

Recent Advancements in Direct Methanol Fuel Cell Catalyst using Noble and Non Noble Metals – A Review

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Abstract

At the moment, one of the most important research questions in the industry is the synthesis of methanol oxidation anode electrocatalysts that have high catalytic activity, high electrical conductivity, long term durability, and are cost effective. This subject has arisen as one of the most major areas of research in the sector, with the goal of reducing the slow kinetics in the direct methanol fuel cell. In particular, the goals of this research are to review information on catalyst size and shape, electrochemical active surface area, electrolyte conditions, support material type, resistance to poisoning species, and synthesis method of noble and non-noble metals, as well as compare the findings of a variety of investigations in order to summarize and contrast the performances of electrocatalysts manufactured from noble and non-noble metals. Additionally, there are other aspects of catalyst modification that researchers are looking into, such as the introduction of nanostructured morphology, the use of metal alloys like metal oxides and support materials like carbon, graphene and graphene oxides, the use of an acidic or basic electrolyte, and the manufacture of the catalyst in its final form. An in-depth assessment of the challenges that are regularly faced in the process of turning direct methanol fuel cells into reliable sources of energy with long-term potential for use is provided by this research. Part of the discussion in this chapter is the strategy that should be used in order to reduce the complexity of synthesising new generations of anode electrocatalysts to the lowest level that is reasonably achievable.

Keywords: DMFCs, Anode Electrocatalyst, Synthesis, Noble and Non Noble Materials

Introduction

The expanding human population and the importance of technology have both increased energy demand. Currently, electricity is used to power electronic devices like laptops, cameras, and phones. The problem of these chargers or rechargeable batteries is that they require external power to charge. The need for an existing power supply and the battery's capacity limit its use. Furthermore, electric power is largely sourced from fossil fuels, which harms the environment as the number of technology users increases. So, researchers are urged to identify sustainable and eco-friendly power sources.

Hence fuel cell is one of the eco-friendly power sources for future. Different types of fuel cells were available in the market. From that Direct Methanol Fuel Cells (DMFC) requires no

power to recharge, is operable at low temperatures, has a long lifetime, and uses a quick refuelling technique [1]. However, problems with DMFCs include high cost, methanol crossover over the proton exchange membrane, heat and water management, and long-term stability and endurance [2]. Other issues include catalyst loading, membrane thickness, diffusion layer, and low power density. The sluggish processes on the cathode (oxygen reduction) and anode (methanol oxidation) have made direct methanol fuel cell operation difficult. Many investigations have been conducted to identify catalysts with adequate functionality and cost to improve the operation and commercialization of fuel cells as renewable energy sources.

Many researchers have researched the synthesis of platinum-based catalysts because Pt has high catalytic efficiency, good electrical characteristics, and is corrosion-resistant [3]. Pure Pt is the most active metal for methanol dissociative adsorption. However, CO produced by low-temperature methanol electro oxidation easily poisons Pt [4]. In recent years, research has focused on developing platinum-free catalysts. Carbon monoxide generated during the electro-oxidation of methanol is another reason to avoid using pure platinum catalysts. They degrade the platinum catalyst in fuel cells by adsorbing CO₂ intermediates. To overcome these issues, metal oxides such as MnO₂, TiO₂, NiTiO₃ and RuO₂ can be used to embed platinum on other noble or non-noble metal alloys [5–7]. From these, materials with a specific geometric layout, shape, and composition have been developed for Nano-sized catalysts. In order to improve catalyst durability and charge transfer efficiency, mesoporous conductive supports are frequently added. Metal oxides, mesoporous silica and non-carbonaceous support materials were used in DMFCs. To be suitable for practical applications, support materials must have the following key features. A strong link between the support and the catalyst, mesoporous structure, excellent water handling, acceptable corrosion resistance and good electrical conductivity [8].

This review will focus on the recent synthesised noble or non-noble metal electrocatalysts for methanol oxidation reactions (MOR) on the anode of DMFC. The effects of catalyst size and shape, electrolyte conditions, support material type, and synthesis method will also be discussed.

MOR Catalysts

The electro-catalyst is one of the most critical factors affecting the reliability of DMFC. New catalysts with superior activity, anti-CO ability, and durability are preferred for catalysing reactions like methanol oxidation. More non-noble metals,

supported or not, are studied and developed for use in DMFC catalysts with less Pt noble metal content. The catalysts discussed are categorised as noble metal such as platinum, rhodium, and palladium, non-noble metal such as nickel oxides, cobalt, and copper. To compare different catalysts, parameters like current densities and peak area will be stated. Various studies also present morphology, composition, thermal stability, durability, electrochemical active surface area, and resistance to poisoning species.

Platinum and Platinum Alloy Catalysts

For mesoporous platinum, researchers have explored and optimised nanoscale structures to increase available surface area and maintain it for longer periods of time [9]. The self-supported one-dimensional architecture is known to be suitable for long-term stability. This structure avoids the loss of catalytic activity caused by oxidation/dissolution of platinum catalysts [10]. The structure also facilitates electron transfer and protects the catalyst structure [11]. Using a mesoporous design increases the electrochemically active area a concave surface for much more reaction sites. The self-assembled one-dimensional structure allows the presence of large electrochemically active surfaces adequate for methanol oxidation [12].

The mesoporous platinum Nanospheres (MPNs) have excellent electrochemical performance and structural thermostability for methanol oxidation. This property is critical to the practical use of catalysts, as their performance is determined by their ability to regain and maintain their initial structure and shape. PtCarbon-20% and PtBlack were treated at 250°C or 350°C for 3 hours to test this result [13].

Recently, platinum and its alloys with other metals have been studied to improve methanol oxidation catalyst activity. Taylor et al. investigated the activity of a series of PtRu bimetallic catalysts prepared via electroless deposition technique [14]. The greatest activity was seen at 50% monodisperse ruthenium surface coverage of 20 wt% platinum and 1.1 wt% ruthenium, which was 7 times that of pure platinum. By reducing the binding energies of intermediates like CO, a lattice mismatch between platinum and ruthenium atoms increases the catalyst's tolerance to them. Ruthenium can also efficiently oxidise CO by supplying oxygen-carrying species with lower potential [15]. Combining platinum with other materials can improve catalytic activity and resistance to deactivate species. Graphene oxide (GO) adds electrochemical stability, surface area, conductivity, and flexibility [16]. The activity and durability of the hybrid were compared to Platinum@GO (metal-carbon) and Platinum@PVP (metal-polymer) catalysts [17]. Other platinum-based catalysts have also been studied in depth for methanol oxidation. In addition, there are catalysts made of platinum, such as Pt-Ru-Ni/C [18], Pt-Sn [19], Pt-WC/C [20], and Pt-MoO₃/C [21].

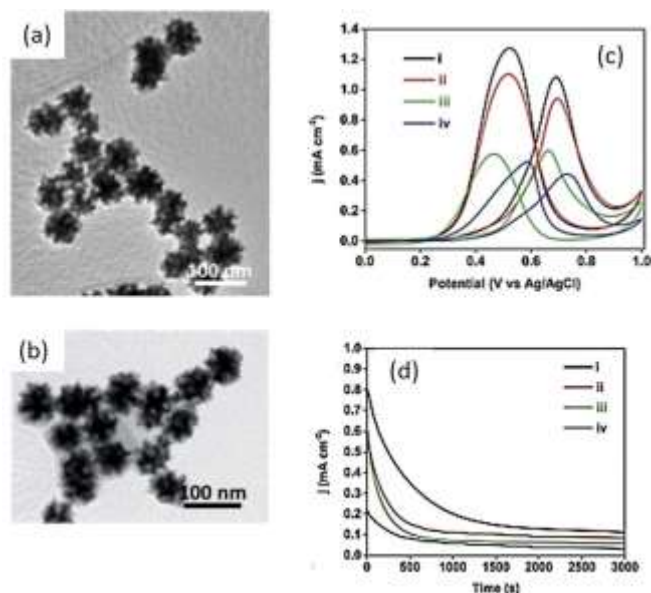


Figure 1 (a) TEM images of Pt sample before reaction, (b) TEM images of Pt sample after 12 h (c) Cyclic voltammograms of MOR recorded in 0.5 M H₂SO₄ + 0.5 M CH₃OH at a scan rate of 50 mV s⁻¹, (d) chronoamperometric curves (recorded at 0.6 V) obtained in 0.5 M H₂SO₄ + 0.5 M CH₃OH [13].

Rhodium and Rhodium alloy catalyst

Rhodium can be used to replace pricey platinum-based catalysts, lowering commercialization costs. Using an alkaline medium can also help solve the previously noted water management issue in DMFCs [22]. Kang's team has synthesised rhodium-based electrocatalyst to examine its catalytic performance toward methanol oxidation process in an alkaline medium. They created rhodium nanodendrites with nanosheet subunits using a simple diethylene glycol reduction technique using polyethyleneimine. After 6000 seconds, the current on rhodium nanodendrites was nearly 20.5 times larger than that on rhodium nanoaggregates, according to the chronoamperometry measurements [23].

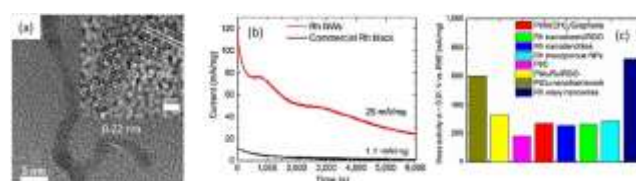


Figure 2 (a) Structural characterizations of ultrathin Rh wavy nanowires from HRTEM image. (b) Chronoamperometry results of the ultrathin Rh wavy nanowires and commercial Rh black in 1 M KOH + 1 M MeOH electrolyte at 0.52 V vs. RHE. (c) The MOR mass activity at ~0.61 V vs. RHE of the Rh and Pt-based electrocatalysts tested in alkaline media.

Rhodium electrocatalysts have low ECSA. Mesoporous and nanodendritic rhodium NPs both have ECSA values of 50 m² g⁻¹ ~43 m² g⁻¹ [24]. Using ultrafine nanostructures may help increase ECSA and hence catalytic activity. Huang et al. and Fu et al. have studied the capabilities of rhodium in the form of ultrathin wavy nanowires for diverse reactions. The catalytic oxidation of benzyl alcohol to benzaldehyde by ultrathin wavy rhodium nanowires was excellent [25]. The ultrathin wavy rhodium nanowires have a mass activity of 722 mA mg⁻¹ (at 0.61 V potential vs. RHE), which is 2.5 times higher than other

rhodium nanomaterials previously investigated [26]. Kang and coworkers developed a one-pot hydrothermal hybrid electrocatalyst comprising rhodium nanosheets on RGO [27].

The hybrid catalysts perform better than the commercial PtCarbon electrocatalyst, according to cyclic voltammetry and chronoamperometry studies. At 0.61 V, the hybrids had 3.6 times the current of the commercial PtCarbon electrocatalyst (264 A g⁻¹_{Rh} and 73 A g⁻¹_{Pt}, respectively) Figure 3 (c). Also, chronoamperometry investigations revealed that hybrids have a higher current value than PtCarbon, which decays in 6000 seconds Figure 3 (d). This shows that not only do the synthesised hybrids have increased activity for longer periods of time, but also stability against harmful carbonaceous molecules like carbon monoxide.

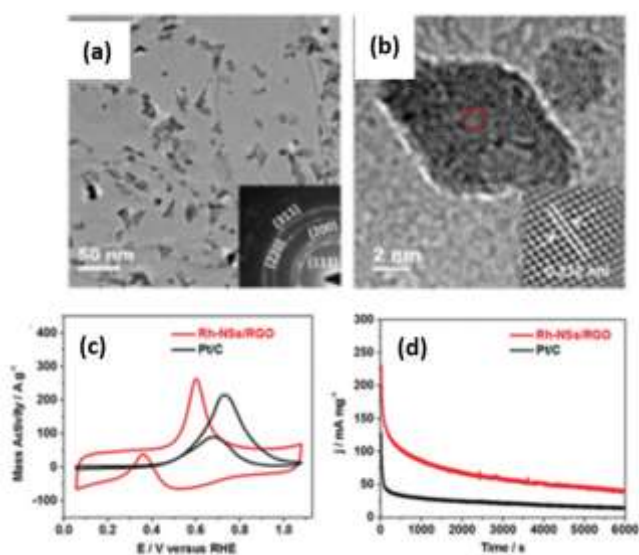


Figure 3 (a) Rh-NSs/RGO hybrids TEM image and its SAED pattern (inset image) (b) Image of Rh-NSs/RGO hybrids obtained using HRTEM along with the magnified version of a region in red square (inset image). (c) Metal mass-normalized (d) Chronoamperometry data of Rh-NSs/RGO hybrids and Pt/C catalyst at 0.61 V potential (in 1 M KOH + 1 M CH₃OH solution) [27].

Palladium and Palladium alloy catalyst

Recently, palladium has been employed as a platinum substitute as a catalyst. Researchers are interested in researching their electrochemical response characteristics for commercial applications because of their nanostructural shape and active sites. Not enough study has been done on palladium nanoporous structures, which are projected to perform better than other palladium structures. However, the time-consuming dealloying procedure and the large dealloying driving power required are some of the disadvantages that need to be overcome. Wang's team created nanoporous palladium (NP Pd) rods electrocatalysts by dealloying a binary Al₈₀Pd₂₀ alloy in a 5 wt% hydrochloric acid solution under free corrosion [28]. Nanoporous rods with interpenetrating ligament-channels were found under scanning and transmission electron microscopy. After that, they were mixed with Vulcan XC-72 Carbon powder to make NP Pd/C catalyst to test in alkaline medium. Adding more than 2 M methanol to the KOH solution reduces the oxidation current density due to competition for hydroxyl

(OH_{ads}) and methoxyl ((CH₃O)_{ads}) intermediates. Zhao's [29] team developed a palladium-based electrocatalyst supported by Mn₃O₄-modified multiwalled carbon nanotubes (Pd-Mn₃O₄/MWCNTs) by wet impregnation.

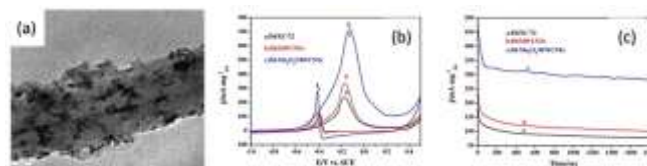


Figure 4 (a) Pd-Mn₃O₄/MWCNT TEM images, (b) CV curves (at 50 mV s⁻¹ scan rate) and (c) CA curves of Pd/XC-72, Pd/MWCNTs, and Pd-Mn₃O₄/MWCNTs catalysts in 0.5 M NaOH + 1 M CH₃OH nitrogen-saturated solution.

The results show that Pd-Mn₃O₄/MWCNTs had a better catalytic performance towards MOR at all potentials utilised (1.0 V to 0.2 V). For Pd-Mn₃O₄/MWCNTs, Pd/MWCNTs, and Pd/XC-72, the methanol forward oxidation mass specific peak currents were 715.8, 332.4, and 236.1 mA mg⁻¹_{Pd}, respectively. For Pd-Mn₃O₄/MWCNTs, 284.14 mA mg⁻¹_{Pd} was reported, 101.03 mA mg⁻¹_{Pd} for Pd/MWCNT, and 77.25 mA mg⁻¹_{Pd} for Pd/XC-72 at Chronoamperometric analysis for 1800 seconds. Other palladium-based catalysts for MOR have also been investigated in the past, with examples including PdNPs/PVP-graphene [30], NPPd [31], Pd/TiO₂-C [32], and Pd/CNF [33] being some of the most well-known examples.

Summary of Platinum, Rhodium and Palladium based catalysts

Finally, numerous synthesis strategies for noble metal anode catalysts have been explored. Mesoporous platinum nanospheres created by a gradual reduction process with shape-directing surfactant showed excellent structural heat stability and electrochemical performance. Due to their resistance to particle aggregation, MPNs could retain 97 percent of their initial ECSA when heated to 350°C. The maximal activity of commercial monometallic Pt/C alloyed with ruthenium is attained at roughly 50% monodisperse ruthenium surface coverage. The activity was seven times that of pure platinum. Combining ruthenium with platinum alters platinum's electrical structure for simple hydrogen-carbon bond breaking and creates a strain effect that lowers intermediate binding energies.

Alkaline medium can be used to test the activity and decay rate of rhodium nanodendritic morphology, one of the cheaper alternatives to platinum. Due to the presence of surface imperfections and a large specific surface area, an ultrathin wavy rhodium nanowire could have a high mass activity and enhanced catalytic performance. So the hybrid structure is not only able to retain fine function for long periods of time, but it can also withstand the poisonous effects of carbonaceous substances. Introduce composites to a support, as illustrated by MWCNT supports modified with Mn₃O₄ to support palladium, may increase resistance to CO poisoning and increase the active surface area of a support. Pd-Mn₃O₄/MWCNTs perform better than Pd/MWCNTs and Pd/XC-72 catalysts due to their superior features, which include a greater methanol forward oxidation mass specific current and a higher current density during an 1800-second CA study.

Catalysts based on Non Nobel Metals

Recently researchers to explore for non-noble metal anode catalysts to avoid the expensive cost and, in some situations, the declining activity of noble metals. Transition metal oxides, such as nickel oxide (NiO), have been recognised for their usage as catalysts [34] and electrochemical performance. Tong's team [35] used a sponge template to generate NiO nanoparticle/nanoflake catalyst on a Ni-P alloy tube. This approach involves electroless plating amorphous Ni-P on sponge and annealing it at 500°C in air. The annealing removes the templates, allowing Ni-P to crystallise and form nanostructures of NiO on the NiP tubes' surfaces. They were also tested as electrocatalysts for methanol oxidation (in alkaline solution) with porous NiO nanoflakes made by chemical bath deposition (CBD-NiO).

EP-M (containing 16.2% Ni-P and 83.8 % NiO) has the biggest specific surface area of 210.03 m² g⁻¹. In alkaline solution (0.5 M KOH and 1.0 M CH₃OH at 50 mV s⁻¹ scanning rate), EP-M for MOR observed a substantially higher current density of around 28.56 mA cm⁻². Simultaneously, the novel catalyst showed high stability (over 20,000 seconds) in chronoamperometry tests. Another explanation for its advantage is the strong electrical interaction of Ni-P and NiO. Das et al [36] tested three supports for methanol oxidation: SPAni, PANi, and Vulcan Carbon. For dispersion, deposition, use, and distribution, Ni catalyst nanoparticles supported by SPAni (Ni/SPAni) showed to be the best. CV data provided 6.1 mA g⁻¹ mass specific current density and 306 μA cm⁻² forward peak area. It has mass specific current densities of 0.6 mA g⁻¹ and a forward peak area of 25.6 μA cm⁻², which is substantially greater than Platinum-Ruthenium/C. The synthesised catalyst's electrocatalytic activity for MOR was improved in alkaline electrolytes, the results showed. A high nickel dispersion and an organised mesoporous structure that enhances methanol and product diffusion are responsible for the increased performance.

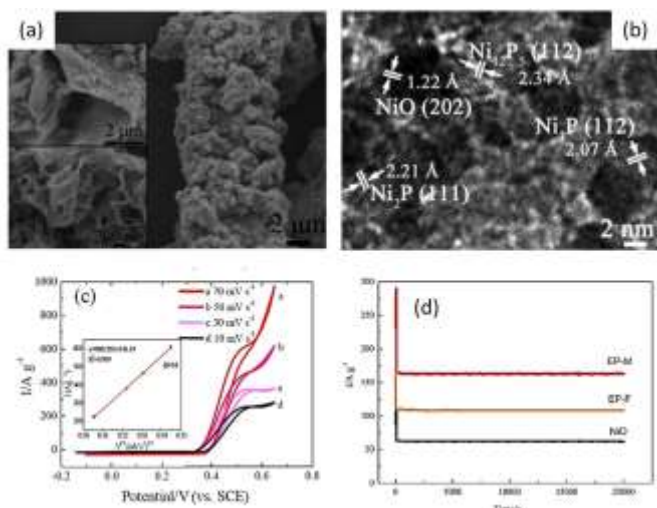


Figure 5 (a) SEM images of CBD-NiO (b) TEM and HRTEM images of the CBD-NiO (c) CVs for methanol electro-oxidation on EP-M in 0.5 M KOH + 1.0 M CH₃OH at different scan rates. Inset: peak currents versus the square roots of the scan rates. (d) Chronoamperometry on EP-M, EP-F, and CBDNiO catalyst in 0.5 M KOH + 1.0 M CH₃OH at 0.5 V for 20,000 s. [35]

A new catalyst based on cobalt and cobalt oxides (Co₃O₄ and CoO) is being developed. High electroactive surface sites and

optimised electronic structure of cobalt oxide contribute to its exceptional catalytic activity. Cobalt has since been described as a major catalyst and co-catalyst in various methanol oxidation processes. Jafarian and colleagues [37] used anodic deposition to make cobalt hydroxide modified glassy carbon electrodes and investigated their activity in an electro-catalytic methanol oxidation reaction. According to Zafeiratos' basic investigation, the former contained more mobile lattice oxygen, which facilitates the partial oxidation of methanol to formaldehyde [38]. Cobalt has been functionalized, and hetero atoms and carbon-based materials have been added to boost its catalytic activity and stability. Due to the increased use of cobalt-based materials, researchers have been looking for ways to improve its properties chemically and physically. Most commonly utilised metals for replacement are nickel, copper, cadmium, and tungsten.

Due to its high reactivity, low cost, low to moderate stability, and ease of synthesising copper is another popular electrocatalyst. Cu has substantially lower CO selectivity than Pt, Pd, Ru, and Rh, for example [39]. This is advantageous for long-term stability runs, where CO can poison or deactivate the active sites of the catalyst, reducing the catalyst's activity. The next section discusses several selected Cu-based catalyst for methanol oxidation. A Pt-free Cu-based catalyst for methanol oxidation has been described lately. It was achieved by Ali Doner's group [40] using electrodeposition. This is higher than Cu/Cu (235.65 mA cm⁻¹) electrode. Because of the larger surface area, increased surface porosity, and strong electrical interaction between Cu and Zn, the reason was postulated.

Summary of Non Nobel Metals

The use of non-noble metals as MOR catalysts allows for the avoidance of pricey noble metals while also benefiting from their stability as anode catalysts. Compared to NiO nanoflakes and porous nanoflakes, micro-spherical nickel oxide has a larger specific surface area. The combination may assist achieve large mass specific current densities by dispersing active sites widely. Furthermore, compared to a carbon-supported platinum-ruthenium catalyst, Ni/SPAni has greater mass specific current densities and forward peak area. Cobalt is another possible catalyst material for high MOR catalytic performance. The electrochemical behaviour of the produced catalyst may surpass that of conventional nickel cobalt alloy structures. The Ni-Co-P-O molecule contains electron tunnelling connections between the phosphates and metal phosphides, allowing for rapid methanol and product transport in and out of the catalysts. Compared to noble metals like palladium, ruthenium, rhodium, and platinum, copper has better long-term stability and less selectivity toward carbon monoxide. This excellent performance may be owing to the surfaces multiple atomic steps, edges, and corner atoms. The polyhedral catalyst has the best CO endurance due to the improved electron transport enabled by the strong copper-platinum interaction. The CoO_x cage provides Co⁴⁺ as an active site for easier methanol oxidation. Copper, on the other hand, is a methanol adsorption centre.

Conclusion

Pt is quite costly, and it quickly degrades when exposed to carbon monoxide created in the process of methanol oxidation. Alloying with other metals, such as Ru, or even employing transition metals or alloys to totally replace Pt could lengthen the catalyst's lifetime by destabilising the CO intermediate.

Catalysts used in water-gas-shift reaction ($\text{CO} + \text{H}_2\text{O} = \text{CO}_2 + \text{H}_2$) and other catalysts used for the dissociation of water and CO_2 production have the advantage of producing harmless CO_2 . The stability, dispersion, and overall conductivity of electrode-catalyst assemblies are influenced by the choice of support for DMFCs. Additionally, resistance to corrosion, metal interaction, and hydrophobicity are all vital for the long-term stability of the product. This review will likely offer a way forward for advances in superb alternative technology by addressing how new insights on electrode catalysts and the impacts of varying parameters can be used in future applications.

REFERENCES:

- Moura, A.S., Fajín, J.L.C., Mandado, M., and Cordeiro, M.N.D.S., "Ruthenium-platinum catalysts and direct methanol fuel cells (DMFC): A review of theoretical and experimental breakthroughs," *Catalysts* 7(2), 2017, doi:[10.3390/catal7020047](https://doi.org/10.3390/catal7020047).
- Kamarudin, S.K., Achmad, F., and Daud, W.R.W., "Overview on the application of direct methanol fuel cell (DMFC) for portable electronic devices," *Int. J. Hydrogen Energy* 34(16):6902–6916, 2009, doi:<https://doi.org/10.1016/j.ijhydene.2009.06.013>.
- Kloke, A., Stetten, F. von, Zengerle, R., and Kerzenmacher, S., "Strategies for the Fabrication of Porous Platinum Electrodes," *Adv. Mater.* 23(43):4976–5008, 2011, doi:<https://doi.org/10.1002/adma.201102182>.
- Basri, S., Kamarudin, S.K., Daud, W.R.W., Yaakob, Z., and Kadhum, A.A.H., "Novel Anode Catalyst for Direct Methanol Fuel Cells," *Sci. World J.* 2014:547604, 2014, doi:[10.1155/2014/547604](https://doi.org/10.1155/2014/547604).
- Li, C., Tan, H., Lin, J., Luo, X., Wang, S., You, J., Kang, Y.-M., Bando, Y., Yamauchi, Y., and Kim, J., "Emerging Pt-based electrocatalysts with highly open nanoarchitectures for boosting oxygen reduction reaction," *Nano Today* 21:91–105, 2018, doi:<https://doi.org/10.1016/j.nantod.2018.06.005>.
- Li, C., Iqbal, M., Lin, J., Luo, X., Jiang, B., Malgras, V., Wu, K.C.-W., Kim, J., and Yamauchi, Y., "Electrochemical Deposition: An Advanced Approach for Templated Synthesis of Nanoporous Metal Architectures," *Acc. Chem. Res.* 51(8):1764–1773, 2018, doi:[10.1021/acs.accounts.8b00119](https://doi.org/10.1021/acs.accounts.8b00119).
- Thiagarajan, V., Karthikeyan, P., Thanarajan, K., Neelakrishnan, S., Manoharan, R., Chen, R., Fly, A., Anand, R., Karuppa Raj, T.R., and Sendhil Kumar, N., "Experimental investigation on DMFCs using reduced noble metal loading with NiTiO₃ as supportive material to enhance cell performances," ISBN 4222573833, 2019, doi:[10.1016/j.ijhydene.2019.03.244](https://doi.org/10.1016/j.ijhydene.2019.03.244).
- Jha, N., Leela Mohana Reddy, A., Shaijumon, M.M., Rajalakshmi, N., and Ramaprabhu, S., "Pt–Ru/multi-walled carbon nanotubes as electrocatalysts for direct methanol fuel cell," *Int. J. Hydrogen Energy* 33(1):427–433, 2008, doi:<https://doi.org/10.1016/j.ijhydene.2007.07.064>.
- Li, C., Imura, M., and Yamauchi, Y., "Displacement Plating of a Mesoporous Pt Skin onto Co Nanochains in a Low-Concentration Surfactant Solution," *Chem. – A Eur. J.* 20(12):3277–3282, 2014, doi:<https://doi.org/10.1002/chem.201303250>.
- Chen, Y.-P., Chen, C.-T., Hung, Y., Chou, C.-M., Liu, T.-P., Liang, M.-R., Chen, C.-T., and Mou, C.-Y., "A New Strategy for Intracellular Delivery of Enzyme Using Mesoporous Silica Nanoparticles: Superoxide Dismutase," *J. Am. Chem. Soc.* 135(4):1516–1523, 2013, doi:[10.1021/ja3105208](https://doi.org/10.1021/ja3105208).
- Li, H.-H., Zhao, S., Gong, M., Cui, C.-H., He, D., Liang, H.-W., Wu, L., and Yu, S.-H., "Ultrathin PtPdTe Nanowires as Superior Catalysts for Methanol Electrooxidation," *Angew. Chemie Int. Ed.* 52(29):7472–7476, 2013, doi:<https://doi.org/10.1002/anie.201302090>.
- Li, C., Malgras, V., Alshehri, S.M., Kim, J.H., and Yamauchi, Y., "Electrochemical Synthesis of Mesoporous Pt Nanowires with Highly Electrocatalytic Activity toward Methanol Oxidation Reaction," *Electrochim. Acta* 183:107–111, 2015, doi:<https://doi.org/10.1016/j.electacta.2015.04.028>.
- Jiang, B., Li, C., Malgras, V., Imura, M., Tominaka, S., and Yamauchi, Y., "Mesoporous Pt nanospheres with designed pore surface as highly active electrocatalyst," *Chem. Sci.* 7(2):1575–1581, 2016, doi:[10.1039/C5SC03779D](https://doi.org/10.1039/C5SC03779D).
- Garrick, T.R., Diao, W., Tengco, J.M., Stach, E.A., Senanayake, S.D., Chen, D.A., Monnier, J.R., and Weidner, J.W., "The Effect of the Surface Composition of Ru-Pt Bimetallic Catalysts for Methanol Oxidation," *Electrochim. Acta* 195:106–111, 2016, doi:<https://doi.org/10.1016/j.electacta.2016.02.134>.
- Ataee-Esfahani, H., Liu, J., Hu, M., Miyamoto, N., Tominaka, S., Wu, K.C.W., and Yamauchi, Y., "Mesoporous Metallic Cells: Design of Uniformly Sized Hollow Mesoporous Pt–Ru Particles with Tunable Shell Thicknesses," *Small* 9(7):1047–1051, 2013, doi:<https://doi.org/10.1002/sml.201202539>.
- Çelik, B., Başkaya, G., Sert, H., Karatepe, Ö., Erken, E., and Şen, F., "Monodisperse Pt(0)/DPA@GO nanoparticles as highly active catalysts for alcohol oxidation and dehydrogenation of DMAB," *Int. J. Hydrogen Energy* 41(13):5661–5669, 2016, doi:<https://doi.org/10.1016/j.ijhydene.2016.02.061>.
- Daşdelen, Z., Yıldız, Y., Eriş, S., and Şen, F., "Enhanced electrocatalytic activity and durability of Pt nanoparticles decorated on GO-PVP hybride material for methanol oxidation reaction," *Appl. Catal. B Environ.* 219:511–516, 2017, doi:<https://doi.org/10.1016/j.apcatb.2017.08.014>.
- Wang, Z.-B., Yin, G.-P., Shao, Y.-Y., Yang, B.-Q., Shi, P.-F., and Feng, P.-X., "Electrochemical impedance studies on carbon supported PtRuNi and PtRu anode catalysts in acid medium for direct methanol fuel cell," *J. Power Sources* 165(1):9–15, 2007,

- doi:<https://doi.org/10.1016/j.jpowsour.2006.12.027>.
19. Antolini, E. and Gonzalez, E.R., "The electro-oxidation of carbon monoxide, hydrogen/carbon monoxide and methanol in acid medium on Pt-Sn catalysts for low-temperature fuel cells: A comparative review of the effect of Pt-Sn structural characteristics," *Electrochim. Acta* 56(1):1–14, 2010, doi:<https://doi.org/10.1016/j.electacta.2010.08.077>.
 20. Cui, G., Shen, P.K., Meng, H., Zhao, J., and Wu, G., "Tungsten carbide as supports for Pt electrocatalysts with improved CO tolerance in methanol oxidation," *J. Power Sources* 196(15):6125–6130, 2011, doi:<https://doi.org/10.1016/j.jpowsour.2011.03.042>.
 21. Justin, P. and Ranga Rao, G., "Methanol oxidation on MoO₃ promoted Pt/C electrocatalyst," *Int. J. Hydrogen Energy* 36(10):5875–5884, 2011, doi:[10.1016/j.ijhydene.2011.01.122](https://doi.org/10.1016/j.ijhydene.2011.01.122).
 22. Shen, M., Zheng, L.-R., He, W., Ruan, C., Jiang, C., Ai, K., and Lu, L., "High-performance oxygen reduction electrocatalysts derived from uniform cobalt–adenine assemblies," *Nano Energy* 17:120–130, 2015, doi:<https://doi.org/10.1016/j.nanoen.2015.08.007>.
 23. Fu, X., Zhao, Z., Wan, C., Wang, Y., Fan, Z., Song, F., Cao, B., Li, M., Xue, W., Huang, Y., and Duan, X., "Ultrathin wavy Rh nanowires as highly effective electrocatalysts for methanol oxidation reaction with ultrahigh ECSA," *Nano Res.* 12(1):211–215, 2019, doi:[10.1007/s12274-018-2204-8](https://doi.org/10.1007/s12274-018-2204-8).
 24. Jiang, B., Li, C., Dag, Ö., Abe, H., Takei, T., Imai, T., Hossain, M.S.A., Islam, M.T., Wood, K., Henzie, J., and Yamauchi, Y., "Mesoporous metallic rhodium nanoparticles," *Nat. Commun.* 8(1):15581, 2017, doi:[10.1038/ncomms15581](https://doi.org/10.1038/ncomms15581).
 25. Huang, X., Zhao, Z., Chen, Y., Chiu, C.-Y., Ruan, L., Liu, Y., Li, M., Duan, X., and Huang, Y., "High Density Catalytic Hot Spots in Ultrafine Wavy Nanowires," *Nano Lett.* 14(7):3887–3894, 2014, doi:[10.1021/nl501137a](https://doi.org/10.1021/nl501137a).
 26. Kang, Y., Li, F., Li, S., Ji, P., Zeng, J., Jiang, J., and Chen, Y., "Unexpected catalytic activity of rhodium nanodendrites with nanosheet subunits for methanol electrooxidation in an alkaline medium," *Nano Res.* 9(12):3893–3902, 2016, doi:[10.1007/s12274-016-1258-8](https://doi.org/10.1007/s12274-016-1258-8).
 27. Kang, Y., Xue, Q., Jin, P., Jiang, J., Zeng, J., and Chen, Y., "Rhodium Nanosheets–Reduced Graphene Oxide Hybrids: A Highly Active Platinum-Alternative Electrocatalyst for the Methanol Oxidation Reaction in Alkaline Media," *ACS Sustain. Chem. Eng.* 5(11):10156–10162, 2017, doi:[10.1021/acssuschemeng.7b02163](https://doi.org/10.1021/acssuschemeng.7b02163).
 28. Wang, X., Wang, W., Qi, Z., Zhao, C., Ji, H., and Zhang, Z., "Electrochemical catalytic activities of nanoporous palladium rods for methanol electro-oxidation," *J. Power Sources* 195(19):6740–6747, 2010, doi:<https://doi.org/10.1016/j.jpowsour.2010.03.098>.
 29. Zhao, Y., Nie, S., Wang, H., Tian, J., Ning, Z., and Li, X., "Direct synthesis of palladium nanoparticles on Mn₃O₄ modified multi-walled carbon nanotubes: A highly active catalyst for methanol electro-oxidation in alkaline media," *J. Power Sources* 218:320–330, 2012, doi:<https://doi.org/10.1016/j.jpowsour.2012.07.012>.
 30. Zhang, Y., Shu, H., Chang, G., Ji, K., Oyama, M., Liu, X., and He, Y., "Facile synthesis of palladium–graphene nanocomposites and their catalysis for electro-oxidation of methanol and ethanol," *Electrochim. Acta* 109:570–576, 2013, doi:<https://doi.org/10.1016/j.electacta.2013.07.068>.
 31. Wang, X., Wang, W., Qi, Z., Zhao, C., Ji, H., and Zhang, Z., "High catalytic activity of ultrafine nanoporous palladium for electro-oxidation of methanol, ethanol, and formic acid," *Electrochem. Commun.* 11(10):1896–1899, 2009, doi:<https://doi.org/10.1016/j.elecom.2009.08.011>.
 32. Liang, R., Hu, A., Persic, J., and Zhou, Y.N., "Palladium Nanoparticles Loaded on Carbon Modified TiO₂ Nanobelts for Enhanced Methanol Electrooxidation," *Nano-Micro Lett.* 5(3):202–212, 2013, doi:[10.1007/BF03353751](https://doi.org/10.1007/BF03353751).
 33. GUO, Q.-H., HUANG, J.-S., and YOU, T.-Y., "Electrospun Palladium Nanoparticle-Loaded Carbon Nanofiber for Methanol Electro-oxidation," *Chinese J. Anal. Chem.* 41(2):210–214, 2013, doi:[https://doi.org/10.1016/S1872-2040\(13\)60629-5](https://doi.org/10.1016/S1872-2040(13)60629-5).
 34. Ge, X., Gu, C.D., Wang, X.L., and Tu, J.P., "Anomalous self-reduction of layered double hydroxide (LDH): from α -Ni(OH)₂ to hexagonal close packing (HCP) Ni/NiO by annealing without a reductant," *Chem. Commun.* 51(6):1004–1007, 2015, doi:[10.1039/C4CC07767A](https://doi.org/10.1039/C4CC07767A).
 35. Tong, Y.Y., Gu, C.D., Zhang, J.L., Tang, H., Wang, X.L., and Tu, J.P., "Thermal growth of NiO on interconnected Ni-P tube network for electrochemical oxidation of methanol in alkaline medium," *Int. J. Hydrogen Energy* 41(15):6342–6352, 2016, doi:[10.1016/j.ijhydene.2016.03.018](https://doi.org/10.1016/j.ijhydene.2016.03.018).
 36. Das, S., Dutta, K., and Kundu, P.P., "Nickel nanocatalysts supported on sulfonated polyaniline: potential toward methanol oxidation and as anode materials for DMFCs," *J. Mater. Chem. A* 3(21):11349–11357, 2015, doi:[10.1039/C5TA01837D](https://doi.org/10.1039/C5TA01837D).
 37. Jafarian, M., Mahjani, M.G., Heli, H., Gopal, F., Khajehsharifi, H., and Hamed, M.H., "A study of the electro-catalytic oxidation of methanol on a cobalt hydroxide modified glassy carbon electrode," *Electrochim. Acta* 48(23):3423–3429, 2003, doi:[https://doi.org/10.1016/S0013-4686\(03\)00399-2](https://doi.org/10.1016/S0013-4686(03)00399-2).
 38. Zafeiratos, S., Dintzer, T., Teschner, D., Blume, R., Hävecker, M., Knop-Gericke, A., and Schlögl, R., "Methanol oxidation over model cobalt catalysts: Influence of the cobalt oxidation state on the reactivity," *J. Catal.* 269(2):309–317, 2010, doi:<https://doi.org/10.1016/j.jcat.2009.11.013>.

39. Carugno, S., Chassaing, E., Rosso, M., and González, G.A., "Enhanced electrochemical oxidation of methanol on copper electrodes modified by electrocorrosion and electrodeposition," *Mater. Chem. Phys.* 143(3):1012–1017, 2014, doi:<https://doi.org/10.1016/j.matchemphys.2013.10.039>.
40. Döner, A., Solmaz, R., and Kardaş, G., "Fabrication and characterization of alkaline leached CuZn/Cu electrode as anode material for direct methanol fuel cell," *Energy* 90:1144–1151, 2015, doi:<https://doi.org/10.1016/j.energy.2015.06.058>.