Platinum-alloy Materials for highly efficient oxygen reduction reaction in fuel cell

Xuan Hu

The Affiliated International School (YHV) of Shenzhen University, shenzhen,513000, China

Abstract. Global climate change and the overuse of fossil fuels have become the most serious challenges of the day. As a result, the search for cleaner and more efficient energy conversion technologies has become more imminent. The advantages of f proton exchange membrane fuel cells, such as zero emission, simple structure and low cost, have attracted the attention of a wide range of scholars. However, the selection of ORR catalysts in fuel cells is the key to its development. Therefore, this paper presents a review of platinum alloy materials for efficient oxygen reduction reaction in proton exchange membrane fuel cells. The advantages and disadvantages of different materials are explored, analyzed and discussed.

Keywords: Pt-based catalysts, clean energy, proton exchange membrane fuel cells (PEMFCs), oxygen reduction reaction (ORR), review.

1. Introduction

The global energy paradigm is shifting towards more sustainable and efficient solutions. As the world grapples with the challenges of climate change and depleting fossil fuel reserves, the search for cleaner and more efficient energy conversion technologies has intensified. Thus, reducing carbon dioxide emissions in the energy sector is a crucial task in the national carbon peak and carbon neutrality policies[1]. The hydrogen economy, based on renewable energy solutions such as hydrogen production, storage, and power generation, is widely regarded as a promising energy solution for the future. If fuel cell technology matures, greenhouse gas emissions from the transportation sector could be reduced to near zero[2-4]. PEMFCs are among the more mature types of fuel cells, characterized by low operating temperatures, ease of operation, high energy density, and diverse fuels, offering broad application prospects.[5] However, the technology is not yet mature, and much research focuses on reducing the manufacturing cost of fuel cells.

Oxygen reduction reaction (ORR) optimization is key to enhancing fuel cell performance. ORR catalysts are pivotal in the realm of fuel cell technology, especially within Proton-Exchange Membrane Fuel Cells (PEMFCs). The efficiency, stability, and comprehensive performance of these fuel cells are deeply influenced by the quality and characteristics of the ORR catalysts in use [6]. Historically, platinum (Pt) and its alloys have been the primary materials harnessed for ORR catalysis due to their superior electrochemical reactivity. Nevertheless, the exorbitant cost and rarity of platinum have compelled researchers to delve into potential alternative materials [7]. Besides, the long-term resilience and resistance to poisoning (from contaminants like CO) are also paramount for ORR catalysts. Several alternative catalysts, such as metal-free nitrogen-doped carbon materials, transition metal-nitrogen-carbon (M-N-C) catalysts, and perovskites, have shown significant promise in contemporary research. Yet, the challenge remains in identifying a catalyst that can either match or outperform platinum, but at a mere fraction of its cost [8].

In summation, the appraisal of ORR catalysts is an ever-adapting domain, with ceaseless research focusing on unearthing efficient, long-lasting, and economically viable alternatives to traditional platinum-based catalysts. Metrics such as SA, MA, and ECSA remain invaluable instruments in gauging the efficacy and potential of these catalysts.

2. Pt-alloy Materials for ORR

2.1 How to improve the activity of Pt-based ORR catalysts

Platinum (Pt) has been the quintessential material for ORR catalysis in fuel cells owing to its outstanding electrochemical activity. Nevertheless, the quest for more efficient, durable, and cost-effective catalysts has driven researchers to alloy platinum with other metals. One of the most promising of these alloys is Pt3Ni [9].

Pt3Ni exhibits a modified surface structure compared to pure Pt. The alloy's surface tends to be enriched with Pt atoms due to the leaching of Ni in acidic conditions, creating a Pt-skin structure. This unique structure leads to a higher density of the desired active sites for the ORR. Electronic Effects: The incorporation of Ni into the Pt lattice induces electronic effects, modifying the d-band center of the Pt atoms. This alteration weakens the binding energy of oxygenated species to the catalyst surface, enhancing ORR kinetics. While Pt3Ni alloys have shown enhanced ORR activity, their durability, especially under fuel cell operating conditions, has been a concern. However, recent advancements in synthesis methods and post-treatment processes have improved the stability of Pt3Ni catalysts, bringing them closer to the durability of pure Pt. The introduction of Ni reduces the overall amount of Pt required in the catalyst, leading to potential cost savings. Given the high cost of platinum, this makes Pt3Ni an attractive choice for commercial applications [10].

2.2 0-dimensional materials reviews

Zero-dimensional Pt nanoparticles are extensively researched catalyst materials. Commercially available as the Pt/C catalyst, these represent nanoparticles supported on carbon materials. The performance of these catalysts, primarily composed of Pt nanoparticles, is deeply influenced by several factors:

The nanoparticle's diameter and its distribution play a crucial role in determining its effectiveness in catalysis. An optimized catalytic activity is observed when the Pt nanoparticle size is minimized and its dispersion is maximized. This optimization increases the number of exposed Pt atoms on the surface, leading to a surge in the number of active sites and ensuring efficient Pt utilization[11]. However, reducing the Pt nanoparticle size beyond a certain limit may not be advantageous. As particle size shrinks, there's an increase in the binding energy with oxygen. When this binding energy becomes excessively strong, it can hinder the oxygen reduction reaction, causing a paradoxical decrease in overall activity[12]. Another significant concern with Pt nanoparticle catalysts is their stability during the catalytic process. Events such as detachment from the support, agglomeration of particles, and phenomena like Ostwald ripening can lead to an increase in particle size. These occurrences can deteriorate the catalyst's stability, representing a pressing issue in the research of nanoparticle catalysts.

2.3 1-dimensional materials reviews

One-dimensional Pt-based catalysts predominantly manifest in structures like nanowires, nanorods, and nanotubes. Historically, nanowires, characterized by their high aspect ratio, were primarily synthesized using templating methods, such as those involving insulin[13]. However, advancements in the growth studies of precious metals have paved the way for non-templated preparations. Contemporary techniques now predominantly leverage liquid-phase chemical synthesis to directly obtain nanowires[14].

Several intrinsic advantages of one-dimensional Pt-based catalysts. Their relatively elongated lengths can induce a path-directed effect, thereby promoting electron transfer. This path-directed effect enhances the reaction kinetics on the catalyst surface. The increased contact area between the one-dimensional Pt-based catalyst and its support enhances electron transfer between the metal and the support. These one-dimensional structures largely circumvent issues like agglomeration and Ostwald ripening, which are often witnessed in nanoparticle catalysts. These attributes contribute to prolonging the catalyst's operational lifespan.

In comparative studies, Huang et al.[15] synthesized both zero-dimensional Pt octahedra and one-dimensional Pt nanowires. Upon electrocatalytic testing, results unequivocally revealed that whether in catalyzing oxygen reduction reactions or methanol oxidation reactions, Pt nanowires consistently outperformed the octahedra, showcasing superior catalytic activity and stability. Through innovative advancements in synthesis techniques, the diameters of these nanowires have been whittled down from about 10 nm to contemporary sizes of 2 nm or even sub-nanometer scales, with a concomitant enhancement in their aspect ratios. In another groundbreaking study, Huang et al.[16] utilized CTAC and Mo(CO)6 to modulate morphology, successfully fabricating Pt and its alloy nanowires with an average diameter of just 0.8 nm. These nanowires exhibited oxygen reduction catalytic activity far surpassing commercial Pt/C and showcased commendable stability. Duan's research group[17] introduced a serrated Pt nanowire with an impressive electrochemically active surface area reaching up to 118 m2 gPt^-1. Its mass activity for ORR catalysis was a staggering 52 times that of commercial Pt/C (13.6 A mgPt^-1), making it one of the most potent oxygen-reducing Pt-based catalysts reported to date. Remarkably, post-durability testing, this nanowire exhibited almost no loss in activity. This exceptional stability is attributed to its unique one-dimensional structure.

2.4 2-dimensional materials reviews

Two-dimensional nanoplates, especially ultra-thin nanoplates with atomic-level thickness, offer a compelling proposition in catalysis. Their design ensures maximum exposure of specific crystal facets that are conducive to enhanced catalytic activity. This design philosophy not only amplifies the catalytic performance but also optimizes the utilization of the precious metal Pt.

However, the challenge escalates when aiming for two-dimensional Pt-based materials for fuel cell catalysts. Most of the currently synthesized monocrystalline two-dimensional Pt-based materials are alloys, wherein Pt is alloyed with other metals. For instance, Wang et al.1 pioneered the synthesis of freestanding (unsupported by any other carrier) ultra-thin monocrystalline PtCu alloy nanoplates. Remarkably, these nanoplates had a thickness of merely 4 to 6 atomic layers, showcasing exceptional electrocatalytic performance.

The immense potential of these 2D nanoplates is rooted in their inherent structural advantages. With their extended surface area and exposure of active facets, they provide an ideal platform for catalytic reactions. The architecture ensures that more catalytic sites are available, fostering efficient reactions even with minimal catalyst material. This efficient site exposure translates to enhanced metal utilization, a crucial aspect given the costs associated with metals like Pt[18].

Moreover, while the achievements with metals like Pd, Ag, and Rh are commendable, Pt, given its exceptional catalytic properties, remains the gold standard in many applications. The challenge with Pt lies in stabilizing its ultra-thin structures without compromising its catalytic attributes. The introduction of alloys, such as the PtCu variant mentioned, can potentially offer a balance between stability and performance. By alloying Pt with metals like Cu, researchers aim to stabilize the 2D structure while still leveraging Pt's superior catalytic properties.

2.5 3-dimensional materials reviews

Three-dimensional (3D) nanostructures, particularly nanoframes and nanowire network systems, have attracted significant attention in various research domains, including catalysis, electronics, and energy storage. These 3D architectures offer distinct advantages, such as a high surface area, excellent electron transfer capabilities, and improved structural integrity, making them ideal candidates for numerous applications[19].

A nanoframe can be visualized as a skeletal nanostructure, where the bulk of the material is selectively etched away, leaving behind a robust frame[20]. These structures retain the advantageous properties of nanoparticles, such as high surface area and active sites, but with reduced metal usage, making them cost-effective[21]. Due to their unique hollowed structure, nanoframes possess an increased number of exposed active sites compared to their solid counterparts. This facilitates more efficient catalytic reactions, especially in scenarios where the surface activity is paramount[22]. The skeletal structure ensures that a larger fraction of the metal atoms is on the surface and directly involved in catalysis, leading to optimized metal utilization. The interconnected nature of nanowire network systems ensures seamless electron transfer pathways, crucial for applications like sensors, catalysis, and energy storage devices.

In recent years, various strategies, including template-based methods, direct growth, and self-assembly, have been employed to synthesize these 3D structures. Additionally, alloying and doping with other metals or non-metals have emerged as effective techniques to enhance their stability and performance.

3. Pt-based ORR catalysts in practical fuel cells

On conventional precious metal platinum (Pt) catalysts, the ORR exhibits extremely slow reaction rates, often requiring overpotentials exceeding 0.4V. Consequently, conventional Pt loadings as high as 0.4 mg/cm2Pt are necessary on the PEMFC cathode, leading to a substantial increase in system costs.The working environment of the PEMFC cathode is highly hostile, combining strong acidity with high voltages. This makes it challenging for materials other than precious metals like platinum, iridium (Ir), and gold (Au) to remain stable under such conditions. This limitation restricts the application potential of non-precious metal catalytic materials in ORR[77-78].Precious metal platinum (Pt) nanoparticles exhibit a high surface area but are plagued by stability issues. This stems from significant electronic structure differences between metallic platinum and the carbon support, resulting in their adhesion relying on weak forces. Due to this relatively weak adhesion, Pt nanoparticle catalysts are prone to migration, aggregation, and enlargement during the operation of fuel cells, leading to a gradual reduction in the catalyst's active surface area. Ultimately, this phenomenon results in a gradual decline in fuel cell performance, limiting its long-term stability and lifespan[23-24].During prolonged operation of Proton Exchange Membrane Fuel Cells (PEMFCs), the surface of the precious metal platinum (Pt) catalyst undergoes an oxidation process, which can ultimately lead to catalyst dissolution. Particularly under high-potential conditions, dissolved Pt ions may migrate to lower potentials during potential cycling and then redeposit onto other Pt nanoparticles. This intricate electrochemical process alters the morphology and structure of the entire catalyst, resulting in a reduction in the activity of Pt catalysts. This phenomenon is one of the primary reasons for the long-term stability and performance degradation in Proton Exchange Membrane Fuel Cells (PEMFCs)[25-26].A portion of dissolved Pt ions will diffuse into the proton exchange membrane, permeating it along with water, and deposit there through the hydrogen reduction reaction from hydrogen gas penetrating from the anode. At times, these Pt ions may even replace hydrogen ions (H+) within the proton exchange membrane, leading to a deterioration in the membrane's performance. This series of intricate processes ultimately has a detrimental impact on fuel cell performance, including the weakening of catalyst activity and the degradation of the proton exchange membrane[27-28].In the cathode of Proton Exchange Membrane Fuel Cells (PEMFCs), air is typically used as the source of oxygen rather than pure oxygen, primarily considering factors such as cost and availability. However, air often contains trace impurities such as sulfur oxides (SOX), nitrogen oxides (NOX), and hydrocarbons. These impurities strongly adsorb onto the surface of the precious metal platinum (Pt) catalyst, covering the active sites of Pt and causing catalyst poisoning, significantly impacting its performance. This poisoning phenomenon limits the efficiency of the catalyst, thereby reducing the overall performance and lifespan of the fuel cell.In addition to the effects of impurities, corrosion of the catalyst support is also a significant issue that can have a notable impact on catalyst stability[29].Developing low-platinum (Pt), high-activity, and high-stability ORR (Oxygen Reduction Reaction) catalysts is a key factor in achieving the commercialization of fuel cells.

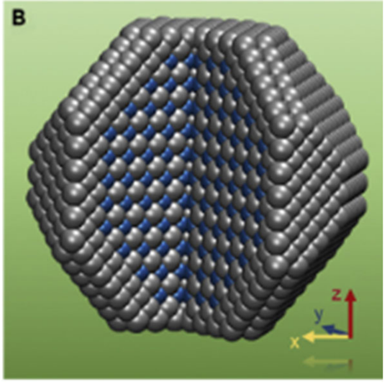

Fig. 3 Schematic of L1 0 -CoPt/Pt NPs with 2 ‒ 3 atomic layers of Pt shell, where the silver-colored atom is Pt and the blue-colored atom is Co[30].

As shown in Figure 3, the fully ordered L10-CoPt has been transformed into a core-shell L10-CoPt/Pt structure through acid treatment and annealing at 400℃. Research indicates that the L10-CoPt structure effectively shields Co from acid corrosion, with only surface Co being removed, significantly enhancing the corrosion resistance of the catalyst support[30].

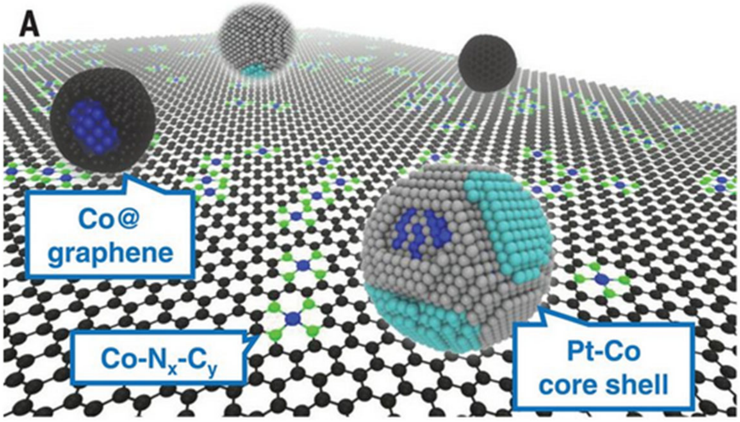

Fig. 4 LP@PF catalyst structure[31]

Research in Figure 4 has shown that Pt-Co alloys not only directly participate in the ORR but also facilitate the reduction of H_2O_2 generated from adjacent PGM-free sites, thereby improving the utilization efficiency of Pt-Co alloys.

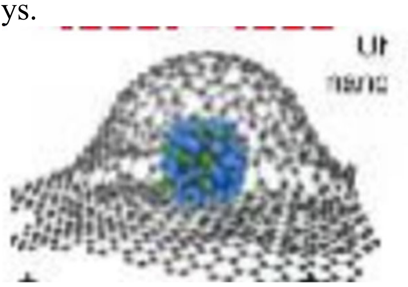

Fig. 5 structure of the PtCo@GnP catalyst[32]

4. Conclusions and Outlook

The global shift towards sustainable energy solutions is evident, with proton-exchange membrane fuel cells (PEMFCs) playing a pivotal role in this transition. While the progress is commendable, there's much work ahead.Catalyst Development. To make PEMFCs commercially viable, there's an urgent need to either find alternatives to Pt or enhance its efficiency and stability, thereby reducing the overall manufacturing costs.Research and Collaboration.Multi-disciplinary collaboration between chemists, physicists, and engineers can lead to breakthroughs in fuel cell technology. By addressing the challenges head-on and continually innovating, the dream of a cleaner, greener world is within reach.

References

[1] Dingxian Xiang. Current situation analysis and development trend path of energy under the goal of carbon peaking and carbon neutrality [J]. Industrial safety and environmental protection,2021,47(S1):20-24.

[2] Eberle U, Müller B, Von Helmolt R. Fuel cell electric vehicles and hydrogen infrastructure: status 2012[J]. Energy & Environmental Science, 2012, 5(10): 8780-8798.

[3] Itaoka K, Saito A, Sasaki K. Public perception on hydrogen infrastructure in Japan: influence of rollout of commercial fuel cell vehicles[J]. International Journal of Hydrogen Energy, 2017, 42(11): 7290-7296.

[4] Staffell I, Scamman D, Abad A V, et al. The role of hydrogen and fuel cells in the global energy system[J]. Energy & Environmental Science, 2019, 12(2): 463-491.

[5] Guo S, Wang E. Functional micro/nanostructures: simple synthesis and application in sensors, fuel cells, and gene delivery[J]. Accounts of Chemical Research, 2011, 44(7): 491-500.

[6] Carrette L, Friedrich K A, Stimming U. Fuel Cells-Fundamentals and Applications[J]. Fuel Cells, 2001, 1(1): 5-39.

[7] McNicol B D, Rand D A J, Williams K R. Direct methanol-air fuel cells for road transportation[J]. Journal of Power Sources, 1999, 83(1-2): 15-31.

[8] Yang Z, Yao Z, Li G, et al. Sulfur-Doped Graphene as an Efficient Metal-free Cathode Catalyst for Oxygen Reduction[J]. ACS nano, 2012, 6(1), 205-211.

[9] Wang R, Wang K, Wang Z, et al. Pig bones derived N-doped carbon with multi-level pores as electrocatalyst for oxygen reduction[J]. Journal of Power Sources, 2015, 297, 295-301.

[10] Bezerra C W B, Zhang L, Lee K, et al. A review of Fe-N/C and Co-N/C catalysts for the oxygen reduction reaction[J]. Electrochimica Acta, 2008, 53(15), 4937-4951.

[11] Latsuzbaia R, Negrol E, Koper G. Synthesis, Stabilization and Activation of Pt Nanoparticles for PEMFC Applications[J]. Fuel Cells, 2015, 15(4): 628-638.

[12] Shao M, Peles A, Shoemaker K. Electrocatalysis on platinum nanoparticles: Particle size effect on oxygen reduction reaction activity[J]. Nano Letters, 2011, 11(9): 3714-3719.

[13] Zhang L, Li N, Gao F, et al. Insulin Amyloid Fibrils: An Excellent Platform for Controlled Synthesis of Ultrathin Superlong Platinum Nanowires with High Electrocatalytic Activity[J]. Journal of the American Chemical Society, 2012, 134(28): 11326-11329.

[14] Huang H, Li K, Chen Z, et al. Achieving Remarkable Activity and Durability toward Oxygen Reduction Reaction Based on Ultrathin Rh-Doped Pt Nanowires[J]. Journal of the American Chemical Society, 2017, 139(24): 8152-8159.

[15] Bu L, Feng Y, Yao J, et al. Facet and dimensionality control of Pt nanostructures for efficient oxygen reduction and methanol oxidation electrocatalysts[J]. Nano Research, 2016, 9(9): 2811-2821.

[16] Jiang K, Zhao D, Guo S, et al. Efficient oxygen reduction catalysis by subnanometer Pt alloy nanowires[J]. Science Advances, 2017, 3(2): e1601705.

[17] Li M F, Zhao Z P, Cheng T, et al. Ultrafine jagged platinum nanowires enable ultrahigh mass activity for the oxygen reduction reaction[J]. Science, 2016, 354(6318): 1414-1419.

[18] Saleem F, Zhang Z, Xu B, et al. Ultrathin Pt-Cu Nanosheets and Nanocones[J]. Journal of the American Chemical Society, 2013, 135(49): 18304-18307.

[19] Wang L, Tang Z, Yan W, et al. Co@Pt Core@Shell nanoparticles encapsulated in porous carbon derived from zeolitic imidazolate framework 67 for oxygen electroreduction in alkaline media[J]. Journal of Power Sources, 2017, 343: 458-466.

[20] Zhang J L, Vukmirovic M B, Xu Y, et al. Controlling the Catalytic of Platinum-Monolayer Electrocatalysts for Oxygen Reduction with Different Substrates[J]. Angew. Chem., Int. Ed. 2005, 44(14): 2132−2135.

[21] Zhao X, Chen S, Fang Z, et al. Octahedral Pd@Pt1.8Ni Core-Shell Nanocrystals with Ultrathin PtNi Alloy Shells as Active Catalysts for Oxygen Reduction Reaction[J]. Journal of the American Chemical Society, 2015, 137(8): 2804-2807.

[22] Strasser P, Koh S, Anniyev T, et al. Lattice-Strain Control of the Activity in Dealloyed Core-Shell Fuel

Cell Catalysts[J]. Nature Chemistry, 2010, 2(6): 454-460.

[23] Kong K J, Choi Y M, Ryu B H, et al. Investigation of metal/carbon-related materials for fuel cell applications by electronic structure calculations[J]. Materials Science & Engineering C-Biomimetic and Supramolecular Systems, 2006,26 (5-7SI):1207-1210.

[24] Kim P, Kim H S, Joo J B, et al. Preparation and application of nanoporous carbon templated by silica particle for use as a catalyst support for direct methanol fuel cell[J]. Journal of Power Sources, 2005,145(2SI):139-146.

[25] Kim M, Park J, Kim H, et al. The preparation of Pt/C catalysts using various carbon materials for the cathode of PEMFC[J]. Journal of Power Sources, 2006,163(1SI):93-97.

[26] Dicks A L, The role of carbon in fuel cells[J]. Journal of Power Sources, 2006,156(2):128-141.

[27] Fan Luo, Shijun Liao. Research progress on the application of surface-modified carbon carriers to fuel cell catalysts [J]. Modern Chemical Industry,2012(07):29-33.

[28] Yi Zhang, Zhenbo Wang. Effects of carbon support on catalytic properties of proton exchange membrane fuel cells: The 22nd Carbon-Graphite Materials Symposium, Ningbo, Zhejiang, China, 2010[C].

[29] Yu Chen, Yawen Tang, Yimin Zhou, et al. Research progress of carbon nanotubes as catalyst carriers for fuel cells [J]. Batteries,2006(01):71-73.

[30] Li J, Sharma S, Liu X, et al. Hard-magnet L10-CoPt nanoparticles advance fuel cell catalysis[J]. Joule, 2019, 3(1): 124-135.

[31] Chong L, Wen J, Kubal J, et al. Ultralow-loading platinum-cobalt fuel cell catalysts derived from imidazolate frameworks[J]. Science, 2018, 362(6420): 1276-1281.

[32] Zhao Z, Liu Z, Zhang A, et al. Graphene-nanopocket-encaged PtCo nanocatalysts for highly durable fuel cell operation under demanding ultralow-Pt-loading conditions[J]. Nature Nanotechnology, 2022, 17(9): 968-975.