

Review

Sustainable Anodes for Direct Methanol Fuel Cells: Advancing Beyond Platinum Scarcity with Low-Pt Alloys and Non-Pt Systems

Liangdong Zhao  and Yankun Jiang * 

School of Energy and Power Engineering, Huazhong University of Science and Technology, Wuhan 430074, China; d202480594@hust.edu.cn

* Correspondence: jykust@hust.edu.cn; Tel.: +86-13886100246

Abstract: Direct methanol fuel cells (DMFCs) represent a promising pathway for energy conversion, yet their reliance on platinum-group metal (PGM)-based anode catalysts poses critical sustainability challenges, which stem from finite mineral reserves, environmentally detrimental extraction processes, and prohibitive lifecycle costs. Current anode catalysts for DMFCs are dominated by platinum materials; therefore, this review systematically evaluates the following three emerging eco-efficient design paradigms using platinum materials as a starting point: (1) the atomic-level optimization of low-Pt alloy surfaces to maximize catalytic efficiency per metal atom, (2) Earth-abundant transition metal compounds (e.g., nitrides and sulfides) and coordination-tunable metal–organic frameworks as viable PGM-free alternatives, and (3) mechanically robust carbon architectures with engineered topological defects that enhance catalyst stability through covalent metal–carbon interactions. Through comparative analysis with pure Pt benchmarks, we critically examine how these strategic material innovations collectively mitigate CO intermediate poisoning risks and improve electrochemical durability. Such fundamental advances in catalyst design not only address immediate technical barriers, but also establish essential material foundations for the development of DMFC technologies compatible with circular economy frameworks and United Nations Sustainable Development Goal 7 targets.

Keywords: direct methanol fuel cells; sustainable catalyst materials; anode catalysts; platinum-group metal alternatives; carbon supports



Academic Editors: Francesco Liberato Cappiello, Francesco Calise, Maria Vicidomini and Rafał Figaj

Received: 28 March 2025

Revised: 28 May 2025

Accepted: 31 May 2025

Published: 1 June 2025

Citation: Zhao, L.; Jiang, Y. Sustainable Anodes for Direct Methanol Fuel Cells: Advancing Beyond Platinum Scarcity with Low-Pt Alloys and Non-Pt Systems. *Sustainability* **2025**, *17*, 5086. <https://doi.org/10.3390/su17115086>

Copyright: © 2025 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (<https://creativecommons.org/licenses/by/4.0/>).

1. Introduction

The global decarbonization imperative has established fuel cell technology as a cornerstone of sustainable energy system transitions [1–4]. Functioning as the fourth-generation power generation successor to hydroelectric, thermal, and nuclear technologies, fuel cells enable direct electrochemical energy conversion through the exploitation of Gibbs free energy—a transformative advancement beyond conventional thermal cycles limited by Carnot efficiency constraints. While theoretical energy conversion efficiencies reach 85–90%, practical systems exhibit operational efficiencies of 40–60% due to multifaceted polarization phenomena. Despite these limitations, the advantages of fuel cells in sustainable energy architectures demand systematic scientific investigations [5]. Hydrogen fuel cells surpass conventional power systems through the following three strategic advantages [6–9]: achieving carbon neutrality via renewable hydrogen integration, enabling silent urban deployment through vibration-free operation, and maintaining peak efficiency across dynamic loads via modular scalability.

As schematically illustrated in Figure 1, the fundamental operating principle involves simultaneous half-cell reactions at spatially separated electrodes: gaseous fuel oxidation (e.g., H_2) at the anode and oxidant reduction (e.g., O_2) at the cathode.

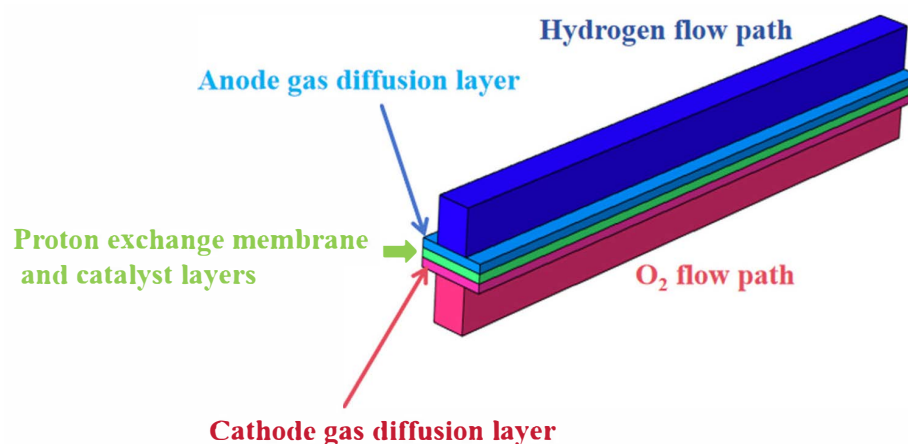
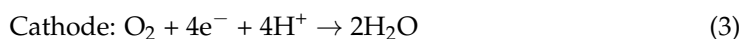


Figure 1. Basic structure of hydrogen fuel cell.

The electrochemical reaction of a hydrogen fuel cell is shown in the following equation:



The rapid growth in multifunctional electronics (e.g., foldable displays and AR/VR) has highlighted lithium-ion batteries' limitations in energy density and cycling stability. Fuel cells emerge as transformative alternatives, leveraging continuous electrochemical conversion to bypass cycle-dependent degradation while achieving a higher energy density. Their operation eliminates flammable electrolytes and dendrite risks, enabling a robust performance under mechanical stress or overcharging. This paradigm shift addresses the dual challenges of energy storage capacity and operational safety inherent to conventional battery systems [10,11].

Fuel cell classification is governed by multidimensional engineering parameters, including fuel phase state (gas/liquid), processing methodology (internal/external reforming), operational thermodynamics (temperature/pressure ranges), and electrolyte material properties. The current technological landscape predominantly features the following six principal fuel cell archetypes: Proton Exchange Membrane (PEMFC), Direct Methanol (DMFC), Alkaline (AFC), Phosphoric Acid (PAFC), Molten Carbonate (MCFC), and Solid Oxide Fuel Cells (SOFCs) [12–14]. AFCs utilize aqueous KOH electrolytes for hydrogen oxidation, but exhibit sensitivity to atmospheric CO_2 . In contrast, PAFCs operate with phosphoric acid electrolytes and are primarily deployed in stationary power plants. High-temperature variants, such as MCFCs (650 °C, carbonate melt electrolytes) and SOFCs (800–1000 °C, ceramic electrolytes), facilitate direct hydrocarbon reforming at the expense of demanding thermal management systems. Among these, PEMFCs have emerged as the leading candidate for portable energy applications due to their exceptional power density ($>1 \text{ W/cm}^2$), moderate operating temperatures (60–80 °C), and sub-second transient response capabilities [15]. DMFCs circumvent the infrastructural challenges associated with hydrogen utilization—such as cryogenic storage inefficiencies, safety risks, and carbon emissions—via direct methanol oxidation. Critically, Alkaline Direct Methanol Fuel Cells differ from conventional AFCs in both fuel type and ion transport mechanism: AFCs rely

on hydrogen fuel with pure OH^- conduction, whereas alkaline DMFCs utilize methanol fuel with hybrid proton–hydroxide transport. This configuration eliminates hydrogen-reforming byproducts, achieving a 30–50% reduction in fuel handling costs. As shown in Figure 2, the system integrates the following five core components: (1) methanol oxidation anode, (2) oxygen reduction cathode, (3) proton-exchange membrane, (4) nanostructured catalysts, and (5) gas diffusion layers with optimized flow fields. This integrated design enables continuous power generation distinct from conventional batteries' charge–discharge cycles, maintaining efficient proton transport and reactant separation through membrane-mediated phase management.

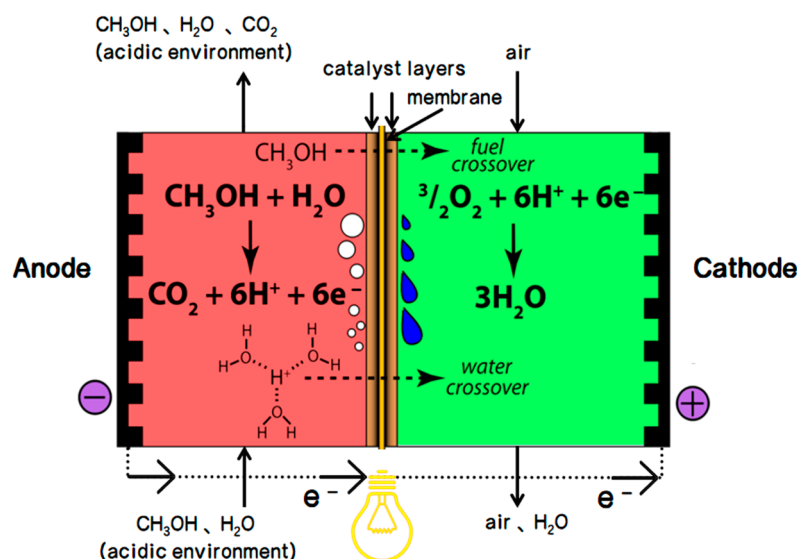
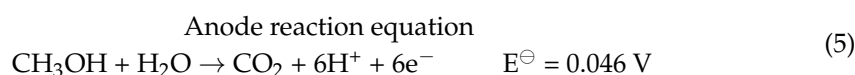
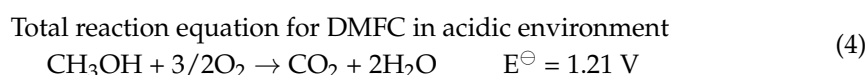
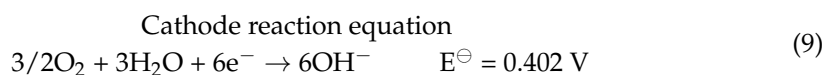
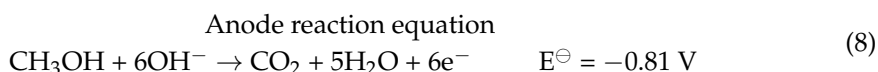
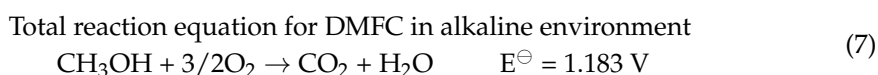


Figure 2. Structure sketch and working principle of DMFC.

The DMFC architecture strategically integrates a methanol oxidation reaction (MOR) catalyst at the anode to orchestrate the multi-step methanol dehydrogenation pathway, while the cathode employs an oxygen reduction reaction (ORR) catalyst to overcome the inherent kinetic limitations of tetra-electron oxygen reduction. The proton-exchange membrane (PEM) fulfills the following dual critical functions: enabling selective proton transport between electrodes while acting as an electronic insulator and methanol diffusion barrier. In DMFC operation, methanol electro-oxidizes at the anode, producing electrons, protons, and CO_2 . Electrons power external circuits while protons traverse the PEM. At the cathode, oxygen undergoes efficient reduction using these protons and electrons to form water. This closed-loop energy conversion process achieves over 90% theoretical efficiency, directly transforming methanol's chemical energy into electricity with minimal environmental impact. Notably, DMFC systems demonstrate unique pH adaptability—their core reaction mechanisms remain electrochemically viable in both acidic and alkaline media, with the respective half-cell and overall reactions governed by the following potential-dependent equations:





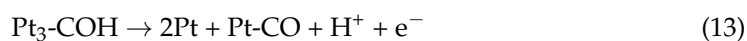
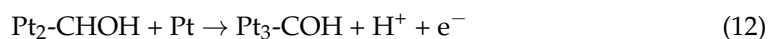
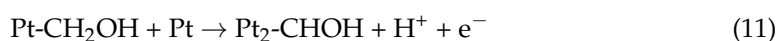
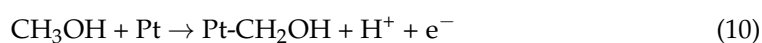
Comparative analysis reveals that methanol electro-oxidation kinetics in acidic environments significantly lag behind those in alkaline systems, primarily due to unfavorable proton transfer mechanisms and insufficient generation of reactive intermediates [16,17]. This kinetic disparity drives the prevalent adoption of alkaline-based DMFC configurations, where nickel or platinum anode catalysts synergize with silver-based cathode materials to enhance methanol oxidation and oxygen reduction processes. However, the alkaline advantage is partially negated by progressive carbonate accumulation within the electrolyte—a phenomenon that physically obstructs catalytic active sites and degrades ionic conductivity, cumulatively impairing cell performance. To mitigate these competing factors, the precise optimization of electrolyte pH and chemical composition becomes essential for balancing reaction kinetics with long-term stability. DMFCs demonstrate a remarkable theoretical energy density (6100 Wh kg^{-1} at 25°C) and near-ideal thermodynamic efficiency (96.68% at 25°C , 1 atm) [18], yet practical systems achieve only 30–40% of these theoretical values due to the following three well-documented limitations [19–22]:

(1) Methanol crossover: Uncontrolled methanol permeation through the membrane induces parasitic reactions at the cathode while poisoning ORR catalysts.

(2) Electrochemical polarization: Combined activation losses (low current density) and concentration polarization (high current density) substantially reduce operational voltage.

(3) Ohmic resistance: Interface resistance between catalyst layers and the membrane contributes 10–20% of total voltage losses, particularly pronounced in alkaline systems.

In operational DMFC systems, mitigating these efficiency limitations constitutes the foremost challenge for performance enhancement. Previous fundamental studies have focused on mechanistic investigations of the MOR at the anode, with a particular emphasis on elucidating the multi-step reaction pathways governing catalyst functionality. Seminal work by Hamnett et al. [23] established platinum-based systems as the prototypical catalyst platform for anode reaction analysis, delineating the following sequential reaction mechanism under acidic conditions:



The generation of CO arises from the direct dehydrogenation of methanol, a process that follows an indirect reaction mechanism. In this mechanism, a hydroxyl (OH) group first reacts with the carbon species on the catalyst surface, forming a series of intermediate products such as dihydroxy hydrocarbons ($\text{C}(\text{OH})_2$) and formic acid (HCOOH). These intermediates undergo a series of dehydrogenation reactions, ultimately converting into carboxyl groups (COOH) or formate esters (HCOO). Through further dehydrogenation steps, these intermediate products are ultimately transformed into CO_2 . Additionally, there is a pathway leading to the generation of CO_2 , where protons and electrons from water molecules are separated, and the resulting hydroxyl group reacts with formaldehyde to

form H_2COOH . This intermediate is subsequently converted into HCOOH or H_2COO^- , and through further dehydrogenation reactions, it is transformed into formate, which undergoes a similar reaction mechanism to ultimately yield CO_2 [24]. This reaction pathway not only reveals the complexity of CO generation, but also provides a theoretical basis for optimizing the methanol electrooxidation reaction. Figure 3 below shows the possible reaction products and reaction pathways for methanol oxidation.

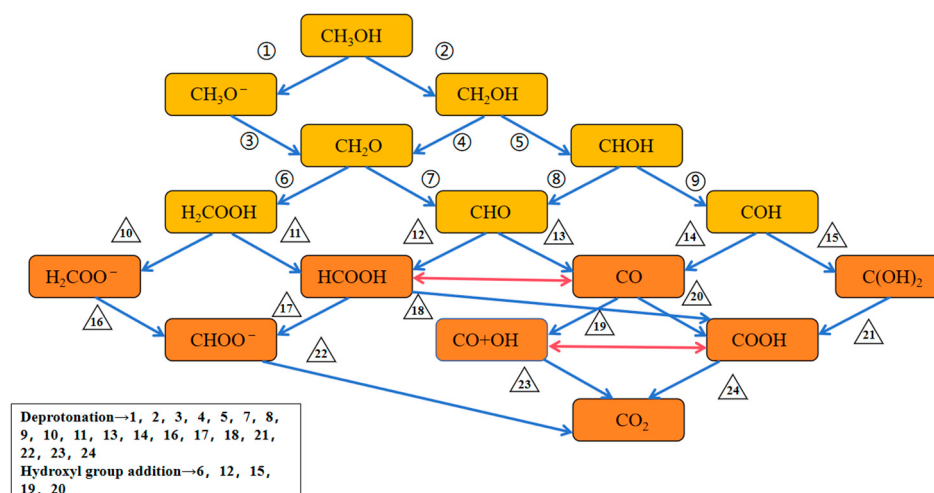


Figure 3. The possible reaction products and reaction paths for methanol oxidation.

Methanol crossover describes the uncontrolled diffusion of methanol fuel from the anode compartment across the PEM to the cathode. This mass transport phenomenon triggers parasitic MOR parallel to the ORR at the cathode, severely degrading DMFC efficiency through the following two synergistic mechanisms: (i) cathodic mixed-potential formation due to competing redox processes and (ii) irreversible electrocatalytic site poisoning through CO-like intermediate adsorption [25,26]. Despite incremental advancements in PEMs, their fundamental material constraints—particularly their compromised methanol-blocking selectivity under mass transport limitations and accelerated carbonate precipitation in alkaline environments—remain persistent technical barriers. This impasse has driven the research paradigm to pivot toward developing anode catalysts with the following dual functionality: superior intrinsic MOR activity and CO intermediate oxidation capability, aiming to simultaneously accelerate reaction kinetics and suppress efficiency losses. Platinum's dominance as the anode catalyst of choice in DMFC systems stems from its unique d-band electronic configuration, which optimally balances methanol adsorption strength and intermediate desorption kinetics in accordance with the Sabatier principle [27–29]. In DMFC anodes, methanol undergoes dual adsorption on Pt surfaces—physisorption followed by chemisorption via Pt–O bonds. Pt's d-band mediates dehydrogenation through orbital hybridization, while its metallic conductivity enables efficient charge transfer during oxidation. However, Pt catalysts face the following two intrinsic limitations: (1) CO intermediate accumulation from incomplete methanol oxidation, blocking active sites at triple-phase boundaries, and (2) surface reconstruction from adsorbed intermediates, altering d-band electronic states. These synergistic effects geometrically obstruct methanol access and electronically destabilize catalytic centers, leading to irreversible performance degradation [30–32].

Platinum-based catalysts remain the primary cost barrier for DMFC commercialization, dominating stack manufacturing expenses and undermining competitiveness against conventional energy systems. Current research prioritizes the following three pathways: enhancing Pt atomic utilization efficiency, developing ultra-low loading architectures via

support engineering, and exploring non-precious alternatives with a protonic functionality comparable to Pt [33–35]. Low-platinum (low-Pt) catalysts represent a strategic material class defined by a reduced precious metal content compared to conventional Pt/C benchmarks. Contemporary catalyst design prioritizes atomic-level Pt utilization through structural engineering and surface coordination modulation, aiming to reconcile the fundamental trade-off between methanol oxidation activity and long-term electrochemical stability [36,37]. The enhanced dispersion of active sites in Pt catalysts—achieved via metal alloying [38], structured oxide [39], and core-shell architectures [40]—has proven essential for improving both catalytic activity and operational stability. Concurrently, non-Pt catalyst exploration has gained momentum, with substantial research efforts targeting transition metal oxides and their modified derivatives for methanol oxidation [41,42]. Recent advances include the design of non-precious metal alloy catalysts such as Pd- [43,44], Ru- [45], and Fe-systems [46] and their derivatives [47,48]. These advancements substantiate the viability of platinum-free catalytic systems for methanol electro-oxidation applications.

The dual challenges of platinum scarcity and CO poisoning have driven extensive research into alternative DMFC catalysts, as evidenced by prior reviews focusing on alloy engineering and surface-modified Pt architectures. While previous review studies have laid an important foundation for activity–structure optimization, the emerging demand for sustainable energy requires a paradigm shift towards system-level integration. As schematically summarized in Figure 4, this review provides a comparative assessment of platinum-based and alternative catalytic platforms, focusing on the following two critical performance metrics: intrinsic MOR activity and CO intermediate tolerance. Furthermore, we critically examine persistent technical barriers in DMFC anode development while elucidating the mechanistic role of catalyst supports in modulating electronic structures and mass transport dynamics. Collectively, these analyses establish fundamental design principles for next-generation catalysts, offering a roadmap for optimizing both atomic efficiency and long-term operational stability in practical DMFC systems.

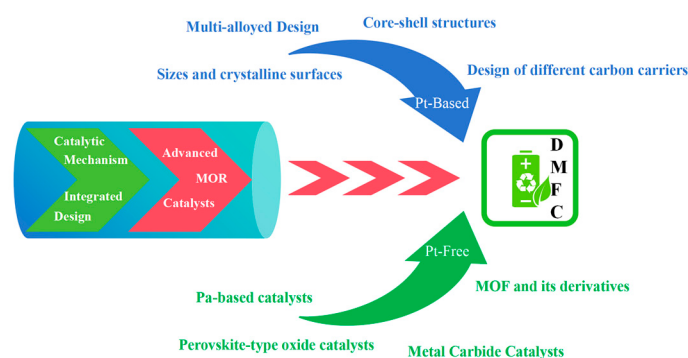


Figure 4. Comparative assessment of DMFC anode catalysts using platinum-based and non-platinum-based catalytic routes.

2. Platinum-Based Catalysts for DMFC Anodes

The methanol electro-oxidation reactions in DMFCs are surface-mediated processes, where exclusively exposed platinum atoms participate in catalytic cycles while bulk atoms remain electrochemically inactive. To mitigate platinum dependency without compromising performance, the following three principal strategies have emerged: (1) the nanostructural control of platinum particles through precise size regulation and crystallographic facet engineering; (2) multi-metallic alloying with metallic elements (Au, Mo, Ag, Pd, Fe, Ni, Co, Rh, Ru, and Sn) to synergistically modulate surface electronic states; and (3) core-shell architectures that confine platinum to atomically thin surface layers over cost-effective core materials. These approaches collectively maximize platinum surface atom accessibility and

intermediate adsorption/desorption kinetics, achieving catalytic efficiencies comparable to pure platinum systems at significantly reduced metal loadings. Table 1 systematically compares the composition–activity relationships of representative platinum alloys under standardized testing conditions.

Table 1. Research results of platinum-based catalysts for DMFC anodes.

No.	Author and Time	Refs	Catalyst Preparation Method or Calculation Method	Metals	Catalyst Size or Catalyst Crystal Spacing of Interest	Catalyst Performance or Key Findings
1	Sanja Stevanović et al., 2021	[49]	Microwave-assisted polyol process	Pt, Sn	PtSnO ₂ /C: <2 nm SnO ₂ : ~2 nm PtSn/C: ~2 nm Pt ₃ Sn: ~3 nm	The methanol oxidation activity on PtSn/C was increased by about two times compared to that on Pt/C catalysts.
2	Huixian Shi et al., 2020	[50]	Silicon monoxide reduction process	Pt, Au	Pt intergranular spacing: 0.226 nm, corresponding to the Pt(111) crystal plane	Pt _{0.05} AuNWs with a Pt content of 1 wt% were used as catalysts for MOR, with mass activities as high as 2282.3 mA·mgpt ^{−1} .
3	L. C. Ordóñez et al., 2016	[51]	Metal carbonyl pyrolysis	Pt, Mo	Microcrystalline size of PtMo/C: 4.7–9.3 nm, Pt/C: ~5.4 nm	In the PtMo/C series, the low molybdenum content had the greatest promoter effect on the electro-oxidation of methanol.
4	Rui Zhang et al., 2018	[52]	Electro-substitution reaction method	Pt, Ag	The d(111)-spacing for PtAg is 0.228 nm	PtAg/graphene demonstrated superior specific/plasmonic activity and CO tolerance versus Pt/C.
5	V.S.Men'shchikova et al., 2020	[53]	Prepared by multi-stage reduction of metal precursors with sodium borohydride	Pt, Cu		The specific activity of this catalyst was 5–7 times higher than that of commercial Pt/C catalysts.
6	Tingting Yang et al., 2022	[54]	Using Density Functional Theory (DFT)	Pt, Pd		PtPd alloys can effectively improve the catalytic efficiency of single metals and also reduce CO poisoning.
7	Mustafa Ercelik et al., 2017	[55]	Sol–gel-synthesized TiO ₂ was integrated into commercial PtRu/C with controlled loadings (5, 15, 25 wt%).	Pt, Ru		Incorporating 5 wt% polyvinyl alcohol stabilized the polymer, while commercial TiO ₂ addition to Pt–Ru/C enhanced catalyst durability.
8	Li Min et al., 2017	[56]	Hydrothermal method	Pt, Fe	The particle size of Fe ₃ O ₄ @Pt is 200–300 nm	The peak current density of the prepared Fe ₃ O ₄ @Pt catalyst was about 1.1 times that of the pure Pt catalyst.

2.1. Platinum Catalysts of Different Sizes and Crystalline Surfaces

The implementation of nanoscale architectures substantially enhances platinum's surface-to-volume ratio, thereby improving mass-normalized catalytic efficiency. This enhancement originates from the intrinsic high surface area characteristics inherent to nanomaterial design. Optimal platinum utilization necessitates the following three critical structural parameters: (1) homogeneous nanoparticle dispersion, (2) constrained particle size distribution (<5 nm), and (3) robust metal–support interfacial interactions. As platinum particle dimensions decrease below 5 nm, corresponding increases occur in atomic utilization efficiency, surface Pt site density, and specific activity—collectively improving overall catalytic efficacy. Frelink et al. [57] systematically investigated carbon-supported Pt catalysts with controlled particle sizes (1.2–10 nm), revealing an inverse correlation between mass activity and a particle diameter below 4.5 nm, beyond which activity plateaued. This size-dependent behavior stemmed from the following two competing phenomena: smaller particles (<4.5 nm) exhibited a heightened surface oxidation susceptibility, promoting Pt–OH species formation at reduced electrode potentials, while larger particles (>4.5 nm) demonstrated CO poisoning resistance through preferential CO nucleation on low-coordination surface sites rather than complete mono-layer coverage.

The structure-sensitive nature of platinum-catalyzed methanol electro-oxidation has been rigorously established through crystallographic surface studies. Pioneering work by Koper's group employed online electrochemical mass spectrometry (OLEMS) to deconvolute pathway selectivity across low-index Pt surfaces [(111), (110), (100)] and stepped configurations (Pt(554), Pt(553)) in H₂SO₄ and HClO₄ electrolytes [58]. Through synchronized cyclic voltammetry (CV) and mass spectrometry-coupled CV (MSCV), they quantified intrinsic activity trends while mapping potential-dependent product distributions. Key mechanistic insights emerged: In H₂SO₄, Pt(111)/(110) preferentially mediated direct oxidation through solution-phase intermediates, whereas Pt(100) favored the CO_{ads}-mediated indirect pathway. Stepped surfaces in H₂SO₄ enhanced total oxidation rates but suppressed direct pathway contributions (<30% current efficiency). HClO₄ electrolytes enabled stepped surfaces to synergistically boost both total activity (>2× vs. flat surfaces) and direct pathway selectivity (>60% current efficiency). This seminal work establishes the following two critical design principles: (i) surface topology (terrace/step ratios) governs intermediate adsorption configurations and (ii) electrolyte anion identity (SO₄^{2−} vs. ClO₄[−]) modulates both pathway competition and surface poisoning dynamics through competitive adsorption.

Jarvi et al. [59] elucidated the interfacial charge transfer kinetics, intermediate poisoning dynamics, and CO₂ evolution selectivity of low-index Pt(111) versus Pt(100) surfaces during methanol electro-oxidation. Their quantitative analysis revealed that Pt(100) exhibited a 2.3-fold higher dissolution charge density across the 0.4–0.8 V potential range compared to Pt(111), indicative of its inherent electrochemical instability. Mechanistic interrogation uncovered the following two distinct reaction regimes on Pt(100): (i) below 0.50 V, methanol dehydrogenation predominantly yielded adsorbed CO (CO_{ad}), with surface coverage reaching $\theta_{\text{CO}} \approx 0.52$, and (ii) above 0.65 V, a critical onset potential triggered CO_{ad} oxidative stripping, enabling CO₂ to dominate the product distribution. These findings underscore Pt(111)'s optimal balance between activity and CO tolerance, contrasting with Pt(100)'s activity–stability trade-off—a critical consideration for durable DMFC operation.

Ferrin et al. [60] employed DFT to analyze the free energy profiles of methanol electro-oxidation intermediates on Pt(111) and Pt(100) surfaces, evaluating the potential thresholds for direct and indirect reaction mechanisms. The computational analysis revealed facet-dependent methanol oxidation mechanisms: Pt(111) favors direct oxidation at lower potentials, while Pt(100) shows lower kinetic barriers for both direct and CO-mediated pathways. These predictions suggest that Pt(111) may offer CO tolerance advantages under specific conditions, though experimental validation under practical DMFC operation (with methanol crossover and dynamic potentials) remains imperative. This facet-governed reactivity dichotomy creates the following intrinsic activity–stability trade-off: high-index facets theoretically enhance CO tolerance through adsorption energetics tuning, yet suffer from thermodynamic instability and accelerated Ostwald ripening [61]. Contemporary approaches prioritizing facet or size control fail to address concurrent DMFC requirements, necessitating alloy architectures that decouple activity–stability constraints through multifunctional site engineering.

2.2. Multi-Alloyed Platinum-Based Catalysts

Recent progress in platinum alloy catalyst development encompasses systems such as Pt-Ge, Pt-In, and Pt-Ru [62–64]. These multicomponent alloys demonstrate a markedly improved CO tolerance compared to their pure platinum counterparts, effectively mitigating catalyst deactivation while achieving enhanced mass activity. The CO poisoning resistance enhancement mechanisms in platinum alloys are predominantly governed by the following two synergistic effects: (1) electronic modulation through heteroatom-induced

d-band center downshifting, which attenuates CO chemisorption strength and lowers CO oxidation overpotential, and (2) bifunctional catalysis, where secondary metal sites facilitate hydroxyl (OH^*) generation at reduced potentials, enabling efficient CO^* oxidation through Langmuir–Hinshelwood-type surface reactions [65]. The bifunctional mechanism postulates that platinum alloys facilitate water dissociation at reduced overpotentials, generating reactive hydroxyl species (OH^*) that oxidize adsorbed CO intermediates (CO^*) through synergistic surface reactions. This dual functionality concurrently scavenges CO poisons while regenerating metallic active sites via Langmuir–Hinshelwood-type mechanisms, thereby enhancing both catalytic efficiency and long-term durability [66].

Platinum–ruthenium alloy systems are one of the most widely used fuel cell catalysts due to their lower onset potentials compared to pure platinum [67]. Pt–Ru alloy catalysts demonstrate superior methanol oxidation activity coupled with enhanced CO poisoning resistance. For decades, these alloys have served as the benchmark anode material in DMFCs [68]. In Pt–Ru alloy catalysts, the bifunctional mechanism enables Ru to oxidize CO—a key methanol oxidation intermediate [69,70]. Common synthesis methods encompass impregnation, microemulsion, colloidal synthesis, electrodeposition, and sputtering techniques [71–74]. Studies demonstrate that dual-potential pulse electrophoretic deposition from $\text{RuCl}_3/\text{H}_2\text{PtCl}_6$ electrolyte solutions produces highly dispersed Pt–Ru particles on carbon electrodes [75]. As illustrated in Figure 5, SEM micrographs reveal the morphological characteristics of a pulsed-electrodeposited Pt–Ru electrode. The observed microstructure originates from simultaneous nucleation at both carbon substrate interfaces and pre-existing catalytic particles during the pulsed potential deposition process. Through systematic variation of the pulse frequency, both the nanoparticle dimensions and the metal deposition density can be precisely engineered.

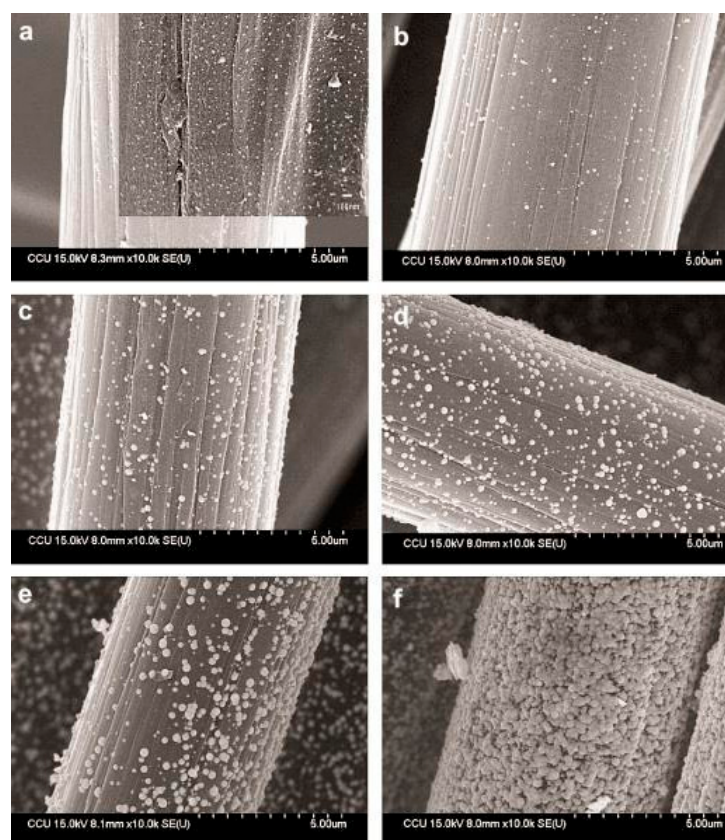


Figure 5. SEM micrographs of Pt–Ru electrodes: (a) 50, (b) 100, (c) 200, (d) 300, (e) 500, and (f) 2000 cycles of repetitive bipotential pulses, with electrolytes of 6.0 mM RuCl_3 and 14.0 mM H_2PtCl_6 [75].

Binary platinum-based catalysts demonstrate an enhanced activity and CO tolerance compared to monometallic systems while maintaining cost efficiency, yet their compositional homogeneity fundamentally restricts further performance optimization. The strategic incorporation of tertiary metallic components creates ternary alloy architectures that effectively mitigate hydrogen underpotential deposition (H₂ UPD)-induced site blocking during methanol oxidation, thereby improving Faradaic efficiency through the selective exposure of Pt active sites [76]. Ternary PtRuM (M = Fe, Co, Ni, Rh, and Ir) exhibits a superior CO tolerance compared to pure platinum and platinum–ruthenium [77]. Iron is a potential candidate material to achieve this goal. The introduction of iron into ternary platinum alloy catalysts for DMFC anodes weakens the Pt–CO bond, thereby enhancing the durability of the catalyst [78]. The strategic incorporation of iron—a cost-efficient alternative to platinum-group metals—significantly enhances the economic viability of DMFC commercialization. Jeon et al. [79] demonstrated this through the synthesis of PtRuFe/C (Pt:Ru:Fe = 2:1:1, 60 wt%) via impregnation, achieving a 2.5-fold mass activity enhancement and 2-fold specific activity improvement over commercial PtRu/C, coupled with a 60 mV reduction in onset potential (0.44 V vs. RHE). Remarkably, the catalyst exhibited negligible iron dissolution in acidic electrolytes, despite Fe precursors costing merely 0.26% (vs. Pt) and 0.71% (vs. Ru) of their noble metal equivalents. Mechanistic analysis attributed the performance enhancement to ruthenium-mediated hydroxyl (OH[−]) adsorption and the iron-induced electronic structure modulation of platinum, which collectively weakened CO binding energetics. Complementing these findings, Cai et al. [80] developed ultrathin branched PtRuFe nanodendrites via solvothermal synthesis, demonstrating exceptional mass (6.02×) and specific (4.95×) activity enhancements relative to Pt/C. X-ray photoelectron spectroscopy revealed a 0.35 eV negative shift in Pt 4f binding energies, indicative of electron-deficient Pt sites that destabilize Pt–CO bonds. Concurrently, ruthenium incorporation promoted OH adsorption kinetics, synergistically accelerating CO oxidation through Langmuir–Hinshelwood mechanisms. Extended chronoamperometry (24 h) and 1000-cycle CV testing confirmed <5% activity decay, underscoring an exceptional structural integrity and poisoning resistance.

Molybdenum's unique combination of low onset potential and exceptional CO tolerance positions it as a promising component for advanced DMFC anode catalysts. Kakati et al. [81] demonstrated this potential through the hydrothermal synthesis of PtRuMo/MWCNT catalysts, which exhibited superior methanol oxidation activity and stability compared to PtRu/MWCNT benchmarks. The ternary system achieved the following three critical performance enhancements: (1) a 12% larger electrochemical active surface area, (2) an 80 mV cathodic shift in onset potential, and (3) a 35% reduction in charge transfer resistance. Chronoamperometric analysis revealed a 40% slower current density decay over 3600 s of operation, while XPS identified MoO_x species that facilitated water dissociation kinetics through electron donation to Pt, thereby weakening Pt–CO adsorption strength. Complementing these findings, Park et al. [82] synthesized Pt₄₃–Ru₄₃–Mo₁₄/MWCNT catalysts displaying the following two key advantages: (1) a 150 mV lower onset potential versus pure Pt and (2) a 2.6-fold enhancement in the forward/reverse current ratio. Electrochemical impedance spectroscopy quantified a 55% lower charge transfer resistance, directly correlating with accelerated methanol oxidation kinetics. These studies collectively establish molybdenum's dual role as both an electronic modulator and hydroxyl radical provider, synergistically mitigating CO poisoning while enhancing reaction thermodynamics. Theoretical studies indicate negligible platinum surface enrichment in PtNi alloys [83,84]. Unlike ruthenium in PtRu catalysts, nickel in PtNi systems demonstrates an enhanced resistance to dissolution in DMFC electrolytes through the formation of stable Ni(OH)₂ passivation layers, thereby improving structural

integrity. Liang et al. [85] synthesized PtRuNi/C catalysts via a microwave-assisted polyol method, with TEM characterization confirming uniform nanoparticle dispersion (3.6 nm average particle size versus 3.2 nm for PtRu/C). XRD analysis revealed lattice contraction compared to PtRu/C, indicative of Ni-induced alloying effects and lattice distortion. A synergistic mechanism involving the following three interconnected processes was identified: (1) conductive Ni(OH)₂ layers enhanced interfacial charge transfer kinetics, (2) hydrogen spillover effects accelerated CO oxidation through adjacent active sites, and (3) nickel alloying modified the electronic structure of platinum, weakening Pt-CO interactions. The dynamic Ni(OH)₂/NiOOH redox cycle further contributed to CO oxidation by supplying reactive oxygen species. The following Table 2 compares the key performance data of the above ternary alloy catalysts.

Table 2. Comparative data between ternary PtRu alloy catalysts and benchmark catalysts.

Catalyst Name	Refs	Mass Activity (Baseline)	Mass Activity (Novel)	Key Improvements/Mechanisms
PtRuFe/C (2:1:1)	[79]	2.28 A/g catal	5.67 A/g catal	2.5× higher mass activity; Fe ₂ O ₃ induces Pt electron deficiency, enhancing CO oxidation.
PtRuFe nanodendrites	[80]	0.19 A/mg Pt (Pt/C)	1.14 A/mg Pt	6× mass activity vs. Pt/C; ultrathin branches and ternary synergy improve CO tolerance.
PtRuMo/MWCNT	[81]	12.6 A/cm ² ·mg (PtRu/C)	15 A/cm ² ·mg	Enhanced ECSA (138 vs. 134 m ² /g); Mo promotes water activation and reduces CO adsorption.
Pt43-Ru43-Mo14/MWCNT	[82]	0.19 A/mg Pt (Pt/C)	1.14 A/mg Pt	6× mass activity vs. Pt/C; flash synthesis improves dispersion; Mo enhances CO tolerance.
PtRuNi/C	[85]	30.6 m ² /g EAS (PtRu/C)	40.7 m ² /g EAS	CO oxidation peak decline; Ni(OH) ₂ enables H-spillover and proton conduction; high stability.

These combined properties enable ternary Pt alloys (PtRuFe, PtRuMo, and PtRuNi) to outperform many of their bimetallic counterparts and pure Pt catalysts in terms of methanol oxidative activity and carbon monoxide tolerance in specific environments, making them favorable candidates for anode catalysts in persistent DMFC systems.

2.3. Platinum-Based Core–Shell Structures

The atomic-level precision of core–shell architectures enables the following dual functionality through interfacial engineering: (1) electron transfer from core to shell induces ligand and strain effects that optimize platinum’s d-band center position, thereby enhancing methanol dehydrogenation kinetics, and (2) subnanometer-scale platinum confinement within the shell achieves a near-unity dispersion efficiency, maximizing surface atom accessibility while minimizing noble metal consumption. This synergistic electronic-geometric modulation establishes an ideal platform for simultaneous activity enhancement and resource economization in DMFC catalysis [86–89].

The precise control of platinum deposition constitutes the cornerstone of this methodology. Wet-chemical synthesis enables atomic-level control over Pt shell formation through the strategic manipulation of precursor chemistry and reduction kinetics, facilitating tunable architectures from sub-mono-layer to multi-layer configurations on transition metal cores. This approach leverages the competitive adsorption dynamics between Pt precursors and core surface binding sites, achieving surface-selective deposition while suppressing parasitic galvanic replacement reactions [90]. Core–shell architectures synergized with alloying technology effectively reduce Pt content while enhancing catalytic efficiency. The Pt shell acts as a corrosion barrier, prolonging core metal stability [90–92]. The integration of alloying effects into epitaxial platinum overlayers preserves the geometric benefits of core–shell architectures while enabling precise electronic structure modulation. This hierar-

chical design strategy demonstrates significant potential for developing high-performance DMFC catalysts with reduced platinum loading. Wu et al. [93] exemplified this approach through the colloidal synthesis of PdPt@Pt/C core-shell catalysts, which exhibited 2.85-fold and 3.91-fold enhancements in methanol oxidation peak currents compared to commercial and laboratory-synthesized Pt/C benchmarks, respectively. At an operational cell voltage of 0.65 V (vs. RHE), the catalyst achieved over an 80% higher current density than commercial Pt/C. Comprehensive characterization via TEM, XPS, and XRD confirmed preserved core-shell interactions and structural integrity during electrochemical operation. Cheng et al. [94] developed dealloyed-annealed PtRuCo_x core-shell nanoparticles, where thermal treatment at 450 °C yielded an ultrathin PtRu shell (~1 nm) with the following two key advantages: (1) a 90 mV cathodic shift in onset potential (0.01 V vs. RHE) relative to bulk PtRuCo alloys and (2) 75% higher steady-state current density retention versus PtRu/C after 5000 s of chronoamperometric testing. As illustrated in Figure 6, the enhanced methanol oxidation activity and structural stability originate from the synergistic combination of cobalt-rich cores and platinum-group metal shells, which collectively optimize intermediate adsorption energetics while suppressing metal dissolution. These studies establish a universal framework for designing multi-metallic core-shell catalysts that transcend conventional activity-stability trade-offs in DMFC applications.

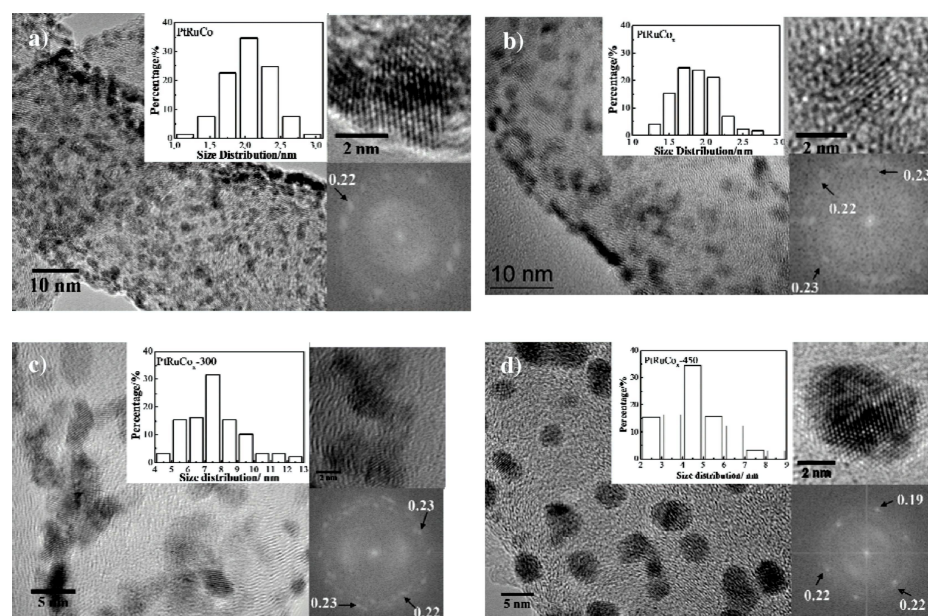


Figure 6. TEM micrographs, histograms, and Fast Fourier Transform (FFT) images of (a) PtRuCo, (b) PtRuCo_x, (c) PtRuCo_x-300, and (d) PtRuCo_x-450 [94].

The catalytic activity of platinum-based catalysts exhibits a direct correlation with compressive strain within platinum-rich surface layers. Strasser et al. [95] established experimental and theoretical correlations between lattice parameter differences in platinum shells compared to bulk platinum, identifying compressive strain—resulting from atomic lattice distortions caused by interfacial forces and thermal gradients—as a critical factor enhancing electrocatalytic activity. Wang et al. [96] demonstrated this concept through Ru-core/Pt-shell nanostructures, where the smaller lattice parameter of Ru cores induced compressive strain in mono-layer Pt shells. This structural modification achieved a 450% increase in DMFC power density and a 0.18 V improvement in open-circuit voltage (OCV) compared to platinum nanoparticles. XRD, SAXS, and HRTEM characterization confirmed the presence of 1.5-layer Pt shells under compressive strain. The performance enhancement was attributed to strain-optimized Pt-Ru electronic interactions that improved

methanol electrooxidation efficiency. Wang et al. [97] engineered Cu@CuPt core-shell concave octahedrons through solvothermal synthesis, achieving nanocrystals with high-index facets containing high-density atomic steps and terraces. These structures demonstrated 8.6-fold higher specific activity and 13.1-fold greater mass activity for methanol oxidation compared to commercial Pt/C, alongside an exceptional durability under prolonged potential cycling. In parallel, dealloying-derived nanoporous metals/alloys have emerged as promising DMFC anode materials. This process selectively dissolves electrochemically active elements from parent alloys to create porous architectures [98]. Singh et al. [99] exemplified this approach through the surface dealloying of PtAg alloys, where preferential Ag dissolution generated nanoporous Pt-rich shells with retained core-shell interfaces. The resulting porous PtAg nanoparticles exhibited intrinsic CO tolerance through optimized *CO intermediate adsorption/desorption energetics, providing new pathways for designing poison-resistant DMFC catalysts.

The systematic optimization of Pt-based catalysts through size engineering (<5 nm nanoparticles), alloy design, and core-shell architectures has established well-defined performance benchmarks for DMFC anodes: mass activities of 1.2–3.5 A mgPt^{−1}, CO oxidation initiation at 0.2–0.4 V vs. RHE, and an operational stability within 0.05–0.4 V. However, evaluating non-Pt catalysts against these Pt benchmarks remains scientifically fragmented due to inconsistent testing protocols. To enable meaningful comparisons, future studies must enforce the following three operational alignments: (1) equivalent methanol concentrations, (2) matched temperature ranges (60–80 °C for practical DMFCs), and (3) identical catalyst loading. Under such standardized conditions, performance metrics, including CO^{*} oxidation efficiency (via in situ spectroscopy) and voltage cycling stability, should be quantitatively contrasted. This framework not only contextualizes non-Pt advancements relative to mature Pt systems, but also identifies condition-specific advantages that may justify Pt-free alternatives.

3. Platinum-Free Catalysts for DMFC Anodes

While platinum-based catalysts exhibit an unparalleled catalytic performance in DMFC anodes, their sustainable deployment has been fundamentally constrained by the following tripartite nexus of limitations: resource scarcity stemming from finite global reserves, the environmental ramifications of carbon-intensive extraction and processing, and economic vulnerabilities exacerbated by market volatility coupled with inadequate closed-loop recovery infrastructure. The exponential proliferation of fuel cell technologies has critically amplified the structural disequilibrium between platinum supply chains and industrial demand. Furthermore, legacy refining protocols generate substantial lifecycle carbon footprints while demonstrating persistently suboptimal recovery rates (<30% in most industrial economies). This synergistic interplay of multidimensional resource–environment–economic constraints creates an imperative mandate for developing non-platinum alternatives that harmonize operational sustainability with technologically viable implementation pathways.

Non-Pt catalyst degradation arises from the following three primary mechanisms [100–103]: (1) acid-driven metal dissolution, (2) CO^{*}/intermediate poisoning through strong adsorption, and (3) nanoparticle coalescence. The strategy for mitigating the degradation of non-Pt catalysts is usually a synergistic approach: alloying modifies electronic structures to resist dissolution and weaken CO binding; heterointerfaces accelerate intermediate desorption via charge redistribution; and confined carbon architectures inhibit agglomeration through spatial anchoring. This multiscale engineering framework—spanning atomic (electronic), nanoscopic (interfacial), and mesoscopic (structural) regimes—overcomes traditional stability–activity trade-offs while preserving sustainable manufacturability.

3.1. Palladium-Based Catalysts

The catalytic activity of palladium-based catalysts originates from synergistic bifunctional and ligand effects [100]. The bifunctional mechanism requires the following two distinct active sites: one for methanol adsorption and dissociation, and another for water adsorption and activation. Ligand effects modify palladium's electronic structure to weaken CO adsorption, enabling CO oxidation at reduced potentials. Although palladium is less expensive than platinum, its cost remains prohibitive for large-scale DMFC commercialization due to inherent material scarcity and insufficient durability under operational conditions [101,102]. This development has propelled research into non-precious metals (Ni and Cu) exhibiting significant methanol oxidation activity in alkaline media combined with cost advantages. Incorporating these metals into palladium-based catalysts has become crucial for reducing DMFC costs. Mandal et al. [103] synthesized Pd-Cu (3:1) nanoalloys via room-temperature soft chemistry, demonstrating superior methanol oxidation activity compared to pure Pd while maintaining an equivalent catalytic efficiency. By significantly reducing palladium usage without compromising performance, this approach effectively lowers material costs. The Pd-Cu alloy system thereby emerges as a promising candidate for commercial DMFC anode catalysts. Mansor et al. [104] prepared NiPd catalysts supported on mesoporous silica via the sol-gel method. Characterization with XRD, FESEM, FTIR, BET, and XPS confirmed high NiPd dispersion. Electrochemical tests showed 61% current retention after 3600 s, enhanced CO removal, a lower Tafel slope, and a higher exchange current density compared to pure Pd. The activity improvement stemmed from NiPd dispersion and synergy, adjustable through Pd content variation, with an optimal performance at the highest Pd concentration due to reduced crystallite sizes. Tan et al. [105] investigated Pd-CeO₂ nanoparticles on nitrogen-doped mesoporous carbon (NMCS) for alkaline methanol oxidation. The NMCS support enabled uniform Pd/CeO₂ dispersion, with optimized Pd(20%)-CeO₂(20%)/NMCS exhibiting a 6× higher current density and 93% activity retention after 1000 cycles versus PtRu/C. Strong Pd-CeO₂ interactions and nitrogen doping reduced CO adsorption energy, enhancing CO tolerance. The strategic encapsulation of catalytic species within ordered mesoporous frameworks enhances active site accessibility through hierarchical mass transport channels while conferring an exceptional structural robustness against electrochemical degradation [106]. These technological breakthroughs establish transformative design principles for palladium-based catalyst systems, simultaneously achieving superior electrode kinetics and economically viable DMFC deployment strategies via precision-engineered material architectures.

3.2. Perovskite-Type Oxide Catalysts

Perovskite-type oxides have emerged as highly promising DMFC anode catalysts owing to their inherently ordered lattice frameworks and superior electronic conductivity. The archetypal ABO₃ structure exhibits A-site occupancy by rare-earth cations (e.g., La³⁺ and Ce⁴⁺) or alkaline-earth species (e.g., Sr²⁺ and Ba²⁺), while transition metal cations (e.g., Co³⁺, Mn³⁺, and Ni³⁺) predominantly populate the B-site sublattice [107]. Such an exceptional compositional flexibility allows for precise control over methanol oxidation activity via strategic A/B-site cation substitution [108]. Advances in synthesis protocols build upon conventional approaches, including hydrothermal, sol-gel, and precipitation routes, which remain industrially relevant due to their optimal balance of manufacturing economy and process scalability. Singh et al. [109] synthesized perovskite-type La_{2-x}Sr_xNiO₄ (0 ≤ x ≤ 1) oxides via a modified citric acid sol-gel method. Through comprehensive physicochemical characterization and systematic electrochemical analysis, they demonstrated exceptional methanol oxidation activity in alkaline media coupled with resistance to intermediate/product poisoning. Sr substitution concomitantly enhanced the oxide's

zero-point charge and methanol electro-oxidation efficacy. Notably, at 0.55 V vs. RHE in 1 M KOH (25 °C), the $\text{La}_{1.5}\text{Sr}_{0.5}\text{NiO}_4$ electrode achieved a sustained current density exceeding 200 mA/cm^2 , substantially surpassing most state-of-the-art electrodes reported to date. Prince et al. [110] fabricated RuNiO_3 -modified nickel foam (RNO/NF) through solid-state synthesis. Combined SEM/XRD/XPS characterization unambiguously confirmed a high crystallinity, wherein Ru^{4+} and Ni^{2+} preferentially occupied perovskite A/B-sites, respectively. As evidenced in Figure 7, the optimized RNO/NF demonstrated high mass-specific current densities while maintaining > 80% activity retention after 10,000 s of continuous methanol oxidation, significantly outperforming commercial Pt/C benchmarks. This performance enhancement originated from the synergistic coupling of $\text{Ni}^{2+}/\text{Ni}^{3+}$ redox catalysis, Ru-induced structural stability, and abundant surface oxygen functional groups, establishing a cost-effective electrocatalyst paradigm for DMFCs.

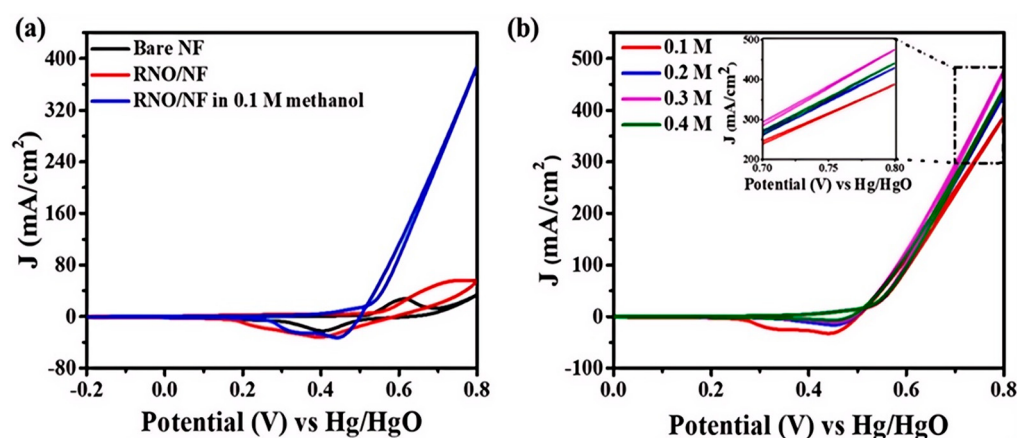


Figure 7. (a) CV of the bare nickel foam and the RNO-modified NF electrode in KOH medium. (b) CV data of the RNO-modified electrode in varying concentrations of methanol with the inset indicating the clear increase in current density at 0.8 V with varying concentrations of methanol [110].

Perovskite-type oxides manifest distinct advantages not merely through enhanced catalytic activity and stability, but more significantly through an exceptional resistance to coking and poisoning phenomena [111]. These materials effectively suppress coke formation during catalytic oxidation by virtue of unique surface electronic configurations that disrupt intermediate aggregation and mitigate carbonization pathways. Rational doping engineering further improves impurity (e.g., sulfides/chlorides) tolerance via the precise control of cationic composition to strategically tailor d-band center positions and surface chemisorption properties. Notably, their structural robustness under harsh thermal/mechanical conditions ensures the preservation of active site coordination environments, thereby guaranteeing a sustained catalytic efficiency throughout prolonged operation.

3.3. Metal Carbide Catalysts

The d-band electronic structure of transition metal carbides closely mimics that of platinum, endowing them with a catalytic performance rivaling that of noble metals in multiphase electrochemical reactions. In particular, tungsten carbide (WC) has garnered sustained scientific attention since the 1960s owing to its atomic hybridization featuring synergistic covalent, ionic, and metallic bonding characteristics, which collectively engender platinum-like adsorption/desorption kinetics [112,113]. These fundamental attributes establish WC as a compelling candidate for next-generation DMFC anode electrocatalysts. Conventionally synthesized via the solid-phase carbothermal reduction of tungsten salts at 1200–1600 °C, WC demonstrates an exceptional acid corrosion resistance coupled with a methanol electro-oxidation activity comparable to benchmark Pt catalysts. Notably,

excessive pyrolytic carbon deposition during gas-phase synthesis encapsulates active sites, necessitating post-synthetic acid leaching protocols to restore surface accessibility. This phenomenon underscores the intrinsic stability compromise dilemma in metal carbide systems under oxidative potentials. Emerging approaches focus on strategic alloying with transition metals to construct W-based bimetallic carbides with tailored electronic structure modulation via synergistic d-band center regulation [114,115]. Nickel-based materials have emerged as economically viable electrocatalysts, exhibiting a methanol oxidation activity approaching noble metal benchmarks. The interfacial charge transfer in Ni-WC heterostructures synergistically ameliorates CO adsorption via electronic coupling effects, thereby boosting electrocatalytic turnover frequency and extending operational durability [116–118]. Figure 8 below shows a tungsten surface species model.

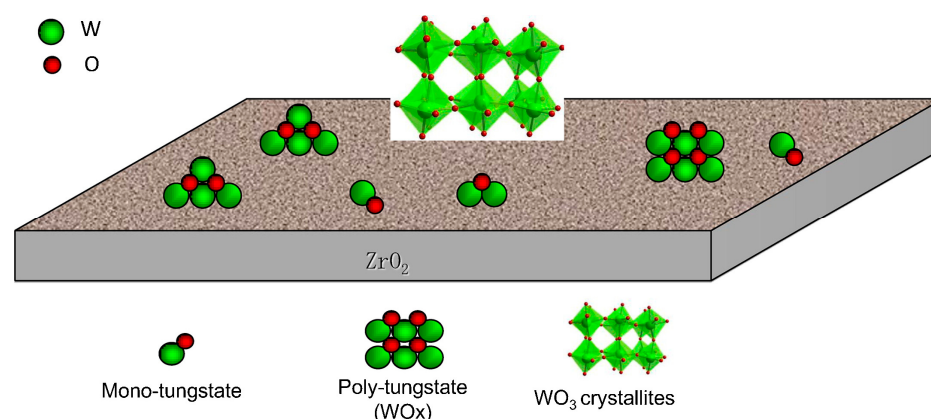


Figure 8. Models of tungsten surface species evidenced by HRTEM [118].

Hou et al. [119] engineered a Ni-WC/CA composite electrode through the sequential impregnation–annealing of nickel-based catalysts and 1.6 nm-average WC nanoparticles onto bacterial cellulose-derived carbon aerogel (CA). When deployed in DMFC and DUFC anode reactions, this architecture alleviated the CO-poisoning-induced activity decay prevalent in conventional Ni catalysts via WC-mediated electron transfer pathways and interfacial Ni-WC charge redistribution that attenuated CO adsorption strength. Advanced material characterization revealed uniform nanoscale WC/Ni distribution accompanied by verifiable interfacial electron transfer via XPS valence band analysis. Electrochemically, the electrode delivered an MOR current density of 105.7 mA cm^{-2} at 0.8 V vs. RHE in 1 M KOH, surpassing Pt-free counterparts by >40%. Accelerated durability testing demonstrated 48.94% peak current retention after 2000 potential cycles in used electrolyte, whereas reactivation through electrolyte replenishment restored its performance to 88.42% of its initial activity. This breakthrough establishes a scalable non-noble-metal catalyst platform with a simultaneously enhanced CO tolerance and regenerative stability for fuel cell applications. Collectively, modified tungsten carbide has been unequivocally validated as a frontier anode material system. Kelly et al. [120] investigated the bond scission sequences (O-H, C-H, and C-O) of methanol on Ni-, Rh-, and Au-modified WC surfaces. Methanol adsorption predominantly occurred at atop sites of both pristine and modified WC surfaces, while methoxy species exhibited varied adsorption configurations. Metal-modified WC surfaces demonstrated stronger methanol/methoxy binding compared to pure metal surfaces, with WC-based systems showing superior overall activity. Notably, Ni/WC and Rh/WC effectively suppressed methane formation, contrasting with the reduced activity of Au/WC. The initial O-H bond cleavage enabling methoxy formation was observed across all systems, where Rh/WC and Ni/WC exhibited enhanced methoxy decomposition activity relative to Au/WC. Al-Enizi et al. [121] synthesized CoCr_7C_3 nanorods encapsulated in carbon nanofibers through electrospinning. Electrochemical evaluation in alkaline media revealed

improved methanol electro-oxidation activity, particularly in surface oxidation processes. CoCr₇C₃-CNF composites are not only cost-effective, but also highly active and stable, highlighting the potential of metal carbides as promising anode catalysts for DMFCs, which deserves further investigation.

While metal carbides demonstrate a compelling catalytic performance in DMFC anodes, their transition from laboratory-scale synthesis to industrial deployment faces significant scalability hurdles. Conventional high-temperature fabrication methods (>800 °C)—essential for achieving phase-pure carbide crystallinity—impose substantial energy penalties (>150 kWh kg^{−1}) and induce irreversible particle agglomeration (e.g., growth from 5 nm to >50 nm during scale-up), thereby diminishing electrochemical surface area. Emerging low-temperature routes (<300 °C), such as solution-phase carburization, partially mitigate sintering but typically yield amorphous or carbon-overloaded phases that degrade methanol oxidation kinetics. Furthermore, lifecycle cost analyses reveal a critical trade-off: while carbide materials circumvent platinum's scarcity, their synthesis energy intensity may offset the cost advantages relative to Pt/C systems produced via established low-energy pathways (e.g., wet impregnation at <100 °C). Addressing these challenges necessitates synergistic advances in scalable reactor designs (e.g., roll-to-roll plasma processing) and carbide structural engineering (e.g., MXene-templated porous architectures) to decouple performance retention from energy-intensive synthesis.

3.4. MOF and Its Derivatives

The optimization of catalytic materials necessitates the synergistic convergence of materials science and electrochemical engineering principles. A maximized specific surface area enhances catalytic efficiency by maximizing active site exposure and facilitating reaction kinetics through an increased electrochemical interface density. Superior charge transfer kinetics and reactant/product diffusion characteristics are imperative: rapid charge transfer mitigates kinetic overpotential limitations, while optimized mass transport alleviates concentration polarization to maintain sustained reaction flux. Crucially, hierarchical porosity dictates methanol adsorption dynamics via molecular-scale anchoring sites that orchestrate subsequent electro-oxidation pathways. Emerging paradigms highlight metal–organic frameworks (MOFs) and their derivatives as structurally programmable candidates for DMFC anode catalysis. MOFs constitute crystalline coordination polymers featuring periodic porous architectures formed through metal cluster/linker coordination assembly [122–126].

The ultrahigh porosity and large specific surface area of MOFs endow them with a superior methanol adsorption capacity, which contributes to an enhanced DMFC energy conversion efficiency. Zhou et al. [127] synthesized MOF-74(Ni)/NiOOH heterostructured composites via the in situ transformation of NiOOH microsphere precursors. As demonstrated in Figure 9, structural characterization revealed a hierarchical porous architecture, with XPS analysis indicating interfacial interaction-induced electronic structure modifications of Ni species. Electrochemical testing in 0.1 M KOH/1.0 M CH₃OH achieved a peak current density of 27.62 mA cm^{−2} and mass activity of 243.8 mA mg^{−1}, representing 1.8-fold and 1.76-fold improvements over pristine MOF-74(Ni), respectively. Mechanistic analysis suggested that heterointerface-induced synergy enhanced active site exposure, optimized charge transport, and facilitated reactant diffusion through the NiOOH structure. This work provides a methodology for designing metal hydroxide/MOF heterostructures via in situ conversion, advancing non-precious metal MOR catalyst development.

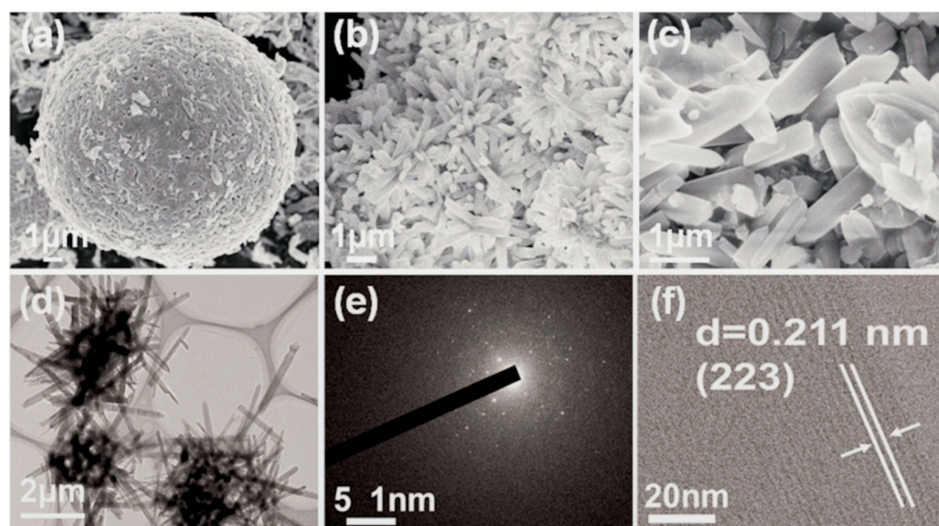


Figure 9. (a) SEM image of NiOOH. (b,c) SEM image of MOF-74(Ni)/NiOOH. (d) TEM image of MOF-74(Ni)/NiOOH, (e) SEAD pattern of MOF-74Ni/NiOOH. (f) HRTEM image of MOF-74Ni/NiOOH [127].

Sheikhi et al. [128] synthesized mesoporous $\text{Cu}_{2-x}\text{Se@PCs}$ through the carbonization–selenization of a Cu-MOF precursor, retaining an octahedral morphology while forming non-stoichiometric $\text{Cu}^+/\text{Cu}^{2+}\text{-Se}^{2-}/\text{C-Se-C}$ active sites. The material exhibited a surface area of $58.2 \text{ m}^2 \text{ g}^{-1}$ with dominant pore sizes of 26.3 nm. In 1 M NaOH/0.5 M CH_3OH electrolyte, it achieved a methanol oxidation current density of 629.3 mA cm^{-2} , tripling the performance of non-selenized $\text{Cu}/\text{Cu}_2\text{O@PCs}$, along with reduced overpotential. The low electronegativity of selenium enhanced OH^- adsorption and transport, facilitating CO oxidation via bifunctional mechanisms, supported by a 66% reduction in charge transfer resistance. Chronopotentiometric testing at 22.3 mA cm^{-2} for 4 h and 88.5% current retention after 300 cycles demonstrated effective protective dispersion by the carbon matrix. This performance exceeds conventional Ni/Co-based catalysts, confirming structural advantages for alkaline methanol oxidation. Rajpure et al. [129] developed a NiCo-MOF-P bimetallic phosphide electrocatalyst via sequential electrodeposition, in situ MOF growth, and the phosphorization of layered double hydroxide (LDH)–MOF precursors. Electrocatalytic evaluation in 1 M KOH/0.5 M CH_3OH revealed an exceptional performance attributed to the following: (i) structural stabilization by NiCo-LDH substrates suppressing particle aggregation, (ii) Ni-P/Co-P active sites generated through phosphorization augmenting interfacial electron transfer, (iii) bimetallic synergy accelerating $\text{Ni}^{2+}/\text{Ni}^{3+}$ and $\text{Co}^{2+}/\text{Co}^{3+}$ redox transitions crucial for methanol dehydrogenation kinetics, and (iv) the three-dimensional porous architecture providing a $3.3\times$ higher electrochemical active surface area than conventional $\text{Ni}(\text{OH})_2$. This methodology establishes a carbonization-free synthetic route for the scalable production of MOF-derived non-precious metal catalysts surpassing state-of-the-art Ni/Co-based materials in activity–stability metrics.

Although significant advancements have been achieved for non-platinum catalysts, practical benchmarking tests reveal that these alternatives exhibit a substantially inferior performance to Pt/C catalysts in actual DMFC operation, demonstrating only 60–80% of the current density attained by their Pt/C counterparts. Furthermore, they lag markedly in durability parameters (displaying 2–3 times faster decay rates than Pt/C catalysts) and onset potential consistency under operational conditions. Tungsten carbides approach Pt-level activity in controlled environments, but suffer voltage hysteresis under dynamic loads. MOF-derived systems maximize surface-area-driven activity, yet underperform in full cell configurations due to mass transport limitations. These gaps necessitate hybrid

strategies blending non-Pt active components with nanoscale Pt stabilization or advanced support engineering to meet commercial viability thresholds.

4. Carbon Carriers for DMFC Anode Catalysts

Carbon-based materials serve as pivotal catalyst supports in DMFCs, systematically categorized into the following four classes: (i) pristine carbon matrices, (ii) composite carbon architectures, (iii) heteroatom-doped (metal/non-metal) carbon frameworks, and (iv) metal oxide/polymer-functionalized carbon materials [130,131]. These structural variants exhibit tailored heterogeneities that govern discrete electrocatalytic performance profiles through the following three mechanistic vectors [132,133]: morphological control of metallic nanoparticles (size regulation, dispersion optimization, alloying precision, and stability enhancement), augmented mass/charge transfer capabilities via enhanced conductivity and nanostructural stabilization, and kinetic pathway modulation enabled by three-dimensional topological effects coupled with surface chemistry engineering. The rational design of carbon carriers—achieved through hierarchical porosity engineering, targeted surface functionalization, and interfacial electronic optimization—represents a critical pathway for developing next-generation DMFC anode catalysts with superior activity–stability metrics [134,135].

4.1. Single Versus Multiple Carbon Loads

While carbon-supported materials are not conventionally rigidly classified in academic research or practical applications, they are operationally categorized into single-carbon-supported and multi-carbon-supported systems based on structural hierarchy. Single-carbon-supported materials comprise mono-layer or few-layer carbon architectures exhibiting a well-defined structural uniformity and enhanced surface reactivity owing to minimized interlayer screening effects. This classification framework provides a foundational basis for rationalizing structure–property relationships in DMFC anode catalyst design [136]. Prototypical single-carbon-supported systems encompass carbon black, mesoporous carbon, carbon nanofibers, single-walled carbon nanotubes (SWCNTs), and graphene [137–139]. Multi-carbon-supported materials, in contrast, are defined by carbon-based architectures with multi-layered atomic configurations or complex hierarchical structuring, characterized by enhanced specific surface areas coupled with a superior mechanochemical robustness. Exemplary implementations include multi-walled carbon nanotubes (MWCNTs) featuring concentric graphitic cylinders and hierarchically porous carbons with three-dimensionally interconnected micro/mesoporous networks [140].

The commonly employed carbon blacks include acetylene black [141], Vulcan XC-72 [142], and Ketjen Black [143]. Vulcan XC-72 carbon black demonstrates an exceptional specific surface area coupled with metallic-grade electronic conductivity, establishing it as the benchmark support material in DMFC catalyst design. However, its propensity for electrochemical corrosion and surface oxidation under prolonged DMFC operation induces precious metal nanoparticle detachment, leading to irreversible performance degradation via active site loss. In contrast, mesoporous carbons (MCs) leverage tunable mesoporous architectures to achieve simultaneous enhancements in the following: (i) accessible surface area, (ii) interfacial charge transfer resistance, and (iii) mass transport kinetics through engineered pore networks, collectively optimizing reactant flux to catalytic active sites [144,145]. The structural taxonomy of mesoporous carbons (MCs) dichotomizes ordered mesoporous carbons (OMCs)—featuring monodisperse pore size distribution and long-range structural periodicity—from disordered mesoporous carbons (DMCs) with polydisperse pore geometries. Carbon nanofibers (CNFs), as one-dimensional carbon allotropes, are classified into the following three microstructural archetypes based on their

graphene layer axial alignment: (i) platelet-type CNFs with basal planes orthogonal to the fiber axis, (ii) herringbone-type CNFs exhibiting multidirectional stacking ($\theta = 0\text{--}90^\circ$), and (iii) tubular-type CNFs containing coaxial graphene layers parallel to the growth axis [146]. SWCNTs manifest seamless cylindrical nanostructures via the helical winding of singular graphene sheets, while MWCNTs comprise concentric graphene cylinders that synergize metallic conductivity with an exceptional Young's modulus. Notwithstanding these merits, practical deployment remains constrained by inherent structural imperfections and inter-tubular Van der Waals interactions, precipitating a compromised macroscopic performance through electron scattering and mechanical failure pathways.

While conventional graphite served as a foundational carbon support in early fuel cell development due to its moderate conductivity and chemical inertness, its limited accessible surface area and sluggish interfacial charge transfer kinetics constrain its applicability in next-generation electrodes requiring atomic-level precision. In contrast, graphene's 2D confinement effect and edge-rich architecture enable unparalleled electrocatalytic functionality, making it a quintessential upgrade over traditional graphite-based systems. Graphene, a two-dimensional monolayer of sp^2 -hybridized carbon atoms arranged in a hexagonal lattice, manifests an exceptional electrical conductivity, ultrahigh specific surface area (theoretical limit: $2630\text{ m}^2\text{ g}^{-1}$), and superior electrochemical stability coupled with mechanical robustness [147]. These intrinsic properties establish it as a paradigm material for electrocatalytic systems, particularly in direct methanol fuel cell applications where simultaneous demands for rapid charge transfer, maximized active site exposure, and structural durability must be reconciled. Extensive studies focus on graphene functionalization strategies to modulate supported nanoparticle morphology and properties. Choi et al. [148] synthesized oxygen-functionalized graphene nanosheets (GNSs) through chemical oxidation and thermal exfoliation, achieving 80 wt% platinum loading. The functionalized GNSs exhibited a specific surface area of $487\text{ m}^2\text{ g}^{-1}$ and electrical conductivity of 3095 S m^{-1} . Surface oxygen groups enabled uniform Pt nanoparticle dispersion with a minimal size of 2.9 nm at 80 wt% loading, outperforming conventional supports that showed 7.0 nm particles under identical conditions. This enhancement originated from the three-dimensional layered GNS structure, which shortened reactant transport pathways through ultrathin catalytic layers while providing high-conductivity electron transfer networks. Figure 10 shows a synthesis schematic of graphene derived from graphite, with structural diagrams and scanning electron microscopy images (inset displays a high-resolution view).

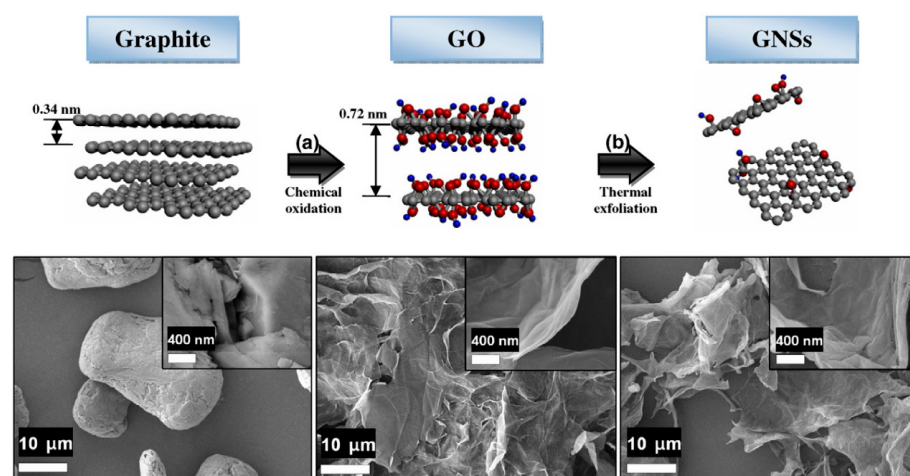


Figure 10. (a) Chemical oxidation to form GO from graphite. (b) Thermal exfoliation to synthesize surface functionalized GNSs from GO. The red- and blue-colored atoms on the surface of graphite oxide and GNSs represent oxygen and hydrogen species, respectively [148].

While graphene and CNTs offer a superior conductivity and surface area, their practical implementation faces cost and manufacturing hurdles. High-quality graphene synthesis remains energy-intensive with a limited throughput, while CNTs require complex post-synthesis purification to remove metal residues. In contrast, conventional carbon black provides cost-effective scalability despite a moderate performance. As a result, researchers have attempted to develop multicarbon composites that synergistically integrate the advantages of multiple carbon qualities. A predominant approach involves grafting one-dimensional carbon materials (e.g., carbon nanotubes) onto substrates to construct hierarchical structures. The coral-like multicarbon material (Coral-C), comprising curled multi-walled carbon nanotubes grown on carbon black, demonstrates an exceptional electronic conductivity, chemical stability, and hydrophobicity [149]. Pt catalysts supported on Coral-C achieve a superior catalytic activity and power output in DMFCs, outperforming single-component MWCNT and carbon black-supported counterparts. Zhang et al. [150] developed a Pt-based catalyst using vertically aligned carbon nanotube/carbon fiber paper (VACNTs/CFP) supports. Ethylene glycol reduction deposited 3.5 nm Pt nanoparticles, while VACNTs formed ordered three-dimensional porous networks. The Pt/VACNTs/CFP system exhibited an enhanced CO tolerance and stability in methanol oxidation, attributed to one-dimensional electron transport pathways reducing intermediate adsorption resistance. This design overcomes conventional carbon limitations such as a low surface area and disordered porosity, thereby improving catalyst utilization.

4.2. Doped Heteroatom Carbon Loading and Metal-Oxide-Modified Carbon Loading

Heteroatom doping effectively modulates carbon material properties by incorporating elements such as nitrogen, boron, and sulfur into nanostructures, altering electronic structure, chemical reactivity, and conductivity while preserving intrinsic characteristics. Nitrogen, with its carbon-comparable atomic radius, is widely adopted for stable doping [151]. A representative approach involves direct nitrogen doping during synthesis [152]. Forootan Fard et al. [153] prepared nitrogen-doped carbon nanotubes (N-CNTs) through ammonia pyrolysis and fabricated PtRu/N-CNT catalysts for passive DMFCs. Nitrogen doping increased structural defects, reducing PtRu nanoparticles to 3.5 nm with a surface area of $91 \text{ m}^2 \text{ g}^{-1}$, representing 32% and 12% enhancements compared to carbon black and undoped CNTs, respectively. The N-CNT-based membrane electrode assembly achieved a peak power density of 26.1 mW cm^{-2} at a 3 M methanol concentration, surpassing CNT- and carbon black-supported systems by 18% and 62%. This work demonstrates that nitrogen doping optimizes electronic structure and enhances metal-support interactions, advancing the design of novel DMFC catalysts.

The development of metal-oxide-modified carbon materials originates from the intrinsic limitations of pure metal oxides, notably their low specific surface area and poor electronic conductivity. Strategic hybridization approaches integrate metal oxides with carbon matrices to synergistically optimize component deficiencies. Transition metal oxides (e.g., Co_3O_4 , CuO , Fe_2O_3 , and MoO_3) demonstrate the capacity to enhance the catalytic activity, stability, and durability of carbon systems through composite formation, thereby improving DMFC performance. CeO_2 has emerged as a prominent co-catalyst for methanol oxidation due to its exceptional corrosion resistance and mechanical robustness. Fluorite-structured CeO_2 enables reversible $\text{Ce}^{3+}/\text{Ce}^{4+}$ redox transitions coupled with an oxygen storage capacity that regulates surface oxygen availability. Manthiram et al. [154] synthesized Pt- CeO_2/C via reverse microemulsion (RME), systematically investigating nanostructure-property relationships in methanol oxidation. Compared to conventional borohydride reduction (CBR), RME employs oil-phase micelles as nanoreactors for spatially controlled Pt- CeO_2 codeposition on carbon, whereas CBR induces Pt/ CeO_2 agglomera-

tion through bulk-phase precipitation. Electrochemical evaluation in 0.5 M H₂SO₄ + 1 M CH₃OH demonstrated that RME-Pt-CeO₂/C achieved a 52% higher mass/specific activity than CBR-derived counterparts, attributed to interfacial oxygen transfer at Pt-CeO₂ junctions. Post 100-cycle durability testing, RME-Pt-CeO₂/C retained 80% of its initial activity, outperforming Pt/C and PtRu/C through CeO₂-mediated Pt stabilization. This study validates microemulsion-enabled interfacial engineering as an effective strategy to balance methanol adsorption–oxidation kinetics.

As a prototypical metal oxide, TiO₂ exhibits the following dual functionality in catalytic enhancement [155]: (i) accelerating Pt-CO bond cleavage via strong metal–support interactions (SMSI) to promote CO intermediate desorption and (ii) stabilizing Pt nanoparticles against Ostwald ripening through interfacial anchoring effects. The synergistic Pt-TiO₂ interaction in Pt-TiO₂/C composite systems has been precisely engineered through advanced synthesis protocols, including co-sputtering deposition, sol–gel assembly, and hydrothermal crystallization [156,157]. These controlled synthetic methodologies enable the optimal dispersion of Pt nanoparticles on TiO₂-modified carbon substrates, maximizing interfacial charge transfer kinetics. Concurrently, MnO₂ has emerged as a multifunctional additive for MOR enhancement, leveraging its inherent proton transport pathways and sustainable redox characteristics [158]. The structural engineering of MnO₂-PtRu/CNT hybrid architectures demonstrates sequence-dependent performance optimization. The sequential deposition of MnO₂ on CNT supports enables conformal oxide coatings that (i) mitigate PtRu dissolution during electrochemical cycling and (ii) inhibit CNT substrate corrosion. Zhou et al. [159] elucidated this protective mechanism through comparative studies of Pt and PtRu catalysts supported on MnO₂-decorated CNTs. Mechanistically, the MnO₂ interlayer serves the following dual functionalities: establishing 3D proton/electron conduction networks to reduce charge transfer resistance and the redox-mediated scavenging of CO-like poisoning species, thereby preserving catalytically active Pt sites.

4.3. Polymer-Modified Carbon Loading

Polymer-modified carbon supports entail the strategic incorporation of polymeric materials into carbon matrices to augment catalytic performance, operational stability, and long-term durability. Polymers are judiciously integrated via physical/chemical methodologies, affording tailored functionalities. These hybrid systems primarily utilize the following two polymer classifications: (i) π -conjugated conductive polymers and (ii) ionomer polyelectrolytes. Conductive polymers emerge as viable DMFC anode catalyst supports owing to extended π -electron delocalization, metallic-range conductivity, reversible redox doping capability, and structure–property tunability. Notably, polyaniline (PANI), a hierarchical nanostructured conductive polymer, has been extensively investigated as a multifunctional catalyst scaffold through precisely controlled aniline oxidative polymerization pathways [160,161]. Prasad [162] and Lin Niu et al. [163] demonstrated PANI's effectiveness as a support for methanol electro-oxidation, with PANI/Pt electrodes showing a superior activity. Zhiani et al. [164] synthesized PANI nanofiber-Pt/C composites via in situ aniline oxidative polymerization. The PANI incorporation significantly enhanced (i) catalytic activity, (ii) intermediate poisoning resistance, and (iii) mechanical robustness. Complementarily, polyelectrolyte-modified carbon architectures enable the precise fabrication of atomically dispersed noble metal catalysts with a high site density through electrostatic confinement phenomena. Zhao et al. [165] demonstrated polypyrrole-functionalized graphene as a high-performance DMFC support, where conductive polymers synergistically enhanced electron transfer kinetics and nucleation uniformity during catalyst deposition. Luo et al. [166] engineered polydiallyldimethylammonium (PDDA)-functionalized graphene nanosheets for precision Pt deposition through the electrostatic self-assembly of PtCl₆^{2−} precursors,

achieving 2.8 nm Pt nanoparticles with <8% size dispersity. The charged polymeric interface amplified functional group density while suppressing Pt aggregation, yielding a 3.2-fold higher methanol oxidation activity compared to conventional carbon supports. This interfacial engineering strategy enhanced catalysis through the following three synergistic mechanisms: spatial confinement effects inhibiting nanoparticle coalescence, electronic structure modulation weakening intermediate adsorption strength, and proton-conductive interfacial networks accelerating reaction kinetics. Current challenges center on establishing quantitative correlations between polymer chain architectures and long-term stability under operational DMFC conditions, particularly regarding polymer backbone degradation during voltage cycling. Future research must integrate operando characterization with multiscale simulations to decipher the dynamic evolution at catalyst/electrolyte/gas interfaces while advancing scalable synthesis methods to translate laboratory innovations into industrially viable DMFC technologies.

While polymeric coatings (e.g., conductive polymers and ionomers) initially enhance catalyst adhesion and corrosion resistance, prolonged operation under acidic, high-potential conditions triggers progressive degradation. The following two dominant failure mechanisms emerge: (i) the temperature-dependent hydrolytic degradation of polymer matrices, which compromises interfacial integrity and promotes catalyst detachment, and (ii) the oxidative decomposition of functional groups, accelerating carbon support corrosion through pore structure deterioration. Recent advancements in crosslinked polymer networks and inorganic–polymer hybrids demonstrate an improved stability, though their durability remains inferior to that of commercial carbon supports under operational voltage cycling. Rigorous evaluation via accelerated stress tests mimicking multi-year DMFC operation—particularly potential cycling across anode-relevant ranges—is essential to establish reliable lifetime predictions for these engineered materials.

5. Conclusions

Recent advancements in DMFC anode catalysts highlight divergent yet complementary development pathways for platinum-based and non-platinum catalytic systems. Platinum-optimized catalysts, despite delivering unparalleled methanol oxidation kinetics and near-term industrial applicability, remain constrained by inherent limitations, including material scarcity, voltage-cycling-induced degradation, and unsustainable long-term cost structures. Conversely, non-platinum alternatives exhibit a superior corrosion resistance and scalable manufacturing potential, but suffer from inconsistent catalytic activity. To reconcile these divergent trajectories, emerging support-engineered low-PGM architectures and hybrid configurations synergistically enhance platinum atom utilization efficiency while establishing transitional pathways toward sustainability. These systems concurrently mitigate CO poisoning and acidic degradation through precisely engineered nanostructures and alloy phase optimization.

Future advancements necessitate a phased, integrated strategy that balances immediate technological pragmatism with next-generation innovation. Near-term priorities should emphasize the following: (1) platinum surface engineering via defect modulation and ultra-low loading techniques to satisfy emission-sensitive applications and (2) industrial-scale catalyst recovery protocols to alleviate supply chain volatility. Parallel efforts must accelerate non-platinum catalyst development through atomic-scale active site engineering, stability-optimized architectures, and alkaline membrane compatibility to resolve intrinsic activity–stability compromises. Critically, system-level integration must align fundamental material breakthroughs with stack engineering innovations. This holistic approach will enable the scalable deployment of DMFC as economically viable and environmentally sustainable energy conversion platforms.

Author Contributions: L.Z.: writing—review and editing, writing—original draft, investigation, methodology, software, conceptualization. Y.J.: supervision, resources, validation, data curation, visualization, project administration, funding acquisition, formal analysis. All authors have read and agreed to the published version of the manuscript.

Funding: This research was funded by the Department of Science and Technology of Hubei Province, China (Grant number 2022BEC010).

Institutional Review Board Statement: Not applicable.

Informed Consent Statement: Not applicable.

Data Availability Statement: No new data were created or analyzed in this study. Data sharing is not applicable to this article.

Conflicts of Interest: The authors declare no conflicts of interest. The funders had no role in the design of the study; in the collection, analyses, or interpretation of data; in the writing of the manuscript; or in the decision to publish the results.

References

- Li, F.; Zhang, J.; Li, X. Energy Security Dilemma and Energy Transition Policy in the Context of Climate Change: A Perspective from China. *Energy Policy* **2023**, *181*, 113624. [\[CrossRef\]](#)
- Chen, L.; Msigwa, G.; Yang, M.; Osman, A.I.; Fawzy, S.; Rooney, D.W.; Yap, P.-S. Strategies to Achieve a Carbon Neutral Society: A Review. *Environ. Chem. Lett.* **2022**, *20*, 2277–2310. [\[CrossRef\]](#)
- Ahmed, A.A.; Al Labadidi, M.; Hamada, A.T.; Orhan, M.F. Design and Utilization of a Direct Methanol Fuel Cell. *Membranes* **2022**, *12*, 1266. [\[CrossRef\]](#)
- Santiago, Ó.; Mosa, J.; Escribano, P.G.; Navarro, E.; Chinarro, E.; Aparicio, M.; Leo, T.J.; Del Río, C. $^{40}\text{SiO}_2$ – $^{40}\text{P}_2\text{O}_5$ – $^{20}\text{ZrO}_2$ Sol-Gel Infiltrated sSEBS Membranes with Improved Methanol Crossover and Cell Performance for Direct Methanol Fuel Cell Applications. *Int. J. Hydrogen Energy* **2020**, *45*, 20620–20631. [\[CrossRef\]](#)
- Abdelkareem, M.A.; Elsaid, K.; Wilberforce, T.; Kamil, M.; Sayed, E.T.; Olabi, A. Environmental Aspects of Fuel Cells: A Review. *Sci. Total Environ.* **2021**, *752*, 141803. [\[CrossRef\]](#) [\[PubMed\]](#)
- Al Shouny, A.; Rezk, H.; Sayed, E.T.; Abdelkareem, M.A.; Issa, U.H.; Miky, Y.; Olabi, A.G. Maximization of Power Density of Direct Methanol Fuel Cell for Greener Energy Generation Using Beetle Antennae Search Algorithm and Fuzzy Modeling. *Biomimetics* **2023**, *8*, 557. [\[CrossRef\]](#) [\[PubMed\]](#)
- Wang, Y.; Ruiz Diaz, D.F.; Chen, K.S.; Wang, Z.; Adroher, X.C. Materials, Technological Status, and Fundamentals of PEM Fuel Cells—A Review. *Mater. Today* **2020**, *32*, 178–203. [\[CrossRef\]](#)
- Kumar, P.; Dutta, K.; Das, S.; Kundu, P.P. An Overview of Unsolved Deficiencies of Direct Methanol Fuel Cell Technology: Factors and Parameters Affecting Its Widespread Use: Unsolved Deficiencies of Direct Methanol Fuel Cells. *Int. J. Energy Res.* **2014**, *38*, 1367–1390. [\[CrossRef\]](#)
- Faghri, A.; Guo, Z. Challenges and Opportunities of Thermal Management Issues Related to Fuel Cell Technology and Modeling. *Int. J. Heat Mass Transf.* **2005**, *48*, 3891–3920. [\[CrossRef\]](#)
- Wang, J.; Wang, H.; Fan, Y. Techno-Economic Challenges of Fuel Cell Commercialization. *Engineering* **2018**, *4*, 352–360. [\[CrossRef\]](#)
- 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. [\[CrossRef\]](#)
- Wang, S.; Jiang, S.P. Prospects of Fuel Cell Technologies. *Natl. Sci. Rev.* **2017**, *4*, 163–166. [\[CrossRef\]](#)
- Chen, F.; Sun, Y.; Li, H.; Li, C. Review and Development of Anode Electrocatalyst Carriers for Direct Methanol Fuel Cell. *Energy Technol.* **2022**, *10*, 2101086. [\[CrossRef\]](#)
- Yaqoob, L.; Noor, T.; Iqbal, N. Recent Progress in Development of Efficient Electrocatalyst for Methanol Oxidation Reaction in Direct Methanol Fuel Cell. *Int. J. Energy Res.* **2021**, *45*, 6550–6583. [\[CrossRef\]](#)
- Sharma, P.; Pandey, O.P. Proton Exchange Membrane Fuel Cells: Fundamentals, Advanced Technologies, and Practical Applications. In *PEM Fuel Cells*; Elsevier: Amsterdam, The Netherlands, 2022; pp. 1–24. ISBN 978-0-12-823708-3.
- Ren, X.; Lv, Q.; Liu, L.; Liu, B.; Wang, Y.; Liu, A.; Wu, G. Current Progress of Pt and Pt-Based Electrocatalysts Used for Fuel Cells. *Sustain. Energy Fuels* **2020**, *4*, 15–30. [\[CrossRef\]](#)
- Tripković, A.V.; Popović, K.D.; Grgur, B.N.; Blizanac, B.; Ross, P.N.; Marković, N.M. Methanol Electrooxidation on Supported Pt and PtRu Catalysts in Acid and Alkaline Solutions. *Electrochim. Acta* **2002**, *47*, 3707–3714. [\[CrossRef\]](#)
- Chen, R.; Zhao, T.S.; Liu, J.G. Effect of Cell Orientation on the Performance of Passive Direct Methanol Fuel Cells. *J. Power Sources* **2006**, *157*, 351–357. [\[CrossRef\]](#)

19. Hu, X.; Wang, X.; Chen, J.; Yang, Q.; Jin, D.; Qiu, X. Numerical Investigations of the Combined Effects of Flow Rate and Methanol Concentration on DMFC Performance. *Energies* **2017**, *10*, 1094. [\[CrossRef\]](#)
20. Ismail, A.; Kee, Y.W. Investigation on Voltage Loss Mechanism for Direct Methanol Fuel Cell. *Energy Rep.* **2023**, *10*, 535–543. [\[CrossRef\]](#)
21. Goor, M.; Menkin, S.; Peled, E. High Power Direct Methanol Fuel Cell for Mobility and Portable Applications. *Int. J. Hydrogen Energy* **2019**, *44*, 3138–3143. [\[CrossRef\]](#)
22. Ud Din, M.A.; Idrees, M.; Jamil, S.; Irfan, S.; Nazir, G.; Mudassir, M.A.; Saleem, M.S.; Batool, S.; Cheng, N.; Saidur, R. Advances and Challenges of Methanol-Tolerant Oxygen Reduction Reaction Electrocatalysts for the Direct Methanol Fuel Cell. *J. Energy Chem.* **2023**, *77*, 499–513. [\[CrossRef\]](#)
23. Hamnett, A. Mechanism and Electrocatalysis in the Direct Methanol Fuel Cell. *Catal. Today* **1997**, *38*, 445–457. [\[CrossRef\]](#)
24. Yuda, A.; Ashok, A.; Kumar, A. A Comprehensive and Critical Review on Recent Progress in Anode Catalyst for Methanol Oxidation Reaction. *Catal. Rev.* **2022**, *64*, 126–228. [\[CrossRef\]](#)
25. Martinaiou, I.; Monteverde Videla, A.H.A.; Weidler, N.; Kübler, M.; Wallace, W.D.Z.; Paul, S.; Wagner, S.; Shahraei, A.; Stark, R.W.; Specchia, S.; et al. Activity and Degradation Study of an Fe-N-C Catalyst for ORR in Direct Methanol Fuel Cell (DMFC). *Appl. Catal. B Environ.* **2020**, *262*, 118217. [\[CrossRef\]](#)
26. Prapainainar, P.; Du, Z.; Theampetch, A.; Prapainainar, C.; Kongkachuichay, P.; Holmes, S.M. Properties and DMFC Performance of Nafion/Mordenite Composite Membrane Fabricated by Solution-Casting Method with Different Solvent Ratio. *Energy* **2020**, *190*, 116451. [\[CrossRef\]](#)
27. Yaqoob, L.; Noor, T.; Iqbal, N.; Nasir, H.; Zaman, N.; Rasheed, L.; Yousuf, M. Development of an Efficient Non-Noble Metal Based Anode Electrocatalyst to Promote Methanol Oxidation Activity in DMFC. *ChemistrySelect* **2020**, *5*, 6023–6034. [\[CrossRef\]](#)
28. Bai, X.; Geng, J.; Zhao, S.; Li, H.; Li, F. Tunable Hollow Pt@Ru Dodecahedra via Galvanic Replacement for Efficient Methanol Oxidation. *ACS Appl. Mater. Interfaces* **2020**, *12*, 23046–23050. [\[CrossRef\]](#)
29. Cui, R.; Liu, S.; Guo, X.; Huang, H.; Wang, J.; Liu, B.; Li, Y.; Zhao, D.; Dong, J.; Sun, B. N-Doping Holey Graphene TiO₂-Pt Composite as Efficient Electrocatalyst for Methanol Oxidation. *ACS Appl. Energy Mater.* **2020**, *3*, 2665–2673. [\[CrossRef\]](#)
30. Alias, M.S.; Kamarudin, S.K.; Zainoodin, A.M.; Masdar, M.S. Active Direct Methanol Fuel Cell: An Overview. *Int. J. Hydrogen Energy* **2020**, *45*, 19620–19641. [\[CrossRef\]](#)
31. Shi, W.; Park, H.-U.; Park, A.-H.; Kwon, Y.-U. Effect of Composition of Pd_{10-x}Cu_x (x = 2, 3, 4, and 5) Alloy Nanoparticles on Their Electrocatalysis for Methanol Oxidation. *J. Electroanal. Chem.* **2020**, *865*, 114144. [\[CrossRef\]](#)
32. Menshchikov, V.; Alekseenko, A.; Guterman, V.; Nechitailov, A.; Glebova, N.; Tomasov, A.; Spiridonova, O.; Belenov, S.; Zelenina, N.; Safronenko, O. Effective Platinum-Copper Catalysts for Methanol Oxidation and Oxygen Reduction in Proton-Exchange Membrane Fuel Cell. *Nanomaterials* **2020**, *10*, 742. [\[CrossRef\]](#)
33. Sayed, E.T.; Abdelkareem, M.A.; Alawadhi, H.; Salameh, T.; Olabi, A.G.; Alami, A.H. Facile and Low-Cost Synthesis Route for Graphene Deposition over Cobalt Dendrites for Direct Methanol Fuel Cell Applications. *J. Taiwan Inst. Chem. Eng.* **2020**, *115*, 321–330. [\[CrossRef\]](#)
34. Raduwan, N.F.; Shaari, N.; Kamarudin, S.K.; Masdar, M.S.; Mohamad Yunus, R.; Wani, A.A. Advances, Progress and Challenges of NiCo₂O₄-Based Composite Materials for Direct Methanol Fuel Cell Applications: A Critical Review. *Int. J. Green Energy* **2024**, *21*, 3391–3413. [\[CrossRef\]](#)
35. Andoh, S.; Kawaji, J.; Suzuki, S.; Kuroda, Y.; Mitsushima, S. Heat and Mass Balance Analysis of 130-W Active-Type Direct-Methanol Fuel Cell. *Electrochemistry* **2022**, *90*, 017007. [\[CrossRef\]](#)
36. Coguplugil, Z.K.; Akin, M.; Bayat, R.; Bekmezci, M.; Karimi-Maleh, H.; Javadi, A.; Sen, F. Synthesis and Characterization of Pt/ZnO@SWCNT/Fe₃O₄ as a Powerful Catalyst for Anodic Part of Direct Methanol Fuel Cell Reaction. *Int. J. Hydrogen Energy* **2023**, *48*, 21285–21293. [\[CrossRef\]](#)
37. Erduran, V.; Bayat, R.; Isik, I.; Bayazit, T.; Şen, F. Production of Sustainable Low-Layer Graphene by Green Synthesis at Room Conditions for Platinum-Based Direct Methanol Fuel Cell. *ACS Eng. Au* **2023**, *3*, 537–545. [\[CrossRef\]](#)
38. Liu, F.; Dang, D.; Tian, X. Platinum-Decorated Three Dimensional Titanium Copper Nitride Architectures with Durable Methanol Oxidation Reaction Activity. *Int. J. Hydrogen Energy* **2019**, *44*, 8415–8424. [\[CrossRef\]](#)
39. Wang, H.; Xue, Y.; Zhu, B.; Yang, J.; Wang, L.; Tan, X.; Wang, Z.; Chu, Y. CeO₂ Nanowires Stretch-Embedded in Reduced Graphite Oxide Nanocomposite Support for Pt Nanoparticles as Potential Electrocatalyst for Methanol Oxidation Reaction. *Int. J. Hydrogen Energy* **2017**, *42*, 20549–20559. [\[CrossRef\]](#)
40. Cheng, Y.; Shen, P.K.; Jiang, S.P. Enhanced Activity and Stability of Core-Shell Structured PtRuNi Electrocatalysts for Direct Methanol Fuel Cells. *Int. J. Hydrogen Energy* **2016**, *41*, 1935–1943. [\[CrossRef\]](#)
41. Gizem Güneştekin, B.; Medetalibeyoglu, H.; Atar, N.; Lütfi Yola, M. Efficient Direct-Methanol Fuel Cell Based on Graphene Quantum Dots/Multi-walled Carbon Nanotubes Composite. *Electroanalysis* **2020**, *32*, 1977–1982. [\[CrossRef\]](#)

42. Raveendran, A.; Jeyapriya, M.; Ramalingan, C.; Ramamoorthy, G.; Chandran, M.; Kamalakannan, D.; Prabu, B.; Siddiqui, M.R.; Wabaidur, S.M.; Dhanusuraman, R. Nickel-Modified Poly(Aniline-Co-Pyrrole) as Electrocatalyst for Electrochemical Oxidation of Methanol in Direct Methanol Fuel Cell Application. *Ionics* **2024**, *30*, 5577–5595. [\[CrossRef\]](#)
43. Wu, Z.; Duan, R.; Cui, J.; Ye, C.; Zhang, S.; Yan, S. An Overview of the Pd Based Electrocatalysts Utilized in Direct Alcohol Fuel Cells. *Electrocatalysis* **2025**, *16*, 197–223. [\[CrossRef\]](#)
44. Calderón Gómez, J.; Moliner, R.; Lázaro, M. Palladium-Based Catalysts as Electrodes for Direct Methanol Fuel Cells: A Last Ten Years Review. *Catalysts* **2016**, *6*, 130. [\[CrossRef\]](#)
45. Jeong, H.; Kim, J.W.; Park, J.; An, J.; Lee, T.; Prinz, F.B.; Shim, J.H. Bimetallic Nickel/Ruthenium Catalysts Synthesized by Atomic Layer Deposition for Low-Temperature Direct Methanol Solid Oxide Fuel Cells. *ACS Appl. Mater. Interfaces* **2016**, *8*, 30090–30098. [\[CrossRef\]](#)
46. Mohamed, M.M.; Amer, A.A. Solid Waste-Derived γ -Al₂O₃ Nanowires Supporting α -Fe₂O₃ as an Efficient Anodic Direct Methanol Fuel Cell Electrocatalyst. *J. Alloys Compd.* **2023**, *966*, 171632. [\[CrossRef\]](#)
47. Shams-Eldin, R.; Ali, A.A.; Hani, A.; Haikal, R.R.; Fahmy, H.M.; El Nashar, R.M.; Alkordi, M.H. Metal–Organic Framework Mediated Ni-Deposition on MWCNTs for Direct Methanol Fuel Cell Catalysis. *SN Appl. Sci.* **2023**, *5*, 166. [\[CrossRef\]](#)
48. Chen, F.; Wang, L.; Yu, S.; Guo, S.; Zhang, C.; Guo, M.; Li, C. Synergistic CoCu Nanocrystals on N-Doped Carbon Nanofibers with Significant Carbon Monoxide-Resistant in Alkaline Direct Methanol Fuel Cell. *Int. J. Hydrogen Energy* **2024**, *72*, 1001–1009. [\[CrossRef\]](#)
49. Stevanović, S.; Tripković, D.; Gavrilović-Wohlmuther, A.; Rogan, J.; Lačnjevac, U.; Jovanović, V. Carbon Supported PtSn versus PtSnO₂ Catalysts in Methanol Oxidation. *Int. J. Electrochem. Sci.* **2021**, *16*, 210222. [\[CrossRef\]](#)
50. Shi, H.; Liao, F.; Zhu, W.; Shao, C.; Shao, M. Effective PtAu Nanowire Network Catalysts with Ultralow Pt Content for Formic Acid Oxidation and Methanol Oxidation. *Int. J. Hydrogen Energy* **2020**, *45*, 16071–16079. [\[CrossRef\]](#)
51. Ordóñez, L.C.; Roquero, P.; Ramírez, J.; Sebastian, P.J. Methanol Electro-Oxidation on Bimetallic PtMo/C Catalysts and Pt/C—Mo/C Mechanical Mixtures. *Int. J. Electrochem. Sci.* **2016**, *11*, 5364–5379. [\[CrossRef\]](#)
52. Zhang, R.; Xia, W.; Kang, W.; Li, R.; Qu, K.; Zhang, Y.; Chen, B.; Wang, H.; Sun, Y.; Li, H. Methanol Oxidation Reaction Performance on Graphene-Supported PtAg Alloy Nanocatalyst: Contrastive Study of Electronic and Geometric Effects Induced from Ag Doping. *ChemistrySelect* **2018**, *3*, 3615–3620. [\[CrossRef\]](#)
53. Men'shchikov, V.S.; Guterman, V.E.; Belenov, S.V.; Spiridonova, O.A.; Rezvan, D.V. De-Alloyed PtCu/C Catalysts of Methanol Electrooxidation. *Russ. J. Electrochem.* **2020**, *56*, 850–858. [\[CrossRef\]](#)
54. Yang, T.; Xue, Q.; Yu, X.; Qi, X.; Wu, R.; Lu, S.; Gu, Z.; Jiang, J.; Nie, Y. DFT Study on Methanol Oxidation Reaction Catalyzed by Pt_mPd_n Alloys. *Coatings* **2022**, *12*, 918. [\[CrossRef\]](#)
55. Ercelik, M.; Ozden, A.; Seker, E.; Colpan, C.O. Characterization and Performance Evaluation of Pt Ru/C TiO₂ Anode Electrocatalyst for DMFC Applications. *Int. J. Hydrogen Energy* **2017**, *42*, 21518–21529. [\[CrossRef\]](#)
56. Min, L.; Yuan, L.; Xu, W.J.; Liu, J.-X. Synthesis of DMFC Anode Catalyst Fe₃O₄@Pt Particles and Catalytic Performance. *J. Inorg. Mater.* **2017**, *32*, 916. [\[CrossRef\]](#)
57. Frelink, T.; Visscher, W.; Van Veen, J.A.R. Particle Size Effect of Carbon-Supported Platinum Catalysts for the Electrooxidation of Methanol. *J. Electroanal. Chem.* **1995**, *382*, 65–72. [\[CrossRef\]](#)
58. Housmans, T.H.M.; Wonders, A.H.; Koper, M.T.M. Structure Sensitivity of Methanol Electrooxidation Pathways on Platinum: An On-Line Electrochemical Mass Spectrometry Study. *J. Phys. Chem. B* **2006**, *110*, 10021–10031. [\[CrossRef\]](#)
59. Jarvi, T.D.; Sriramulu, S.; Stuve, E.M. Reactivity and Extent of Poisoning during Methanol Electro-Oxidation on Platinum (100) and (111): A Comparative Study. *Colloids Surf. A Physicochem. Eng. Asp.* **1998**, *134*, 145–153. [\[CrossRef\]](#)
60. Ferrin, P.; Mavrikakis, M. Structure Sensitivity of Methanol Electrooxidation on Transition Metals. *J. Am. Chem. Soc.* **2009**, *131*, 14381–14389. [\[CrossRef\]](#)
61. Mikita, K.; Nakamura, M.; Hoshi, N. In Situ Infrared Reflection Absorption Spectroscopy of Carbon Monoxide Adsorbed on Pt(S)-[n (100) × (110)] Electrodes. *Langmuir* **2007**, *23*, 9092–9097. [\[CrossRef\]](#)
62. Veizaga, N.S.; Paganin, V.A.; Rocha, T.A.; Scelza, O.A.; De Miguel, S.R.; Gonzalez, E.R. Development of PtGe and PtIn Anodic Catalysts Supported on Carbonaceous Materials for DMFC. *Int. J. Hydrogen Energy* **2014**, *39*, 8728–8737. [\[CrossRef\]](#)
63. Patel, P.P.; Datta, M.K.; Jampani, P.H.; Hong, D.; Poston, J.A.; Manivannan, A.; Kumta, P.N. High Performance and Durable Nanostructured TiN Supported Pt₅₀–Ru₅₀ Anode Catalyst for Direct Methanol Fuel Cell (DMFC). *J. Power Sources* **2015**, *293*, 437–446. [\[CrossRef\]](#)
64. Wang, Q.; Zhou, Y.-W.; Jin, Z.; Chen, C.; Li, H.; Cai, W.-B. Alternative Aqueous Phase Synthesis of a PtRu/C Electrocatalyst for Direct Methanol Fuel Cells. *Catalysts* **2021**, *11*, 925. [\[CrossRef\]](#)
65. Muthukumar, V.; Chetty, R. Impregnated Electroreduced Pt on Ru/C as an Anode Catalyst for Direct Methanol Fuel Cells. *J. Electrochem. Soc.* **2019**, *166*, F1173–F1179. [\[CrossRef\]](#)

66. Feng, Y.; Zhang, S.; Chen, M.; Zhu, L.; Pei, A.; Wu, F.; Liao, X.; Gao, Q.; Wang, W.; Yang, Z.; et al. Revealing the Mechanism of Bifunctional PtLa Electrocatalyst for Highly Efficient Methanol Oxidation, Hydrogen Evolution, and Coupling Reaction. *J. Colloid Interface Sci.* **2025**, *679*, 918–928. [\[CrossRef\]](#) [\[PubMed\]](#)
67. Eudora Khotseng, L. (Ed.) *Electrocatalysis and Electrocatalysts for a Cleaner Environment—Fundamentals and Applications*; IntechOpen: London, UK, 2022; ISBN 978-1-83968-127-1.
68. Petrii, O.A. Pt–Ru Electrocatalysts for Fuel Cells: A Representative Review. *J. Solid State Electrochem.* **2008**, *12*, 609–642. [\[CrossRef\]](#)
69. Wang, H.; Gao, C.; Liu, Z.; Li, B.; Dok Kim, Y.; Feng, J.; Sun, K.; Peng, Z. Pt–Ru Atomic Alloys Confined in Mesoporous Carbon Hollow Spheres for Accelerating Methanol Oxidation. *J. Colloid Interface Sci.* **2025**, *678*, 1004–1011. [\[CrossRef\]](#)
70. Xu, H.; Zheng, D.J.; Iriawan, H.; Fang, J.-H.; Kim, J.; Wang, X.; Román-Leshkov, Y.; Li, J.; Shao-Horn, Y. A Cobalt–Platinum–Ruthenium System for Acidic Methanol Oxidation. *Chem. Mater.* **2024**, *36*, 6938–6949. [\[CrossRef\]](#)
71. Cui, Z.; Liu, C.; Liao, J.; Xing, W. Highly Active PtRu Catalysts Supported on Carbon Nanotubes Prepared by Modified Impregnation Method for Methanol Electro-Oxidation. *Electrochim. Acta* **2008**, *53*, 7807–7811. [\[CrossRef\]](#)
72. Rojas, S.; García-García, F.J.; Järas, S.; Martínez-Huerta, M.V.; Fierro, J.L.G.; Boutonnet, M. Preparation of Carbon Supported Pt and PtRu Nanoparticles from Microemulsion. *Appl. Catal. A Gen.* **2005**, *285*, 24–35. [\[CrossRef\]](#)
73. Schmidt, T.J.; Gasteiger, H.A.; Behm, R.J. Methanol Electrooxidation on a Colloidal PtRu-Alloy Fuel-Cell Catalyst. *Electrochem. Commun.* **1999**, *1*, 1–4. [\[CrossRef\]](#)
74. Caillard, A.; Coutanceau, C.; Brault, P.; Mathias, J.; Léger, J.-M. Structure of Pt/C and PtRu/C Catalytic Layers Prepared by Plasma Sputtering and Electric Performance in Direct Methanol Fuel Cells (DMFC). *J. Power Sources* **2006**, *162*, 66–73. [\[CrossRef\]](#)
75. Jow, J.; Yang, S.; Chen, H.; Wu, M.; Ling, T.; Wei, T. Co-Electrodeposition of Pt–Ru Electrocatalysts in Electrolytes with Varying Compositions by a Double-Potential Pulse Method for the Oxidation of MeOH and CO. *Int. J. Hydrogen Energy* **2009**, *34*, 665–671. [\[CrossRef\]](#)
76. Cai, G.; Hua, C.; Ren, H.; Yu, R.; Xu, D.; Khan, M.A.; Guo, J.; Sun, Y.; Tang, Y.; Qian, H.; et al. Ultrathin Ternary PtNiRu Nanowires for Enhanced Oxygen Reduction and Methanol Oxidation Catalysis via D-Band Center Regulation. *J. Colloid Interface Sci.* **2025**, *678*, 599–608. [\[CrossRef\]](#)
77. Strasser, P.; Fan, Q.; Devenney, M.; Weinberg, W.H.; Liu, P.; Nørskov, J.K. High Throughput Experimental and Theoretical Predictive Screening of Materials—A Comparative Study of Search Strategies for New Fuel Cell Anode Catalysts. *J. Phys. Chem. B* **2003**, *107*, 11013–11021. [\[CrossRef\]](#)
78. Watanabe, M.; Zhu, Y.; Uchida, H. Oxidation of CO on a Pt–Fe Alloy Electrode Studied by Surface Enhanced Infrared Reflection–Absorption Spectroscopy. *J. Phys. Chem. B* **2000**, *104*, 1762–1768. [\[CrossRef\]](#)
79. Jeon, M.K.; Won, J.Y.; Lee, K.R.; Woo, S.I. Highly Active PtRuFe/C Catalyst for Methanol Electro-Oxidation. *Electrochem. Commun.* **2007**, *9*, 2163–2166. [\[CrossRef\]](#)
80. Cai, Z.; Kuang, Y.; Qi, X.; Wang, P.; Zhang, Y.; Zhang, Z.; Sun, X. Ultrathin Branched PtFe and PtRuFe Nanodendrites with Enhanced Electrocatalytic Activity. *J. Mater. Chem. A* **2015**, *3*, 1182–1187. [\[CrossRef\]](#)
81. Kakati, N.; Maiti, J.; Oh, J.Y.; Yoon, Y.S. Study of Methanol Oxidation of Hydrothermally Synthesized PtRuMo on Multi Wall Carbon Nanotubes. *Appl. Surf. Sci.* **2011**, *257*, 8433–8437. [\[CrossRef\]](#)
82. Park, S.-H.; Jung, H.-M.; Um, S.; Song, Y.-W.; Kim, H.-S. Rapid Synthesis of Pt-Based Alloy/Carbon Nanotube Catalysts for a Direct Methanol Fuel Cell Using Flash Light Irradiation. *Int. J. Hydrogen Energy* **2012**, *37*, 12597–12604. [\[CrossRef\]](#)
83. Li, Z.; Yu, K.; Leng, Y.; Chen, Z. Platinum-Nickel Bimetallic Nanowire Electrocatalyst Enables Methanol Oxidation. *J. Electroanal. Chem.* **2025**, *980*, 118989. [\[CrossRef\]](#)
84. Li, L.; Gao, W.; Wan, X.; Wen, D. Pt Nanoparticles Dispersed on Ni/C Nanoflowers as Stable Electrocatalysts for Methanol Oxidation and Oxygen Reduction. *ACS Appl. Nano Mater.* **2021**, *4*, 10960–10968. [\[CrossRef\]](#)
85. Liang, Y.; Zhang, H.; Tian, Z.; Zhu, X.; Wang, X.; Yi, B. Synthesis and Structure–Activity Relationship Exploration of Carbon-Supported PtRuNi Nanocomposite as a CO-Tolerant Electrocatalyst for Proton Exchange Membrane Fuel Cells. *J. Phys. Chem. B* **2006**, *110*, 7828–7834. [\[CrossRef\]](#)
86. Xie, J.; Zhang, Q.; Gu, L.; Xu, S.; Wang, P.; Liu, J.; Ding, Y.; Yao, Y.F.; Nan, C.; Zhao, M.; et al. Ruthenium–Platinum Core–Shell Nanocatalysts with Substantially Enhanced Activity and Durability towards Methanol Oxidation. *Nano Energy* **2016**, *21*, 247–257. [\[CrossRef\]](#)
87. Ren, Y.; Chen, K.; Zhang, Y.; Shi, D.; Wu, Q.; Liang, D.; Hu, C.; Li, H. N-Doped Carbon Confined CoFe@Pt Nanoparticles with Robust Catalytic Performance for the Methanol Oxidation Reaction. *J. Mater. Chem. A* **2022**, *10*, 13345–13354. [\[CrossRef\]](#)
88. Wang, Z.; Kang, J.S.; Göhl, D.; Paciok, P.; Gonçalves, D.S.; Lim, H.; Zanchet, D.; Heggen, M.; Shao-Horn, Y.; Ledendecker, M.; et al. Platinum/Tantalum Carbide Core–Shell Nanoparticles with Sub-Monolayer Shells for Methanol and Oxygen Electrocatalysis. *Adv. Energy Mater.* **2024**, *14*, 2304092. [\[CrossRef\]](#)
89. El Sawy, E.N.; Birss, V.I. Nanoengineered Ircore @Ptshell Nanoparticles with Controlled Pt Shell Coverages for Direct Methanol Electro-Oxidation. *ACS Appl. Mater. Interfaces* **2018**, *10*, 3459–3469. [\[CrossRef\]](#)

90. Gawande, M.B.; Goswami, A.; Asefa, T.; Guo, H.; Biradar, A.V.; Peng, D.-L.; Zboril, R.; Varma, R.S. Core–Shell Nanoparticles: Synthesis and Applications in Catalysis and Electrocatalysis. *Chem. Soc. Rev.* **2015**, *44*, 7540–7590. [\[CrossRef\]](#)
91. Cao, K.; Zhu, Q.; Shan, B.; Chen, R. Controlled Synthesis of Pd/Pt Core Shell Nanoparticles Using Area-Selective Atomic Layer Deposition. *Sci. Rep.* **2015**, *5*, 8470. [\[CrossRef\]](#)
92. Xue, Y.; Chen, L.; Zhang, L.; Zheng, G.; Zhang, X.; Zhou, Z. Activity and Stability Origin of Core–Shell Catalysts: Unignorable Atomic Diffusion Behavior. *Chem. Sci.* **2025**, *16*, 3323–3328. [\[CrossRef\]](#)
93. Wu, Y.-N.; Liao, S.-J.; Liang, Z.-X.; Yang, L.-J.; Wang, R.-F. High-Performance Core–Shell PdPt@Pt/C Catalysts via Decorating PdPt Alloy Cores with Pt. *J. Power Sources* **2009**, *194*, 805–810. [\[CrossRef\]](#)
94. Cheng, Y.; Shen, P.K.; Saunders, M.; Jiang, S.P. Core–Shell Structured PtRuCo Nanoparticles on Carbon Nanotubes as Highly Active and Durable Electrocatalysts for Direct Methanol Fuel Cells. *Electrochim. Acta* **2015**, *177*, 217–226. [\[CrossRef\]](#)
95. Strasser, P.; Koh, S.; Anniyev, T.; Greeley, J.; More, K.; Yu, C.; Liu, Z.; Kaya, S.; Nordlund, D.; Ogasawara, H.; et al. Lattice-Strain Control of the Activity in Dealloyed Core–Shell Fuel Cell Catalysts | Nature Chemistry. *Nature Chem.* **2010**, *2*, 454–460. [\[CrossRef\]](#) [\[PubMed\]](#)
96. Wang, J.-J.; Liu, Y.-T.; Chen, I.-L.; Yang, Y.-W.; Yeh, T.-K.; Lee, C.H.; Hu, C.-C.; Wen, T.-C.; Chen, T.-Y.; Lin, T.-L. Near-Monolayer Platinum Shell on Core–Shell Nanocatalysts for High-Performance Direct Methanol Fuel Cell. *J. Phys. Chem. C* **2014**, *118*, 2253–2262. [\[CrossRef\]](#)
97. Wang, Q.; Zhao, Z.; Jia, Y.; Wang, M.; Qi, W.; Pang, Y.; Yi, J.; Zhang, Y.; Li, Z.; Zhang, Z. Unique Cu@CuPt Core–Shell Concave Octahedron with Enhanced Methanol Oxidation Activity. *ACS Appl. Mater. Interfaces* **2017**, *9*, 36817–36827. [\[CrossRef\]](#)
98. Erlebacher, J.; Aziz, M.J.; Karma, A.; Dimitrov, N.; Sieradzki, K. Evolution of Nanoporosity in Dealloying. *Nature* **2001**, *410*, 450–453. [\[CrossRef\]](#)
99. Singh, B.; Seddon, B.; Dempsey, E.; Redington, W.; Dickinson, C. Porous Core-Shell Platinum-Silver Nanocatalyst for the Electrooxidation of Methanol. *Electroanalysis* **2015**, *27*, 135–143. [\[CrossRef\]](#)
100. Sarkar, A.; Murugan, A.V.; Manthiram, A. Synthesis and Characterization of Nanostructured Pd–Mo Electrocatalysts for Oxygen Reduction Reaction in Fuel Cells. *J. Phys. Chem. C* **2008**, *112*, 12037–12043. [\[CrossRef\]](#)
101. Sikeyi, L.L.; Ntuli, T.D.; Maxakato, N.W.; Coville, N.J.; Maubane-Nkadimeng, M.S. Highly Active Bimetallic Nanocatalysts (Pd/Ag and Pd/ZnO) Decorated Nitrogen-Doped Onion-like Carbon Nanoparticles for Enhanced Methanol Oxidation in Alkaline Media. *J. Power Sources* **2024**, *613*, 234802. [\[CrossRef\]](#)
102. Yao, C.; Li, M.; Xue, Z.; Yang, Z.; He, K.; Chen, Q.; Cheng, B.; Wang, R.; Cai, S.; Qiao, X.; et al. Three-Dimensional MXene-Based Pd/Ni/Cu Electrocatalyst for Methanol Oxidation Reaction with Efficient Performance. *ACS Appl. Nano Mater.* **2024**, *7*, 19628–19636. [\[CrossRef\]](#)
103. Mandal, K.; Bhattacharjee, D.; Roy, P.S.; Bhattacharya, S.K.; Dasgupta, S. Room Temperature Synthesis of Pd–Cu Nanoalloy Catalyst with Enhanced Electrocatalytic Activity for the Methanol Oxidation Reaction. *Appl. Catal. A Gen.* **2015**, *492*, 100–106. [\[CrossRef\]](#)
104. Mansor, M.; Timmiati, S.N.; Wong, W.Y.; Mohd Zainoodin, A.; Lim, K.L.; Kamarudin, S.K. NiPd Supported on Mesoporous Silica Nanoparticle as Efficient Anode Electrocatalyst for Methanol Electrooxidation in Alkaline Media. *Catalysts* **2020**, *10*, 1235. [\[CrossRef\]](#)
105. Tan, Q.; Shu, C.; Abbott, J.; Zhao, Q.; Liu, L.; Qu, T.; Chen, Y.; Zhu, H.; Liu, Y.; Wu, G. Highly Dispersed Pd-CeO₂ Nanoparticles Supported on N-Doped Core–Shell Structured Mesoporous Carbon for Methanol Oxidation in Alkaline Media. *ACS Catal.* **2019**, *9*, 6362–6371. [\[CrossRef\]](#)
106. Gao, Z.; Li, A.; Liu, X.; Peng, M.; Yu, S.; Wang, M.; Ge, Y.; Li, C.; Wang, T.; Wang, Z.; et al. Shielding Pt/ γ -Mo₂N by Inert Nano-Overlays Enables Stable H₂ Production. *Nature* **2025**, *638*, 690–696. [\[CrossRef\]](#)
107. Kumar, S.; Sharma, V.; Kumari, N.; Kaur, G.A.; Saha, A.; Thakur, S.; Shandilya, M. Recent Advances in Perovskite Materials: Exploring Multifaceted Properties for Energy Harvesting Applications. *Ionics* **2024**, *30*, 5159–5188. [\[CrossRef\]](#)
108. Li, L.; Tan, S.; Salvatore, K.L.; Wong, S.S. Nanoscale Perovskites as Catalysts and Supports for Direct Methanol Fuel Cells. *Chem. A Eur. J* **2019**, *25*, 7779–7797. [\[CrossRef\]](#)
109. Singh, R.N.; Sharma, T.; Singh, A.; Anindita, R.; Mishra, D.; Tiwari, S.K. Perovskite-Type La_{2–x}Sr_xNiO₄ (0 ≤ x ≤ 1) as Active Anode Materials for Methanol Oxidation in Alkaline Solutions. *Electrochim. Acta* **2008**, *53*, 2322–2330. [\[CrossRef\]](#)
110. Prince, A.G.; Durai, L.; Badhulika, S. Solid State Synthesis of a RuNiO₃ Perovskite Nanomaterial as an Electro-Catalyst for Direct Alcohol (Ethanol, Methanol and Ethylene Glycol) Fuel Cell Applications. *New J. Chem.* **2023**, *47*, 3870–3879. [\[CrossRef\]](#)
111. Ekrami-Kakhki, M.-S.; Yavari, Z.; Saffari, J.; Ekrami-Kakhki, S.A. Perovskite-Type LaFeO₃ and LaFeO₃-CNTs Nanocrystals as Active Anode for Methanol Oxidation in Alkaline Solutions. *J. Electr. Eng.* **2016**, *4*, 88–99. [\[CrossRef\]](#)
112. Stottlemeyer, A.L.; Weigert, E.C.; Chen, J.G. Tungsten Carbides as Alternative Electrocatalysts: From Surface Science Studies to Fuel Cell Evaluation. *Ind. Eng. Chem. Res.* **2011**, *50*, 16–22. [\[CrossRef\]](#)
113. Antolini, E.; Gonzalez, E.R. Tungsten-Based Materials for Fuel Cell Applications. *Appl. Catal. B Environ.* **2010**, *96*, 245–266. [\[CrossRef\]](#)

114. Can, F.; Courtois, X.; Duprez, D. Tungsten-Based Catalysts for Environmental Applications. *Catalysts* **2021**, *11*, 703. [\[CrossRef\]](#)
115. Elezovic, N.R.; Zabinski, P.; Ercius, P.; Wytrwal, M.; Radmilovic, V.R.; Lačnjevac, U.Č.; Krstajic, N.V. High Surface Area Pd Nanocatalyst on Core-Shell Tungsten Based Support as a Beneficial Catalyst for Low Temperature Fuel Cells Application. *Electrochim. Acta* **2017**, *247*, 674–684. [\[CrossRef\]](#)
116. Wang, L.; Zhu, S.; Marinkovic, N.; Kattel, S.; Shao, M.; Yang, B.; Chen, J.G. Insight into the Synergistic Effect between Nickel and Tungsten Carbide for Catalyzing Urea Electrooxidation in Alkaline Electrolyte. *Appl. Catal. B Environ.* **2018**, *232*, 365–370. [\[CrossRef\]](#)
117. Zhou, W.; Wachs, I.E.; Kiely, C.J. Nanostructural and Chemical Characterization of Supported Metal Oxide Catalysts by Aberration Corrected Analytical Electron Microscopy. *Curr. Opin. Solid State Mater. Sci.* **2012**, *16*, 10–22. [\[CrossRef\]](#)
118. Del Angel, P.; Hernandez-Pichardo, M.L.; Montoya De La Fuente, J.A. Aberration-Corrected HRTEM Study of Mn-Doped Tungstated Zirconia Catalysts. *Catal. Today* **2013**, *212*, 201–205. [\[CrossRef\]](#)
119. Hou, G.; Shen, Z.; Tang, Y.; Chen, Q.; Cao, H.; Zhang, H.; Zheng, G.; Zhang, J. Ni-WC Nanoparticles/Carbon Aerogel Electrocatalytic Electrode for Methanol and Urea Electrooxidation. *Int. J. Hydrogen Energy* **2023**, *48*, 991–1000. [\[CrossRef\]](#)
120. Kelly, T.G.; Stottlemeyer, A.L.; Ren, H.; Chen, J.G. Comparison of O–H, C–H, and C–O Bond Scission Sequence of Methanol on Tungsten Carbide Surfaces Modified by Ni, Rh, and Au. *J. Phys. Chem. C* **2011**, *115*, 6644–6650. [\[CrossRef\]](#)
121. Al-Enizi, A.M.; Brooks, R.M.; El-Halwany, M.M.; Yousef, A.; Nafady, A.; Hameed, R.M.A. CoCr₇C₃-like Nanorods Embedded on Carbon Nanofibers as Effective Electrocatalyst for Methanol Electro-Oxidation. *Int. J. Hydrogen Energy* **2018**, *43*, 9943–9953. [\[CrossRef\]](#)
122. Zhou, H.-C.; Long, J.R.; Yaghi, O.M. Introduction to Metal–Organic Frameworks. *Chem. Rev.* **2012**, *112*, 673–674. [\[CrossRef\]](#)
123. Liu, C.; Wang, J.; Wan, J.; Yu, C. MOF-on-MOF Hybrids: Synthesis and Applications. *Coord. Chem. Rev.* **2021**, *432*, 213743. [\[CrossRef\]](#)
124. Ding, M.; Cai, X.; Jiang, H.-L. Improving MOF Stability: Approaches and Applications. *Chem. Sci.* **2019**, *10*, 10209–10230. [\[CrossRef\]](#) [\[PubMed\]](#)
125. Chai, L.; Pan, J.; Hu, Y.; Qian, J.; Hong, M. Rational Design and Growth of MOF-on-MOF Heterostructures. *Small* **2021**, *17*, 2100607. [\[CrossRef\]](#)
126. Yu, J.; Mu, C.; Yan, B.; Qin, X.; Shen, C.; Xue, H.; Pang, H. Nanoparticle/MOF Composites: Preparations and Applications. *Mater. Horiz.* **2017**, *4*, 557–569. [\[CrossRef\]](#)
127. Zhou, W.-Q.; Xi, B.-J.; Chang, X.-W.; Wang, B.; Wu, X.-Q.; Li, S.; Wu, Y.-P.; Li, D.-S. Facile in Situ Transformation of NiOOH into MOF-74(Ni)/NiO OH Heterogeneous Composite for Enhancing Electrocatalytic Methanol Oxidation. *Molecules* **2022**, *27*, 2113. [\[CrossRef\]](#) [\[PubMed\]](#)
128. Sheikhi, S.; Jalali, F. Copper Selenide—Porous Carbon Derived from Metal-Organic Frameworks as an Efficient Electrocatalyst for Methanol Oxidation. *Int. J. Hydrogen Energy* **2024**, *55*, 864–874. [\[CrossRef\]](#)
129. Rajpure, M.M.; Jadhav, H.S.; Kim, H. Advanced LDH-MOF Derived Bimetallic NiCoP Electrocatalyst for Methanol Oxidation Reaction. *Colloids Surf. A Physicochem. Eng. Asp.* **2022**, *654*, 130062. [\[CrossRef\]](#)
130. Khan, M.E. State-of-the-Art Developments in Carbon-Based Metal Nanocomposites as a Catalyst: Photocatalysis. *Nanoscale Adv.* **2021**, *3*, 1887–1900. [\[CrossRef\]](#)
131. Trogadas, P.; Fuller, T.F.; Strasser, P. Carbon as Catalyst and Support for Electrochemical Energy Conversion. *Carbon* **2014**, *75*, 5–42. [\[CrossRef\]](#)
132. Wildgoose, G.G.; Banks, C.E.; Compton, R.G. Metal Nanoparticles and Related Materials Supported on Carbon Nanotubes: Methods and Applications. *Small* **2006**, *2*, 182–193. [\[CrossRef\]](#)
133. Karczmarzka, A.; Adamek, M.; El Houbbadi, S.; Kowalczyk, P.; Laskowska, M. Carbon-Supported Noble-Metal Nanoparticles for Catalytic Applications—A Review. *Crystals* **2022**, *12*, 584. [\[CrossRef\]](#)
134. Huang, H.; Wang, X. Recent Progress on Carbon-Based Support Materials for Electrocatalysts of Direct Methanol Fuel Cells. *J. Mater. Chem. A* **2014**, *2*, 6266–6291. [\[CrossRef\]](#)
135. Xiong, J.; Wang, Y.; Yang, C.; Yang, L.; Zhang, C.; Jiang, Q.; He, H.; Ying, G.; Huang, H. Confining Rhodium Nanocrystals into Polyaniline Nanorod-Embedded MXene Nanoarchitectures Enables Efficient Methanol Electrooxidation. *J. Colloid Interface Sci* **2025**, *695*, 137809. [\[CrossRef\]](#) [\[PubMed\]](#)
136. Belenkov, E.A.; Greshnyakov, V.A. Classification of Structural Modifications of Carbon. *Phys. Solid State* **2013**, *55*, 1754–1764. [\[CrossRef\]](#)
137. Dresselhaus, M.S.; Dresselhaus, G.; Avouris, P. (Eds.) *Carbon Nanotubes: Synthesis, Structure, Properties, and Applications*; Topics in Applied Physics; Springer: Berlin/Heidelberg, Germany; New York, NY, USA, 2001; ISBN 978-3-540-41086-7.
138. Hirsch, A. Functionalization of Single-Walled Carbon Nanotubes. *Angew. Chem. Int. Ed.* **2002**, *41*, 1853. [\[CrossRef\]](#)

139. Zhang, J.; Terrones, M.; Park, C.R.; Mukherjee, R.; Monthieux, M.; Koratkar, N.; Kim, Y.S.; Hurt, R.; Frackowiak, E.; Enoki, T.; et al. Carbon Science in 2016: Status, Challenges and Perspectives. *Carbon* **2016**, *98*, 708–732. [[CrossRef](#)]
140. Ramli, Z.A.C.; Kamarudin, S.K. Platinum-Based Catalysts on Various Carbon Supports and Conducting Polymers for Direct Methanol Fuel Cell Applications: A Review. *Nanoscale Res. Lett.* **2018**, *13*, 410. [[CrossRef](#)]
141. Wissler, M. Graphite and Carbon Powders for Electrochemical Applications. *J. Power Sources* **2006**, *156*, 142–150. [[CrossRef](#)]
142. Zainoodin, A.M.; Kamarudin, S.K.; Daud, W.R.W. Electrode in Direct Methanol Fuel Cells. *Int. J. Hydrogen Energy* **2010**, *35*, 4606–4621. [[CrossRef](#)]
143. Cao, R.; Lee, J.; Liu, M.; Cho, J. Recent Progress in Non-Precious Catalysts for Metal-Air Batteries. *Adv. Energy Mater.* **2012**, *2*, 816–829. [[CrossRef](#)]
144. Antolini, E. Carbon Supports for Low-Temperature Fuel Cell Catalysts. *Appl. Catal. B Environ.* **2009**, *88*, 1–24. [[CrossRef](#)]
145. Liu, Y.; Ji, C.; Gu, W.; Jorne, J.; Gasteiger, H.A. Effects of Catalyst Carbon Support on Proton Conduction and Cathode Performance in PEM Fuel Cells. *J. Electrochem. Soc.* **2011**, *158*, B614–B621. [[CrossRef](#)]
146. De Volder, M.F.L.; Tawfick, S.H.; Baughman, R.H.; Hart, A.J. Carbon Nanotubes: Present and Future Commercial Applications. *Science* **2013**, *339*, 535–539. [[CrossRef](#)] [[PubMed](#)]
147. Su, H.; Hu, Y.H. Recent Advances in Graphene-based Materials for Fuel Cell Applications. *Energy Sci. Eng.* **2021**, *9*, 958–983. [[CrossRef](#)]
148. Choi, S.M.; Seo, M.H.; Kim, H.J.; Kim, W.B. Synthesis of Surface-Functionalized Graphene Nanosheets with High Pt-Loadings and Their Applications to Methanol Electrooxidation. *Carbon* **2011**, *49*, 904–909. [[CrossRef](#)]
149. Chen, W.-F.; Wang, J.-P.; Hsu, C.-H.; Jhan, J.-Y.; Teng, H.; Kuo, P.-L. Nanostructured Coral-like Carbon as Pt Support for Fuel Cells. *J. Phys. Chem. C* **2010**, *114*, 6976–6982. [[CrossRef](#)]
150. Zhang, J.; Yi, X.; Liu, S.; Fan, H.-L.; Ju, W.; Wang, Q.-C.; Ma, J. Vertically Aligned Carbon Nanotubes/Carbon Fiber Paper Composite to Support Pt Nanoparticles for Direct Methanol Fuel Cell Application. *J. Phys. Chem. Solids* **2017**, *102*, 99–104. [[CrossRef](#)]
151. Wang, Y.; Shao, Y.; Matson, D.W.; Li, J.; Lin, Y. Nitrogen-Doped Graphene and Its Application in Electrochemical Biosensing. *ACS Nano* **2010**, *4*, 1790–1798. [[CrossRef](#)]
152. Pan, C.; Qiu, L.; Peng, Y.; Yan, F. Facile Synthesis of Nitrogen-Doped Carbon–Pt Nanoparticle Hybrids via Carbonization of Poly([Bvim][Br]-Co-Acrylonitrile) for Electrocatalytic Oxidation of Methanol. *J. Mater. Chem.* **2012**, *22*, 13578. [[CrossRef](#)]
153. Forootan Fard, H.; Khodaverdi, M.; Pourfayaz, F.; Ahmadi, M.H. Application of N-Doped Carbon Nanotube-Supported Pt–Ru as Electrocatalyst Layer in Passive Direct Methanol Fuel Cell. *Int. J. Hydrogen Energy* **2020**, *45*, 25307–25316. [[CrossRef](#)]
154. Lee, E.; Manthiram, A. One-Step Reverse Microemulsion Synthesis of Pt–CeO₂ /C Catalysts with Improved Nanomorphology and Their Effect on Methanol Electrooxidation Reaction. *J. Phys. Chem. C* **2010**, *114*, 21833–21839. [[CrossRef](#)]
155. Ito, Y.; Takeuchi, T.; Tsujiguchi, T.; Abdelkareem, M.A.; Nakagawa, N. Ultrahigh Methanol Electro-Oxidation Activity of PtRu Nanoparticles Prepared on TiO₂-Embedded Carbon Nanofiber Support. *J. Power Sources* **2013**, *242*, 280–288. [[CrossRef](#)]
156. Park, K.-W.; Han, S.-B.; Lee, J.-M. Photo(UV)-Enhanced Performance of Pt–TiO₂ Nanostructure Electrode for Methanol Oxidation. *Electrochem. Commun.* **2007**, *9*, 1578–1581. [[CrossRef](#)]
157. Zhang, H.; Zhou, W.; Du, Y.; Yang, P.; Wang, C.; Xu, J. Enhanced Electrocatalytic Performance for Methanol Oxidation on Pt–TiO₂/ITO Electrode under UV Illumination. *Int. J. Hydrogen Energy* **2010**, *35*, 13290–13297. [[CrossRef](#)]
158. Zhou, C.; Peng, F.; Wang, H.; Yu, H.; Peng, C.; Yang, J. Development of Stable PtRu Catalyst Coated with Manganese Dioxide for Electrocatalytic Oxidation of Methanol. *Electrochem. Commun.* **2010**, *12*, 1210–1213. [[CrossRef](#)]
159. Zhou, C.; Wang, H.; Peng, F.; Liang, J.; Yu, H.; Yang, J. MnO₂/CNT Supported Pt and PtRu Nanocatalysts for Direct Methanol Fuel Cells. *Langmuir* **2009**, *25*, 7711–7717. [[CrossRef](#)]
160. Lee, H.-Y.; Vogel, W.; Chu, P.P.-J. Nanostructure and Surface Composition of Pt and Ru Binary Catalysts on Polyaniline-Functionalized Carbon Nanotubes. *Langmuir* **2011**, *27*, 14654–14661. [[CrossRef](#)] [[PubMed](#)]
161. Zhang, X.; Xia, G.; Huang, C.; Wang, Y. Preparation and Characterization of Pt Nanoparticles Supported on Modified Graphite Nanoplatelet Using Solution Blending Method. *Int. J. Hydrogen Energy* **2013**, *38*, 8909–8913. [[CrossRef](#)]
162. Rajendra Prasad, K.; Munichandraiah, N. Electrooxidation of Methanol on Polyaniline without Dispersed Catalyst Particles. *J. Power Sources* **2002**, *103*, 300–304. [[CrossRef](#)]
163. Niu, L.; Li, Q.; Wei, F.; Chen, X.; Wang, H. Electrochemical Impedance and Morphological Characterization of Platinum-Modified Polyaniline Film Electrodes and Their Electrocatalytic Activity for Methanol Oxidation. *J. Electroanal. Chem.* **2003**, *544*, 121–128. [[CrossRef](#)]
164. Zhiani, M.; Rezaei, B.; Jalili, J. Methanol Electro-Oxidation on Pt/C Modified by Polyaniline Nanofibers for DMFC Applications. *Int. J. Hydrogen Energy* **2010**, *35*, 9298–9305. [[CrossRef](#)]

165. Zhao, Y.; Zhan, L.; Tian, J.; Nie, S.; Ning, Z. Enhanced Electrocatalytic Oxidation of Methanol on Pd/Polypyrrole–Graphene in Alkaline Medium. *Electrochim. Acta* **2011**, *56*, 1967–1972. [[CrossRef](#)]
166. Luo, B.; Yan, X.; Xu, S.; Xue, Q. Polyelectrolyte Functionalization of Graphene Nanosheets as Support for Platinum Nanoparticles and Their Applications to Methanol Oxidation. *Electrochim. Acta* **2012**, *59*, 429–434. [[CrossRef](#)]

Disclaimer/Publisher’s Note: The statements, opinions and data contained in all publications are solely those of the individual author(s) and contributor(s) and not of MDPI and/or the editor(s). MDPI and/or the editor(s) disclaim responsibility for any injury to people or property resulting from any ideas, methods, instructions or products referred to in the content.