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Novel Pt and Pd Based Core-Shell Catalysts with Critical New Issues of Heat Treatment, Stability and Durability for Proton Exchange Membrane Fuel Cells and Direct Methanol Fuel Cells

Nguyen Viet Long, Cao Minh Thi, Masayuki Nogami and Michitaka Ohtaki

Additional information is available at the end of the chapter

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1. Introduction

Traditionally, Pt and Pd based catalysts are widely studied in the continuous developments of next fuel cells (FCs) with the critical issues of energy and environment technologies. So far, Pt and Pd based catalysts have been mainly used in the anodes and the cathodes in FCs by a electrode-membrane technology. In spite of the large advantages of Pt based catalysts in electro-catalysis for FCs, many problems of high cost remain. In addition, so far Pt and Pd catalysts have still exhibited very good catalytic activity and selectivity of hydrogen and oxygen adsorption as well as hydrogen evolution reaction (HER), hydrogen oxidation reaction (HOR) for the dissociation of hydrogen into protons (H^+) and electrons (e^-), and oxygen reduction reaction (ORR). At present, FC technologies and applications are polymer electrolyte fuel cell (PEFC) or also known as proton exchange membrane FC (PEMFC), phosphoric acid FC (PAFC), alkaline FC (AFC), molten carbonate FC (MCFC), solid oxide FC (SOFC). The typical features include operating temperature ($^{\circ}C$) for low-temperature PEMFC and DMFC of about 50-80 $^{\circ}C$, power density ~ 350 Mw/cm², fuel efficiency ~ 40 -65%, lifetime $>40,000$ hr, capital cost >200 \$/kW [5,49,52,173], and other practical applications. According to hydrogen and oxygen reaction, electro-oxidation of carbon monoxide (CO) is intensively studied in low temperature FCs. In DMFCs, methanol oxidation reaction (MOR) in catalytic activity of Pt catalyst is very crucial to improve the whole performance. Therefore, scientists have considerably focused on the various ways of improving HOR, ORR, and MOR in the catalyst layers of various FCs, PEMFCs, and DMFCs [1-3]. So far, ORR has become an important mechanism investigated in PEMFCs and DMFCs for their large-scale commercialization. Recently, U.S. Department of Energy Fuel Cell Technologies

Program (DOE Program), and New Energy and Industrial Technology Development Organization (NEDO Program) in Japan have supported large Research and Development programs (R&D) of FCs and FC systems for stationary, portable and transportation applications, such as FC vehicles. In addition, FCs become promising technology to address global environmental challenges in energy, science and nature issues [4-8]. Now, various DMFCs can work at low and intermediate temperatures up to 150 °C [9]. Thus, next fuel cells also can meet the urgent demands for green energy.

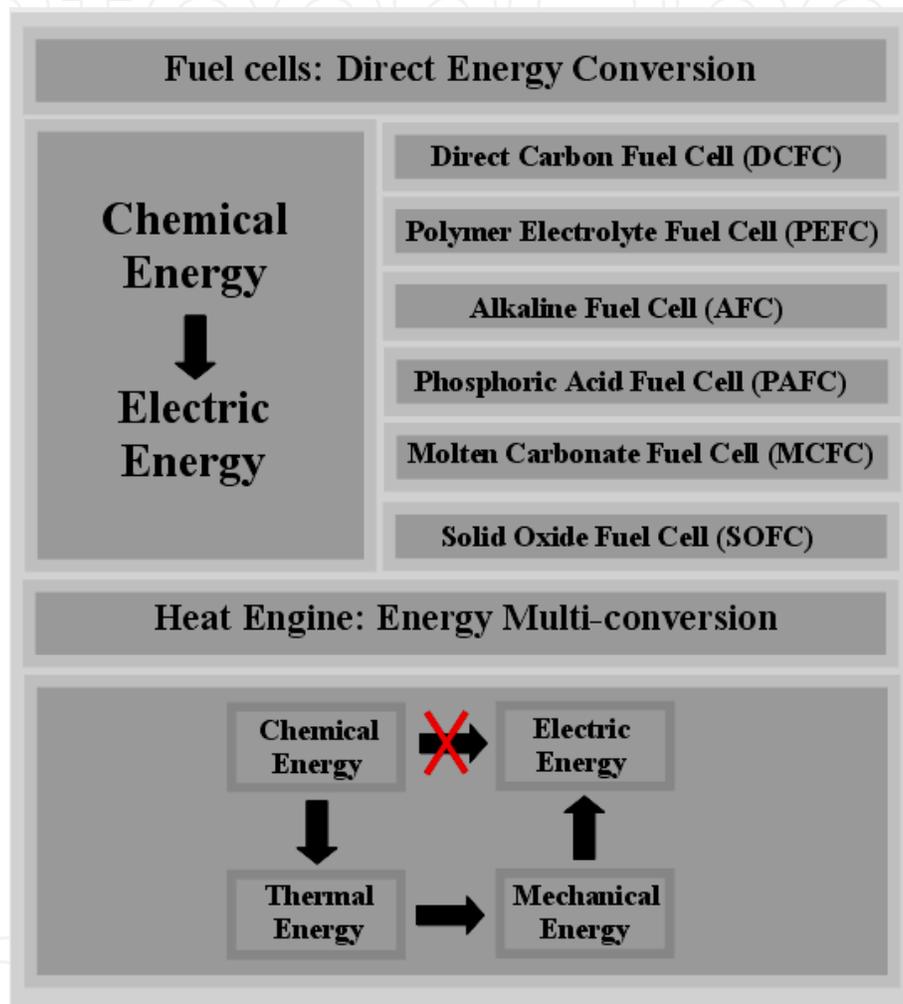


Figure 1. Features of fuel cells and heat engine in the direct or indirect conversion processes from chemical energy into electric energy. Excellent advantage of fuel cells is direct energy conversion

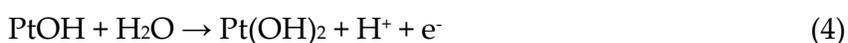
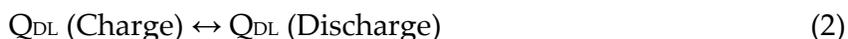
Today, the proton exchange membranes, typically such as perfluorosulfonic acid (PFSA) membranes or Nafion® for FC applications are presented [51-53]. Interestingly, charge carriers in FCs are various kinds of H^+ (PEMFC), H^+ (DMFC), OH^- (AFC), H^+ (PAFC), CO_3^- (MCFC), and O^- (SOFC) [4-9,49,52,173]. Figure 1 shows various energy conversion processes from chemical energy into electric energy through both FCs and heat engine. The operation principle of simple low-temperature FCs mainly depends on the chemical reactions of hydrogen and oxygen with direct conversion into electricity without mediate conversions of thermal energy and mechanical energy.

Fuel cells	Applications
AFC, PAFC, MCFC, SOFC PEMFC, DMFC	AFC: Space, mobile; PAFC: Distributed power; MCFC: Distributed power generation; SOFC: Power generation; PEMFC and DMFC: Portable, mobile, stationary
PEMFC, DMFC	Special use in compact mobile devices and handphoned in future

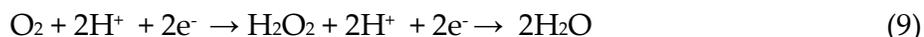
Table 1. Potential applications for various fuel cells [4-9,49,52,173]

2. Pt and Pd based catalysts

In recent years, novel Pt and Pd metals have been known as the best electrocatalysts to important chemical reactions for synthesis of new chemicals as well as the FC reactions. The electrocatalytic properties are typically characterized by hydrogen evolution reaction/hydrogen oxidation reaction (HER/HOR), ORR, and electro-oxidation of CO at the surfaces of Pt(hkl) facets of the as-prepared catalysts as well as the typical oxidations of methanol and formic acid on the surfaces of Pt (hkl) facets of the prepared catalysts. The (111), (100) and (110) low-index facets were proved in high stability and durability in catalysis, and good re-construction in the catalytic FC reactions [10,81,82]. The HER on the Pt catalyst is known by the important Volmer, Tafel, and Heyrovsky mechanisms. In addition, Volmer-Tafel and Volmer-Heyrovsky mechanisms can occur in the complex combinations of the above basic mechanisms [10]. The surface kinetics and chemical activity occurring at the electrode surface containing Pt/support catalyst are characterized as follows [10-14,140].



To evaluate catalytic activity of the pure Pt catalysts or Pt based catalysts, the electrochemical active surface area (ECSA) is used as $\text{ECSA} = Q_{\text{H}} / (0.21 \times L_{\text{Pt}})$ [10-14,140]. Therefore, ECSA can be significantly enhanced by the use of a low L_{Pt} loading, and a low content of CO intermediates generated, and new discoveries of highly strong hydrogen reactions in the improvements of the Pt based catalysts. Clearly, the particle size of Pt NPs of 10 nm is crucial in catalysis and FCs, PEMFCs, and DMFCs because the metal NPs showed very large quantum and size effects in the size range of around 10 nm. The ORR is observed in two main pathways in acidic electrolytes as follows [10-15].



For the ORR, the relationship between kinetic current (i) and potential (E) can be investigated as rate expression

$$i = nFkc(1 - \theta_{\text{ad}})^x \exp(-\beta FE/RT) \exp(-\gamma \Delta G_{\text{ad}}/RT) \quad (10)$$

Where n , F , K , c , x , β , and γ are constants. In addition, n , F , c , and θ_{ad} indicated the mole (n), Faraday's constant (F), the concentration of O_2 (c), and coverage of adsorbed species (θ_{ad}), respectively. Here, ΔG_{ad} indicated the weak or strong adsorption. We can choose $x=1$ and $\gamma=1$ in the simplification. According to the adsorption degree, the rate may be changed. Thus, it may be change from positive (Weak adsorption) to negative (Strong adsorption). It means that the reaction rate declines when the coverage of intermediates (θ_{ad}) rises [13,173].

At present, the phenomena of ORR kinetics and mechanisms occurring on the Pt catalysts are intensively investigated but a very high overpotential loss observed. Thus, the very high loadings of Pt must be supplied in the high requirements of the FCs operation with large current. It is known that the Pt catalyst has showed the highest activity to the ORR mechanism. Most of research has led to understand ORR on catalytic systems of Pt designed catalysts using the ultra-low Pt loading at minimal level. The issues of the low Pt-catalyst loading, high performance, durability and effective-cost design in FCs systems are very crucial for their large-scale commercialization. The CV results of various Pt NPs (sphere, cube, hexagonal and tetrahedral-octahedral morphology ...) in H_2SO_4 showed the strong structural sensitivity of the as-prepared Pt NPs. The most basic (111), (100) and (110) planes were confirmed in the active sites of catalytic activity such as in the edges, corners, and terraces [15]. In particular, monolayer bimetallic surfaces were investigated in the experimental and theoretical studies of the surface monolayer, subsurface monolayer, and inter-mixed bimetallic structures, especially by DFT theoretical approaches [16,17]. So far, the characterization of size, structure, surface structure, internal structure, shape, and morphology has been discussed in various the as-prepared metal NPs by various strategies of syntheses. The noble NPs (Pt, Pd, Ru, Ir, Os, Rh, Au, Ag), and their combinations with cheaper metals (Ni, Co, Cu, Fe ...) as alloy and core-shell nanostructures can be used as potential Pt based catalysts for further studies of ORR and CO oxidation reaction in various FCs for long-term physical-chemical stability and durability, such as PEMFCs and DMFCs [18-21]. Besides, the investigations of both theory and applications of alloy clusters and nanoparticles showed potential applications in catalysis and FCs [22]. In various FCs, noble Pt metal is the key to large-scale commercialization of PEMFCs and DMFCs because of its unusually high catalytic properties. Therefore, scientists and researchers try to create highly active and stable catalysts with a low Pt loading. To enhance its catalytic activity, Pt catalyst NPs were supported on various high-surface-area carbon materials, such as carbon black (e.g. Vulcan XC-72) [23-27]. The Pt based catalysts of various nanostructures are discussed in the developments of PEMFCs and DMFCs. Interestingly, electricity is directly generated in PEMFCs by hydrogen oxidation and oxygen reduction reactions through membrane-electrode assembly (MEA) [1-14].

2.1. Preparation methods of Pt and Pd based nanoparticles

Essentially, various top-down physical or bottom-up chemical methods, such as polyol method, and chemical-physical combined methods are widely used for making Pt and Pd based catalysts for homogeneous and heterogeneous catalysis, FCs, PEMFCs, and DMFCs involving in both theory and practice [28-33,173-188]. The core-shell nanostructures of bimetallic nanoparticles can be synthesized by phase-transfer protocol method [34]. The relatively facile method with microwave and ultrasound supports or sonochemical method in the synthesis of nanoparticles without focusing on much consideration of the basic issues of the homogeneity of typical size and morphology for catalysis and FCs has been very attractive to researchers and scientists [35,36]. In the methods, the nanosized ranges of the as-prepared nanoparticles are crucial to practical applications in catalysis, biology and medicine. So far, no comprehensive survey of the effects of heat treatments to achieve the significant enhancements of catalytic activity of Pt and Pd based catalysts has been presented in detail.

2.2. Size, shape and morphology

At present, it is known that the as-prepared Pt nanostructures show a variety of particle morphologies and shapes in homogeneous and heterogeneous characterizations. The main morphology and shape were prepared in the broad forms of cube, octahedra, cubo-octahedra, tetrahedra, prisim, sphere, icosahedra, decahedra, rod, tube, wire, fiber, dendrite, flower, plate, twin, belt, disk etc... in the non-polyhedral and non-polyhedral or irregular shapes and morphologies in the near same size range. The spherical and non-spherical morphologies and shapes are observed in the near same range of particle size. The particle size is discovered in various nanosized ranges of from 10 nm, 20 nm, 30 nm, 40 nm, 50 nm, and 100 nm ... to 1 μm , 10 μm , up to 100 μm ..., especially particle size of around 10 nm for potential promising applications in catalysis, biology, and medicine. In our proposals, catalytic activity and selectivity of interesting homogeneous and heterogeneous morphologies and shapes of the Pt based nanoparticles in the nanosized ranges of 10 nm and 20 nm become important topics for scientific research because their structural transformations in that certain ranges of 1-30 nm are difficult to understand transparently unknown phenomena and properties [37,38]. When the size of Pt nanoparticles is decreased into the range of 10 nm, the total fraction of Pt atoms on the Pt catalyst surfaces is very large. This leads a very significant enhancement of electro-catalytic activity. Most of sizes, shapes, morphologies, nanostructures of the as-prepared Pt nanoparticles are significantly changed in normal conditions after the *in situ* TEM and HRTEM measurements. Clearly, the important effects of temperature on characterization of the pure Pt NPs and Pt/supports need to be studied at different temperatures for one optimum temperature range while keeping their good catalytic characterization. The new discoveries of surface-structure changes of polyhedral Pt shapes and morphologies are crucial in the further catalysis investigations [39-41]. The influence of hydrogen on the morphology of Pt or Pd nanoparticles was found in the structural transformations [42,43]. Therefore, alloy and core-shell nanoparticles with various Pt metal compositions are crucial to practical applications

in catalysis and FCs. Nevertheless, most of the as-prepared metal nanoparticles possibly change their certain good shapes and morphologies (e.g. cube, tetrahedra, octahedra ...) into hetero-shapes and hetero-morphologies. In fact, the issues of catalytic activity, durability, and stability of the as-prepared metal nanoparticles in various media have become very important to most of current scientific research. For example, non-platinum anode catalysts or without the use of Pt metal for DMFC and PEMFC applications were developed [44]. It has been known that they are transition metal carbides (e.g. WC and W₂C ...) and the promoted transition metal oxides (e.g. TiO₂, SiO₂, CeO₂, Zr₂O₃, CeO₂-Zr₂O₃ ...) that have the advantages of low prices and strong resistance to poisonous substances such as carbon dioxide (CO) poisoning or CO adsorption on the catalysts.

2.3. Structure and composition

Among metal noble nanoparticles (Pt, Pd, Ru, Rh, Ir, Os, Au, and Ag NPs) as well as various cheap metal nanoparticles, metals show a face centered cubic (fcc) structure. The strong emphasis is that they can be used as metal catalysts for catalysis and FCs. Thus, Pt and Pd based alloy and core-shell nanoparticles can be engineered in a variety of composition using various metals (Co, Ni, Fe, Cu ...) or oxides, ceramics, and glasses in the next significant efforts of researches according to the discoveries and improvements of catalytic activity, selectivity, durability, and stability in catalysis.

3. Proton exchange membrane fuel cell

At present, PEMFCs are used for mobile, portable, and automobile applications because of generated high power densities. For instance, they can operate at low and high temperatures of 60-100 °C or up to 200 °C [45-50]. In addition, the PEMFC is used for transportation applications when pure hydrogen as fuel can be used in PEMFCs for their operation. The conventional fuels are used as liquid, natural gas or gasoline. Therefore, the direct use of methanol can lead to develop PEMFCs into DMFCs. In particular, DMFCs proved that they can offer potential applications, such as cameras, notebook computers, and portable electronic applications [45-50]. The nanostructured membranes have been extensively reviewed in potential FC applications [50]. In addition, proton exchange membranes for PEMFCs operated at medium temperatures are discussed [51-53]. It is likely that the fast developments of new membrane technology can be realized in FCs, PEMFCs, and DMFCs.

3.1. Operation principle

A simple hydrogen and oxygen PEMFC includes the catalytic anode, membrane electrode assembly (MEA), and the catalytic cathode. Fuel is hydrogen fed to the anode that generates protons (H⁺). They travel through proton exchange membrane and combine with electrons (e⁻) and oxygen at the cathode to form water (H₂O). Electrons travel through an external circuit. This leads to that electricity is generated by a FC. Figure 2 shows chemical reactions on the anode and the cathode of a PEMFC. The electrochemical reactions typically occur in a PEMFC as follows.

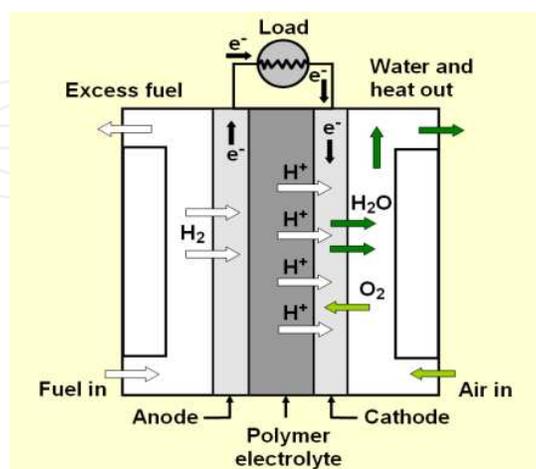
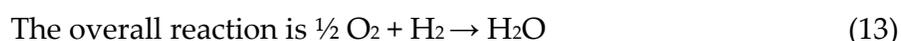
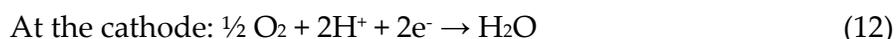


Figure 2. Basic configuration and chemical reaction of PEMFC

3.2. Catalysts in proton exchange membrane fuel cell

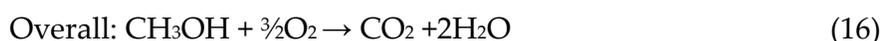
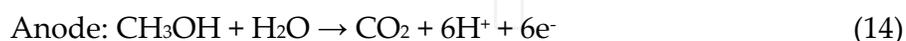
Of great interest is the study of the Pt nanoparticles with controlled size and shape around 10 nm because of its importance in electro-catalysis. So far, the Pt and Pt catalysts have showed the best catalytic activities in the HOR and ORR mechanisms for PEMFCs comparable to other metal catalysts. Therefore, new Pt and Pd based catalysts are developed by using various metals combined in alloy nanostructures. Now, various kinds of Pt and Pd core-shell nanoparticles or nanostructures are prepared in the proofs of improving catalytic activities of HOR and ORR. The cost of Pt and Pd catalysts is very high for the large-scale commercialization of FCs. Therefore, cheaper metals such Cu, Co, Fe, Ni ... can be studied in the uses in the alloy and core-shell catalysts with the Pt shells for reducing the Pt loading [54,55]. The thermal cathodic treatments on Pt/C and Pt-Ru/C catalysts were used to enhance methanol electro-oxidation in sulfuric acid solution in electrochemical activation [56-58]. Clearly, Pt/support catalysts are preferred in many applications. Bimetallic catalysts such as PtNi, PtCo, and PtCu have been very important to the ORR activity at cathode in PEMFC. The as-prepared nanoparticles were studied in the de-alloying phenomena of Pt binary alloys with the different nanostructures [59-62]. The nanostructured catalysts were reviewed in various FCs. The next catalysts with the Pt loadings for low-temperature PEMFCs and DMFCs will be proposed in various alloy, multi-composition, and core-shell structures. Here, Pt bimetallic catalysts were prepared by impregnating a commercial Pt/C with various transition metals (Pt/M = 3, M: V, Cr, Mn, Fe, Co, Ni, Cu, Zr, Ag and W), and sintering at 900 °C. An increase in electrode activity in ORR tests using a half cell in phosphoric acid solution at 190 °C at the initial stage was observed for PtCr, PtFe and PtAg catalysts due to the surface roughening effect [63]. So far, the Pt catalysts of high cost have

been successfully used in both the anode and the cathode in PEMFCs with high cost. Therefore, binary alloy catalysts with Pt are developed for PEMFCs. Thus, Pt-Ni, Pt-Co or Pt-Cr bimetallic nanoparticles can be used as binary alloy catalysts for the significant enhancement of ORR. In particular, the Pt₃Ni catalysts of the very high ORR activity are investigated [64-66]. A thin-film rotating disc electrode (TF-RDE) method was used for investigating the electrocatalytic activity of high surface area catalysts, and the highest catalytic activity on Pt/C catalysts towards ORR [67]. In PEMFCs, the catalytic activity and stability of the Pt based catalysts are very important. In the cathode of PEMFCs, Pt based alloy catalysts are developed for PEMFCs. Consequently, the issues of sizes, internal nanostructures, surface nanostructures, shapes and morphologies are also important to the stable operations of PEMFCs for the long periods. In addition, the Pt based catalysts with the core-shell nanostructures of the thin Pt shell of around several nanometers have been developed for the next PEMFCs. In particular, the non-Pt catalysts without noble Pt metal are developed. Because noble Pt and Pd metals have the near same catalytic activity of HOR, the Pd based catalysts are studied for the improvements of ORR of PEMFCs [68]. The electro-active sites on carbon nanomaterials electro-catalyzed the reduction of peroxide intermediated from ORR on Pt [69]. The Pd based catalysts can be also used in a combination of Fe, Co, and Cu metals for the improvements of ORR, especially methanol tolerant ORR catalysts. It is clear that stability and durability of the catalysts in the cathodes have importance of the operations of PEMFCs. Therefore, PEMFCs can be improved in high stability in the uses of the special supports such as various kinds of carbon supports (e.g. CNTs ...). It is clearly admitted that Pt-Ru, Pt-Mo, Pt-Ni catalysts ... are used as reformate-tolerant catalysts or impure-hydrogen tolerant catalysts for good stability of next PEMFCs. In addition, Pt based ternary catalysts were discussed for the development of various low and high temperature FCs, PEMFCs, and DMFCs involving in their performance, durability and cost [70-73]. Now, an emergence of the hugely urgent demands of the Pt or Pd based catalysts after high heat treatment processes in both low and high temperatures less than 1000 °C, or up to more than 2000 °C offering better characterizations of catalytic activity and stability can be predicted in future due to the catalysts exhibiting the pristine surfaces, shapes and morphologies in the electrode catalysts. The re-constructions, e.g. (111), (110), and (100) planes [10-12], or collapses of the Pt or Pd based nanoparticles and nanostructures with or without heat treatment in the preparation will be very attractive to research and development of new catalysts for PEMFCs and DMFCs [10-12,41]. There are little evidences of the size, structure and morphology of Pt or Pd based catalysts after high heat treatments in media of H₂ or N₂/H₂. These are major challenges in catalysis science, and Pt or Pd based catalysts for FCs, PEMFCs, and DMFCs. Our catalyst preparation gave a better catalytic activity and stability of HER, ORR, and MOR in an environment of mixture H₂/N₂ avoiding the formation of PtO by heat treatment. In future, the Pt catalysts can be treated at high temperature but their size, nanostructure and morphology in the 10 nm range kept [128-130]. Therefore, the pure Pt or Pd based catalysts used in the electrodes of FCs, PEMFCs, and DMFCs can give better catalytic activity, stability, and good performance of the whole FC systems.

4. Direct methanol fuel cell

4.1. Operation principle

In general, PEMFCs can be categorized into various kinds of hydrogen/oxygen FCs, DMFCs, and direct formic acid fuel cells (DFAFC) according to the use of liquid or gas fuels etc. [74-76]. So far, the economic uses of Pt, Pt-Pd, and Pt-Ru based catalysts as well as catalyst supports have been very crucial to MOR at the anode in DMFCs. To date, methanol can be used in direct chemical-electrical energy conversion in a DMFC in figure 3. The electrochemical reactions occurring in a DMFC are:



The DMFC is attractive because methanol, being a liquid fuel, is easy to transport and handle. In DMFCs, the MOR mechanism at the anode is crucial. Due to the low operating temperature ~60-150 °C, the Pt based catalysts are sensitive to poisoning. Since CO is formed during electro-oxidation of methanol, CO-tolerant catalysts are used for DMFCs. Nevertheless, these have a much lower power density despite the typically high noble metal loading of the electrodes. In addition, the energy efficiency of DMFCs suffers from high electrode over-potential (voltage losses), and from methanol losses by transfer (by permeation) through the membrane used in DMFCs [77-80].

4.2. Catalysts in direct methanol fuel cell

So far, Pt and Pd catalysts have been known as the most important catalysts for the direct methanol oxidation in electrodes, such as anodes and cathodes. The interesting hydrogen adsorption on Pt or Pd catalyst was studied [81-83]. In this context, PVP and TTAB polymer-Pt nanoparticles were synthesized with the same cubic shape and similar particle size (8.1 and 8.6 nm, respectively). They can be used as the potential Pt catalysts for chemical synthesis [84]. The PVP-Pt nanoparticles of good cubic, tetrahedral, and octahedral morphology in the size range of 10 nm were prepared by polyol method with the use of commercial chemicals for potential catalysts for FCs [85-87]. At such very small scale, the well-controlled synthesis of Pd nanoparticles by polyol synthesis routes using PVP polymer proved that the shapes of Pd NPs provide a good opportunity of investigating their catalytic property [88]. The catalytic reactions of Pt and Pd catalyst have been studied in the different combinations of various metals such as Ru, Rh, and Sn etc. with support materials such as carbon nanomaterials or oxides and glasses in both homogeneous and heterogeneous catalysis [89-97]. The new Pt-monolayer shell electrocatalysts of high stability were developed for the FC cathodes. The role of the Pt shell is to reduce the Pt loading significantly in PEMFCs and DMFCs but synergic effects for enhancing catalytic activity and stability. However, it is very difficult to make the Pt monolayers on the core nanoparticles.

Therefore, scientists and researchers have tried to study the easy-to-use chemical and physical methods for highly homogeneous core-shell nanosystems with the use of the thin Pt shells of several nanometers in the size range of 10 nm for PEMFCs and DMFCs. In addition, the good characterization of the engineered nanostructure of the Pt based core-shell nanosystems need to be stabilized after the high heat treatments and preparation processes for obtaining the best catalysts for PEMFCs and DMFCs [98-103], leading to the FC durability up to 200,000 cycles with core-shell catalysts with the Pt-monolayers shells [99]. In all cases, the as-prepared Pt nanoparticles are supported on various carbon nanomaterials for catalytic enhancement. The improvements of Pt catalyst can be performed through by the use of the core-shell nanoparticles or core-shell catalysts that have been proposed. The systems of Pt based, binary, ternary, and quaternary catalysts are proposed in both homogeneous and heterogeneous catalysis [104,105]. Therefore, the Pt based multi-metal catalysts (PtRu or PtRuIr/C) exhibiting high catalytic activities are developed for the MOR [106,107]. A comparison of catalytic activity of Pt, Ru, and PtRu catalysts using $\text{Pt}(\text{NH}_3)_2(\text{NO}_2)_2$ and $\text{Ru}(\text{NO}_3)_3$ precursors for DMFCs was performed. The Pt₅₀Ru₅₀/C catalyst prepared at 200 °C has the maximum electrocatalytic activity toward MOR. The Pt-Ru catalysts have shown the excellent MOR in the stable operations of DMFCs but very high cost [108]. For methanol electro-oxidation, binary, ternary, and quaternary Pt alloy catalysts were prepared. As a result, quaternary alloy catalysts (Pt-Ru-Os-Ir) were considered to be far superior to Pt-Ru in DMFCs [109]. In particular, the successful process of Pt based cubic nanoparticles (Pt-Fe NPs, Pt-Fe-Co NPs), Pt-Fe-Co branched nano cubes, Pt-Fe-Co NPs of low and high Co content was presented. Overall, Pt-Fe-Co branched cubes were used as a good catalyst to show best activity and durability for electrocatalytic MOR [110]. In one study, the evidences of linear sweep voltammetry (LSV) tests indicated that the high peak current density on Pt₂Rh/C is about 2.4 times higher than that of Pt/C in alkaline media direct methanol FCs [111]. So far, the Pt-Au catalysts engineering has become very important to the developments of PEMFCs and DMFCs [112]. For the continuous developments of DMFCs, the Pt-Ru alloy and core-shell electrocatalysts for FCs are discussed in a critical survey [113]. The as-prepared catalysts of PtRuMo NPs supported on graphene-carbon nanotubes (G-CNTs) nanocomposites were developed for DMFCs. The results showed that the catalytic activity and stability of the PtRuMo/G-CNTs catalyst are higher than those of PtRuMo/G and PtRuMo/CNTs catalysts. However, the new trends of using Pt based multi-component catalysts without considering the structural issues lead to the complexity of preparation and synthesis [114]. The Pd-Pt catalysts are recognized as potential candidates for PEMFCs and DMFCs operating at low temperatures [115]. Electrocatalytic activity for ORR and oxygen binding energy was intensively studied in the metal catalysts among the different combinations of W, Fe, Mo, Co, Ru, Ni, Rh, Cu, Ir, Pd, Pt, Ag, and Au. According to the oxygen binding energy by density functional theory (DFT), the volcano-type dependence of ORR was discovered in a high catalytic activity of Pt, Ir, and Ag metal, especially for the very thin Pt and Pd layers as the monolayers. The structural investigation of ORR and oxygen binding energy by the *d*-band model or calculation method of *d*-band center is very crucial to the issues of engineering a novel catalyst [116-118]. In particular, a X-ray absorption spectroscopy (XAS) method was employed in the

characterization of a number of catalysts for low temperature FCs to determine the existent oxidation state of metal atoms in the catalyst, or in the case of Pt, the d-band vacancy per atom. It is a good tool for confirming the structures of the catalyst *in situ* [119]. There is an important discovery of a synergistic effect to being studied. In theory and practice, synergistic effect needs to be intensively investigated in quantum property in respective to the development of bimetallic catalysts of alloy and core-shell nanostructures. In this context, the synergistic effect of core-shell bimetallic nanoparticles gives an excellent catalytic enhancement. In catalytic activity, the shell provides strongly catalytic sites. The core element gives an electronic effect (a ligand effect) on the shell element because the surface atoms of the shell are coordinated to the core in their catalytic reactions. Therefore, the shell is an important factor to control the catalytic properties. In addition, the core-shell bimetallic structures cause better suppression of adsorbed poisonous species [120,140-143]. This effect is discussed in the metallic NPs of hetero-morphologies and hetero-structures that can be as new types of important catalyst [121]. Of all catalysts, the bimetallic nanoparticles have played important roles in promising applications of catalysis, and FCs [122]. The core-shell nanoparticles and nanostructures were intensively investigated [123-124]. The Pt-Ni-graphene catalysts were prepared for the high MOR activity observed [125]. In particular, an important role on the MOR activity of Pt-Co and Pt-Ni alloy electrocatalysts for DMFCs has to be ascribed to the degree of alloying [126]. The interaction of Pd NPs and Pd(111) with CH₃OH and CH₃OH/O₂ mixtures was examined from ultrahigh vacuum conditions up to ambient pressures [127]. Here, the particle size and structure dependent effects in methanol oxidation and decomposition are very crucial to the use of the supported Pd catalysts as well as the good incorporation of the pure Pt into various supports with high homogeneous distribution. In addition, we should find suitable heat treatment in good experimental conditions, and Pt based catalyst engineering to increase catalytic activity and durability.

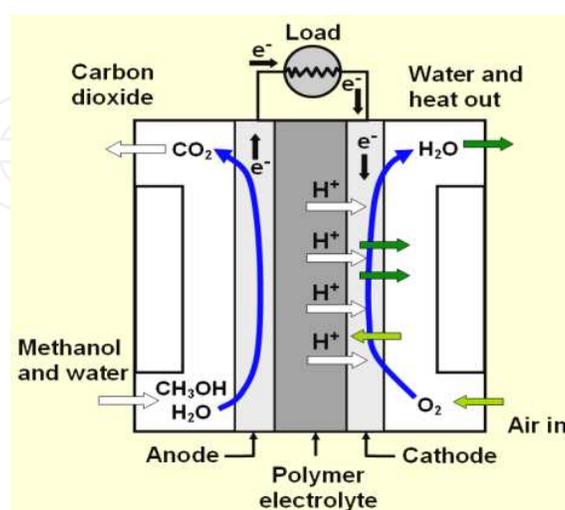


Figure 3. Chemical reactions of direct methanol fuel cell (DMFC)

5. Catalysts and heat treatment

Of interest to scientists, at present the Pt catalysts are used in both the anode and the cathode in DMFCs. However, the Pt NPs showed a variety of sizes, shapes, and morphologies in the different size ranges. The shapes and morphologies of Pt NPs are synthesized in the forms of cube, octahedra, tetrahedra, plate, wire, flower, rod, fiber etc. The certain issues of their particle sizes are studied in the nanosized ranges of 10 nm, 20 nm, 50 nm etc as well as the homogeneous nucleation, growth, and formation of polyhedral nanoparticles. In particular, the range of the Pt NPs of about 10 nm exhibit the highest catalytic activity with the good morphology and shape such as sphere, cube, octahedra, tetrahedra, and polyhedra etc. The high stability and durability of the shape-dependent catalytic activity are needed to be confirmed in the homogeneity of the particle size in a whole nano-system. In the heat treatments of the Pt NPs, the characterization of size, surface, structure, shape, and morphology of Pt NPs need to be preserved to obtain the Pt catalysts of good catalytic activity, stability, and durability for a long time. The new generations of the Pt-Pd core-shell catalysts with the thin Pd shells of less than several nanometers were developed. They showed the excellent catalytic activity. In our recent research, the Pt NPs of less than 10 nm in size were used as the Pt catalysts, which can be used as the standards for any comparison of catalytic activity of new Pt based catalysts. So far, the heat treatment procedures and methods of heat treatments of the as-prepared metal nanoparticles for catalyst engineering in catalysis have not been considered in their very crucial issues of the size, surface, structure, shape, and morphology. The transformations of structure and property of the as-prepared metal nanoparticles in the ranges of 10 nm and 20 nm through heat treatments or sintering of Pt nanoparticles are very critical to nanoparticles as electro-catalysts or catalytic nanosystems for PEMFCs and DMFCs [128]. We need to confirm that Pt nanoparticles with the rough curved surfaces exhibit catalytic activity much better than Pt nanoparticles with flat and smooth surface through the measurement results. The important effects of heat treatment and the removal of poly(vinylpyrrolidone) (PVP) polymer on electrocatalytic activity of polyhedral Pt NPs towards the ORR mechanism have been investigated. The methods of keeping the size, surface structure, internal structure, shape, and morphology were proposed in our catalyst engineering processes, especially heat treatments of the as-prepared PVP-Pt nanoparticles at 300 °C. The loaded electrodes were carefully dried in air for 3 h at 25 °C and heated with the heating rate of 1 °C/min up to 450 °C in air and a keeping time of 2 h in order to remove any organic species. The pure Pt nanoparticles need to be kept in their good characterization of size and morphology in the size range of 10 nm. We proposed that the polyhedral Pt NPs of around 10 nm can be used the standard Pt catalyst in all research of electrocatalysts in PEMFCs and DMFCs due to their higher concentration of surface steps, kinks, islands, terraces, and corners [129-137]. In our research, Pt-Au NPs were prepared by polyol method, which can be used as Pt-Au catalysts for DMFCs [138]. In particular, Pt-Pd alloy and core-shell NPs were synthesized by polyol method. The core-shell NPs can be used for low temperature PEMFCs and DMFCs for the excellent advantages of reducing the Pt total metal weight. Therefore, it is an economic solution of the suitable use of Pt based core-shell catalysts for next FCs. The new

Pt monolayer Pd-Au catalyst of a core-shell structure with double shells was found in a good stability and activity of ORR. The double shells have an outermost shell of Pt monolayer and a sub-layer shell of Pd-Au alloy [139,140]. In our new results and findings, new evidence of fast enhancement of ORR on the electrode of the new Pt-Pd core-shell catalyst in the size range of 25 nm is clearly observed in a comparison with the prepared Pt catalyst in the size range of 10 nm. Therefore, it is important to use core-shell bimetallic catalysts to increase the ORR rate in the electrode catalyst. For the case of Pt-Pd core-shell catalysts, the fast hydrogen-desorption response and high sensitivity in our results after reaching the stable characterization after only the first CV cycle in a comparison to Pt catalyst. This enables the realization of robust and efficient Pt- or Pd-based core-shell catalysts that are extremely sensitive to the fast hydrogen desorption. Most of the alternative method of improving the hydrogen reaction by the core-shell nanostructures can be clearly realized. During the measurement, the electrodes are swept from -0.2 to 1.0 V with respective to the kinds of saturated standard electrodes. There are the specific regions in the cyclic voltammogram (Figures 4 and 5). They show highly and good catalytic activity and surface kinetics for the case of both the Pt catalysts of 10 nm and the Pt-Pd core-shell catalysts of 25 nm. It is clear that the high heat treatments of our catalyst preparation in H₂/N₂ offer the good characterization of the size, surface, structure, and morphology. Therefore, the highly long-term catalytic activity, stability, and durability in chemical and physical Pt or Pd based catalysts are needed in the catalyst layers of FCs, DMFCs, and PEMFCs. The effects of using a suitable temperature range in heat treatment should be suitable to various FCs, for example the better ORR activity. This depends on the operating temperature of various FCs. They were characterized by the chemical activity occurring at the electrode surface. In the forward sweep, the first region assigned to hydrogen desorption is crucial to confirm catalytic activity of the Pt catalysts. The slow kinetics of hydrogen desorption of the case of Pt catalyst was confirmed in the cell before the stabilization of CV was achieved from the first cycle to the twentieth cycle, and the fast kinetics of hydrogen desorption of the case of Pt-Pd core-shell catalyst. Indeed, the results proved the good desorption and adsorption of hydrogen of both Pt catalysts and Pt-Pd core-shell catalyst as evidences of good catalytic activity of two kinds of important catalysts in the preparation process and heat treatment in figures 4 and 5. To evaluate the catalytic activity of the prepared catalysts, the electrochemical active surface area (ECSA) of the Pt catalyst is calculated to be (10.5 m²g⁻¹) in a comparison with that of the Pt-Pd core-shell catalysts (27.7 m²g⁻¹) in our catalytic investigations. Thus, suitable heat treatments or sintering processes of the Pt or Pd based catalysts for obtaining good catalytic activity and stability in the desirable nano and micro structures are very crucial to enhance, and improve the continuous operation of direct chemical-into-electrical energy conversion, high stability and durability of various FCs, PEMFCs and DMFCs for the urgent global challenges of energy and environment. Obviously, the heat treatments can lead to significantly reduce the effects of CO poisoning to the electrodes in PEMFCs and DMFCs. One of the most challenging goals in the heat treatment is to develop successful protocols for keeping the good characterization of the as-preparation Pt NPs such as surface, structure, size, and shape in their nanosized ranges. In our research, the polyol method was used for our

synthesis of the Pt and Pd bimetallic nanoparticles with alloy and core-shell structure. In comparison, we also can control the time and temperature of convenient heat-treatments to the pure Pt or Pt/support catalysts for their better catalytic activity. Clearly, the temperature plays an important role in heat treatments for making the better Pt based catalysts. The shape and morphology of polyhedral-like or spherical-like Pt nanoparticles are crucial in the further study of electro-catalytic activity.

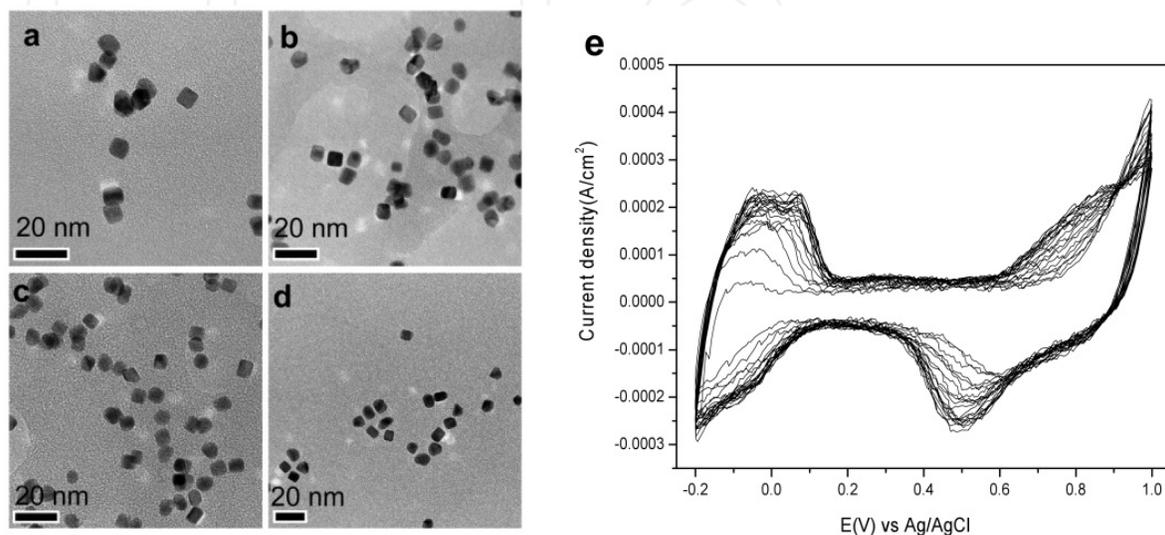


Figure 4. TEM images of the polyhedral Pt nanoparticles. Scale bars: (a)-(d) 20 nm. (e) Cyclic voltammograms of the pure Pt catalysts in 0.5 M H_2SO_4 from -0.2 V to 1.0 V. Reprinted from: Long NV, Ohtaki M, Hien TD, Randy J, Nogami M, *Electrochim. Acta.* 56:9133-9143. Copyright 2011 with permission from Elsevier [140]

It means that the high heat treatment to the as-prepared Pt nanoparticles for the good catalyst can be performed in the ways with various solvents or pure water during their preparation. However, the desirable characterization of size, shape, morphology, and structure need to be kept for the better catalytic activity. Therefore, scientists need provide more research results of Pt based catalysts with heat treatment effects in electro-catalysis. Thus, new Pt based catalysts, electrodes, and membranes need to be considerably studied for the reduction of their high costs but the high whole performance. The effects of heat treatments on size, shape, surface, and structure of the pure Pt nanoparticles (pure Pt catalyst) or Pt based catalysts for catalytic activity, durability and stability can be intensively analyzed by *in situ* TEM and electrochemical measurements as well as the chemical reactions and their kinetics at the surfaces of the only Pt catalyst or Pt/support catalysts in fuel cells.

In electrochemical measurements, we can use electrolyte solution of using 0.5 M H_2SO_4 +1.0 M CH_3OH (a scan rate of 50 mV s^{-1}). Our comparisons of cyclic voltammograms were done between the pure Pt catalysts in the nanosized range of 10 nm, and the pure Pt-Pd core-shell catalysts in the nanosized range of 25 nm in the mixture of 0.5 M H_2SO_4 and 1 M CH_3OH in figure 6. A stable voltammogram was attained after 20 cycles of sweeping between 0 and 1 V. Two oxidation peaks are observed. The good MOR was confirmed in the evidences of the typical peaks at 0.6 V and 0.8 V in the forward sweep, and the other peaks at 0.4 and 0.5 V in

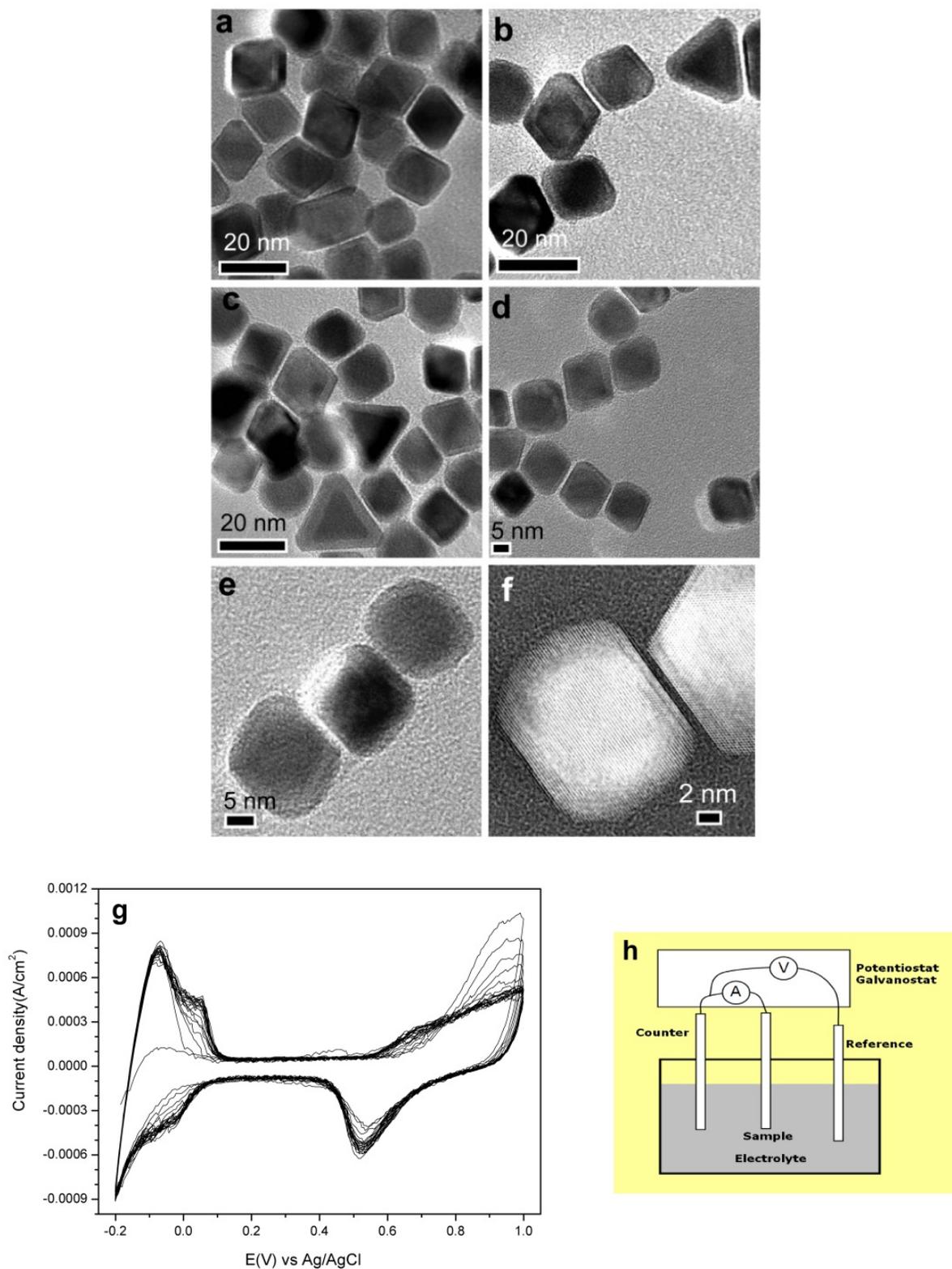


Figure 5. (a)-(f) TEM and HRTEM images of the as-prepared Pt-Pd core-shell. The thin Pd shells protect polyhedral Pt cores. The nucleation and growth of Pd shells are controlled by a chemical synthesis. Scale bars: (a)-(c) 20 nm. (d) 5 nm. (e) 5 nm. (f) 2 nm. (h) Schematic of a standard three-electrode electrochemical cell. Reprinted from: Long NV, Ohtaki M, Hien TD, Randy J, Nogami M, *Electrochim. Acta.* 56:9133-9143. Copyright 2011 with permission from Elsevier [140]

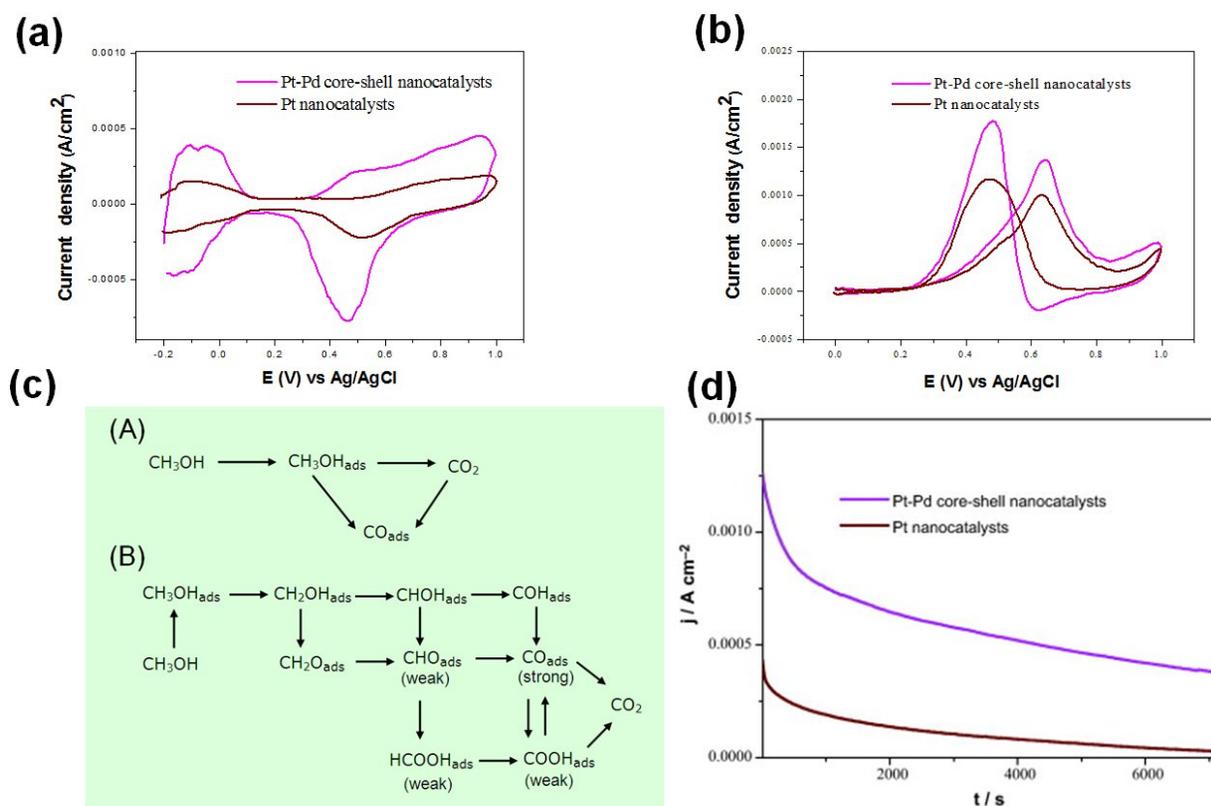


Figure 6. (a) Cyclic voltammogram of Pt catalysts, and Pt-Pd core-shell catalysts on glassy carbon electrode in N₂-bubbled 0.5 M H₂SO₄ electrolyte (scan rate: 50 mV s⁻¹). (b) Cyclic voltammogram towards methanol electro-oxidation of Pt catalyst and Pt-Pd core-shell catalyst. (c) Simple pathways of MOR (A). Possible reaction pathways of MOR (B). (d) Chronoamperometry data of Pt and Pt-Pd catalysts in 0.5 M H₂SO₄+1.0 M CH₃OH and polarization potential about 0.5 V. Reprinted from: Long NV, Ohtaki M, Hien TD, Randy J, Nogami M, *Electrochim. Acta.* 56:9133-9143. Copyright 2011 with permission from Elsevier [140]

the backward sweep. Our results of the MOR mechanisms showed that the two peaks are directly related to methanol oxidation and the associated intermediates. The fascinating high stable characterization was observed for Pt-Pd core-shell catalysts. They showed a very high initial current about 1.29×10^{-3} A cm⁻² in comparison with the Pt catalyst of initial current about 4.33×10^{-4} A cm⁻². In all our research, the samples with the Pt or Pt based catalysts were carried out in the heat treatment procedures at 300 °C and up to 450 °C. The loaded electrodes were dried in air for 3 h at 25 °C and heated with the heating rate of 1 °C/min up to 450 °C in air and a keeping time of about 2 h for the complete removal of any organic species. After heat treatment, the specific size, shape, structure and morphology of Pt nanoparticles were retained in the good conditions of the Pt based catalyst for the CV measurements [141-143]. New hydrogen absorption was found in the Pt-Pd bimetallic nanoparticles [144]. In our research, we suggested that there are the relationships and dependences of electro-catalytic properties on issues of size, internal structure and surface structure, shape and morphology, and composition of Pt or Pd based catalysts in catalysis, biology, and medicine. The homogeneous properties of size, internal structure and surface structure, shape and morphology, and composition of nanoparticles can create novel and

promising properties in catalysis, biology and medicine. According to our research, the effects of the nanostructures can be confirmed in the better catalytic activity. In general, the Frank-van der Merwe (FM), Volmer-Weber (VW), and Stranski-Krastanov (SK) growth modes show the formation of various nanostructures of core-shell nanoparticles [141], such as core-shell bimetallic NPs and oxide-metal NPs [104,141]. It is clear that the formations of novel Pt based core-shell bimetallic nanoparticles the thin-based metal or alloy shells can be controlled in both the FM and SK growth modes for the utilization of Pt metal. The FM overgrowth mode or the epitaxial overgrowth of the thin Pt shells on the metal or oxide cores due to the layer-by-layer mechanism are very crucial to discover most of new Pt based core-shell catalysts for FCs, such as PEMFCs or DMFCs. The core-shell engineered nanoparticles in the nanosized ranges of about 10 nm and 20 nm with the Pt metal shell or the Pt based bimetallic shells or the Pt based multi-metallic shells become an important topic of next research and scientific investigations for FCs. The thin shells can be noble metals such as Pt, Pt-Au, Pt-Pd, Pt based alloys with the use of Ag, Au, Rh, Ru, and Pd metal. The thick cores can be cheap metals such as Ni, Co, Fe, Cu .. and alloys, even and ceramics and glasses. With regards to low-cost issues, we suggest that typical core-shell configurations of bimetallic nanoparticles are proposed in the main goals of designing Pt and Pd based catalysts with the shells of using ultra-low mass of Pt metal or Pt-noble (Pd, Ru, Rh, Au, Ag) bimetals [140-143, 190]. Thus, a variety of the core-shell configurations with the thin Pt shell or the thin Pt based bimetallic shells controllably created in chemical and physical engineering is one of the best ways of the realization of large-scale commercialization and development of FCs, such as PEMFCs and DMFCs. We suggest that noble Au NPs can be used the good core for the Pt shells for DMFCs and PEMFCs. In most cases, Pt-based bimetallic NPs were supported on carbon nanomaterials such as MWCNTs for the catalytic enhancement in the operations of various DMFCs due to their large surface area and good conductivity [145,146]. In addition, the Co-Pt core-shell nanoparticles can be used as potential catalysts in cathode of PEMFCs because of their high stability and durability [147-149]. In many efforts, the catalysts such as Pt-Pd, Pt-Ru, Pt-Rh and Pt-Sn/C exhibiting an improved performance in MOR as anode materials were prepared by ultrasonic method [150,151]. Importantly, the catalytic properties of well-characterized Ru-Pt core-shell NPs were demonstrated for preferential CO oxidation [152]. The metal-oxide nanostructures of Pd or Pt metals and TiO₂ or Zr₂O₃ oxides by self-assembly are proposed for catalysis and FCs. The core-shell nanoparticles and nanostructures will offer potentially promising applications in homogeneous and heterogeneous catalysis, biology and medicine [153,154]. The recent developments of polymer electrolyte membranes for FCs were discussed for improving the long-term stability [155]. The new methanol-tolerant catalysts with the use of Pd nano cubes exhibiting high electro-activity for ORR in the 0.5 M H₂SO₄ solution were confirmed [156,157]. Thus far, the catalysts with the use of the Pt-Pd nanoparticles or the Pt-Pd nanostructures of various size, internal structure, surface structure, shape, morphology, and composition by various preparation methods have been intensively studied for practical applications in various FCs, PEMFCs, and DMFCs. There are the very huge demands of high-surface area catalysts of Pt-Pd NPs supported on carbon nanomaterials that have been used in various FCs, PEMFCs and PEMCs [158-170,188,189]. The nano-porous SiO₂ solids

with Pt or Pd metal nanoparticles were also used [171-172], and they offered higher electro-oxidation current densities for both methanol and ethanol.

5.1. Heat treatment

Before the TEM and HRTEM measurements, copper grids with the prepared nanoparticles were annealed in the heat treatment at 300 °C for 4 h, 6 h or even a half day. The evidences and results of the characterization of size, structure, shape, morphology with the only Pt composition by TEM and HRTEM show the uniform polyhedral Pt nanoparticles synthesized by polyol method with the controlled size in the nanosized range of 10 nm and 20 nm, and sharp shapes and morphologies through an introduction of low contents of AgNO₃ as size, structure, morphology and shape-controlling reagent and the gradual addition of the precursors of PVP and H₂PtCl₆ in the suitable volume ratio. In the characterizations of homogeneous polyhedral morphology and shape, the appearances of the main sharp cubic, octahedral, and tetrahedral shapes of Pt NPs in the controlled growth of (100), (110), and (111) selective surfaces are very good for their applications in catalytic activity, e.g. the ORR and MOR chemical reactions because the polyhedral Pt nanoparticles have at a higher concentration of surface steps, kinks, islands, terraces, and corners [10-12,188]. In addition, the TEM and HRTEM images of Pt NPs by polyol method show interestingly important phenomena of particle-particle surface attachment, self-aggregation, and assembly in the case of the use of the pure Pt NPs or the PVP-Pt NPs. Most of Pt NPs showed various large morphologies and shape after heat treatment at high temperature from 20 to 60 nm for the case of the PVP-Pt NPs [128-130]. The clear overgrowths and structural transformation in the nanosized range of polyhedral Pt nanoparticles annealed at 300 °C for 4 h were observed. Clearly, the morphology of PVP-Pt nanoparticles was significantly changed by heat treatment. During their synthesis, PVP polymer is used to stabilize and control the size and morphology of Pt nanoparticles against their aggregation. In addition, the amount of PVP polymer can bind the nanoparticle surface after the catalyst synthesis. Therefore, PVP or other polymers for the protections of the as-prepared nanoparticles should be removed in the minimal content before the catalytic reactions. In our research, PVP polymer plays an important role to stabilize their morphology and size of these Pt nanoparticles. Despite the fact that these Pt nanoparticles were put on copper grids, they still have their interfacial interactions to their particle-particle surface attachments, aggregation, and self-assembly leading to form the larger and irregular Pt particles or the larger particles in the forms of hetero-morphologies and hetero-nanostructures in the final formation by the heat treatment. It is known that Pt nanostructures with the issues of size, shape and morphology under heat treatment procedures become important to further investigation in the confirmation of catalytic activity in catalysis. The critical issues of size, shape and morphology of colloidal nanoparticles need to be intensively studied in different media (condense, liquid, and gas) for the certain confirmations of high and long-term stability, high durability, and safety in their practical applications in catalysis, biology and medicine. In our experimental methods, in order to obtain the pure Pt catalyst for the standard catalyst of the standard nanosized range of 10 nm in investigations of catalytic

activity, PVP polymer of the as-prepared product of PVP-Pt nanoparticles was removed. Therefore, the pure Pt nanoparticles for electrochemical measurements can be obtained by using centrifuge. The resultant solution of as-prepared nanoparticle was washed by using the suitable mixtures of acetone and followed by centrifugation at 5,000 rpm up to 15,000 rpm. Next, the black solid product was re-dispersed in the ethanol/hexane mixtures with a suitable volume rate. The resultant mixture was centrifuged in order to obtain the fresh product. Experimentally, the procedures of washing and clean Pt nanoparticles in the mixture of ethanol and hexane were done many times. After washing PVP polymer and contaminations in the as-prepared product, the nanoparticles were dispersed in milli-Q water in order to achieve the fixed density of colloidal Pt nanoparticles at 1 mg/mL with the aid of ICPS analyzer. The working electrode was a glassy carbon rod (RA-5, Tokai Carbon Co., Ltd.) with a diameter of 5.2 mm. Then, the electrode surface was cleaned and activated by using a kind of polishing-cloth (Buehler Textmet) with alumina slurry (Aldrich, particle size of 50 nm), followed by washing any contaminations with milli-Q water. The step-by-step procedures were repeated until the surface looked like a mirror. Then, a fixed weight of some μg (e.g. 5 μg or 10 μg) of the Pt loading was set onto the surface of the polished electrode for the electrochemical measurements. The loaded electrodes were dried in air for 3 h at 25 °C and heated with the heating rate of 1 °C/min up to 450 °C or 723 K in air and a keeping time of 2 h in order to remove organic species [128-130]. We used a very slow heating rate to avoid the serious problem of sintering of the pure nanoparticles so that the layer catalyst is the nanoparticles. The electrodes were allowed to cool normally and then exposed into the flow of the mixture of H₂/N₂ gases (20%,80%) at 100 °C for 3 h to reduce the existence of PtO and ensure a pristine catalyst surface. In order to improve the mechanical stability of electrode surfaces, Nafion® solution, e.g. 10 μL of 5 wt.%, was added onto the electrode and followed by drying in air for a long time, e.g. overnight, before the electrochemical measurements. The cyclic voltammetry experiment was performed at room temperature using a typical setup of three-electrode electrochemical system in figure 5(h) connected to Potentiostat (SI-1287 Electrochemical Interface, Solartron). The cell was a 50-mL glass vial, which was carefully treated with the mixture of H₂SO₄ and HNO₃, and then washed generously with milli-Q water. A leak-free AgCl/Ag/NaCl electrode (RE-1B,ALS) served as the reference and all the potentials were reported vs. Ag/AgCl. The counter electrode was a Pt coil (002234,ALS) [128-130, 140-143]. The electrolyte solution was bubbled with N₂ gas for 30 min before every measurement. This N₂ blanket was kept during the actual course of potential sweeping. For the base voltammetry, the electrolyte was a solution of 0.1 M HClO₄ that was diluted from 70% concentrated solution (Aldrich) using milli-Q water. Additionally, 0.5 M H₂SO₄, H₂SO₄ and 1 M CH₃OH are prepared for electrochemical measurements. The potential window between -0.2 to 1.0 V with a sweep rate of 50 mV/s was used. For the methanol oxidation, the electrolyte was added with 1.0 M methanol in milli-Q water. The system measurements were cycled until the stable voltammograms were achieved. The electrochemical surface area (ECA) or ECSA was estimated by considering the area under the curve in the hydrogen desorption region of the forward scan and using 0.21 mC/cm² for the monolayer of hydrogen adsorbed on the surface of Pt catalyst [13,174]. The CO poisoning issues or phenomena of CO-stripping voltammetry of the Pt catalysts cause a

significant decrease in the overall efficiency of DMFCs. In all CV research, we did not observe CO poisoning in the CV data. The evidences proved that heat treatments are very important to engineer the best Pt catalyst or the better Pt based catalyst for FCs, PEMFCs, and DMFCs. In the developments of FCs, PEMFCs, DMFCs, novel Pt and Pd based core-shell bimetallic nanosystems or Pt and Pd core-shell catalysts will be the next catalysts with use of the thin Pt or Pt-Pd shells on the thick cores (metals, oxides, glasses, and ceramics) in the nanosized ranges of 10 nm, 20 nm and 30 nm. The thin Pt metal shells or Pt based noble bimetal (noble Pt-Pd, Pt-Ir, Pt-Ru, Pt-Rh, Pt-Au, Pt-Ag) thin shells can be tuned to be several nanometers on the metal or alloy cores in the ranges of 10 nm, 20 nm and 30 nm, and so on through the controlled synthesis and preparation processes. Unfortunately, quantum-size, structural and surface effects of metal nanoparticles around 10 nm in electro-catalysis are not fully understood in their chemical and structural changes.

5.2. Stability and durability

With respect to the heat treatment, electrocatalytic characterizations of the pure catalyst with our as-prepare products of Pt nanoparticles showed highly good quality, long-term stability and durability. Thus, the significant effects of time and temperature during heat treatment for the pure Pt catalyst or Pt/support catalysts are crucial. In our research, the findings and results involve in the cyclic voltammograms of polyhedral Pt nanoparticles with the different removal of PVP polymer acquired at 50 mV/s in 0.1 M HClO₄ solution (or in 0.5 H₂SO₄ or in 0.5 H₂SO₄ and 1 M CH₃OH). The voltammograms data proved the typical shape for the base voltammetry for the high activity, stability and durability of our catalysts used [98,99,129]. The very high activity, durability and stability in FCs described were achieved up to 200,000 cycles with the use of core-shell catalysts with the Pt-monolayers shells in the cathode as important scientific evidences [99]. In our interesting research, the structural effects of low and high-index planes of the fcc structure of Pt catalyst were confirmed in electrochemical measurements, typical low-index planes of (111), (110), and (100) or more high index planes (hkl). The Volmer-Tafel and Volmer-Heyrovsky mechanisms are observed in hydrogen reactions. Most of ORR evidences showed good oxygen reduction. Therefore, our results showed the important evidences of the catalytic activity of the Pt catalyst or Pt based catalysts with alloy structures or core-shell structures. The ECA of the Pt catalyst the use of the Pt nanoparticles washed and heated showed the best catalytic activity (ECA=10.53 m²/g), better than Pt catalyst the use of the Pt nanoparticles heated only-Pt nanoparticles (8.56 m²/g), and better than Pt catalyst the use of the Pt nanoparticles of washed-only Pt nanoparticles (6.75 m²/g). The values proved that the high stability and durability of the catalyst preparation, processes of heat treatment, methods of washing and clean the as-prepared Pt nanoparticles for the pure Pt catalyst. However, we should find a good process of heat treatment to avoid particle sintering in the electrodes at high temperature more than 450 °C and keep the good characterizations of size, internal structure, surface structure, shape and morphology of the Pt nanoparticles or the Pt based nanoparticles for the pure Pt based catalysts for FCs, PEMFCs and DMFCs. Therefore, we propose that homogeneous

polyhedral Pt nanoparticles under control in the size, shape and morphology in the nanosized range of 10 nm should be used the standard catalyst in the scientific investigations of catalysis for FCs, PEMFCs and DMFCs. Our electrochemical measurements were performed by the use of the pure Pt catalysts of polyhedral Pt nanoparticles or the Pt based catalysts in alloy and core-shell structure in the mixture of 0.1 M HClO₄/1 M methanol (or 0.5 H₂SO₄/1 M methanol). In these CV measurements, the stable voltammograms are attained after about 10-20 cycles of sweeping between -0.2 to 1.0 V potential range. The typical two oxidation peaks are observed in the evidences of methanol oxidation. The first one is between 0.6 and 0.7 V in the forward scan, and the other at around 0.4 V and 0.5 V in the reverse scan [129]. The two peaks showed the good methanol oxidation and its associated intermediate species. Our results of methanol oxidation with the use of the pure Pt catalyst prepared are agreement with other scientific reports. The peak current density in the forward scan serves as benchmark for the catalytic activity of Pt nanoparticles during methanol dehydrogenation. For the prepared catalyst samples, its values are 7.62×10^{-4} A/cm² (washed-only samples), 8.75×10^{-4} (heated-only samples), and 9.90×10^{-4} (washed and heated samples), respectively [129]. Therefore, the as-prepared Pt nanoparticles should be washed with organic solvents before heating them at a specific temperature. It is known that PVP can be polymer that only protects the as-prepared Pt nanoparticles in the solution products that seriously decrease the catalytic activity of Pt nanoparticles in MOR. Therefore, PVP or other polymers should be completely removed in the centrifugation processes by centrifuge systems for the pure Pt and Pd based catalyst before high heat treatments for to enhance catalytic activity of Pt nanoparticles for FCs, PEMFCs, and DMFCs, primarily towards methanol electro-oxidation (MOR) in DMFCs.

6. Prospects and conclusion

In the development and commercialization of various FCs, PEMFCs, and DMFCs, the next Pt and Pd based bimetal nanoparticles of internal structure, surface structure, shape and morphology in the nanosized ranges, typically 10 nm, 20 nm, and 30 nm are the best potential catalysts for a significant reduction of the very high costs of various FCs, PEMFCs, and DMFCs. The aim of this chapter is to demonstrate that the urgent demands of studying and synthesizing for the next Pt based catalysts of highly long-term stability and durability are crucial to create low-cost products of PEMFCs and DMFCs. The low cost of low and high temperature FCs, PEMFCs and DMFCs is an extremely important factor for large-scale commercialization. The low-cost Pt and Pd based catalysts can be the good solution to the big challenges of the costs of low and high temperature FCs, PEMFCs, and DMFCs. The modifications and improvements of the catalyst layer materials, and their synthesis become important factors. It should be stressed that next low and high temperature FCs for direct conversion from chemical energy into electrical energy will be very crucial to offer potential applications in portable power supply for mobile use or portable devices or transportation vehicles. Thus, large-efficiency FCs for direct energy conversion via chemical reaction into electricity can be commercially realized in near future.

Author details

Nguyen Viet Long

Department of Molecular and Material Sciences, Interdisciplinary Graduate School of Engineering Sciences, Kyushu University, 6-1 Kasugakouen, Kasuga, Fukuoka, Japan

Department of Education and Training, Posts and Telecommunications Institute of Technology, Nguyen Trai, Ha Dong, Hanoi, Vietnam

Department of Materials Science and Engineering, Nagoya Institute of Technology, Gokiso-cho, Showa-ku, Nagoya, Japan

Laboratory for Nanotechnology, Ho Chi Minh Vietnam National University, Linh-Trung, Thu-Duc, Ho Chi Minh, Vietnam

Cao Minh Thi

Ho Chi Minh City University of Technology, Dien-Bien-Phu, Binh-Thach, Ho Chi Minh City, Vietnam

Masayuki Nogami

Department of Materials Science and Engineering, Nagoya Institute of Technology, Gokiso-cho, Showa-ku, Nagoya, Japan

Michitaka Ohtaki

Department of Molecular and Material Sciences, Interdisciplinary Graduate School of Engineering Sciences, Kyushu University, 6-1 Kasugakouen, Kasuga, Fukuoka, Japan

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