The Study of Pt and Pd based Anode Catalysis for Formic Acid Fuel Cell

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Abstract
Detailed investigation of HCOOH electro-oxidation started about five decades ago, with the advent of modern potentiodynamic techniques, driven initially by the purpose of elucidating some of the most interesting and challenging electrode kinetic problems. Many pioneering works that withstood the test of time and the continuous sophistication of surface electrochemistry techniques were published in the 1960s. Stimulated results were obtained, such as: (i) phenomenological interpretation of anodic polarization curves (e.g., Determination of Tafel parameters), HCOOH oxidation on Pd and Pt catalysts; (ii) discovery of the catalytic effect with respect to Pt and Pd for HCOOH oxidation; (iii) investigation of the potential dependent adsorption of HCOOH on Pt and Pd catalysts which are accompanied by a dual pathway mechanism and (iv) formic acid concentration, temperature effects and crossover of nafion membrane.

Keywords: Formic acid; Fuel cell; Anode catalysis; Platinum; Palladium

Introduction

Overview

The energy demand in daily life grows very fast, research on new energy sources has attracted most attention in the past few years. Formic acid fuel cells are categorized into proton exchange membrane fuel cell, using formic acid as fuel. Formic acid fuel cell has special features when compare with methanol and hydrogen fuel cells and it is studied widely, due to its high energy conversion rate, fast response rate, easily be transported and stored, is less poisoning to Pt-based anode catalysts and it is environmental friendly [1-3].

The catalyst is one of the main concerns for fuel cell system to perform properly. Many researchers are stressed to find out the best formic acid fuel cell catalyst. Pt nanoparticles show high catalytic activity on the anodic oxidation reaction of formic acid. However, the formic acid fuel cell anode catalyst has some challenges, such as high cost, the low catalytic activity, and easily poisoned by carbon monoxide (CO), which is one of the intermediate products of the fuel cells [4]. In order to handle these issues, some effective methods including incorporating transition metals into Pt, the addition of transition metal oxides and sulfides, using supporting substrate, and replacement of Pt incorporating transition metals into Pt, the addition of transition metal oxides and sulfides, using supporting substrate, and replacement of Pt based catalyst by Pd catalyst have been successfully used to reduce the amount of Pt used, enhance catalytic activity and show their excellent electrochemical properties.

It is well known that Pt and Pd are the two most effective electrocatalysts for the formic acid oxidation [4-6]. On Pt surface, the formic acid oxidation via the indirect pathway is limited by significant amounts of CO as poisoning intermediate accumulating on the catalyst surface and blocking active sites of Pt, whereas the formic acid oxidation on Pd surface proceeds in the direct dehydrogenation pathway to form CO2 [7-9]. By bearing in mind this special characteristic of Pd catalyst together with its low cost and high abundance impress more researchers to use Pd as a primary catalytic metal for formic acid fuel cell. Several approaches exist to further increase the formic acid oxidation efficiency of Pd: (1) alloying to combine the merits of Pd with other metals, including Pd-Pt [10], Pd-Au [11], Pd-Cu [12], and Pd-Ni [13]; (2) developing better catalyst supports to disperse these nanostructures to prevent aggregation and maximize electro catalytic activity of Pd, with graphene as an excellent choice due to its huge surface area, high electrical conductivity, and excellent catalytic activity [14]; (3) building specific shape, architecture and structural arrangement, such as core-shell structure [15], Pd Nano chain networks [16], three dimensional palladium nanoflowers [17] and Pd nanorods [18], (4) adding co-catalyst to the catalyst system, through which a strong electronic interaction between them may lead to better performance, e.g., TiO2 [19] and Ni2P [20].

Transition metal carbides (TMCs) have attracted a significant amount of attention over the past few years as electrocatalyst support materials. TMCs are interesting because of their similar electronic structures to noble metals near the Fermi level (i.e., WC and Pt). WC has been studied as catalysts support, and as catalyst for oxygen reduction reaction (ORR) [21,22], methanol oxidation reaction ( MOR) [23], formic acid oxidation [24] and hydrogen evolution reaction (HER) [25]. It is important to mention that catalytic performance of electrocatalysts is closely related to their shape and configuration, therefore formation of WC Nano crystals with controllable shape and structure is of considerable research interests. Wang et al. [26] reported the synthesis WC Nano rods through size-controlled hydrothermal reaction of WO3 Nano rods, mesoporous WC/C by a hydrothermal reaction route [27], and WC nanowall using high-vacuum chemical vapor deposition [28]. However, they faced some difficulties to obtain small WC Nano crystals (especially sub-10 nm) with controllable morphology and structure. Recently, He et al. [24] synthesized hexagonal prism-shaped WC Nano crystals of 5 nm in size via a microwave assisting route. Their finding showed that WCP Nano crystals were dominated by (01-10), (10-10) and (1-100) facets with a preferred orientation of [0001]. Furthermore, Pd NP’s were loaded onto the WCP/G to produce the Pd-WCP/G catalyst, its electrochemical catalytic activity studied via formic acid oxidation. Compared to Pd/C, the Pd-WCP/G displays a remarkable promotion as catalyst for formic acid oxidation [29].

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The mechanism of the direct formic acid fuel cells

Formic acid is a strong electrolyte, expected to promote the transport of electrons and protons on the anode of the fuel cell. The anodic catalysts for formic acid fuel cell oxidation with an observed 7-fold increase in peak current density on Pt-WO3/G electrode and significant enhancement in durability as well. The main purpose of this work is to introduce the catalytic activity of different Pt and Pd-based catalysts for formic acid fuel cell oxidation.

The scope of this review

Briefly, Section 1 of the present review summarizes the functioning of formic acid fuel cell, the benefits of DFAFCs, and the main challenges hinder the commercialization of DFAFCs catalysts. Section 2, explains Cell configuration of Direct Formic Acid Fuel Cells (DFAFCs). In section 3, Crossover of formic acid through Nafion® membranes is presented, section 4 contains some Challenges in the Operation of DFAFCs, section 5 covers intermediate of formic acid oxidation, section 6 reports some catalytic activity of different Pt and Pd-based anode catalysts for formic acid fuel cell oxidation extracted from recent publications. The last section describes the formic acid fuel cell design and motivation of our study.

The theoretical open circuit potential (OCP) for DFAFCs from the Gibbs free energy, equals 1.48 V. OCP for formic acid fuel cell is higher than the direct methanol fuel cell from the point of dynamics, only with two protons a molecular formic acid could be oxidized, in some cases, it can be done in one step reaction, so the electrochemical polarization is smaller than direct methanol fuel cells. Compared with the other proton exchange membrane fuel cells, formic acid showed many advantages as a fuel. Electro-oxidation of formic acid has attracted much attention, in the early research, the electro-oxidation of formic acid proved to be occurred via bifunctional mechanism, including dehydrogenation (direct pathway), and dehydration (indirect pathway). In the former way, formic acid is directly oxidized to form CO2 via dehydrogenation reaction without forming CO intermediate (COad's) on the anode. While the indirect pathway proceeds first through the formation of CO poisonous intermediate which is oxidized into CO2 as a final product. The direct and indirect pathways are highlighted here after [31-33]:

Direct pathway: HCOOH→CO2+2H++2e−
Indirect pathway: HCOOH→COads+H2O→CO2+2H++2e−

COad’s produced in dehydration reaction, is easily to be adsorbed on electrode, which could lead to poison the catalyst, as a consequence the catalytic activity decreases. Because the potentials for indirect pathway is higher than the potential for the direct pathway, active sites of catalyst is covered by COad’s, so decrease of poison. In order to overcome this problem, researchers do a lot of works to improve the performance of formic acid fuel cell. The main factors which cause the poisoning of anodic catalyst are formic acid concentration and the type of catalyst used.

The effects of concentration towards DFAFC performance: In the study conducted by Hong et al. it has been proven that 5.0 M of formic acid is the optimum concentration for 4-cell stack [34]. While Rice et al. experimented that 2M formic acid produce relatively and the activity increase with the feed concentration of the formic acid. The maximum current that have been observed by Rice et al. [35] at 12 M of formic acid is 134 mA/cm² and the open circuit potential, OCP of the cell is relatively high, 0.72 V. The decreasing of cell performance with the increasing formic acid concentration might be due to some reasons such as catalyst poisoning, formic acid crossover from the anode to cathode through the membrane, diffusion barriers within the carbon cloth and dehydration of the membrane [35]. Higher concentration of formic acid required higher fuel supply rate which will cause higher fuel crossover [36], and hence reduces the cell performance.

Table 1: Performance of direct formic acid fuel cells for different catalyst.

| Catalyst | Open OCP (V) | Current density at 0.5 V (mA/cm²) | Power density at 0.26 V (mW/cm²) |
|----------|-------------|-----------------------------------|----------------------------------|
| Pt/Pd    | 0.91        | 62                                | 41                               |
| Pt       | 0.71        | 33                                | 43                               |
| Pt/Ru    | 0.59        | 38                                | 70                               |

Table 1 shows that Pt/Pd catalyst obtains higher open potential, 0.91 V compared pure platinum and Pt/Ru while Pt/Ru catalyst gives the most power at low voltage 70 mW/cm² at 0.2 V compared to pure platinum and Pt/Pd. Hence, it shows that the addition of palladium
enhances the rate of formic acid electroxidation through direct reaction mechanism [38]. Andante et al. reported a good catalyst which demonstrates high oxidation and low onset potential. From their study, they observed that by adding tin (Sn) even in a small amount into carbon supported Pd catalyst can vigorously increase the current density of formic acid oxidation and shift the onset potential toward negative compared with that of Pd/C [39].

Cell Configuration of Direct Formic Acid Fuel Cells (DFAFCs)

Direct formic acid fuel cells (DFAFCs) can be classified into three type of operation which are active DFAFCs, active air breathing DFAFCs and passive air breathing DFAFCs. For active DFAFC to operate, formic acid is supplied to the anode side by liquid pump and the air is supplied straightly to cathode side by using compressed gas cylinder. While for active air breathing DFAFC, the cathode is exposed to ambient air instead of using a cathode by using cathode flow field [2]. The general configuration of the formic acid fuel cell is shown in Figure 2.

Current collector

Current collector is a crucial part in a fuel cell. It enables the conduction of current while delivering fuel and oxygen. For conventional current collectors using titanium foil coated with gold, stainless steel plate and graphite plate [36].

Gasket

Gasket should be chosen of suitable thickness and material in order to ensure the cell sealing and reducing the contact resistance [36,40]. The optimum gasket should have the combination of thickness, hardness, chemical compatibility with formic acid and bolt torque [40]. Gasket is functioned to ensure that the cell have sufficient sealing and good contact between the current collector and catalyst layer [36].

Membrane

It is not surprising to say that formic acid has a good compatibility with Nafion® membrane. Fundamentally, the flux of formic acid through a Nation® membrane rise with the increasing formic acid concentration and temperature. Kim et al. examined the effect of membrane thickness on the cell performance and found that Nafion® 117 is the optimized membrane at 12 M of formic acid concentration which is 84 mw/cm² at 0.43 V [41].

Membrane electrode assembly

Membrane electrode assembly consists of membrane, and both electrode of anode and cathode which is combined by hot-pressed [42]. Initially, catalysts ink is prepared by sonication of small chain alcohols, monomer solution and catalyst powder [40]. The widespread method in the fabrication of membrane electrode assembly (MEA) by using ‘direct catalyst paint’ technique to apply the catalysts layers [1,35,41,43]. Usually, MEA is hot-pressed at 135°C for 2 minutes at appropriate pressure. The anode catalyst ink is prepared by using Pd black at some suitable ratio. Then, the solution is ultrasonicated in an ice bath. The cathode catalyst ink also is prepared in the same approach using Pt black instead of Pd black [41].

Reservoir

Poly(methyl methacrylate) (PMMA) board is strong enough to support the fuel of formic acid as it is acid resistant to prevent the eroding of the cell. In other hand, PMMA have low conductivity of 19 Wm⁻¹K⁻¹ which prepared the cell to withstand high temperature. Single cells in series will produce higher voltage with independent fuel reservoir for each cell will improved the situation water electrolysis since formic acid is a good electrical conductor [34,36].

Crossover of Formic Acid through Nafion® Membranes

The common feature of the PEM-based fuel cell is that, the fuel fed to the negative electrode (anode) can permeate the membrane to the positive electrode (cathode). This phenomenon reduces fuel utilization, results in a detrimental mixed potential, competes for and potentially poisons the cathode catalyst and thereby decreases the efficiency of the oxygen reduction reaction [44,45]. For liquid fuels, it can also cause flooding of the cathode catalyst layer [44]. One of extreme advantage of formic acid for use in PEM fuel cells is low crossover through Nafion® membranes. However, this does not mean that the crossover of formic acid is negligible, and crossover is still a significant issue limiting the performance of DFAFCs. Recent research work examined and quantified the crossover behavior of formic acid in DFAFCs [46-49]. Rhee et al. [49] studied the permeation of formic acid through Nation® 112 and Nafion 117 membranes at room temperature. Wang et al. [48] performed experiment on formic acid crossover through a Nation® 115 membrane at different temperatures and formic acid concentrations. Generally, the flux of formic acid through a Nation membrane increases with increasing formic acid concentration and temperature [48,49].

Jong et al. [47] studied the crossover of formic acid in a real DFAFC operating environment under various operating conditions. The crossover behavior of formic acid was similar to that under the non-fuel cell conditions used by Rhee et al. [49] and Wang et al. [48]. As summarized in Figure 3, crossover of formic acid increases with increasing formic acid concentration, but decreases with increasing current density as more formic acid is consumed at the anode. Methanol crossover was found to be ca. 6 times greater than that of formic acid under the same cell operating conditions, when expressed in terms of the crossover current (i.e., the current required to oxidize the fuel reaching the cathode) [47]. When fluxes (molcm⁻² s⁻¹) are compared, the difference is only a factor of two [47,48] or less [46], because oxidation of formic acid to CO₂ requires only two electrons while oxidation of methanol requires six electrons. This is contrary to Rhee et al. [49] original report of a two order of magnitude difference because they used an inaccurate crossover value for methanol in their comparison.

Challenges in the Operation of DFAFCs

The decreasing of cell performance might be cause of decreasing formic acid concentration, catalyst dissolution, fuel crossover and
flooding at cathode [36]. The crossover problem is the main barrier which hinders the liquid fuel cell operation.

**Mass transport limitation in DFAFC**

The discussion of Rice et al. stated that the constraint to the mass transport in formic acid to the anode side might be arisen either the Nafion® within the catalyst layer or carbon cloth or both [35]. The mass transfer limitation on the anode side of DFAFCs is very significant and it is dependent on the anode diffusion media property as well as formic acid concentration. The formic acid hygroscopic property of hydrophobic diffusion media is the reason of this limitation on the anode diffusion media [50]. Mass transfer resistance can be managed by using high concentration of formic acid to reduce the diffusion force effect from the gradients of formic acid concentration [36]. Hence, the mass transport limitation of formic acid in catalyst layer and hydroscopicity of concentration formic acid fed on the anode will assign the applicable range for formic acid concentration. The MEA is damaged by a high concentration of formic acid due the dehydration process [1].

Crossover problem that occurs in DFAFCs may be due to the different methods of gas diffusion layer (GDL) preparation, loading of the catalysts, MEA fabrication and pre-conditioning [40]. In Rhee’s et al. experiment, it has been concluded that permeation rate of formic acid through Nafion® membrane is depending on formic acid concentration and also the membrane thickness [49]. At higher flow rate of fuel, the consumption of oxygen decreases but resulting a better performance due to great reduction of fuel crossover [51,52].

**Critical water management and crossover of formic acid**

The internal resistance in the cell is contributed by water content in the membranes. For a long-term operation, water is accumulated at cathode side. To manage the water that is processed, a coating process is done on at carbon cloth at the cathode side with Teflon. Highly concentrated formic acid produces easier water management because it has less influence on the activity of some catalysts [1,33,36,49].

**Catalysts poisoning**

To improve the performance of Formic acid fuel cell, Pd-based catalysts are recommended while reducing the cost of Pt based catalyst. However, there is still some inquiries about using Pd catalysts due to their deactivation during formic acid electro-oxidation. Zhou et al. conclude that deactivation of Pd catalyst could be improved by regeneration with pure water [51].

**Intermediate of Formic Acid Oxidation**

Formic acid can be oxidized via three different paths. These three paths are illustrated in Figure 4 (a schematic adopted from Behm [53]). The first path, depicted in the middle of Figure 4, involves the direct decomposition of formic acid into CO$_2$+2H$^+$ and 2e. The second, depicted at the bottom of Figure 4, involves an indirect route in which formic acid is first dehydrated to CO. CO is then re-oxidized in a second step to form CO$_2$. The third path, depicted at the top of Figure 4, involves the conversion of formic acid into a surface formate intermediate that can subsequently react to form CO$_2$.

**Reactive intermediate of FAO (controversy over formate)**

With regard to the reactive intermediate of FA oxidation on Pt electrodes, Sun et al., and Lipkowski and Ross stated that a carboxylic acid species adsorbed via the carbon atom (–COOH) [54-56] is the rate determining intermediate for the direct pathway. In 2002, Osawa et al. [57] investigated adsorbed formate (HCOO) as the reactive intermediate of formic acid oxidation at Pt film electrode and they concluded that formate is the rate determining step based on the detailed in situ electrochemical ATRSEIRAS investigations, which finally results CO$_2$ as the end product.

Later on the same research team also identified formate as intermediate at Pd electrode by using the same method at highly applied potential [58]. The contribution of formate in the direct pathway mechanism remain controversial. Cuesta’s group [59,60] was not agreed with the opinion of Osawa; they claimed that the adsorbed formate is the key intermediate in both the dehydrogenation and dehydration pathways and bimolecular decomposition of adjacent adsorbed formate with a subsequent electron transfer contributes to...
the oxidation current in the dehydrogenation pathway on Pt and Au, suggesting that no free metal site is necessary for formate oxidation.

More recently, Grozovski et al. [61] demonstrated that the current for FA oxidation is directly proportional to the formate coverage on Pt single crystal electrodes by comparing the charge for adsorbed formate and the recorded oxidation current. Chen et al. [53] used the same techniques coupled with a thin layer electrochemical flow cell to find out the intermediate of formic acid oxidation through direct pathway mechanism. Their outcome showed that formate is a spectator rather than a reactive intermediate and a three-pathway mechanism has been proposed. A schematic representation of a three-pathway mechanism is presented in Figure 4.

Neurock et al. [62] used DFT and suggested that the adsorbed formate is relatively stable while an experimentally undetectable *COOH intermediate is the active intermediate.

The DFT calculation which has been done by Wang et al. [63] to study FA oxidation on the Pt (111)/H2O interface with a continuum solvation model. According to these authors formate is neither a reactive intermediate nor a spectator for FA oxidation, but a template that promotes the adsorption of FA in a CH-down configuration, which is a reactive precursor leading to CO2. In the most recent work done by Chen et al. [64], they proposed that the oxidative adsorption of formic acid is the rate-determining step and that the reactive intermediate in the direct pathway is ascribed to the corresponding unspecified X species, based on a potential oscillation modeling on the Pt.

**Poisoning Intermediate CO**

Adsorbed CO (COad) is identified as the major poisoning species formed through the dehydrogenation pathway. Such COad can be removed only by applying a high potential at anode catalyst resulting to a significantly suppressed dehydrogenation pathway and low catalytic activity at lower potentials. Because the dehydrogenation pathway is highly desired for the best utilization of the chemical energy stored in FA, many efforts have been made to promote this pathway.

The concept of the "ensemble effect" was initially borrowed from the hydrocarbon catalysis on Bi modified Pt surfaces [65], referred to the effect that a reaction requiring a large ensemble of surface active sites can be suppressed by diluting the active sites with a second inert metal, the so-called “third-body”.

On Pt electrodes, it is widely accepted that the "ensemble effect" or "third-body effect" plays a major role in improving the FA oxidation performance, which has been extensively reviewed by Markovic and Ross [66].

Diverse proposals have been put forward to explain the deactivation during (electro)chemical dehydrogenation of FA on Pd surfaces such as the aggregation of Pd nanoparticles [67] and surface blocking by CO2 bubbles [68]. Other than these physical inhibitions, another important suggestion points to the accumulation of inactive (poisoning or spectator) intermediates on surfaces. It has been widely recognized that the dehydrogenation pathway of FA oxidation is not much favored on the Pd-based electrode surfaces and the absence of CO poisoning leads to a much higher initial catalytic activity on Pd at lower potentials as compared to that on Pt surfaces [69]. In 2004, Masei’s group [43] first explored the use of Pd black as an alternative anode catalyst for DFAFCs and demonstrated significant performance enhancements. Further investigations reveal that the deactivation during FA oxidation is a severe obstacle on Pd catalysts for their practical applications [2,3]. Hence much efforts have been paid to disclose the nature of the deactivation process. In 1988, Solis et al. [70] studied FAO on Pd electrodes with on-line mass spectroscopy and suggested the presence of strongly adsorbed residues at a small coverage. Recently, anodic stripping measurements [42,67,71] on carbon supported Pd nanoparticles that were pre-polarized in a concentrated FA solution for hours and then transferred to a HClO4 solution revealed the presence of so-called "COad-like residues" on Pd surfaces. It was also reported that the existence of Pd-O(H) species [72] or the application of a positive potential treatment [51,67,73] to the Pd electrode may facilitate the removal of such "CO-like" species and hence recover the performance of a DFAFC. In contrast, COad was not detected on ultrathin Pd overlay(s) on Pt [74] or Au [75] electrodes in the electrooxidation of FA at varying potentials with external IRAS and ATR-SEIRAS, respectively.

**Anode Catalysts for Electro-Oxidation of Formic Acid**

**Unsupported Pt-based catalysts**

In the early stages of DFAFC development, Pt-based catalysts were employed in the anode layer. The first report of formic acid fuel cell oxidation at Pt electrode was announced by Weber et al. [76] in 1996. They found that formic acid was electrochemically more active than methanol on both Pt-black and Pt/Ru catalysts. Additionally, the Pt/Ru catalyst was more active than Pt-black for formic acid oxidation. The results are summarized in Figure 5 [76]. Surprisingly, no other research published on DFAFC until 2002, although interest in the fundamentals of formic acid electro-oxidation continued [77].

In 2002, a group of researchers at the University of Illinois again reported that formic acid is an excellent fuel for a fuel cell, and that formic acid fuel cells were attractive alternatives for small portable applications [35]. In their research, they used a proprietary Pt-based catalyst named as ‘UIUC-B’ in the anode layer to improve the electro-oxidation of formic acid [35,78]. Through their effort, a current up to 134 mA cm⁻² and power outputs up to 48.8 mW cm⁻² were obtained with their first DFAFC demonstration [35].

Following their successful implementation in the first DFAFC,
systems, Pt-based catalysts have been widely studied, and continue to be an important aspect of DFAFC anode catalyst research. A lot of research used Pt–M (M=a second metal other than platinum) bimetallic catalysts to increase the activity of catalyst for of DFAFCs oxidation and reduce the amount of Pt catalyst used [38,79-82]. Pt/Ru, Pt/Pd, Pt/Au and Pt/Pb have recently been probed as the anode catalysts in DFAFCs, and the effects of Ru, Pd, Au, Pb on the catalytic activities have accordingly been invented. A series of Pt-based catalysts by spontaneous deposition of Pd and/or Ru to decorate platinum nanoparticles have been synthesized by Waszczuk et al. [82]. Decoration of the Pt surface with Pd provided the greatest increase in activity. Rice et al. [77] investigated the effect of Ru and Pd decorated Pt catalysts for formic acid oxidation in more detail, and a representative comparison of the DFAFC performances of the Pt-black, Pt/Ru and Pt/Pd catalysts is mentioned in Figure 6 and in Table 2. Both Ru and Pd were found to significantly enhance the catalytic activity, with Pt/Pd providing the best performance at high cell potentials. Pt/Ru provided the best maximum power density of 70 mWcm\(^{-2}\), but this was at a very low cell potential of 0.26 V. The rate of current decays also varied between catalysts, with Pt/Ru showing the fastest decay while the current at Pt/Pd became quite stable after an initial rapid decay. From a fundamental point of view, Rice et al. [38] concluded that addition of palladium to platinum enhanced the electro-oxidation rate of formic acid via a direct reaction mechanism (dehydrogenation pathway). A group of Thomas and Masel [83] showed that the energy barrier for decomposition of formic acid to CO\(_2\) decreases with increasing palladium coverage. In contrast, addition of ruthenium appears to suppress the direct pathway and enhance the electro-oxidation of formic acid via a reactive CO intermediate (dehydration pathway) [38]. Thomas and Masel [83] proved that there were no synergistic effects between platinum and palladium in a bimetallic Pt/Pd catalyst with respect to formic acid oxidation activity, and suggested that the improved activity was due to resistance to poisoning.

Unsupported Pt-Au alloy prepared by borohydride reduction as an anode catalyst for formic acid oxidation in a DFAFC has been studied by Choi et al. [79]. From their study, compared with Pt-Ru, the Pt-Au catalyst showed a higher catalytic activity, and this is confirmed by the results presented in Figure 7 Moreover, the synthesized catalyst Pt-Au was more stable during a long-term operation of the cell. These authors suggested that the oxidation of formic acid on a Pt-Au catalyst occurs mainly through the direct dehydrogenation pathway, without significant formation of adsorbed CO [79].

A variety of intermetallic phases of Pt with Bi, Pb, In, Sn, Mn and Sb have been evaluated for formic acid oxidation, with PtBi, PtBi\(_2\), PtPb, and PtIn being identified as the most promising candidates [84]. Surface treatment methods to improve the activities of PtBi and PtPb have been investigated, and methods for the synthesis of PtPb nanoparticles have been developed and compared [85,86]. A study of a Pt-Bi alloy produced by induction melting revealed the importance of dissolution and underpotential deposition (upd) of Bi atoms at the surface, as well as the formation of Bi oxides. Surface modification of PtRu with irreversibly adsorbed Bi atoms increases its activity for formic acid oxidation, apparently by hindering CO adsorption on Pt sites [87]. Bimetallic PtPb prepared by arc-melting has been shown to provide much higher and more stable (over 1000°C) formic acid oxidation activity than Pt [87]. PtPb nanoparticle catalysts also show high activity for formic acid oxidation and more stable performance (over 9 h) than Pt, PtRu, and Pd [88].

The enhancement of formic acid oxidation by Bi (and As) has been attributed to the so-called ‘third-body effect’ in which the addition of a second element (third-body) to Pt reduces the number of adsorption sites for CO due to geometrical hindrance and their surface is poisoned by the adsorbed CO to a lesser extent than a pure Pt surface [89]. In contrast, the activity enhancement of Pt–Pb for formic acid oxidation has been attributed to an electronic interaction between Pb and Pt [90]. The high catalytic activity for a Bi modified Pt catalyst has also been explained by electronic effects working in addition to a ‘third-body effect’ [91].

The fundamental mechanism of formic acid oxidation remains an important and challenging topic, and has been intensively studied by employing Pt single crystals modified with up to a monolayer of a second metal. The Pt (111)–Pd system as well as Pt–Pd alloy single crystals have been investigated in more detail by Arenz et al. [74,92]. Pd atoms at the surface were found to be 3–5 times more active than Pt.

### Table 2: Current density and power density comparison for DFAFCs with Pt, Pt-Ru and Pt-Pd anode catalysts running at voltages of 0.4 and 0.5 V.

| Catalyst | Current density (mA cm\(^{-2}\)) | Power density (mW cm\(^{-2}\)) |
|----------|---------------------------------|---------------------------------|
|          | 0.4V | 0.5V | 0.4V | 0.5V |
| Pt       | 37.44 | 22.02 | 15.69 | 10.3 |
| Pt-Ru    | 60.61 | 35.14 | 25.04 | 16.44 |
| Pt-Pd    | 67.32 | 46.39 | 28.24 | 21.71 |

### Figure 6: Constant voltage tests on a DFAFC at cell potentials of (a) 0.5 V and (b) 0.4 V. Catalysts: platinum black, PtRu, and PtPd; fuel: 5M formic acid at 0.2 mlin min\(^{-1}\); cell temperature: 30°C. Reprinted from with permission from Elsevier.

### Figure 7: Single cell performances of PtAu-based and PtRu-based MEAs with 6M formic acid and oxygen at 30°C. Reprinted from with permission from Elsevier.
atoms at 0.4 V. FTIR revealed that CO is not on Pt sites but adsorbed on Pt sites. In the study conducted by Macia et al. [91], the effects of Bi adlayers on formic acid oxidation at stationary and rotating Pt (111) electrodes have been investigated. Their findings reveal that activity increased with increasing Bi coverage up to 0.1–0.25 of a monolayer, depending on the formic acid concentration. Current–time transients indicated that no poisoning occurred for the modified electrodes. They examined adsorbed formate as a reactive intermediate without significant accumulation of adsorbed CO.

Gojkovic et al. [93] showed that a Pt$_x$Mo$_y$ alloy possess high activity for formic acid oxidation. The formation of a hydrous Mo oxide on the surface was found to increase the rate of the direct pathway for formic acid oxidation and also decrease poisoning by absorbed CO. From a theoretical point of view, Demirci [94] has predicted that the Pt–Ag bimetallic system might be a promising catalyst for DFAFCs, but there have not yet been any experimental studies to investigate this hypothesis.

Unsupported Pd-based catalysts

Electro-oxidation of formic acid on Pd catalysts has been extensively studied [69,95–97]. Use of pure Pd as the anode catalyst in DFAFCs was first reported by Ha et al. [43]. Compared with Pt-based catalysts, the Pd-black generated unusually high-power densities at ambient (22°C) and higher (30–50°C) temperatures. A representative comparison between Pd black, Pd–Au, and Pt–Ru is shown in Figure 8. In reference 20, it has shown that the activity of the Pd black catalyst decreased with the cell operation time, with a consequent loss of DFAFC performance. However, the lost activity could largely be recovered by applying a high anodic potential. The same group also studied the effects of operating temperature and formic acid concentration on the performances of a Pt–Ru anode and a H$_2$/air fuel cell [73]. The results were summarized in Table 3. The use of Pd catalyst to oxidize FA in DFAFC not only generated much higher power density than either the DFAFC or DMFC using the Pt–Ru catalyst, but also approached the performance of the hydrogen-PEM fuel cell. When operating with high formic acid concentration, the deactivation of Pd catalyst becomes a serious problem in DFAFC system, but again it was investigated that the initial cell performance could be recovered by applying a potential equal to 1.2 V to the anode side for a few seconds [73].

Carbon-supported Pt-based and Pd-based catalysts

The attractive features of high electrical conductivity, chemical stability and low cost have led to the extensive application of high surface-area carbon materials as supports for precious metal fuel cell catalysts, in order to reduce the noble metal loading and reduce the system cost [98,99]. In 2005, Lovic et al. [33] have conducted experiment on kinetics study of formic acid oxidation on Pt/C catalysts and confirmed that they were consistent with those on pure platinum, with the reaction occurring via the dual pathway mechanism comprising direct dehydrogenation of HCOOH as the main reaction and formation of poisoning species as a parallel reaction.

Pt–Pb catalysts obtained by modifying supported platinum electrodes with under potential deposition(upd) lead has been developed by Uhm et al. [81]. The resulted Pt–Pb upd catalysts showed higher electrocatalytic activities than pure platinum or Pt–Ru catalysts. Furthermore, the development of cell stability was performed by synthesizing a Pt/Pbupd/Pt multi-layer anode structure and enhancement of the cell performance which was stable over a 5 h period of evaluation was observed [81]. Pt modified Au nanoparticles supported on carbon have also been found to be effective for formic acid oxidation [100].

In References [30,37,88,99,101,102], Carbon supported palladium catalysts have become a very hot research topic in DFAFC catalyst and a good activity along with the potential for more efficient palladium metal utilization and lower metal loadings were reported. Pd/C or Pd–M/C (M=a second metal other than Pd) catalysts are generally obtained through chemical solution phase impregnation syntheses. Recent advances in Pd/C and Pd-M/C catalyst synthesis are summarized in Table 4.

In 2005, Ha et al. [37] successfully synthesized finely dispersed Pd particles on a Vulcan XC-72 carbon support, with palladium loadings of 20 and 40 wt%. Using these two Pd/C catalysts, DFAFCs generated a maximum power density of 145 mWcm$^{-2}$ (with 20% Pd/C) and 172 mWcm$^{-2}$ (with 40% Pd/C), as summarized in Figure 9a [30].

Results for the carbon-supported catalysts were compared with those for pure palladium in a DFAFC. Although the total power density generated by the 20% Pd/C catalyst was lower, the power density per unit mass of noble metal was much higher than for the Pt black catalyst, as summarized in Figure 9b. In addition to the benefits of higher palladium utilization efficiency, it was also found that the Pd/C catalysts showed less deactivation than for pure palladium during operation of the cell, especially for high concentrations of formic acid [37]. Larsen et al. [30] reported that the addition of gold to Pd/C can further improve the activity of the catalyst, and these results are also summarized in Figure 10.

An aqueous solution phase synthesis of a Pd/C catalyst with NH$_4$F
and H$_3$BO$_3$ as additives has been reported by Zhang et al. [88]. NH$_4$F forms a complex with PdCl$_2$ and this promotes the formation of finely dispersed Pd particles with smaller average sizes (3.2 nm) and relatively less crystallinity. Consequently, the catalytic activity and stability of the Pd/C catalyst synthesized in the presence of NH$_4$F were enhanced. A representative result is illustrated in Figure 9a. The same research group [101] also reported a Pd–P/C catalyst prepared via a solution phase synthesis with NaH$_2$PO$_2$ as a co-precursor. Combining palladium with the non-metal element phosphorus improved both the activity and stability of the catalyst as shown in Figure 9b.

A novel synthesis method for a carbon supported Pd–Pt catalyst using the surfactant 3-(N,N-dimethyl)dodecylammonio)propanesulfonate (SB12) as the stabilizer has been figured out by Li and Hsing [102]. Compared with a commercial (E-TEK) Pt$_{0.5}$Pd$_{0.5}$/C catalyst, the SB12 stabilized Pt–Pd/C catalysts have the advantages of better Pt–Pd dispersion and higher catalytic performance [102].

**Other supporting tactics for Pt-based and Pd-based catalysts**

Other than carbon supports, supporting substrates of platinum or palladium based catalysts have been recently reported. A novel titanium-supported nanoporous bimetallic Pt-Ir/Ti catalyst has been developed by Yi et al. using a hydrothermal process. H$_2$PtCl$_6$ and IrCl$_3$ have been used as the precursors, and formaldehyde played the function of reduction agent. Compared to pure platinum, the titanium-supported Pt-Ir catalysts mark a significantly higher catalytic activity for formic acid oxidation. The authors concluded that electro-oxidation of formic acid on Pt-Ir catalysts followed the dehydration pathway via a CO$^*$ intermediate.

Highly active palladium based catalysts tend to be passivated under DFAFC conditions, which leads to a decay of the DFAFC performance with the cell operation time. In order to increase the stability of palladium catalysts, Larsen et al. [30] experimented the stability of palladium deposited as a sub-monolayer on various metal foil supports such as V, Mo, W, and Au. Among all the studied metal foil supported catalysts, Pd-V has the best stability and Figures 10 and 11 summarized

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**Table 4:** Recent syntheses of Pd/C and Pd–M/C catalysts with impregnation methodologies.

| Catalyst   | Precursor | Reducing agent | Additive | References |
|------------|-----------|----------------|----------|------------|
| Pd/C       | PdCl$_2$  | NaBH$_4$       | -        | [21,73]    |
| Pd/C       | PdCl$_2$  | Ethylene glycol| -        | [26]       |
| Pd/C       | PdCl$_2$  | NaBH$_4$ H$_3$BO$_3$ NH$_4$F | [27]       |
| Pd-P/C     | H$_2$PtCl$_6$ (NH$_4$I) PdCl$_2$ | Methanol SB 12 | [74]       |
| Pd-P/C     | PdCl$_2$ NaH$_2$PO$_2$ | NaBH$_4$ H$_3$BO$_3$ NH$_4$F | [28]       |

**Figure 9:** Chronoamperometric curves for oxidation of 0.5M HCOOH in 0.5M H$_2$SO$_4$ solution on various Pd/C catalyst electrodes. (a) Comparison of Pd/C catalysts prepared with or without NH$_4$F, H$_3$BO$_3$ additives. Fixed potential: 0.10 V. (b) comparison of Pd/C and Pd-P/C catalyst electrodes. Fixed potential: 0.3 V. Reprinted from with permission from Elsevier.

**Figure 10:** Output power densities for a single cell operating at (a) 25°C and (b) 50°C. Anode: Pt/C or Pd/C (8 mg cm$^{-2}$), 3M HCOOH, 2 ml min$^{-1}$. Cathode: Pt/C (E-TEK) (4 mg cm$^{-2}$), O$_2$ 500 cm$^{-3}$ min$^{-1}$. Reprinted from with permission from Elsevier.

**Figure 11:** Chronoamperometric activity of Pd-M catalysts at 0.3 V vs. RHE. (a) per mass of Pd: (b) per surface area with Pd=0.6 (M=Ti, Zr, Hf, V, Nb, Ta, Cr, Mo, W, Au). The i-t curves were measured in a solution containing 5M HCOOH and 0.1M H$_2$SO$_4$. Reproduced by permission of The Electrochemical Society.
the obtained findings. In the authors’ opinion, the results obtained for these Pd/metal foil catalysts provide important information for the development of highly stable palladium based catalysts by alloying a second metal phase, such as vanadium.

Yin et al. [103] prepared tungsten carbide (WC) promoted palladium (Pd) and palladium-cobalt (PdCo) nanocatalysts for formic acid electrooxidation. The WC as the dopant to carbon supports is found to enhance the CO tolerance and promote the activity of the Pd-based catalysts for formic acid oxidation. Alloying of Pd with Co further improves the electrocatalytic activity and stability of the WC supported catalysts, attributable to a synergistic effect of the carbide support and PdCo alloy nanoparticles. Figure 12a and 12b summarized the results of CV and I-t curve measurement for different catalyst used to study formic acid oxidation.

Later on, He et al. [24] used a microwave assisting method, to synthesize tungsten carbide Nano crystals with a hexagonal prism shape on graphene (WCP/G). The WCP Nano crystals are 5 nm in size and dominated by (01-10), (10-10) and (1-100) facets with a preferred orientation of [0001]. An intermittent microwave heating (IMH) method was also utilized to load Pd nanoparticles (NPs) onto WCP/G to produce Pd–WCP/G, which displays a significant improvement as a catalyst for formic acid oxidation with peak current density increasing.

Figure 12: a) CVs of each catalyst in N$_2$-saturated 0.5 M HCOOH and 0.5 M H$_2$SO$_4$ solutions at a scan rate of 50 mV s$^{-1}$. The current density is based on the electrochemical surface area. Inset: Tafel plots of each catalyst at a scan rate of 1 mV s$^{-1}$. The current (j) is normalized to the geometric electrode area. b) Amperometric i-t curves of HCOOH electro-oxidation on each catalyst in N$_2$-saturated 0.5 M HCOOH and 0.5 M H$_2$SO$_4$ at a fixed potential of 0.445 V vs RHE. The current density is based on the electrochemical surface area.

Figure 13: (a) Typical cyclic voltammograms (CVS) of Pd/C, Pd–WCP/G and Pt/C in N$_2$-saturated 0.5 mol L$^{-1}$ H$_2$SO$_4$ with the scan rate of 20 mV s$^{-1}$ at 30°C, (b) CVs recorded at 20 mV s$^{-1}$ of Pd/C, Pd–WCPG and Pt/C in 0.5 mol L$^{-1}$ H$_2$SO$_4$+1.0 mol L$^{-1}$ HCOOH solution, (c) comparison of specific activities.
by a factor of 7 as presented in Figure 13, and notably enhanced durability. It is believed that this synthesis method of WCP/G opens new door for searching shape-controlled and high-surface-area transition metal carbide Nano crystals (TMCs) and developing them as efficient and low-cost catalysts or catalyst supports in a broad range of sustainable energy technologies.

**Conclusion**

This review paper represents a general overview of formic acid fuel cells on Pt and Pd based catalyst, fundamental mechanism of formic acid fuel cell, basic design of formic acid fuel cell, membrane crossover and some challenges of formic acid fuel cell, debates about intermediates formed during formic acid oxidation at Pt and Pd electrodes, some results from other publications about formic acid oxidation in way of finding the best catalyst with low cost, high activity and high stability. The demands of fuel cell are rapidly growth equivalent to invention of fuel cell performance. DFAFCs appear to be attractive candidates in order to increase power density demands. By all the advantages of direct formic acid fuel cell such as high in electromotive force and low fuel crossover, it is advised to put more effort in research which focus on DFAFC so that it may become a solution of many problems related to energy crisis for future market.

**Conflicts and Interest**

The authors declare that there is no conflict of interest.

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