We are IntechOpen, the world's leading publisher of Open Access books Built by scientists, for scientists

6,900
Open access books available

185,000
International authors and editors

200M
Downloads

Our authors are among the

154
Countries delivered to

TOP 1%
most cited scientists

12.2%
Contributors from top 500 universities



WEB OF SCIENCE™

Selection of our books indexed in the Book Citation Index in Web of Science™ Core Collection (BKCI)

Interested in publishing with us?
Contact book.department@intechopen.com

Numbers displayed above are based on latest data collected.
For more information visit www.intechopen.com



Chapter

Recent Advances in Pt-Based Binary and Ternary Alloy Electrocatalysts for Direct Methanol Fuel Cells

Dang Long Quan and Phuoc Huu Le

Abstract

The direct methanol fuel cell (DMFC) is among the most promising alternative energy sources for the near future owing to its advantages of simple construction, compact design, high energy density, and relatively high energy-conversion efficiency. Typically, the electrodes in DMFC is comprised of a Pt-based catalysts supported on great potential of carbon materials such as multi-walled carbon nanotubes (MWCNTs), carbon black (CB), graphene, etc. It is desired to develop an electrode with high surface area, good electrical conductivity and suitable porosity to allow good reactant flux and high stability in the fuel cell environment. This chapter will provide recent advances in Pt-based binary and ternary electrocatalysts on carbon supports for high-performance anodes in DMFC. Through studying the effects of composition-, support-, and shape dependent electrocatalysts, further fundamental understanding and mechanism in the development of anode catalysts for DMFC will be provided in details.

Keywords: direct methanol fuel cell (DMFC), electrocatalysts, Pt-based binary and ternary alloys, carbon based supports

1. Introduction

1.1 Structure and operating principles of direct methanol fuel cell

Today, population growth and economic growth lead to an increased energy demand. Current energy sources are mainly from fossil fuels (coal, oil and gas), which produce carbon dioxide (CO_2) and other greenhouse gases that are responsible for global climate change. In order to minimize the bad impact of greenhouse effects (e.g. acid rain, ozone damage), the world needs an appropriate transition of the energy sources being used. Therefore, the development of clean energy is a common concern for balancing economic, social development, and environmental protection. Fuel cells are one of the most promising energy sources for use in transportation and communication applications. Compared with internal combustion engine, fuel cells are environmentally friendly, durable, reducing noise, and so on [1]. Currently, the main fuel cells include alkaline fuel cell (AFC), polymer electrolyte membrane fuel cell (PEMFC), direct methanol fuel cell (DMFC), phosphoric acid fuel cell (PAFC) and solid oxide fuel cell (SOFC).

IntechOpen

Among the fuel cells, DMFC, apart from the advantage of being environmentally friendly, also has a high energy density [2, 3]. DMFC is one of the popular types of fuel cells using methanol directly as fuel. DMFC with liquid fuel can operate at ambient air temperature, has good energy density and is easy to store and transport. The membrane electrode assembly with acid or alkaline membranes is a main component of DMFC, in which both side of the polymer electrolyte membrane contact to anode and cathode catalyst layers. Conventionally, PtRu/C or PtRu catalyst is used in the anode, while Pt/C or Pt in the cathode [4]. The gas diffusion layers are closely aligned with the catalyst layers to aid reactant distribution, current collection and catalytic protection.

In DMFC, an electrochemical reaction will occur at the anode due to the interaction between methanol and water to produce protons and electrons. Specifically, at the anode, six protons and six electrons are formed by a methanol molecule reacting to a water molecule. These protons can move freely through the electrolyte toward the cathode, while electrons can travel through the external load (**Figure 1**). In addition, carbon dioxide will be also formed by oxidization of methanol. Meanwhile, at the cathode, water is formed by oxygen electrocatalytic reduction reaction. Therefore, the number of electrons at the anode is larger than the number of electrons at the cathode, resulting in a potential established between the two electrodes. Reaction formulas in DMFC are shown as follows [5]:

$$\text{Anode reaction}: CH_3OH + H_2O \rightarrow CO_2 + 6H^+ + 6e^- \quad (1)$$

$$\text{Cathode reaction}: 3/2\,O_2 + 6H^+ + 6e^- \rightarrow 3H_2O \quad (2)$$

$$\text{Overall reaction}: CH_3OH + 3/2\,O_2 \rightarrow CO_2 + 2H_2O \quad (3)$$

1.2 Electrocatalytic materials in DMFC

In the early 1950s, the anode and cathode electrocatalysts used for methanol fuel cell began to be investigated. Initially, methanol fuel cell used an alkaline electrolyte with an anode catalyst of nickel or platinum for methanol electro-oxidation reaction, and silver for the oxygen reduction process. At the same time, studies of acidic electrolyte replacement have shown that the kinetics of methanol electro-oxidation are slower in this environment than in alkaline [6]. However, DMFC using liquid alkaline electrolyte has a main drawback of carbonate formation, meanwhile, DMFC using an acid electrolyte presents better perspectives. The Pt-Sn bimetallic catalyst has been systematically studied by Jansen and Molhuysen [7], which promoted the use of bimetallic catalysts for DMFC. Along with Pt-Sn, Pt-Ru was the most potential bimetallic catalyst for anode formulations, but it was still underestimated compared with Pt-Sn bimetallic catalyst.

During the 1960s, Pt-Ru system, particularly Pt combining Ru in solid solution, revealed great potential applications supported by the studies of Watanabe and Motoo [8]. In the 1960s and 1970s, the study of anode's processes was carried out by many different groups through the search or improvement of a suitable catalyst as a premise for the construction of the bifunction theory for bimetallic catalysts based on methanol oxidation. In twenty years later, the structural, surface and electronic properties of the most promising systems for DMFC, essentially Pt-Ru were investigated. Besides, the studies of electrode structure including diffusion and backing layers also attracted a lot of attention. Most of these studies aimed to enhance the catalytic activity, improve reaction rate, and minimize poisoning due to methanol

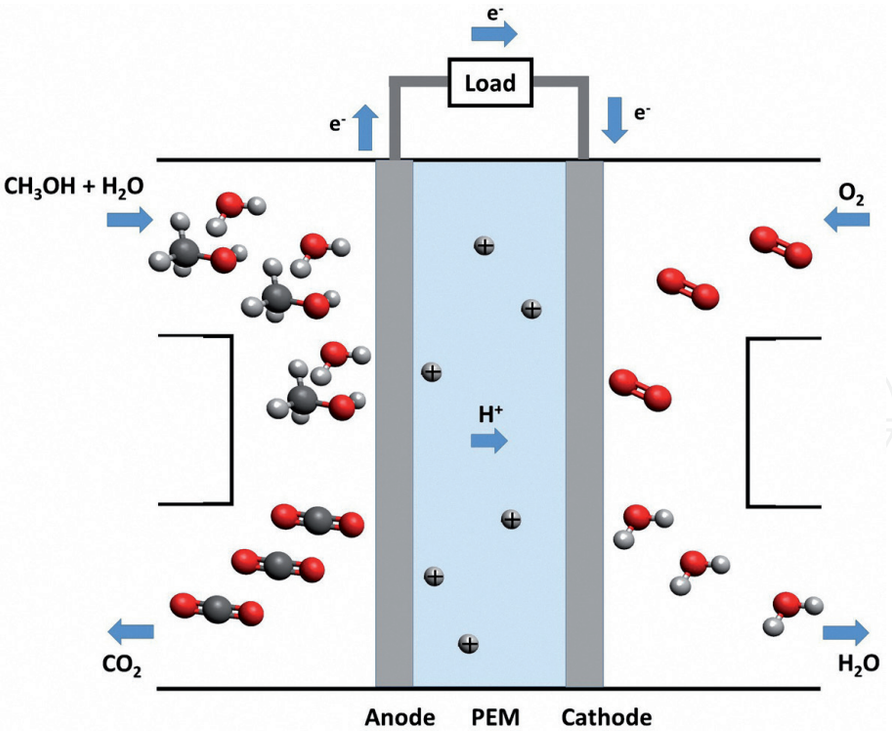


Figure 1.
Structure and operating principle of DMFC.

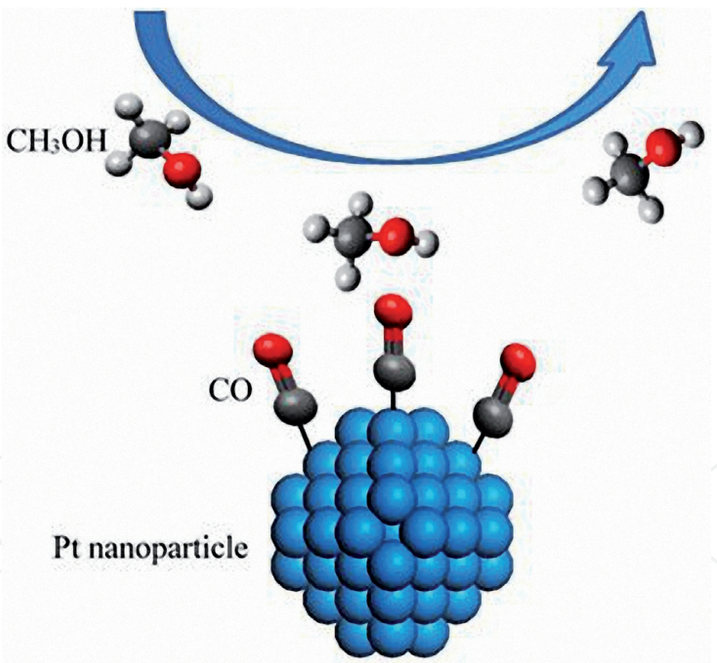


Figure 2.
Poisoning CO on Pt surface to prevent methanol oxidation catalysis.

residues by combining different metals with platinum. It has been found that the use of metal alloys can modify electronic surface structure, physical structure to prevent CO poisoning and absorb oxygen/hydroxyl species. The 1990s marked significant advances in DMFC technology with early applications for portable electronic devices. Briefly, fuel cells (including DMFC) were widely studied in the early 20th century.

DMFC is one of the most potential candidate of fuel cells, however, slow electro-oxidation kinetics, methanol crossover, and gas management on the anode side in DMFC need to be improved. In methanol electro-oxidation, various surface

intermediates as CO, COH_{ads}, HCO_{ads}, $HCOO_{ads}$ are formed and strongly adsorbed to the surfaces of catalysts. As a result, methanol molecules are prevented from the next actions, leading to slow down the oxidation reaction [5]. In addition, fuel efficiency is decreased because of small percentage of the intermediates desorbing before being oxidized to CO_2. Therefore, research on developing suitable catalysts to prevent CO poisoning and improve efficiency for DMFC is one of the critical issues. One of the most popular intermediates, carbon monoxide was produced by adsorption and de-protonation on the anode catalyst, which limits the rate of methanol oxidation. Specifically, if CHO or COH are directly dehydrogenated, carbon monoxide will be formed, as shown in **Figure 2**. Consequently, the active sites of the catalyst will be decreased that limits the next reactions to be occurred.

2. The binary Pt-based and ternary PtRuM alloy electrocatalysts for DMFC

2.1 The binary Pt-based alloy electrocatalysts for DMFC

2.1.1 Advantages of binary Pt-based alloy catalysts compare to platinum catalyst

Around the middle of the nineteenth century, the first model of a fuel cell using a platinum wire as an electrode was investigated [4]. Since then, the application of platinum in fuel cells is great of interest for scientists. In strongly acidic electrolytes, platinum nanoparticles are higher catalytic activity and better stability than other noble metals. Therefore, it was used as an optimal catalyst in the first most studies of DMFC. However, platinum's cost is high and easy to dissolve and agglomerate under poor operating conditions, resulting in the commercialization of DMFC based on platinum catalyst is still limited. Especially, Pt-based anode can be poisoned by a carbonaceous intermediate as CO, COH_{ads}, HCO_{ads}, $HCOO_{ads}$, leading to decreasing DMFC efficiency. To overcome the above obstacles, many studies have been conducted to improve catalysts in DMFC. As a result, binary catalysts are one of the most effective catalysts, in which Pt-Ru system is the most common.

According to the bifunctional mechanism, each metal in surface of Pt-M will promote various steps in the overall reaction. The Pt – CO strength bond and the reaction activation energy can be modified by energy perturbations of the surface d-band of Pt due to ligand effect from M metal. As a result, CO on the platinum surface requires less energy to oxidize to CO_2 compared with pure platinum. In addition, the attachment of metal M on the substrate can induce changes in the catalytic properties of the substrate, which is attributed to establishing a new equilibrium state for occurring the electronic and strain effects simultaneously. The presence of metal M significantly reduces the onset potential for the reaction because the oxidation of CO on the surface with more metal M is greatly affected compared to pure Pt.

Therefore, bimetallic catalysts have been developed over many decades. Specifically, the combination of platinum with transition metals (Fe, Co, Ni) not only improves electrochemical performance but also decreases the Pt mass loading and enhances methanol tolerance in the oxygen reduction reaction (ORR) [9–11]. ORR activity and stability of the Pt catalyst can be increased in the presence of Cr and Pd. In addition, the bimetallic catalyst offers advantages to the reactions occurring at the DMFC electrode with outstanding features such as improving methanol dissociative chemisorption, reducing CO poison adsorption and CO removal via its oxidation by adsorbed OH [12–14].

Survey results of methanol oxidation ability by cyclic voltammetry (CV) measurement showed that the methanol oxidation capacity of all Pt-M alloys was superior to that of pure Pt. Many research groups have in turn fabricated the Pt-M alloys such as PtFe, PtCo, PtNi, PtCu, PtMo, PtRu, PtRh, PtPd, etc., and investigated their activity to oxidize methanol comparing to pure Pt catalyst [15–22]. The obtained CV spectra results are shown in **Table 1** and **Figure 3**. Clearly, although there were differences in the selection of substrate, the composition percentage in the alloy, or the concentration of the investigated solution, the ability to oxidize methanol of pure Pt is always lower than that of Pt-M alloys. Here, in the CV results, methanol oxidation capacity is realized by the spectral peak position during the forward sweeping/positive sweeping (maximum current density - j_f). The value of j_f in CV spectrum of PtFe, PtCo, PtNi, PtCu, PtMo, PtRu, PtRh, PtPd alloys and pure Pt are listed in **Table 1**. It can be clearly seen that the j_f values of PtFe, PtNi, PtCu, and PtRu alloys were about twice that of pure Pt. The difference is about 3–5 times for Pt67% Mo33% and Pt54% Rh46%. Especially, PtCo (1: 9) and Pt3Pd1 offered the enhancement of ~10 times. In adition, the CV spectra of PtRu alloys almost had no current density peak for reverse sweeping. This indicates that the high tolerance to CO poisoning led to the increased efficiency of methanol oxidation and the enhanced DMFC performance. Furthermore, the CV results of the PtCo, PtMo, PtRh and PtPd alloys show that the ability to oxidize methanol was also strongly influenced by the composition ratios in the alloy. It is clear to conclude that

Pt alloy	Support	Size (nm)	Electrooxidation			Reference
			Condition	Current density of Pt ($mA\ cm^{-2}$)	Current density of PtM ($mA\ cm^{-2}$)	
PtFe	Multi-walled carbon nanotubes (MWCNT)	2	0.5 M H_2SO_4 + 1 M CH_3OH	0.12	0.24	[15]
PtCo	Graphene oxide (GO)	2.1–3.4	1 M H_2SO_4 + 2 M CH_3OH	3.85	38 PtCo (1:9)	[16]
PtNi	Functionalized carbon nanotubes (FCNTs)	2.7–3.9	0.5 M H_2SO_4 + 1 M CH_3OH	300	500	[17]
PtCu	Graphene oxide (GO)	3	0.5 M H_2SO_4 + 0.5 M CH_3OH	0.83	1.6	[18]
PtMo	Single-wall carbon nanotubes (SWCNT)	—	0.5 M H_2SO_4 + 0.5 M CH_3OH	0.1	0.55 Pt67%Mo33%	[19]
PtRu	Carbon (C)	4.5	1 M H_2SO_4 + 2 M CH_3OH	7.5	17.5	[20]
PtRh	—	4.3–6	0.5 M H_2SO_4 + 1 M CH_3OH	140.7	404.9 Pt54%Rh46%	[21]
PtPd	Vulcan XC-72R	6.5	0.5 M H_2SO_4 + 0.5 M CH_3OH N_2-saturated	25	200 Pt3Pd1	[22]

Table 1.
Various studies of advantages of binary Pt-based alloy compare to platinum catalyst.

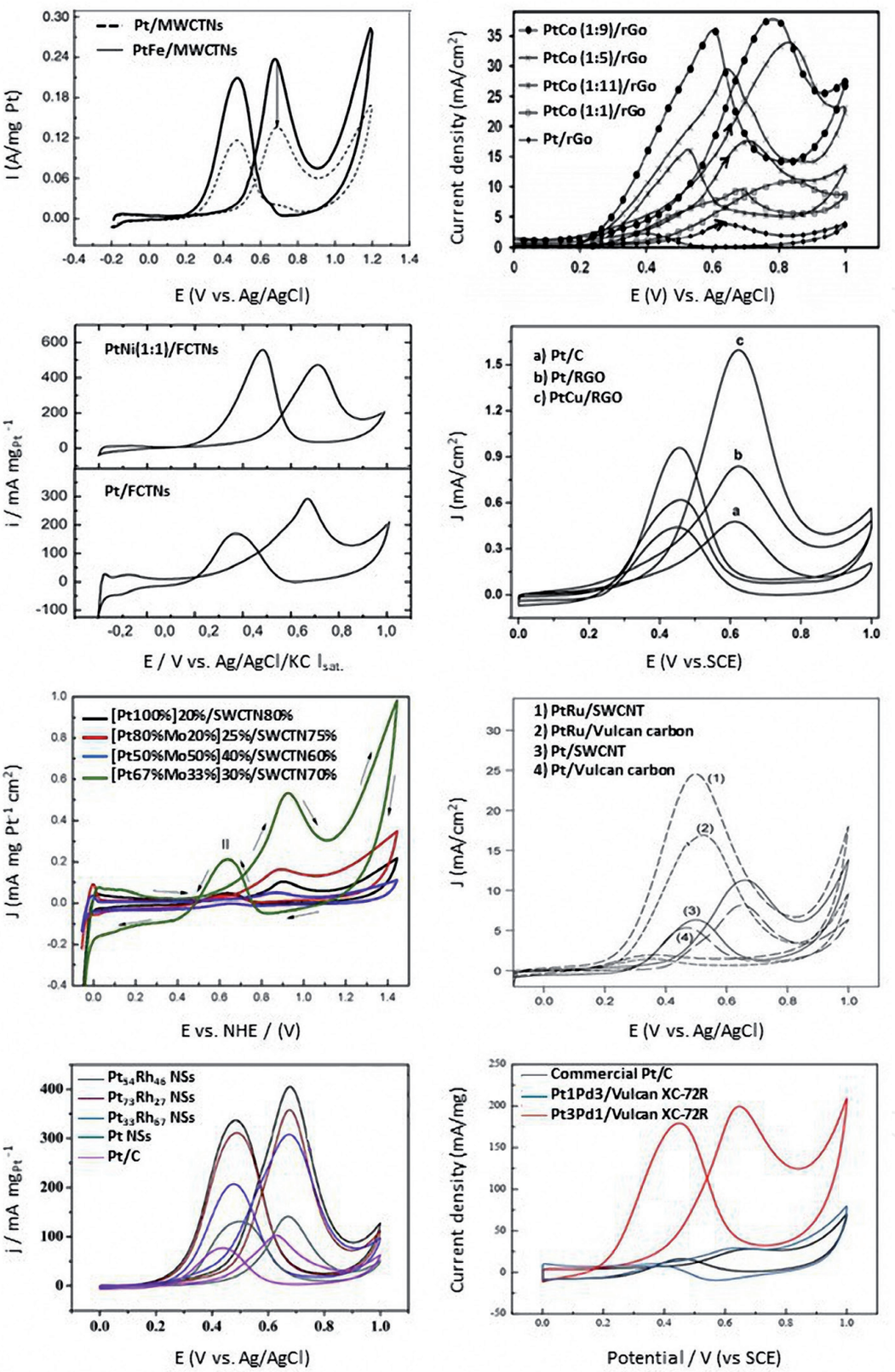


Figure 3.
Results of methanol oxidation ability by CV spectra of PtFe/MWCNTs, PtCo/rGO, PtNi/FCNTs, PtCu/RGO, PtMo/SWCNT, PtRu/Vulcan carbon, PtRh, and PtPd/Vulcan XC-72R in comparison with pure Pt [15–22].

Pt-M alloys exhibited higher methanol oxidation performance than that of pure Pt. However, it is not suitable to make a comparison among the different alloys because some alloys require careful examination of the composition ratios. Also, it is worthy of note that the differences in the onset potential position of j_f, the j_f/j_r ratio, and the substrate can influence the evaluation of methanol oxidation performance.

2.1.2 Dominances of PtRu catalyst compare to other binary Pt-based alloy catalysts

Pt-Ru has been interested in research since the late 19th century with the first mention in thermoelectric materials. In 1930s, the physical and chemical properties of this material system were explored, setting the stage for more detailed studies in the following decades.

First, the Pt-Ru system is one of the most common alloys used for fuel cells owing to its lower potential onset than Pt or Pt alloys. Indeed, **Table 2** shows that the strongest synergetic effects belonged to Pt-Ru. Specifically, their onset potentials in 1 M H_2SO_4 at 100°C and current density 20 mA/cm^2 about 0.24–0.32 V, while this value of Pt is 0.44 V, and Pt-M (M belongs to group IVB, VB, VIB, VIIB and some other metals) have the onset potentials in range of 0.3–0.44 V. The electrolytic activity of Pt and its alloy related to the oxidation of methanol has been established the foundation for further studies. The extensive studies of combining Pt with multiple elements in the periodic table to find the most suitable catalysts (including Pt-Ru) for organic fuel oxidation were also carried out in the 1960s by Batelle group [24].

Second, the Pt-Ru system is often used for fuel cell catalysis because Ru and its alloy can be used as an effective catalyst. In parallel with Pt-Ru studies, the other Ru systems (i.e. Ru-Ta, Ru-Ni, Ru-Rh and Ru-Ir) were also investigated. Corrosion and electrochemical properties were strongly influenced in Ru systems doped with Pb, Tl, Ag [24]. A ruthenium electrode with a high surface area was successfully synthesized by a research team from Moscow [24], and the effect of heat treatment on ruthenium dispersion was also studied. In addition, the effect of temperature on ruthenium properties was also studied [24]. The calculation of electronic structures combined with density function theory was used to investigate the free-energy landscape of the electrochemical oxygen reduction reaction over Pt (111), in which the changes of applied bias confirmed that noble metals were suitable for the peroxide mechanism [25]. In this mechanism, the oxygen reduction on the surface of Pt or noble metals is performed through peroxy intermediates according to the following scheme:

$$O_2 + {}^* \rightarrow O_2{}^* \tag{4}$$

$$O_2{}^* + \left(H^+ + e^-\right) \rightarrow HO_2{}^* \tag{5}$$

$$HO_2{}^* + \left(H^+ + e^-\right) \rightarrow H_2O + O^* \tag{6}$$

$$O^* + \left(H^+ + e^-\right) \rightarrow HO^* \tag{7}$$

$$HO^* + \left(H^+ + e^-\right) \rightarrow H_2O + {}^* \tag{8}$$

Here, the "*" symbol indicates a site on the surface. This is an important basis for the application of Pt and noble metals for fuel cell catalysis.

Finally, the strain effect caused by the lattice mismatch between platinum and ruthenium reduced the binding energy of intermediates such as carbon monoxide, resulting in the increased tolerance to CO poisoning for PtRu bimetallic [26, 27]. Bifunctional theory of the electrocatalysis was formulated based on an investigation of Pt-Ru activity by Watanabe and Motoo [26, 27]. According to this mechanism,

Catalyst	The onset potential at 100°C at 20 $mA.cm^{-2}$ (V)
Pt	0.44
PtM M in group IVB and VB	0.37–0.39
PtM M in group VIB and VIIB	0.20–0.38
PtM M: Fe, Co, Ni, Be, Pb, Cu, Bi, Sb	≥ 0.44
PtRu	**0.24–0.32**
PtOs	0.30–0.35
PtRh	0.44
PtIr	0.33

Table 2.
The catalytic activity of Pt and Pt alloys in methanol oxidation [23].

generation of active oxygen species belongs to ruthenium, while the adsorbed methanol species are kept by platinum. Hence, methanol oxidation takes place by the following reactions [28]:

$$Pt + CH_3OH \rightarrow Pt - CH_3OH_{ads} \rightarrow Pt - COH_{ads} + 3H^+ + 3e^- \quad (9)$$

$$Pt - COH_{ads} \rightarrow Pt - CO_{ads} + H^+ + e^- \quad (10)$$

$$Ru + H_2O \rightarrow Ru - OH_{ads} + H^+ + e^- \quad (11)$$

$$Pt - COH_{ads} + Ru - OH_{ads} \rightarrow Pt + Ru + CO_2 + 2H^+ + 2e^- \quad (12)$$

$$Pt - CO_{ads} + Ru - OH_{ads} \rightarrow Pt + Ru + CO_2 + H^+ + e^- \quad (13)$$

The invent of the bimechanism has underpinned the profound and extensive studies of the Pt-Ru catalyst for DMFC.

2.2 The ternary PtRuM electrocatalysts for DMFC

From the above analysis, PtRu is the most commonly alloy for the anode methanol oxidation electrocatalyst in DMFC. However, both platinum and ruthenium are precious metals, so in order to increase performance and reduce costs, the studies of searching effective ternary PtRuM electrocatalysts have been attracting a lot of attention. It has been found that ternary Pt alloys can improve catalytic performance as compared to Pt or PtRu because the additional metals can change the electronic properties or the surface structure of the Pt or PtRu [29]. Indeed, from theoretical screening results, Strasser et al. showed that ternary PtRuM (M = Fe, Co, Ni, Rh, Ir) which had better CO-tolerance than pure Pt or PtRu to result in a superior catalytic activity [30]. This is the key platform for driving the fabrication of ternary catalysts toward improving the efficiency and reducing the cost of DMFC.

Due to some outstanding properties such as low potential onset, CO-tolerance, and ability to participate in oxygen reduction reaction at a fuel cell cathode, molybdenum (Mo) is also one of popular elements of interest for the development of DMFC. Binary PtRu has been successfully formulated and exhibited the better tolerate CO poisoning than pure Pt [31–34]. Differ from PtRu, the main oxidation peak of PtMo shifts toward a lower potential, while the oxidation of CO in PtMo occurs in two steps to form two peaks in the voltamperometric sample [31]. It was found that Mo species also reduced easily due to the undergo oxygen transfer. In addition, CO oxidized by Mo at a low voltage had weakly bonding, and thus the CO occupied a very low proportion of the total CO absorbed to the catalyst [31–35]. Therefore, PtMo has a lower methanol oxidation activity than PtRu. However, the two different CO oxidation mechanisms in PtRu and PtMo at different potentials can induce a co-catalytic effect by combining Ru and Mo to form a ternary PtRuMo alloy [36]. This was the basis for a series of studies on ternary PtRuMo catalysts. Specifically, PtRuMo/C was prepared by a two-steps reduction method, and PtRuMo/C possessed a decrease of CO poisoning as compared to PtRu and Pt [37]. Moreover, DMFC with PtRuMo/CNTs anode had higher performance than DMFC with PtRu/CNTs or PtRu/C anodes [38]. The successful synthesis of PtRuMo nanoparticles on MWCNTs by chemical reduction under hydrothermal synthesis method, and the PtRuMo/MWCNTs exhibited superior catalytic activity and durability for methanol oxidation in H_2SO_4 solution over PtRu/MWCNTs [39]. The CV and electrochemical impedance spectroscopy (EIS) results for $Pt_{43}Ru_{43}Mo_{14}$/MWCNTs, $Pt_{50}Ru_{50}$/MWCNTs, and Pt/MWCNTs presented that $Pt_{43}Ru_{43}Mo_{14}$/MWCNTs obtained the highest activity and stability [40].

Iron (Fe) is also one of the good candidates for electrode catalysis in DMFC anode. The presence of iron as the third element in the platinum alloy can weaken the Pt-CO bonding [41, 42]. It is known that, if platinum and iron combine, the orbital mixing will occur. Due to electron-rich platinum and electron-poor iron, Pt electron density and electron density hinders the electron back-donation from Pt to CO to result in weakening Pt-CO bonding. In addition, the cost of iron-containing precursors is much lower than that of Pt and Ru. Therefore, the cost of DMFC using PtRuFe catalyst will significantly reduce, and thus expand the commercialization capability of the DMFC. For these reasons, the study of PtRuFe alloys was promoted. In particular, PtRuFe/C (2:1:1 atomic ratio, 60 wt% metal) was synthesized by impregnation method [43]. **Figure 4** shows that the PtRuFe nanoparticles were uniformly formed with an average size of approximately 2.5 nm. For CO-stripping results, Jeon et al. [43] obtained the onset potentials of PtRuFe/C and PtRu/C were 0.44 V and 0.49 V, respectively. In addition, current intensity of PtRuFe/C was also higher than that of PtRu/C under the similar experimental conditions. The obtained results confirmed that PtRuFe/C exhibited the better methanol electro-oxidation activity [43]. In another study, PtRuFe nanodendrites which was prepared via a one-pot solvothermal method also presented the higher specific and mass activities than those of PtFe and Pt [44].

In order to minimize CO poisoning and increase the performance of the DMFC, ternary catalyst including platinum, ruthenium and cobalt is also considered. The PtRuCo/GC catalysts was successfully prepared by the one-step electrochemical CV co-deposition method, and it exhibited higher electrochemical activity and stability for methanol oxidation than PtRu/GC [45]. PtRuCo/C was successfully synthesized by the electro-deposition process with controlling the deposition potential and deposition time to control Pt and Ru galvanic displacements [46]. It was found that PtRuCo/C presented superior catalytic activity and tolerance to CO poisoning as compared to those of the commercial PtRu/C [46].

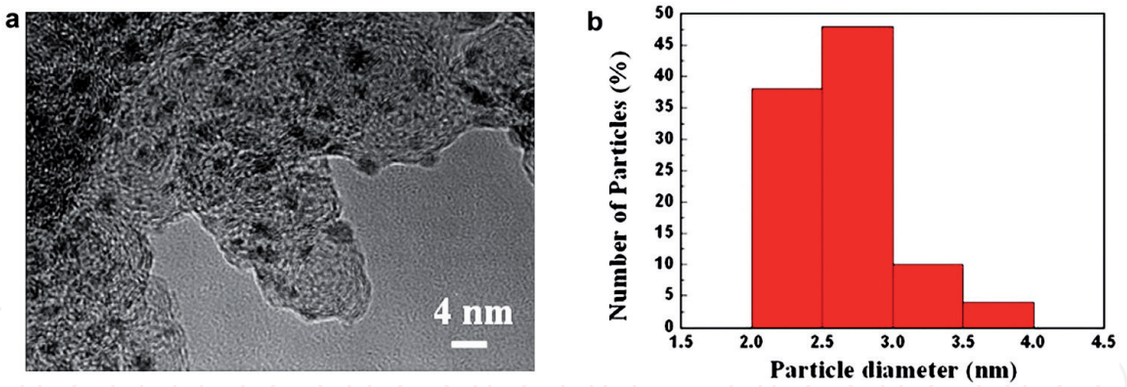


Figure 4.
A TEM image (a) and particle size distribution (b) of PtRuFe/C (2:1:1) catalyst [43].

The theoretical investigation found that the segregation processes for creating Pt surface enrichment was unlikely to take place in the PtNi system [47]. Additionally, unlike Ru in PtRu, Ni in PtNi was not dissolved in the electrolyte due to the nickel-hydroxide-passivated surface and the increased stability of Ni in the Pt network [48]. Furthermore, the use of Ni as the third metal in a ternary alloy will reduce the amount of noble metals of Pt and Ru that allows reducing the DMFC cost and supports for its commercialization. Therefore, ternary PtRuNi alloys have been developed and characterized [49–51]. Specifically, PtRuNi/C catalyst can significantly improve the methanol oxidation performance compared with PtRu/C [49–51]. Liang et al. were successfully synthesized a carbon-supported PtRuNi nanocomposite via a microwave-irradiated polyol plus annealing synthesis strategy, and the nanocomposite exhibited an enhanced tolerance to CO [52]. The impedance patterns of methanol electrooxidation for PtRuNi/C proved its superior performance to that of PtRu/C [53]. Similar results were also obtained for PtRuNi and PtRu on CNTs [54]. Adding a third metal to PtRu is one of the effective approaches to improve DMFC performance. Therefore, in addition to the aforementioned three-component alloys, the other three-component alloys such as PtRuCu, PtRuW, PtRuMn, etc. were also investigated in the literature [55–57].

Briefly, the ternary platinum alloy exhibited superiority in catalytic activity and resistance to CO compared with bimetallic or pure metals. It is worthy to note that each type of catalytic substrate also provides certain advantages for the DMFC application. Therefore, it is essential to study ternary platinum alloy on different catalytic supports to look for the optimal material system with excellent DMFC performance and cost effectiveness.

3. Effects of supports, shape, and structure on methanol oxidation activity of catalysts

3.1 Effects of supports on methanol oxidation activity of catalysts

In the early stages of fuel cell development, only Pt nanoparticles were used as catalysts for the anodes and cathodes. The Pt catalyst showed higher activity and durability than any other metals [58]. However, without a substrate, the increased Pt concentration leads to the agglutination of the Pt nanoparticles, and consequently reduces the surface area, which in turn affects the catalytic performance [59]. Therefore, the use of carbon-based materials (i.e. carbon black (CB), carbon nanotubes (CNTs), carbon nanofibers (CNFs), and graphene, etc.) allows reducing the amount of Pt used, while increasing the activity of the electrolytes.

Carbon materials with high surface area, suitable porosity, high corrosion resistance, and excellent electrical conductivity, allow for multiple dispersing of Pt nanoparticles and accelerate electronically charge transfer from electrode to membrane electrolysis [60]. Oxide materials are also good candidates for serving as the substrates of Pt catalyts because they can improve corrosion resistance to carbon materials [61, 62]. Since the 1990s, CB materials have been widely used as catalysts for Pt and its alloys in PEMFC because of the large area surface area, good electrical conductivity, porous structure, and low cost. Therefore, CB has been widely used for many decades as a base material for fuel cell catalysis [63]. Under the normal conditions, CNTs has the same advantages as CB, but it supports for minimizing the agglomeration of Pt nanoparticles. Specifically, Shao et al. found that Pt/CNTs were more stable than Pt/C for PEMFC primarily because the impedance of CNTs was higher than CB [64]. Furthermore, CNTs appears to be a good support material for fuel cells because of their high electrical conductivity, purity, and durability compared with the conventional substrates [65–72]. It is well-known that the main component of DMFC is the membrane electrode assembly (MEA), where the anode and cathode reactions occur to generate electrical energy. The ideal MEA material has the following prerequisites: (1) An efficient anode catalyst is for oxidation of methanol completely, (2) solid polymer electrolyte has a high proton conductivity and low methanol permeability, (3) the cathode catalyst is methanol-tolerant with a high deoxygenation activity [73]. Therefore, it is important to develop suitable support materials for catalysts in DMFC, which currently attracts a lot of attention.

A variety of support materials for PtRu catalysts such as Carbon Vulcan, CNTs, graphene, and oxides has been developed and used. **Table 3** and **Figure 5** show that the catalytic performance, durability, and even CO-tolerance varied depending on the support catalysts.

By comparing the different morphologies of carbon supports, Alegre and Kang's group found that methanol oxidation of carbon xerogels and carbon nanofiber substrates was respectively about 1.2 to 1.3 times higher than that of carbon substrate [74, 75]. Meanwhile, the CMK-8-II mesoporous carbon substrate fabricated by Maiyalagan's group gave superior methanol oxidation activity up to 2.2 times over carbon substrate [76]. CMK-8 mesoporous carbons with 3-D cubic Ia3d mesostructure consists of two interpenetrating continuous networks of chiral channels also called bicontinuous gyroidal. This structure possesses high surface area, well-defined pore size, high thermal stability, flexible framework composition, and intrinsic conductivity. With its distinct structure, CMK-8 mesoporous carbons have better diffusion and deposition of nanoparticles. In addition, the highly conductive Ia3d symmetric structure enhances electron transfer. Meanwhile, carbon xerogels have excellent properties such as high surface area, mesopore structure and high purity, allowing for high dispersion and efficient diffusion.

For the substrate of CNTs, the CV results show that the methanol oxidation capacity of the catalyst on CNTs substrate was 1.3–1.6 times higher than carbon Vulcan substrate [77–79]. CNTs possesses the higher graphite degree and the better electrical conductivity when it had the higher diffraction peaks than carbon black. Moreover, the smaller average particle size of PtRu/CNTs than that of pure Pt was one of the reasons for the high methanol oxidation capacity of this material system. In addition, a large specific surface area and high mechanical strength are also the preeminent properties of PtRu/CNTs that is attributed to the improved performance of the DMFC using PtRu/CNTs.

Graphene with its unique properties such as outstanding surface area, consistent porosity, good electrical conductivity and rich surface chemistry has become an excellent candidate for DMFC. Wang and Lee et al. reported that the current densities of PtRu/G or PtRu/GS were about 4 times and 1.5 times higher than those

Catalyst	Support	Particle/crystal size (nm)	Catalyst performance		Reference
			Measurement condition	Current density	
PtRu/E-Tek	Vulcan XC-72R	-	2 M CH_3OH + 0.5 M H_2SO_4, v = 0.02 V s^{-1}	0.29 mA/cm^2	[74]
PtRu/CX	Carbon xerogels	3.5		0.36 mA/cm^2	
PtRu/C	Carbon	2.0	1 M CH_3OH and 0.5 M H_2SO_4, 2 mV sL1	340 mA/cm^2	[75]
PtRu 70%/CNF	Carbon nanofiber	2.9		390 mA/cm^2	
PtRu/XC-72	Vulcan XC-72R Mesoporous Carbon	4.0	0.5 M H_2SO_4 + 1 mol dm^{-3} methanol at 50 mV^{-1}	27 mA/cm^2	[76]
PtRu/CMK-8-II		5.0		60 mA/cm^2	
PtRu/C	Vulcan XC-72R	3.0	20 mV/s in 1 M CH_3OH + 0.5 M H_2SO_4	22.5 mA/cm^2	[77]
PtRu/CNTs	Carbon nanotube	2.5		33.5 mA/cm^2	
PtRu/CB	Carbon	4.5	0.5 M H_2SO_4 and 1 M methanol, 50 mV/s	27.5 mA cm^{-2}	[78]
PtRu/CNT	Carbon nanotube	3.9		44.1 mA cm^{-2}	
PtRu/N-CNTs	Carbon nanotube doping N	3.5		82.7 mA cm^{-2}	
PtRu/C	Carbon	-	1 M CH_3OH + 0.5 M H_2SO_4, 20 mV s^{-1}	42.7 mA mg^{-1}	[79]
PtRu/CNTs	Carbon nanotubes	-		56.0 mA mg^{-1}	
PtRu/GS	Graphene sheet	2.9		78.7 mA mg^{-1}	
PtRu/CTNs-GS	Carbon nanotubes + Graphene sheet	2.4		136.7 mA mg^{-1}	
PtRu/MWCNTs	Carbon nanotubes	3.75	N_2-saturated, 0.5 M H_2SO_4 + 1.0 M CH_3OH, 10 mV/s	4.82 mA/cm^2	[80]
PtRu/Graphene	Graphene	2.25		20.8 mA/cm^2	
PtRu/C	Carbon	-	0.5 M H_2SO_4 + 1 M CH_3OH	430 mA mg^{-1}	[81]
PtRu/RGO	Reduced graphene oxide (RGO)	2.8		570 mA mg^{-1}	
PtRu/C	Carbon	4.39	1 M CH_3OH + 0.5 M H_2SO_4, 50 mV s^{-1}	8.21 mA cm^{-2}	[82]
PtRu/FGSs	Functionalized graphene sheets	2.87		14.05 mA cm^{-2}	
PtRu/AO-MWCNTs	Carbon nanotubes	4.19	N_2-saturated, 0.5 M H_2SO_4 + 1.0 M CH_3OH,	112 mA/cm^2	[83]
PtRu/PEI-MWCNTs	Functionalized carbon nanotubes	3.17	50 mV s^{-1}.	636 mA/cm^2	

Table 3.
Results of methanol oxidation ability by CV measurement of PtRu on different supports.

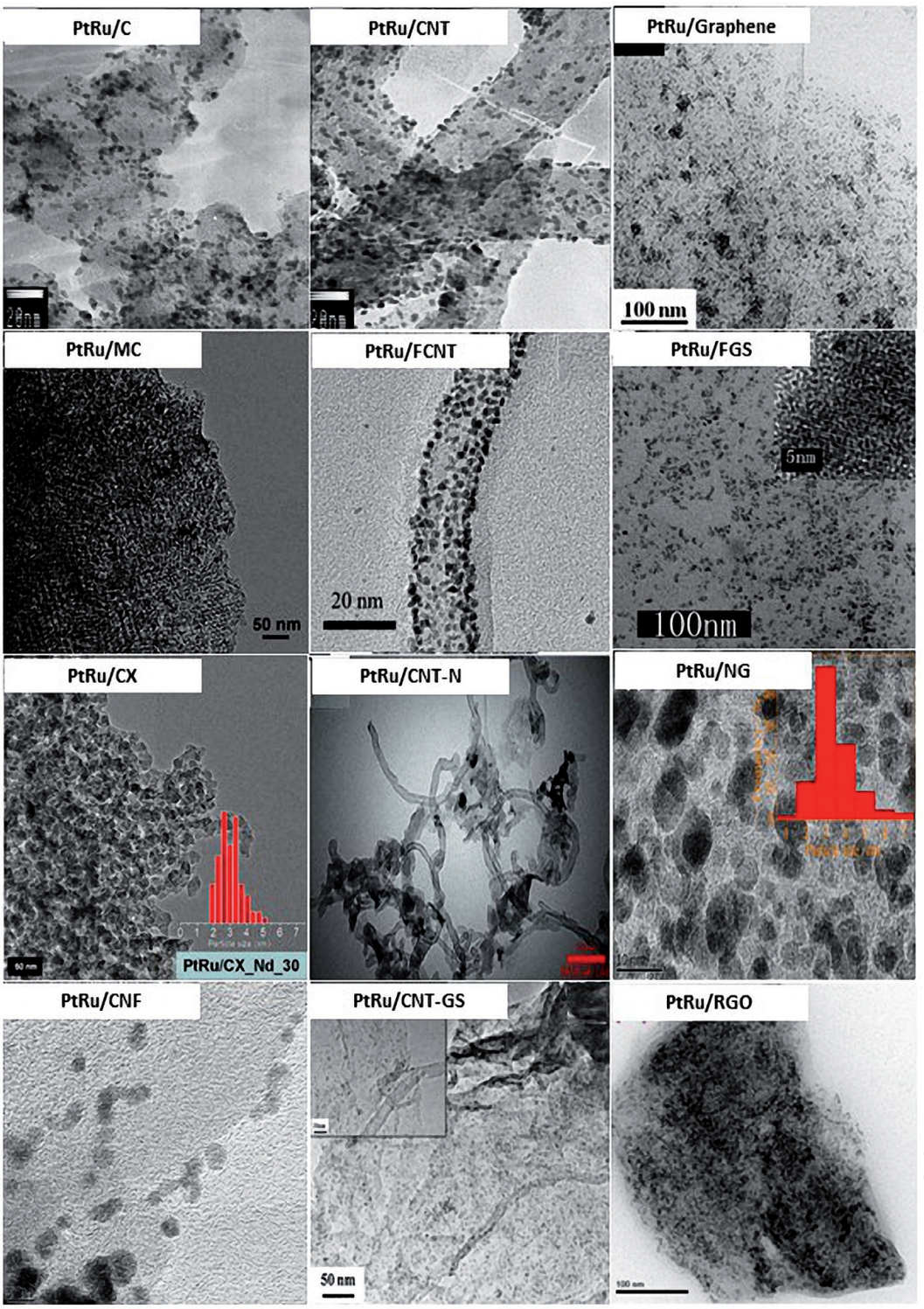


Figure 5.
TEM images of PtRu on different supports: Carbon (C), mesoporous carbon (MC), carbon xerogels (CX), carbon nanofiber (CNF), carbon nanotube (CNT), functionalized carbon nanotubes (FCNT), carbon nanotube doping N (CNT-N), carbon nanotube - graphene sheet (CNT-GS), graphene, functionalized graphene sheet (FGS), graphene doping N (NG) and reduced graphene oxide (RGO) [74–83].

of PtRu/CNTs [79, 80]. Similarly, the current density of reduced graphene oxide (RGO) substrate was about 1.3 times higher than carbon substrate one [81].

For comparison between carbon Vulcan substrate and graphene substrate, Zhao et al. found that the functionalized graphene sheets (FGSs) were 1.7 times higher in current density than carbon substrates [82]. The current density of N-doped carbon nanotube substrates was nearly 3 times higher than that of the conventional carbon substrates [78]. Due to the lack of bonding sites, namely -COOH, C = O and -OH

groups on CNTs, the deposition of metal nanoparticles on the surface of CNTs is very difficult. To solve this problem, various methods have been implemented to functionalize CNTs in order to hold metal nanoparticles on its surfaces. Commonly, HNO_3 or H_2SO_4 was used to activate CNTs at an appropriate temperature and processing time. In addition, the functionalization of CNTs by various surfactants, aromatic compounds, functional polymers, and biomolecules have been proposed [83–86]. These methods can maintain the CNTs properties, allows to control the particle size, and create more uniform distribution for enhancing the DMFC efficiency. Consequently, the functionalized CNTs and graphene generally presented the improved methanol oxidation activity.

Combination of various materials is an approach toward developing effective support materials. For example, a highly porous architecture which was formed by combining CNTs and graphene sheets, provided a large exposure surface area, so the aggregation of metallic nanoparticles decreased to result in the enhanced catalytic performance [79]. Indeed, composite substrate of CNTs and graphene sheet resulted in current intensity 3.2 times higher than that of carbon substrate [79], suggesting that composite substrate materials can complement each component's advantages and suppress the disadvantages of each ingredient.

3.2 Effects of shape and structure on methanol oxidation of catalysts

Surface structure of catalysts is closely related to the catalytic activity. It is essential to find the optimal surface structures that can enhance methanol oxidation efficiency. For manipulating the morphology of nanoparticles, the key fabricating factors include precursors, ligand, capping agent, reductant, reaction time, and temperature. Up to now, nanoparticle catalysts have been successfully synthesized with many different morphologies such as nanopolyhedrons, nanowires, nanoplatelets, porous structure, hollow structure, concave structure, nanoframes, dendrites, monolayer, and core-shell structure [87–90]. **Figure 6** shows several various interesting morphologies of PtRu and their CV results [87–90]. Obviously, the maximum current densities j_f of the new morphologies were higher than that of the traditional catalysts on carbon substrates. Because the new morphologies resulted in the differences in CO poisoning tolerance and methanol oxidation efficiency. Specifically, PtRu nanowires (NWs), PtRu nanorods (NRs) and PtRu nanocubes (NCs) were successfully fabricated by a one-step solvothermal method [87]. As shown in **Figure 6**, the PtRu NWs possessed higher methanol oxidation reaction activity than PtRu NRs and PtRu NCs. In addition, the onset potential of PtRu NWs is lower and its j_f/j_b ratio is greater compared with PtRu NRs and PtRu NCs. Based on density functional theory, calculations show a transition state (Pt-CO ••• OH-Ru) that is only formed from the interaction between Pt-COads and Ru-OHads species if the distance between Pt and Ru atoms is less than or equal to 4 Å. Therefore, the close connection between Pt and Ru atoms in PtRu alloy structure is more beneficial than heterostructure. In addition, the methanol oxidation catalytic activity for PtRu NWs was higher than that of PtRu NCs because the adsorption energy of CO_{ads} and OH_{ads} on {111} facets enclosed PtRu NWs reached near the optimal value compared to the adsorption energy of CO_{ads} and OH_{ads} on {100} facets enclosed PtRu NCs. Moreover, compared with PtRu NRs, the PtRu NWs had more {111} active sites facets due to their longer and thinner structure to result in the higher electrocatalytic activity. **Figure 6** also shows that PtRu nanodendrites have higher methanol oxidation efficiency than PtRu NCs or Pt/C because PtRu nanodendrites with the staggered branches can facilitate guest accessibility and tolerance to undesired agglomeration [89]. Furthermore, PtRu nanodendrites has surface area and atom utility is larger than PtRu NCs to get

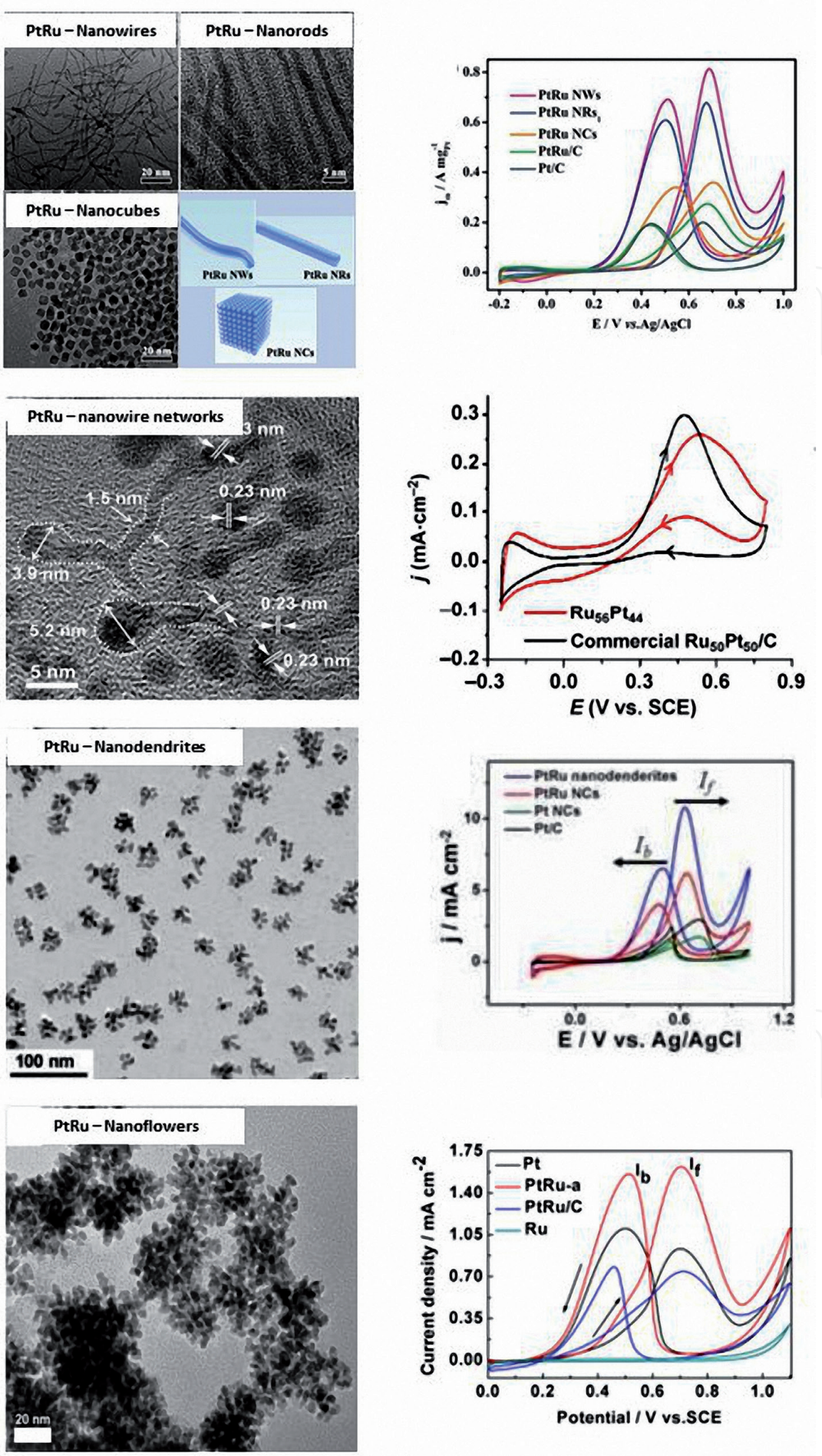


Figure 6.
TEM images and CV curves of the various morphologies of PtRu [87–90].

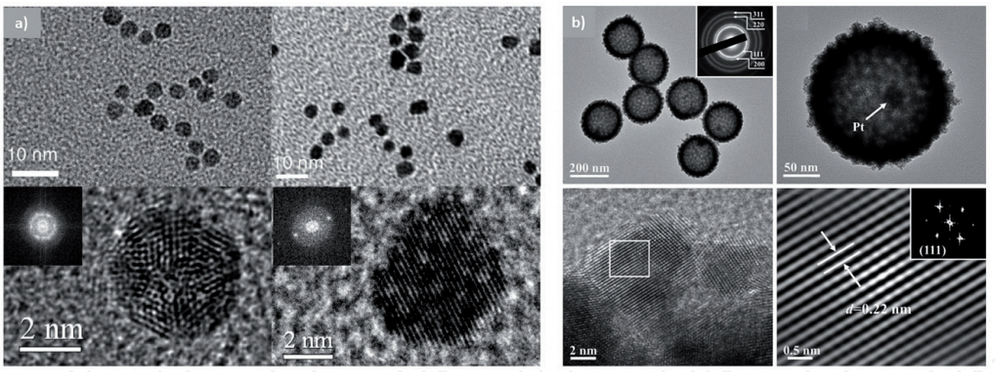


Figure 7.
TEM and HR-TEM images of core-shell (a) and Pt@mPtRu Yolk – Shell (b) nanostructures [93, 94].

better facilitate electron catalysis. PtRu nanoflower catalysts synthesized by a facile one-pot solvothermal method exhibited superior methanol oxidation efficiency compared to PtRu/C, as shown in **Figure 6** [90].

In order to improve fuel cell performance and reduce their cost, the fuel cell catalysis primarily needs to optimize its composition and structure – morphology. The core-shell structure has attracted much attention owing to its wide applications in electrochemical energy devices. Various works on Ru@Pt nanoparticles have demonstrated that Ru@Pt has superior CO tolerance and higher methanol oxidation efficiency than that of PtRu [91–94]. A demonstrated Ru@Pt structure is shown in **Figure 7**. An increase of active sites is a necessary requirement to enhance the Pt-based electrocatalyst utilization. Hollow nanostructures not only meet this requirement but also reduce the amount of Pt, while porous nanostructures can reduce diffusion resistance and increase contact area [92, 93]. A combination of core-shell and hollow structures is of great interest and become a potential new research direction. Recently, yolk–shell nanostructures have been successfully synthesized by a facile approach (**Figure 7**) [94]. As a result, this structure has better catalytic activity, durability and tolerance to CO comparing to PtRu nanocages and Pt/C [94].

4. Conclusion

In summary, the two-component Pt alloy has generally better methanol oxidation efficiency and tolerances to CO poisoning than pure Pt. Among PtM alloys, PtRu is the most notable due to its superior properties of a low potential onset, high catalytic activity, and high CO tolerance. The performance of DMFC can be further improved when PtRu is combined with a third suitable metal. Up to now, PtRuM nanoparticles with different morphologies have been successfully synthesized, and they exhibited higher methanol oxidation activities than those of traditional PtRu. Substrate and morphology are also the important factors in manipulating fuel cell performance, and thus a variety of substrates has been used for DMFC catalyst. It is found that CNTs and graphene are the two most common support materials to mitigate the disadvantages of carbon Vulcan (a traditional support material (or substrate)) and thereby enhancing the fuel cell efficiency. Functionalization and doping approaches are the next developments to improve and search for the optimal substrates. Interestingly, the combination of CNTs and graphene substrates possesses as an excellent substrate for methanol oxidation. The demonstrated results in this book chapter open up a new research direction that involves in simultaneously optimization of nanocatalysts, substrates, and their structures – morphologies toward the developments of DMFC.

Acknowledgements

This research is funded by Vietnam National Foundation for Science and Technology Development (NAFOSTED) under grant number 103.02-2019.374, and Ho Chi Minh City University of Technology (HCMUT), VNU-HCM under grant number BK-SDH-2021-2080906. We acknowledge the support of time and facilities from Ho Chi Minh City University of Technology (HCMUT), VNU-HCM for this study.

Author details

Dang Long Quan[1,2,3] and Phuoc Huu Le[4*]

1 Ho Chi Minh City University of Technology (HCMUT), Ho Chi Minh City, Vietnam

2 Vietnam National University Ho Chi Minh City, Ho Chi Minh City, Vietnam

3 Department of Physics, College of Natural Sciences, Can Tho University, Can Tho City, Vietnam

4 Department of Physics and Biophysics, Faculty of Basic Sciences, Can Tho University of Medicine and Pharmacy, Can Tho, Vietnam

*Address all correspondence to: lhuuphuoc@ctump.edu.vn

IntechOpen

© 2021 The Author(s). Licensee IntechOpen. This chapter is distributed under the terms of the Creative Commons Attribution License (http://creativecommons.org/licenses/by/3.0), which permits unrestricted use, distribution, and reproduction in any medium, provided the original work is properly cited. CC BY

References

[1] Almeida TS, Garbim C, Silva RG, De Andrade AR. Addition of iron oxide to Pt-based catalyst to enhance the catalytic activity of ethanol electrooxidation. Journal of Electroanalytical Chemistry. 2017; *796*: 49-56.

[2] Zhang C, Shen X, Pan Y, Peng Z. A review of Pt-based electrocatalysts for oxygen reduction reaction. Frontiers in Energy. 2017; *11*: 268-285.

[3] Seselj N, Engelbrekt C, Zhang, J. Graphene-supported platinum catalysts for fuel cells. Science Bulletin. 2015; *60*: 864-876.

[4] Aricò AS, Baglio V, Antonucci V. Direct methanol fuel cells: history, status and perspectives. Electrocatalysis of direct methanol fuel cells. Wiley 2009; 1-78. ISBN: 9783527627707

[5] Tiwari JN, Tiwari RN, Singh G, Kim KS. Recent progress in the development of anode and cathode catalysts for direct methanol fuel cells. Nano Energy. 2013; *2*: 553-578.

[6] 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. Sustainable Energy & Fuels. 2020; 4: 15-30.

[7] Janssen MMP, Moolhuysen J. Platinum—tin catalysts for methanol fuel cells prepared by a novel immersion technique, by electrocodeposition and by alloying. Electrochimica Acta. 1976; 21: 861-868.

[8] Watanabe M, Motoo S. Electrocatalysis by ad-atoms: Part III. Enhancement of the oxidation of carbon monoxide on platinum by ruthenium ad-atoms. J. Electroanal. Chem. Interf. Electrochem. 1975; *60*: 275-283.

[9] Nassr ABAA, Sinev I, Grünert W, Bron M. PtNi supported on oxygen functionalized carbon nanotubes: in depth structural characterization and activity for methanol electrooxidation. Appl Catal B Environ. 2013; *142-143*:849-860.

[10] Baronia R, Goel J, Tiwari S, Singh P, Singh D, Singh SP, Singhal SK. Efficient electro-oxidation of methanol using PtCo nanocatalysts supported reduced graphene oxide matrix as anode for DMFC. Int. J. Hydrog Energy. 2017; *42*:10238-10247.

[11] Baglio V, Stassi A, Di Blasi A., Durso C, Antonucci V, Aricò AS. Investigation of bimetallic Pt–M/C as DMFC cathode catalysts. Electrochimica Acta. 2007; 53(3):1360-1364.

[12] Sahin O, Kivrak H.. A comparative study of electrochemical methods on Pt–Ru DMFC anode catalysts: the effect of Ru addition. International journal of hydrogen energy. 2013; 38(2):901-909.

[13] Jia H, Chang G, Shu H, Xu M, Wang X, Zhang Z, Liu X, He H, Wang K, Zhu R, He Y. Pt nanoparticles modified Au dendritic nanostructures: facile synthesis and enhanced electrocatalytic performance for methanol oxidation. Int. J. Hydrog Energy. 2017; 42: 22100-22107.

[14] Alekseenko AA, Guterman V.E., Belenov S.V., Menshikov V. S., Tabachkova N.Y., Safronenko O.I., Moguchikh E.A. Pt/C electrocatalysts based on the nanoparticles with the gradient structure. International Journal of Hydrogen Energy. 2018; 43(7): 3676-3687.

[15] Xu J, Hua K, Sun G, Wang C, Lv X, Wang Y. Electrooxidation of methanol on carbon nanotubes supported Pt–Fe alloy electrode. Electrochemistry communications. 2006; 8(6): 982-986.

[16] Baronia R, Goel J, Tiwari S, Singh P, Singh D, Singh SP, Singhal SK.

Efficient electro-oxidation of methanol using PtCo nanocatalysts supported reduced graphene oxide matrix as anode for DMFC. International Journal of Hydrogen Energy. 2017; 42(15): 10238-10247.

[17] Nassr A.B.A.A, Sinev I, Grünert W, Bron M. PtNi supported on oxygen functionalized carbon nanotubes: in depth structural characterization and activity for methanol electrooxidation. Applied Catalysis B: Environmental. 2013; 142: 849-860.

[18] Li F, Guo Y, Chen M, Qiu H, Sun X, Wang W, Gao J. Comparison study of electrocatalytic activity of reduced graphene oxide supported Pt–Cu bimetallic or Pt nanoparticles for the electrooxidation of methanol and ethanol. International journal of hydrogen energy. 2013; 38(33): 14242-14249.

[19] Maya-Cornejo J, Garcia-Bernabé A, Compañ V. Bimetallic Pt-M electrocatalysts supported on single-wall carbon nanotubes for hydrogen and methanol electrooxidation in fuel cells applications. International Journal of Hydrogen Energy. 2018; 43(2): 872-884.

[20] Liu Z, Ling XY, Guo B, Hong L, Lee JY. Pt and PtRu nanoparticles deposited on single-wall carbon nanotubes for methanol electro-oxidation. Journal of power sources. 2007; 167(2): 272-280.

[21] Lu Q, Huang J, Han C, Sun L, Yang X. Facile synthesis of composition-tunable PtRh nanosponges for methanol oxidation reaction. Electrochimica Acta 2018; 266: 305-311.

[22] Zhao H, Qi W, Zhou X, Wu H, Li Y. Composition-controlled synthesis of platinum and palladium nanoalloys as highly active electrocatalysts for methanol oxidation. Chinese Journal of Catalysis. 2018; 39(2): 342-349.

[23] Wroblowa H. Electrocatalysis. Journal of Electroanalytical Chemistry. 1964; 7(6): 428-451.

[24] Petrii OA. Pt–Ru electrocatalysts for fuel cells: a representative review. Journal of Solid State Electrochemistry. 2008; 12(5): 609.

[25] Nørskov JK, Rossmeisl J, Logadottir A, Lindqvist LRKJ, Kitchin JR, Bligaard T, Jonsson H. Origin of the overpotential for oxygen reduction at a fuel-cell cathode. The Journal of Physical Chemistry B 2004; 108(46): 17886-17892.

[26] Watanabe M, MoToo S. Correlation between Electro-Catalytic Activity of Platinum-Ruthenium Alloys and Coverage of Organic Substances. Denki Kagaku oyobi Kogyo Butsuri Kagaku. 1973; 41(3): 190-196.

[27] Watanabe MA, Motoo S. Electrocatalysis by ad-atoms: Part II. Enhancement of the oxidation of methanol on platinum by ruthenium ad-atoms. J. Electroanal. Chem. Interf. Electrochem. 1975; 60(3): 267-273.

[28] Ramli ZAC, Kamarudin SK. Platinum-based catalysts on various carbon supports and conducting polymers for direct methanol fuel cell applications: a review. Nanoscale research letters. 2018; *13*(1): 410.

[29] Stamenkovic V, Mun BS, Mayrhofer KJ, Ross PN, Markovic NM, Rossmeisl J, Nørskov JK. Changing the activity of electrocatalysts for oxygen reduction by tuning the surface electronic structure. Angewandte Chemie. 2006; 118: 2963-2967.

[30] Strasser P, Fan Q, Devenney M, Weinberg WH, Liu P, Nørskov JK. High throughput experimental and theoretical predictive screening of materials– a comparative study of search strategies for new fuel cell anode catalysts. The Journal of Physical Chemistry B. 2003; 107: 11013-11021.

[31] Samjeské G, Wang H, Löffler T, Baltruschat H. CO and methanol oxidation at Pt-electrodes modified by Mo. Electrochimica Acta. 2002; *47*: 3681-3692.

[32] Ordóñez LC, Roquero P, Sebastian PJ, Ramírez J. CO oxidation on carbon-supported PtMo electrocatalysts: effect of the platinum particle size. International journal of hydrogen energy. 2007; 32: 3147-3153.

[33] Liu Z, Hu JE, Wang Q, Gaskell K, Frenkel AI, Jackson GS, Eichhorn B. PtMo alloy and MoOx@ Pt Core– shell nanoparticles as highly CO-tolerant electrocatalysts. Journal of the American Chemical Society 2009; 131: 6924-6925.

[34] Zhou ZH, Li WS, Fu Z, Xiang XD. Carbon nanotube-supported Pt-$HxMoO_3$ as electrocatalyst for methanol oxidation. International Journal of Hydrogen Energy. 2010; *35*(3): 936-941.

[35] Ordóñez LC, Roquero P, Sebastian PJ, Ramírez J. Carbon-supported platinum-molybdenum electro-catalysts for methanol oxidation. Catalysis Today. 2005; *107*: 46-52.

[36] Mukerjee S, Urian RC. Bifunctionality in Pt alloy nanocluster electrocatalysts for enhanced methanol oxidation and CO tolerance in PEM fuel cells: electrochemical and in situ synchrotron spectroscopy. Electrochimica Acta. 2002; *47*(19): 3219-3231.

[37] Tsiouvaras N, Martínez-Huerta MV, Paschos O, Stimming U, Fierro JLG, Peña MA. PtRuMo/C catalysts for direct methanol fuel cells: Effect of the pretreatment on the structural characteristics and methanol electrooxidation. International journal of hydrogen energy. 2010; *35*(20):11478-11488.

[38] Chen S, Ye F, Lin W. Effect of operating conditions on the performance of a direct methanol fuel cell with PtRuMo/CNTs as anode catalyst. International Journal of Hydrogen Energy. 2010; *35*(15): 8225-8233.

[39] Kakati N, Maiti J, Oh JY, Yoon YS. Study of methanol oxidation of hydrothermally synthesized PtRuMo on multi wall carbon nanotubes. Applied Surface Science. 2011; *257*: 8433-8437.

[40] Park SH, Jung HM, Um S, Song YW, Kim HS. Rapid synthesis of Pt-based alloy/carbon nanotube catalysts for a direct methanol fuel cell using flash light irradiation. International Journal of Hydrogen energy. 2012; *37*(17): 12597-12604.

[41] Watanabe M, Igarashi H, Fujino T. Design of CO tolerant anode catalysts for polymer electrolyte fuel cell. Electrochemistry. 1999; *67*(12): 1194-1196.

[42] Watanabe M, Zhu Y, Uchida H. Oxidation of CO on a Pt– Fe alloy electrode studied by surface enhanced infrared reflection– absorption spectroscopy. The Journal of Physical Chemistry B. 2000; *104*(8): 1762-1768.

[43] Jeon MK, Won JY, Lee KR, Woo SI. Highly active PtRuFe/C catalyst for methanol electro-oxidation. Electrochemistry Communications. 2007; *9*(9): 2163-2166.

[44] Cai Z, Kuang Y, Qi X, Wang P, Zhang Y, Zhang Z, Sun X. Ultrathin branched PtFe and PtRuFe nanodendrites with enhanced electrocatalytic activity. Journal of Materials Chemistry A. 2015; 3(3): 1182-1187.

[45] Huang T, Wang X, Zhuang J, Cai WB, Yu A. Preparation of Porous PtRuCo Catalyst by One-Step

Codeposition and Its Electrocatalytic Performance for Methanol Oxidation. Electrochemical and Solid State Letters. 2009; *12*(7): B112.

[46] Ahn SH, Kwon OJ, Kim SK, Choi I, Kim JJ. Electrochemical preparation of Pt-based ternary alloy catalyst for direct methanol fuel cell anode. International Journal of Hydrogen Energy 2010; *35*(24): 13309-13316.

[47] Paulus UA, Wokaun A, Scherer GG, Schmidt TJ, Stamenkovic V, Radmilovic V, Markovic NM, Ross PN. Oxygen reduction on carbon-supported Pt−Ni and Pt−Co alloy catalysts. The Journal of Physical Chemistry B. 2002; 106: 4181-4191.

[48] Park KW, Choi JH, Kwon BK, Lee SA, Sung YE, Ha HY, Hong SA, Kim H, Wieckowski A. Chemical and electronic effects of Ni in Pt/Ni and Pt/Ru/Ni alloy nanoparticles in methanol electrooxidation. The Journal of Physical Chemistry B. 2002; 106: 1869-1877.

[49] Wang ZB, Yin GP, Shi PF, Sun YC. Novel Pt–Ru–Ni/C catalysts for methanol electro-oxidation in acid medium. Electrochemical and Solid State Letters. 2005; *9*(1): A13.

[50] Wang ZB, Yin GP, Zhang J, Sun YC, Shi PF. Co-catalytic effect of Ni in the methanol electro-oxidation on Pt–Ru/C catalyst for direct methanol fuel cell. Electrochimica Acta. 2006; *51*(26): 5691-5697.

[51] Ye F, Chen S, Dong X, Lin W. Carbon nanotubes supported Pt-Ru-Ni as methanol electro-oxidation catalyst for direct methanol fuel cells. Journal of Natural Gas Chemistry. 2007; *16*(2): 162-166.

[52] 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. The Journal of Physical Chemistry B. 2006; 110: 7828-7834.

[53] Wang ZB, Yin GP, Shao YY, Yang BQ, Shi PF, Feng PX. Electrochemical impedance studies on carbon supported PtRuNi and PtRu anode catalysts in acid medium for direct methanol fuel cell. Journal of Power Sources. 2007; *165*(1): 9-15.

[54] Ye F, Chen S, Dong X, Lin W. Carbon nanotubes supported Pt-Ru-Ni as methanol electro-oxidation catalyst for direct methanol fuel cells. Journal of Natural Gas Chemistry. 2007; 16(2): 162-166.

[55] Roth C, Goetz M, Fuess H. (2001). Synthesis and characterization of carbon-supported Pt–Ru–WOx catalysts by spectroscopic and diffraction methods. Journal of Applied Electrochemistry; 31(7): 793-798.

[56] Xue S, Deng W, Yang F, Yang J, Amiinu IS, He D, Tang H, Mu S. Hexapod PtRuCu nanocrystalline alloy for highly efficient and stable methanol oxidation. ACS Catalysis. 2018; 8(8): 7578-7584.

[57] Jeon MK, Lee KR, Woo SI. Ternary Pt 45 Ru 45 M 10/C (M = Mn, Mo and W) catalysts for methanol and ethanol electro-oxidation. Korean journal of chemical engineering. 2009; 26(4): 1028-1033.

[58] Yu X, Ye S. Recent advances in activity and durability enhancement of Pt/C catalytic cathode in PEMFC: Part I. Physico-chemical and electronic interaction between Pt and carbon support, and activity enhancement of Pt/C catalyst. Journal of power sources. 2007; 172(1): 133-144.

[59] Jung N, Chung DY, Ryu J, Yoo SJ, Sung YE. Pt-based nanoarchitecture and catalyst design for fuel cell applications. Nano Today. 2014; 9(4): 433-456.

[60] Antolini E. Carbon supports for low-temperature fuel cell catalysts. Appl. Catal. B. 2009; 88(1-2): 1-24.

[61] Yang WH, Zhang QH, Wang HH, Zhou ZY, Sun SG. Preparation and utilization of a sub-5 nm PbO_2 colloid as an excellent co-catalyst for Pt-based catalysts toward ethanol electro-oxidation. New Journal of Chemistry. 2017; 41(20): 12123-12130.

[62] Antoniassi RM, Silva JCM, Neto AO, Spinacé EV. Synthesis of Pt+SnO_2/C electrocatalysts containing Pt nanoparticles with preferential (100) orientation for direct ethanol fuel cell. Applied Catalysis B: Environmental. 2017; 218: 91-100.

[63] Luo Y, Alonso-Vante N. The effect of support on advanced Pt-based cathodes towards the oxygen reduction reaction. State of the art. Electrochimica Acta. 2015; 179: 108-118.

[64] Shao Y, Yin G, Gao Y, Shi P. Durability study of Pt/ C and Pt/ CNTs catalysts under simulated PEM fuel cell conditions. Journal of the Electrochemical Society. 2006; 153(6): A1093.

[65] Li W, Liang C, Zhou W, Qiu J, Zhou Z, Sun G, Xin Q. Preparation and characterization of multiwalled carbon nanotube-supported platinum for cathode catalysts ofdirect methanol fuel cells. J. Phys. Chem. B. 2003; 107: 6292-6299.

[66] Tian ZQ, Jiang SP, Liang YM, Shen PK. Synthesis and characterization of platinum catalysts on multiwalled carbon nanotubes by intermittent microwave irradiation for fuel cell applications. J. Phys. Chem. B. 2006; 110: 5343-5350.

[67] Li W, Liang C, Qiu J, Zhou W, Han H, Wei Z, Sun G, Xin Q. Carbon nanotubes as support for cathode catalyst of a direct methanol fuel cell. Carbon. 2002; 40: 791-794.

[68] Li L, Xing Y. Electrochemical durability of carbon nanotubes at 80°C. J. Power Sources. 2008; 178: 75-79.

[69] Li L, Xing Y. Electrochemical durability of carbon nanotubes in noncatalyzed and catalyzed oxidations. J. Electrochem. Soc. 2006; 153: A1823–A1828

[70] Kongkanand A, Kuwabata S, Girishkumar G, Kamat P. Single-wall carbon nanotubes supported platinum nanoparticles with improved electrocatalytic activity for oxygen reduction reaction. Langmuir. 2006; 22: 2392-2396.

[71] Shao Y, Yin G, Gao Y, Shi P. Durability study of Pt/C and Pt/CNTs catalysts under simulated PEM fuel cell conditions. J. Electrochem. Soc. 2006; 153: A1093–A1097.

[72] Wang X, Li W, Chen Z, Waje M, Yan Y. Durability investigation of carbon nanotube as catalyst support for proton exchange membrane fuel cell. J. Power Sources. 2006; 158: 154-159.

[73] Rambabu G, Bhat DS, Figueiredo FM. Carbon Nanocomposite Membrane Electrolytes for Direct Methanol Fuel Cells—A Concise Review. Nanomaterials. 2019; 9(9): 1292.

[74] Alegre C, Calvillo L, Moliner R, González-Expósito JA, Guillén-Villafuerte O, Huerta MM, Pastor E, Lázaro MJ. Pt and PtRu electrocatalysts supported on carbon xerogels for direct methanol fuel cells. Journal of Power Sources. 2011; *196*(9): 4226-4235.

[75] Kang S, Lim S, Peck DH, Kim SK, Jung DH, Hong SH, Jung HG, Shul Y.

Stability and durability of PtRu catalysts supported on carbon nanofibers for direct methanol fuel cells. International journal of hydrogen energy. 2012; *37*(5): 4685-4693.

[76] Maiyalagan T, Alaje TO, Scott K. Highly stable Pt–Ru nanoparticles supported on three-dimensional cubic ordered mesoporous carbon (Pt–Ru/CMK-8) as promising electrocatalysts for methanol oxidation. The Journal of Physical Chemistry C. 2012; 116(3): 2630-2638.

[77] 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. Electrochimica Acta. 2008; *53*(27): 7807-7811.

[78] Fard HF, Khodaverdi M, Pourfayaz F, Ahmadi MH. Application of N-doped carbon nanotube-supported Pt-Ru as electrocatalyst layer in passive direct methanol fuel cell. International Journal of Hydrogen Energy. 2020; 45(46): 25307-25316.

[79] Wang YS, Yang SY, Li SM, Tien HW, Hsiao ST, Liao WH, Liu CH, Chang KH, Ma CCM, Hu CC. Three-dimensionally porous graphene–carbon nanotube composite-supported PtRu catalysts with an ultrahigh electrocatalytic activity for methanol oxidation. Electrochimica Acta. 2013; 87: 261-269.

[80] Lee SH, Kakati N, Jee SH, Maiti J, Yoon YS. Hydrothermal synthesis of PtRu nanoparticles supported on graphene sheets for methanol oxidation in direct methanol fuel cell. Materials Letters. 2011; 65: 3281-3284.

[81] Reddy GV, Raghavendra P, Ankamwar B, Chandana PS, Kumar SS, Sarma LS. Ultrafine Pt–Ru bimetallic nanoparticles anchored on reduced graphene oxide sheets as highly active electrocatalysts for methanol oxidation. Materials Chemistry Frontiers. 2017; 1(4): 757-766.

[82] Zhao J, Zhang L, Xue H, Wang Z, Hu H. Methanol electrocatalytic oxidation on highly dispersed platinum–ruthenium/graphene catalysts prepared in supercritical carbon dioxide–methanol solution. *RSC Advances*. 2012; 2(25): 9651-9659.

[83] Cheng Y. Highly effective and CO-tolerant PtRu electrocatalysts supported on poly(ethyleneimine) functionalized carbon nanotubes for direct methanol fuel cells. Electrochimica Acta. 2013; 99: 124-132.

[84] Prabhuram J, Zhao TS, Liang ZX, Chen R. A simple method for the synthesis of PtRu nanoparticles on the multi-walled carbon nanotube for the anode of a DMFC. Electrochimica Acta. 2007; *52*(7): 2649-2656.

[85] Carmo M, Paganin VA, Rosolen JM, Gonzalez ER. Alternative supports for the preparation of catalysts for low-temperature fuel cells: the use of carbon nanotubes. Journal of Power Sources. 2005; *142*(1-2): 169-176.

[86] Gan L, Lv R, Du H, Li B, Kang F. High loading of Pt–Ru nanocatalysts by pentagon defects introduced in a bamboo-shaped carbon nanotube support for high performance anode of direct methanol fuel cells. Electrochemistry Communications. 2009; *11*(2): 355-358.

[87] Huang L, Zhang X, Wang Q, Han Y, Fang Y, Dong S. Shape-control of Pt–Ru nanocrystals: tuning surface structure for enhanced electrocatalytic methanol oxidation. Journal of the American Chemical Society. 2018; 140(3): 1142-1147.

[88] Zhao W, Huang D, Yuan Q, Wang X. Sub-2.0-nm Ru and composition-tunable RuPt nanowire

networks. Nano Research. 2016; 9(10): 3066-3074.

[89] Lu S, Eid K, Ge D, Guo J, Wang L, Wang H, Gu H. One-pot synthesis of PtRu nanodendrites as efficient catalysts for methanol oxidation reaction. Nanoscale. 2017; 9(3): 1033-1039.

[90] Li M, Zheng H, Han G, Xiao Y, Li Y. Facile synthesis of binary PtRu nanoflowers for advanced electrocatalysts toward methanol oxidation. Catalysis Communications. 2017; 92: 95-99.

[91] Dang LQ, Nguyen MT, Truong NV, Le PH, Long N. Investigation of Carbon Supported Ru–Pt Nanoparticles for High–Performance Electrocatalytic Oxidation of Methanol. Int. J. Electrochem. Sci. 2017; 12: 10187-10198.

[92] Yin HJ, Zhou JH, Zhang YW. Shaping well-defined noble-metal-based nanostructures for fabricating high-performance electrocatalysts: advances and perspectives. Inorganic Chemistry Frontiers. 2019; 6(10): 2582-2618.

[93] Alayoglu S, Zavalij P, Eichhorn B, Wang Q, Frenkel AI, Chupas P. Structural and architectural evaluation of bimetallic nanoparticles: a case study of Pt– Ru core– shell and alloy nanoparticles. Acs Nano. 2009; 3(10): 3127-3137.

[94] Yin S, Kumar RD, Yu H, Li C, Wang Z, Xu Y, Li X, Wang L, Wang H. Pt@Mesoporous PtRu Yolk–Shell Nanostructured Electrocatalyst for Methanol Oxidation Reaction. ACS Sustainable Chemistry & Engineering. 2019; 7(17): 14867-14873.