitecture and catalyst design for fuel cell applications. Nano Today 2014, 9, 433–456.

52. Gao, P.; Pu, M.; Chen, Q.; Zhu, H. Pt-Based Intermetallic Nanocrystals in Cathode Catalysts for Proton Exchange Membrane Fuel Cells: From Precise Synthesis to Oxygen Reduction Reaction Strategy. Catalysts 2021, 11, 1050.
53. Wang, D.; Xin, H.L.; Hovden, R.; Wang, H.; Yu, Y.; Muller, D.A.; Disalvo, F.J.; Abruña, H.D. Structurally ordered intermetallic platinum–cobalt core–shell nanoparticles with enhanced activity and stability as oxygen reduction electrocatalysts. Nat. Mater. 2013, 12, 81–87.
54. Wang, X.X.; Hwang, S.; Pan, Y.T.; Chen, K.; He, Y.; Karakalos, S.; Zhang, H.; Spendelow, J.S.; Su, D.; Wu, G. Ordered Pt3Co Intermetallic Nanoparticles Derived from Metal-Organic Frameworks for Oxygen Reduction. Nano Lett. 2018, 18, 4163–4171.
55. Li, X.; An, L.; Wang, X.; Li, F.; Zou, R.; Xia, D. Supported sub-5nm Pt–Fe intermetallic compounds for electrocatalytic application. J. Mater. Chem. 2012, 22, 6047–6052.
56. Jung, C.; Lee, C.; Bang, K.; Lim, J.; Lee, H.; Ryu, H.J.; Cho, E.; Lee, H.M. Synthesis of Chemically Ordered Pt3Fe/C Intermetallic Electrocatalysts for Oxygen Reduction Reaction with Enhanced Activity and Durability via a Removable Carbon Coating. ACS Appl. Mater. Interfaces 2017, 9, 31806–31815.
57. Kuang, Y.; Cai, Z.; Zhang, Y.; He, D.; Yan, X.; Bi, Y.; Li, Y.; Li, Z.; Sun, X. Ultrathin Dendritic Pt3Cu Triangular Pyramid Caps with Enhanced Electrocatalytic Activity. ACS Appl. Mater. Interfaces 2014, 6, 17748–17752.
58. Sun, X.; Jiang, K.; Zhang, N.; Guo, S.; Huang, X. Crystalline Control of Bounded Pt3Cu Nanocrystals: Multiply-Twinned Pt3Cu Icosahedra with Enhanced Electrocatalytic Properties. ACS Nano 2015, 9, 7634–7640.
59. Toshima, N.; Ito, R.; Matsushita, T.; Shiraishi, Y. Trimetallic nanoparticles having a Au-core structure. Catal. Today 2007, 122, 239–244.
60. Zhao, X.; Sasaki, K. Advanced Pt-Based Core–Shell Electrocatalysts for Fuel Cell Cathodes. Accounts Chem. Res. 2022, 55, 1226–1236.
61. Zhang, L.; Doyle-Davis, K.; Sun, X. Pt-Based electrocatalysts with high atom utilization efficiency: From nanostructures to single atoms. Energy Environ. Sci. 2018, 12, 492–517.
62. Abdelkareem, M.A.; Wilberforce, T.; Elsaid, K.; Sayed, E.T.; Abdelghani, E.A.M.; Olabi, A.G. Transition metal carbides and nitrides as oxygen reduction reaction catalyst or catalyst support in proton exchange membrane fuel cells (PEMFCs). Int. J. Hydrog. Energy 2021, 46, 23529–23547.
63. Mohanta, P.K.; Regnet, F.; Jörissen, L. Graphitized Carbon: A Promising Stable Cathode Catalyst Support Material for Long Term PEMFC Applications. Materials 2018, 11, 907.
64. Grigoriev, S.A.; Fateev, V.N.; Pushkarev, A.S.; Pushkareva, I.V.; Ivanova, N.A.; Kalinichenko, V.N.; Presnyakov, M.Y.; Wei, X. Reduced Graphene Oxide and Its Modifications as Catalyst Supports

and Catalyst Layer Modifiers for PEMFC. Materials 2018, 11, 1405.

65. Zhang, J.; Yuan, Y.; Gao, L.; Zeng, G.; Li, M.; Huang, H. Stabilizing Pt-Based Electrocatalysts for Oxygen Reduction Reaction: Fundamental Understanding and Design Strategies. Adv. Mater. 2021, 33, e2006494.
66. Xue, Q.; Huang, J.-B.; Yang, D.-J.; Li, B.; Zhang, C.-M. Enhanced PEMFC durability with graphitized carbon black cathode catalyst supports under accelerated stress testing. RSC Adv. 2021, 11, 19417–19425.
67. Zhao, J.; Tu, Z.; Chan, S.H. Carbon corrosion mechanism and mitigation strategies in a proton exchange membrane fuel cell (PEMFC): A review. J. Power Sources 2021, 488, 229434.
68. Majlan, E.H.; Rohendi, D.; Daud, W.R.W.; Husaini, T.; Haque, M.A. Electrode for proton exchange membrane fuel cells: A review. Renew. Sustain. Energy Rev. 2018, 89, 117–134.
69. Liang, Z.; Zheng, H.; Cao, R. Importance of Electrocatalyst Morphology for the Oxygen Reduction Reaction. ChemElectroChem 2019, 6, 2600–2614.
70. Lin, R.; Wang, H.; Zhu, Y. Optimizing the structural design of cathode catalyst layer for PEM fuel cells for improving mass-specific power density. Energy 2021, 221, 119909.
71. Jiang, H.; Luo, R.; Li, Y.; Chen, W. Recent advances in solid–liquid–gas three-phase interfaces in electrocatalysis for energy conversion and storage. EcoMat 2022, 4, e12199.
72. Ren, H.; Teng, Y.; Meng, X.; Fang, D.; Huang, H.; Geng, J.; Shao, Z. Ionomer network of catalyst layers for proton exchange membrane fuel cell. J. Power Sources 2021, 506, 230186.
73. Suter, T.A.M.; Smith, K.; Hack, J.; Rasha, L.; Rana, Z.; Angel, G.M.A.; Shearing, P.R.; Miller, T.S.; Brett, D.J.L. Engineering Catalyst Layers for Next-Generation Polymer Electrolyte Fuel Cells: A Review of Design, Materials, and Methods. Adv. Energy Mater. 2021, 11, 2101025.
74. Shi, Y.; Lu, Z.; Guo, L.; Yan, C. Fabrication of membrane electrode assemblies by direct spray catalyst on water swollen Nafion membrane for PEM water electrolysis. Int. J. Hydrog. Energy 2017, 42, 26183–26191.
75. Sassin, M.B.; Garsany, Y.; Gould, B.D.; Swider-Lyons, K.E. Fabrication Method for Laboratory-Scale High-Performance Membrane Electrode Assemblies for Fuel Cells. Anal. Chem. 2017, 89, 511–518.
76. Vierrath, S.; Breitwieser, M.; Klingele, M.; Britton, B.; Holdcroft, S.; Zengerle, R.; Thiele, S. The reasons for the high power density of fuel cells fabricated with directly deposited membranes. J. Power Sources 2016, 326, 170–175.
77. Wei, Z.; Su, K.; Sui, S.; He, A.; Du, S. High performance polymer electrolyte membrane fuel cells (PEMFCs) with gradient Pt nanowire cathodes prepared by decal transfer method. Int. J. Hydrog. Energy 2015, 40, 3068–3074.

78. Chen, G.-Y.; Wang, C.; Lei, Y.-J.; Zhang, J.; Mao, Z.; Mao, Z.-Q.; Guo, J.-W.; Li, J.; Ouyang, M. Gradient design of Pt/C ratio and Nafion content in cathode catalyst layer of PEMFCs. Int. J. Hydrog. Energy 2017, 42, 29960–29965.
79. Zheng, Z.; Yang, F.; Lin, C.; Zhu, F.; Shen, S.; Wei, G.; Zhang, J. Design of gradient cathode catalyst layer (CCL) structure for mitigating Pt degradation in proton exchange membrane fuel cells (PEMFCs) using mathematical method. J. Power Sources 2020, 451, 227729.
80. Chen, M.; Zhao, C.; Sun, F.; Fan, J.; Li, H.; Wang, H. Research progress of catalyst layer and interlayer interface structures in membrane electrode assembly (MEA) for proton exchange membrane fuel cell (PEMFC) system. ETransportation 2020, 5, 100075.
81. Zeng, Y.; Zhang, H.; Wang, Z.; Jia, J.; Miao, S.; Song, W.; Xiao, Y.; Yu, H.; Shao, Z.; Yi, B. Nano-engineering of a 3D-ordered membrane electrode assembly with ultrathin Pt skin on open-walled PdCo nanotube arrays for fuel cells. J. Mater. Chem. A 2018, 6, 6521–6533.

Retrieved from https://encyclopedia.pub/entry/history/show/93101