

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

Uwitonze N and Chen YX*

Hefei National Laboratory for Physical Sciences at Microscale, Department of Chemical Physics, University of Science and Technology of China, Hefei, 230026, China

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 HCCOH 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 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 grapheme 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 NPs 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

*Corresponding author: Yan-Xia Chen, Hefei National Laboratory for Physical Sciences at Microscale, Department of Chemical Physics, University of Science and Technology of China, Hefei, 230026, China, Tel: +8615656576310; E-mail: uwitonze@mail.ustc.edu.cn

Received July 14, 2017; Accepted July 17, 2017; Published September 14, 2017

Citation: Uwitonze N, Chen YX (2017) The Study of Pt and Pd based Anode Catalysis for Formic Acid Fuel Cell. Chem Sci J 8: 167. doi: 10.4172/2150-3494.1000167

Copyright: © 2017 Uwitonze N, et al. This is an open-access article distributed under the terms of the Creative Commons Attribution License, which permits unrestricted use, distribution, and reproduction in any medium, provided the original author and source are credited.

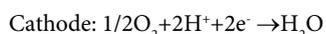
acid oxidation with an observed 7-fold increase in peak current density on Pd-WCP/G electrode and significant enhancement in durability as well. The main purpose of this work is to introduce the catalytic activity of different Pt and Pd -based anode catalysts for formic acid fuel cell oxidation.

The scope of this review

Briefly, Section 1 of the present review summarizes the functioning of formic acid fuel cell, the benefits of DFAFC, 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.

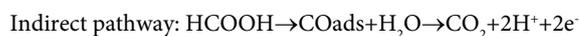
The mechanism of the direct formic acid fuel cells

Formic acid is a strong electrolyte, expected to promote the transport of electrons and protons on the anode of the fuel cell. Formic acid fuel cell uses oxygen (O₂) as cathode. On the cathode, by getting two electrons from anode, O₂ transform into water by reduction reaction. On the anode side of fuel cell, each molecular formic acid is oxidized to provide two electrons. The anodic, cathodic and overall reaction is shown in the following equations [29,30] (Figure 1):



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]:



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.

Catalysts effect on cells' performance: Generally, cell performance improved by the increasing of the anode or cathode catalyst loadings [36]. For initiation stage, Pt-based catalysts are employed in the anode layer such as Pt-black and Ru [2]. Yet, the poisoning of CO is overcome by using palladium (Pd) catalyst which produces the unusually high performance in DFAFCs [37]. Usually, Pt catalysts is used as the cathodic catalyst since it possesses high electrocatalytic activity for oxygen reduction. The intermediate CO causes Pt catalyst poisoned. Pd-black results unusually high power compared to Pt-based catalyst. Catalyst activity for Pd-black is decreasing in time at the same time the DFAFC performance drops slowly. Carbon supported Pd catalysts demonstrate good activity along with the potential for more efficient Pd metal utilization and lower metal loadings [2]. Larsen et al. [30] have compared the previous result of Pt-based catalysts in DFAFCs, the performance of Pd catalysts are greater. Rice et al., have experimented the behavior of platinum black, platinum-ruthenium and platinum-palladium towards the performance of the DFAFCs as illustrated in Table 1 [38].

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 0.26 V compared to pure platinum and Pt/Pd. Hence, it shows that the addition of palladium

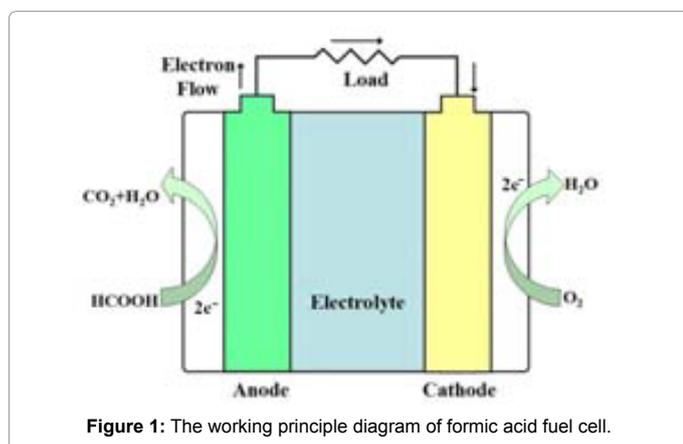


Figure 1: The working principle diagram of formic acid fuel cell.

Catalyst	Open OCP (V) Circuit potential	Current density at 0.5 V (mA/cm ²)	Power density at 0.26 V (mW/cm ²)
Pt/Pd	0.91	62	41
Pt	0.71	33	43
Pt/Ru	0.59	38	70

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

enhances the rate of formic acid electrooxidation 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 Nafion® 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

Polymethyl 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 Nafion® 112 and Nafion 117 membranes at room temperature. Wang et al. [48] performed experiment on formic acid crossover through a Nafion® 115 membrane at different temperatures and formic acid concentrations. Generally, the flux of formic acid through a Nafion 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

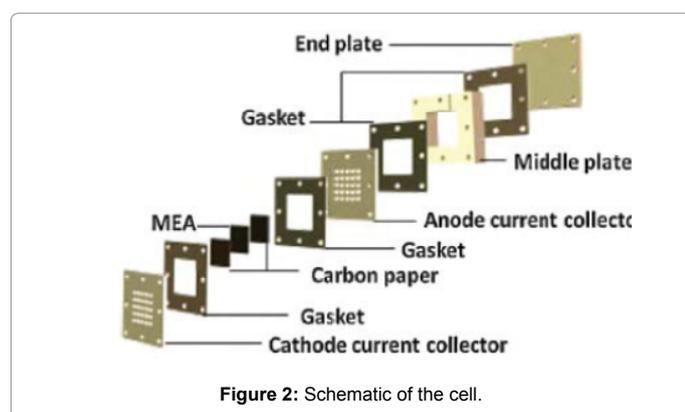


Figure 2: Schematic of the cell.

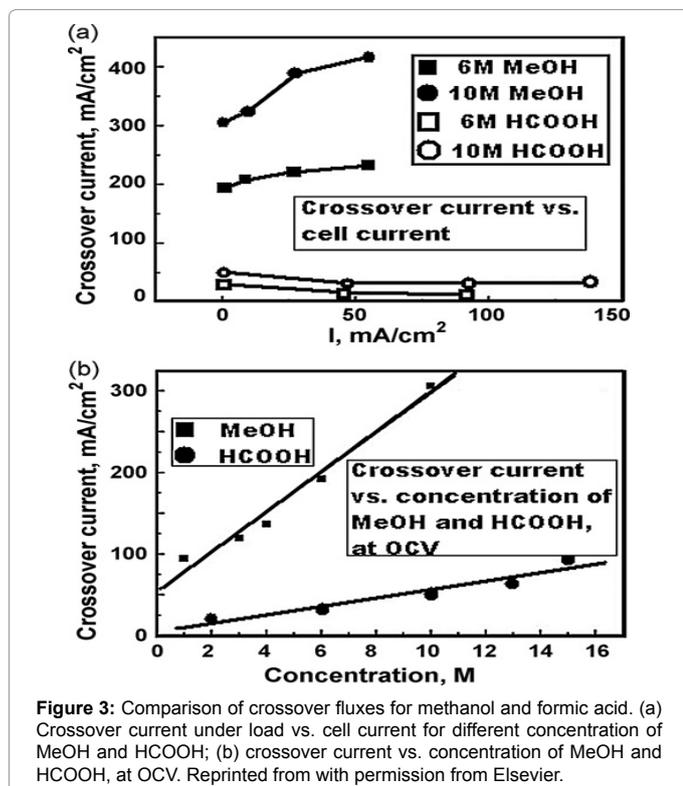


Figure 3: Comparison of crossover fluxes for methanol and formic acid. (a) Crossover current under load vs. cell current for different concentration of MeOH and HCOOH; (b) crossover current vs. concentration of MeOH and HCOOH, at OCV. Reprinted from with permission from Elsevier.

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 CO₂+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 CO₂. 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 CO₂.

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 CO₂ 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

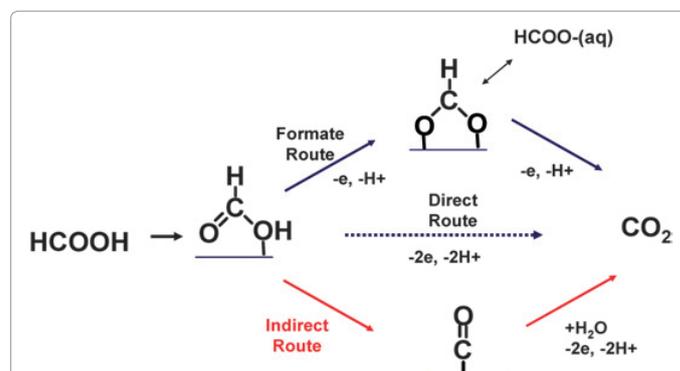


Figure 4: The reaction paths involved in the electro catalytic oxidation of formic acid to CO₂. (A) Direct path (center) to CO₂, (B) indirect path through CO (bottom), and (C) formate path through the formation of the formate intermediate (top).

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 dehydration 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 the 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 dehydration 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, Masel'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 of 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 overlayer(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 mAcm⁻² and power outputs up to 48.8 mWcm⁻² were obtained with their first DFAFC demonstration [35].

Following their successful implementation in the first DFAFC

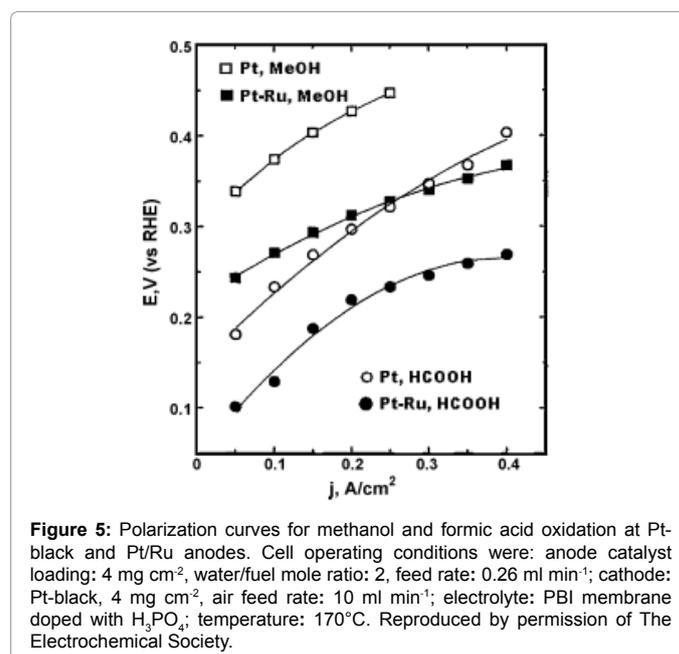


Figure 5: Polarization curves for methanol and formic acid oxidation at Pt-black and Pt/Ru anodes. Cell operating conditions were: anode catalyst loading: 4 mg cm⁻², water/fuel mole ratio: 2, feed rate: 0.26 ml min⁻¹; cathode: Pt-black, 4 mg cm⁻², air feed rate: 10 ml min⁻¹; electrolyte: PBI membrane doped with H₃PO₄; temperature: 170°C. Reproduced by permission of The Electrochemical Society.

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 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 mWcm², 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 CO₂ 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.

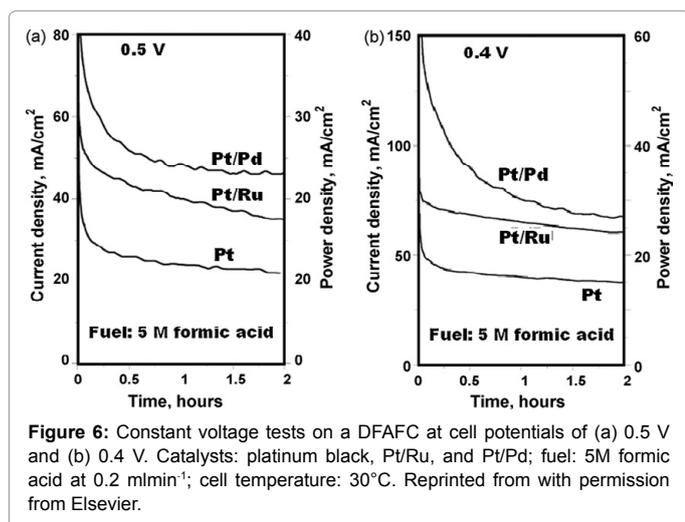


Figure 6: Constant voltage tests on a DFAFC at cell potentials of (a) 0.5 V and (b) 0.4 V. Catalysts: platinum black, Pt/Ru, and Pt/Pd; fuel: 5M formic acid at 0.2 mlmin⁻¹; cell temperature: 30°C. Reprinted from with permission from Elsevier.

	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

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.

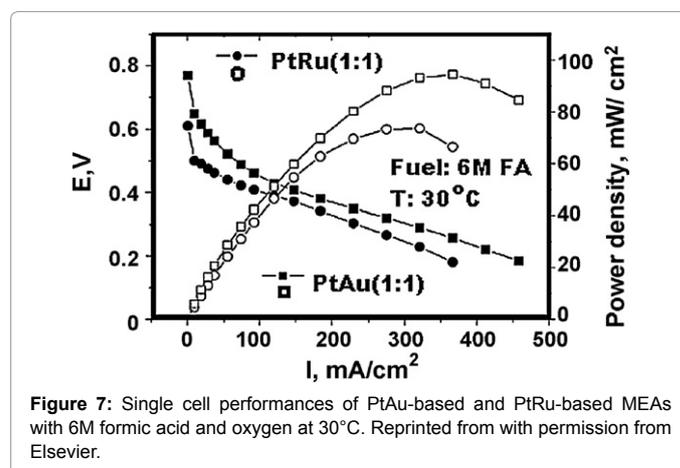


Figure 7: Single cell performances of PtAu-based and PtRu-based MEAs with 6M formic acid and oxygen at 30°C. Reprinted from with permission from Elsevier.

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, PtBi₂, 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

atoms at 0.4 V. FTIR revealed that CO is not on Pd 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 Pt₄Mo 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 adsorbed 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 DFAFC with a Pd anode, a DFAFC with a Pt–Ru anode, a DMFC (direct methanol fuel cell) with a Pt–Ru anode and a H₂/air fuel cell [73]. The results are 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

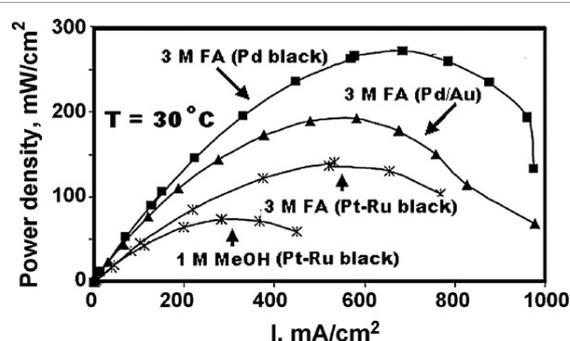


Figure 8: Power density curves for fuel cells fed with 1M methanol, 3M formic acid and hydrogen gas. Flow rates of methanol, formic acid and hydrogen were 1 ml min⁻¹, 3.5 ml min⁻¹ and 200 sccm, respectively. Dry air was supplied to the cathode at a flow rate of 390 sccm. The cell operation temperature was 30°C. Anodic catalysts used in the cell are indicated, while a Pt-black catalyst was used for cathode.

Fuel Cell	Anode Catalyst	Temperature (°C)	Fuel Concentration (M)	Peak power density (mW cm ⁻²)
H ₂ -air	Pd	20	-	320
MeOH-air	Pt-Ru	20	1	50
FA-air	Pt-Ru	20	3	84
FA-air	Pd	20	3	253
FA-air	Pd	30	3	300
FA-air	Pd	40	3	350
FA-air	Pd	50	3	375
FA-air	Pd	20	10	255
FA-air	Pd	20	15	230
FA-air	Pd	20	20	103

Table 3: Comparison of power densities for different types of fuel cell, and power densities of DFAFCs under different operating conditions.

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 syntheses 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 Pd 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 NH₄F

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-Pt/C	H ₂ PtCl ₆ , (NH ₄) ₂ PdCl ₆	Methanol	SB 12*	[74]
Pd-P/C	PdCl ₂ , NaH ₂ PO ₂	NaBH ₄	H ₃ BO ₃ , NH ₄ F	[28]

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

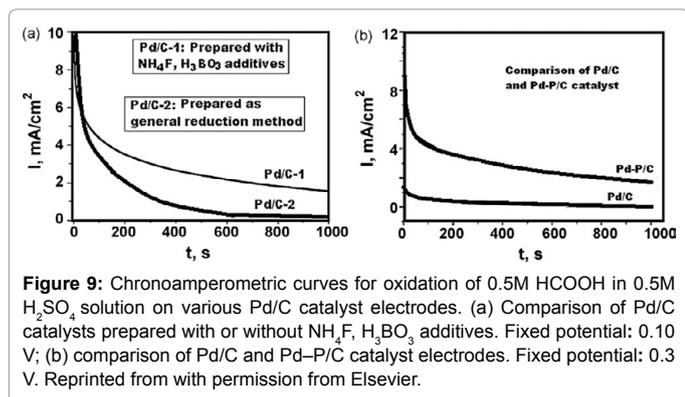


Figure 9: Chronoamperometric curves for oxidation of 0.5M HCOOH in 0.5M H₂SO₄ solution on various Pd/C catalyst electrodes. (a) Comparison of Pd/C catalysts prepared with or without NH₄F, H₃BO₃ additives. Fixed potential: 0.10 V; (b) comparison of Pd/C and Pd-P/C catalyst electrodes. Fixed potential: 0.3 V. Reprinted from with permission from Elsevier.

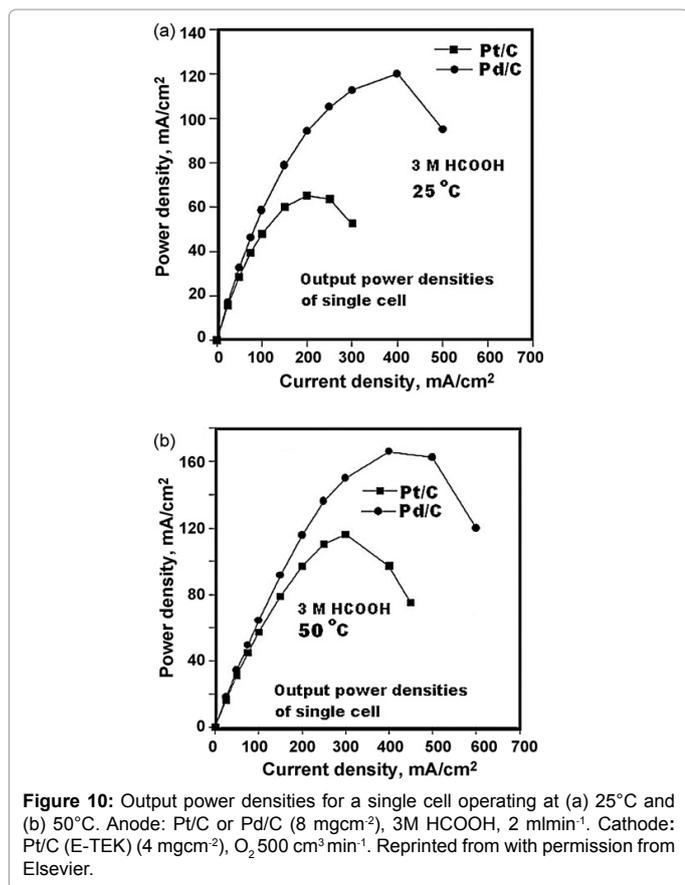


Figure 10: Output power densities for a single cell operating at (a) 25°C and (b) 50°C. Anode: Pt/C or Pd/C (8 mg/cm²), 3M HCOOH, 2 mlmin⁻¹. Cathode: Pt/C (E-TEK) (4 mg/cm²), O₂ 500 cm³min⁻¹. Reprinted from with permission from Elsevier.

and H₃BO₃ as additives has been reported by Zhang et al. [88]. NH₄F forms a complex with PdCl₂ 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 NH₄F 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 NaH₂PO₂ 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-dimethyldodecylammonio) 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. H₂PtCl₆ and IrCl₃ 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

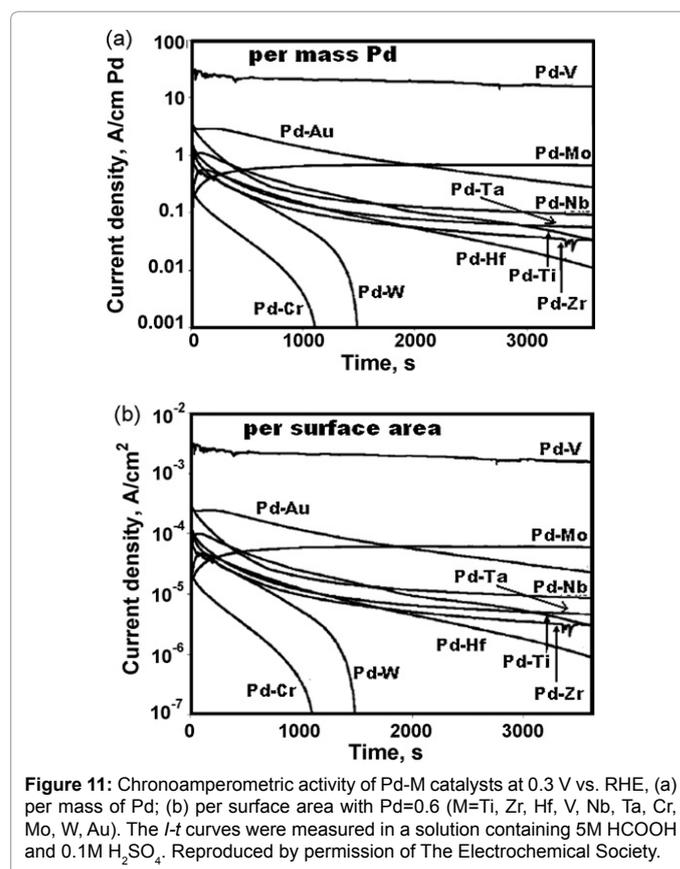


Figure 11: Chronoamperometric activity of Pd-M catalysts at 0.3 V vs. RHE, (a) per mass of Pd; (b) per surface area with Pd=0.6 (M=Ti, Zr, Hf, V, Nb, Ta, Cr, Mo, W, Au). The *I-t* curves were measured in a solution containing 5M HCOOH and 0.1M H₂SO₄. Reproduced by permission of The Electrochemical Society.

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 palladiumcobalt (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

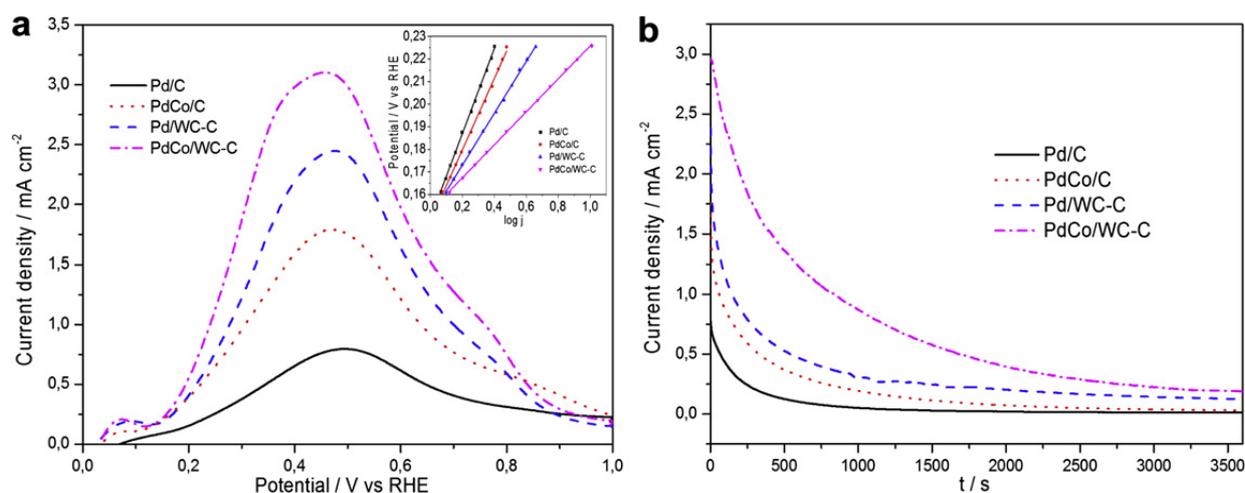


Figure 12: a) CVs of each catalyst in N_2 -saturated 0.5 M HCOOH and 0.5 M H_2SO_4 solutions at a scan rate of 50 $mV s^{-1}$. The current density is based on the electrochemical surface area. Inset: Tafel plots of each catalyst at a scan rate of 1 $mV s^{-1}$. The current (j) is normalized to the geometric 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_2SO_4 at a fixed potential of 0.445 V vs RHE. The current density is based on the electrochemical surface area.

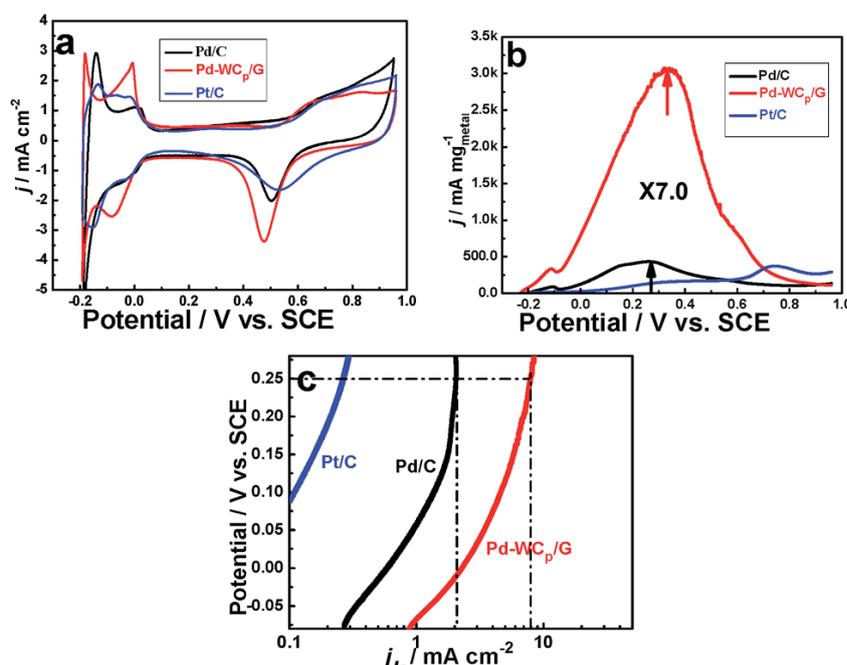


Figure 13: (a) Typical cyclic voltammograms (CVs) of Pd/C, Pd-WCP/G and Pt/C in N_2 -saturated 0.5 mol L^{-1} H_2SO_4 with the scan rate of 20 $mV s^{-1}$ at 30°C, (b) CVs recorded at 20 $mV s^{-1}$ of Pd/C, Pd-WCP/G and Pt/C in 0.5 mol L^{-1} H_2SO_4 + 1.0 mol L^{-1} HCOOH solution, (c) comparison of 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.

Acknowledgements

The authors are grateful for the financial support by the National Basic Research Program of China (2012CB932900, 2009CB220100, 2011CB933700), Hefei National Laboratory for Physical Sciences at Microscale, Department of Chemical Physics (University of Science and Technology of China), and of the National Science Foundation of China (NSFC 20973142, 21061120456, 21021002).

References

- Zhu Y, Ha SY, Masel RI (2004) High power density direct formic acid fuel cells. *Journal of Power Sources* 130: 8-14.
- Yu X, Pickup PG (2008) Recent advances in direct formic acid fuel cells (DFAFC). *Journal of Power Sources* 182: 124-132.
- Uhm S, Lee HJ, Lee J (2009) Understanding underlying processes in formic acid fuel cells. *Phys Chem Chem Phys* 11: 9326-9336.
- Mazumder V, Lee Y, Sun S (2010) Recent development of active nanoparticle catalysts for fuel cell reactions. *Advanced Functional Materials* 20: 1224-1231.
- Jiang K, Cai WB (2014) Carbon supported Pd-Pt-Cu nanocatalysts for formic acid electrooxidation: Synthetic screening and componential functions. *Applied Catalysis B: Environmental* 147: 185-192.
- Yuan W, Cheng Y, Pei KS, Chang ML, San PJ (2015) Significance of wall number on the carbon nanotube support-promoted electrocatalytic activity of Pt NPs towards methanol/formic acid oxidation reactions in direct alcohol fuel cells. *Journal of Materials Chemistry A* 3: 1961-1971.
- Samjeské G, Osawa M (2005) Current Oscillations during Formic Acid Oxidation on a Pt Electrode: Insight into the Mechanism by Time-Resolved IR Spectroscopy. *Angewandte Chemie* 117: 5840-5844.
- Okamoto H, Kon W, Mukoyama Y (2005) Five current peaks in voltammograms for oxidations of formic acid, formaldehyde, and methanol on platinum. *J Phys Chem B* 109: 15659-15666.
- Kim J, Changhoon J, Choong KR, Tae-hoon L (2007) Electrocatalytic oxidation of formic acid and methanol on Pt deposits on Au (111). *Langmuir* 23: 10831-10836.
- Xu C, Hao Q, Duan H (2014) Nanoporous PdPt alloy as a highly active electrocatalyst for formic acid oxidation. *Journal of Materials Chemistry A* 2: 8875-8880.
- Lee SY, Namgee J, Jinwon C, Hee-Young P, Jaeyune R, et al. (2014) Surface-rearranged Pd₃Au/C nanocatalysts by using CO-induced segregation for formic acid oxidation reactions. *ACS Catalysis* 4: 2402-2408.
- Xu, D, Bliznakov S, Liu Z, Fang J, Dimitrov N (2010) Composition-Dependent Electrocatalytic Activity of Pt-Cu Nanocube Catalysts for Formic Acid Oxidation. *Angew Chem Int Ed Engl* 122: 1304-1307.
- She Y, Zhonguang L, Wenguang F, Simon J, Michael KH, et al. (2014) Facile preparation of PdNi/rGO and its electrocatalytic performance towards formic acid oxidation. *Journal of Materials Chemistry A* 2: 3894-3898.
- Yang S, Chengmin S, Yuan T, Xiaogang Z, Hong-Jun G (2014) Synthesis of cubic and spherical Pd nanoparticles on graphene and their electrocatalytic performance in the oxidation of formic acid. *Nanoscale* 6: 13154-13162.
- Sneed BT, Allison PY, Daniel J, Matthew CG, Shunja M, et al. (2014) Shaped Pd-Ni-Pt core-sandwich-shell nanoparticles: influence of Ni sandwich layers on catalytic electrooxidations. *ACS nano* 8: 7239-7250.
- Lan F, Deli W, Shanfu L, Jin Zhang, Dawei Liang, et al. (2013) Ultra-low loading Pt decorated coral-like Pd nanochain networks with enhanced activity and stability towards formic acid electrooxidation. *Journal of Materials Chemistry A*. 1: 1548-1552.
- Zhang B, Hongliang P, Lijun Y, Hualing L, Haoxiong N, et al. (2015) Three dimensional palladium nanoflowers with enhanced electrocatalytic activity towards the anodic oxidation of formic acid. *Journal of Materials Chemistry A* 3: 973-977.
- Tang Y, Edelmann RE, Zou S (2014) Length tunable penta-twinned palladium nanorods: seedless synthesis and electrooxidation of formic acid. *Nanoscale* 6: 5630-5633.
- Matos J, Andrzej B, Anna MZ, Piotre K, Boguslaw M et al. (2015) Direct formic acid fuel cells on Pd catalysts supported on hybrid TiO₂-C materials. *Applied Catalysis B: Environmental* 163: 167-178.
- Chang J, Liang F, Changpeng L, Wei X, Xile H (2014) An effective Pd-Ni₂P/C anode catalyst for direct formic acid fuel cells. *Angewandte Chemie* 53: 122-126.
- He C, Shen PK (2014) Pt loaded on truncated hexagonal pyramid WC/graphene for oxygen reduction reaction. *Nano Energy*. 8: 52-61.
- Yin S, Mei C, Chengxin W, Pei KS (2011) Tungsten carbide promoted Pd-Fe as alcohol-tolerant electrocatalysts for oxygen reduction reactions. *Energy & Environmental Science* 4: 558-563.
- He C, Meng H, Yao X, Kang SP (2012) Rapid formation of nanoscale tungsten carbide on graphitized carbon for electrocatalysis. *International Journal of Hydrogen Energy* 37: 8154-8160.
- He C, Tao J, Ke Y, Qiu Y (2015) Graphene-supported small tungsten carbide nanocrystals promoting a Pd catalyst towards formic acid oxidation. *RSC Advances* 5: 66695-66703.
- Esposito DV, Hunt ST, Alan LS, Kelvin DD, Brain EM, et al. (2010) Low-Cost Hydrogen-Evolution Catalysts Based on Monolayer Platinum on Tungsten Monocarbide Substrates. *Angewandte Chemie* 49: 9859-9862.
- Yan Y, Lan Z, Xiang Q, Song H, Wang JY, et al. (2012) Template-Free Pseudomorphic Synthesis of Tungsten Carbide Nanorods. *Small* 8: 3350-3356.
- d'Arbigny JB, Gilles T, Mathieu M, Deborah JJ, Jacques R (2011) Hollow microspheres with a tungsten carbide kernel for PEMFC application. *Chemical Communications* 47: 7950-7952.
- Sun Y, Cui H, Jin SX, Wang CX (2012) Eutectic solidification applied to nanofabrication: a strategy to prepare large-scale tungsten carbide nanowalls. *Journal of Materials Chemistry* 22: 16566-16571.
- Wang Y, Bing W, Ying G, Yawen T, Tianhong L, et al. (2009) Kinetic study of formic acid oxidation on carbon supported Pd electrocatalyst. *Journal of Power Sources* 192: 372-375.
- Larsen R, Su H, Joseph Z, Richard IM (2006) Unusually active palladium-based catalysts for the electrooxidation of formic acid. *Journal of Power Sources* 157: 78-84.
- Liu M, Zhang R, Chen W (2014) Graphene-supported nanoelectrocatalysts for fuel cells: synthesis, properties, and applications. *Chemical reviews* 114: 5117-5160.
- Shen L, Huanzhi L, Liang L, Yafen L, Yawen T, et al. (2013) Improvement and mechanism of electrocatalytic performance of Pd-Ni/C anodic catalyst in direct formic acid fuel cell. *Electrochimica Acta* 89: 497-502.

33. Lović J, Tripkovic AV, Gojkovic SL, Popovic KD, Olszewski P, et al. (2005) Kinetic study of formic acid oxidation on carbon-supported platinum electrocatalyst. *Journal of Electroanalytical Chemistry* 581: 294-302.
34. Hong P, Yiliang Z, Shijun L, Jianhuang Z, Xueyi L, et al. (2011) A 4-cell miniature direct formic acid fuel cell stack with independent fuel reservoir: Design and performance investigation. *Journal of Power Sources* 196: 5913-5917.
35. Rice C (2002) Direct formic acid fuel cells. *Journal of Power Sources* 111: 83-89.
36. Hong P, Shijun L, Jianhuang Z, Xinjian H (2010) Design, fabrication and performance evaluation of a miniature air breathing direct formic acid fuel cell based on printed circuit board technology. *Journal of Power Sources* 195: 7332-7337.
37. Ha S, Larsen R, Masel R (2005) Performance characterization of Pd/C nanocatalyst for direct formic acid fuel cells. *Journal of Power Sources* 144: 28-34.
38. Rice C, Ha S, Masel RI, Wieckowski A (2003) Catalysts for direct formic acid fuel cells. *Journal of Power Sources* 115: 229-235.
39. Wu B (2011) A highly active carbon-supported PdSn catalyst for formic acid electrooxidation. *Applied Catalysis B: Environmental* 103: 163-168.
40. Miesse CM, Won SJ, Kyoung-Jin J, Kwang LJ, Jaeyoung L et al. (2006) Direct formic acid fuel cell portable power system for the operation of a laptop computer. *Journal of Power Sources* 162: 532-540.
41. Kim HS, Robert DM, Bogdan G, Richard IM (2009) A miniature direct formic acid fuel cell battery. *Journal of Power Sources* 188: 118-121.
42. Yu X, Pickup PG (2009) Deactivation/reactivation of a Pd/C catalyst in a direct formic acid fuel cell (DFAFC): Use of array membrane electrode assemblies. *Journal of Power Sources* 187: 493-499.
43. Ha S, Adams B, Masel R (2004) A miniature air breathing direct formic acid fuel cell. *Journal of Power Sources* 128: 119-124.
44. McGrath KM, Prakash GS, Olah GA (2004) Direct methanol fuel cells. *Journal of Industrial and Engineering Chemistry* 10: 1063-1080.
45. Heinzl A, Barragan V (1999) A review of the state-of-the-art of the methanol crossover in direct methanol fuel cells. *Journal of Power Sources* 84: 70-74.
46. Song C, Khanfar M, Pickup PG (2006) Mo oxide modified catalysts for direct methanol, formaldehyde and formic acid fuel cells. *Journal of Applied Electrochemistry* 36: 339-345.
47. Jeong KJ (2007) Fuel crossover in direct formic acid fuel cells. *Journal of Power Sources* 168: 119-125.
48. Wang X, Hu JM, Hsing IM (2004) Electrochemical investigation of formic acid electro-oxidation and its crossover through a Nafion® membrane. *Journal of Electroanalytical Chemistry* 562: 73-80.
49. Rhee YW, Ha SY, Masel RI (2003) Crossover of formic acid through Nafion® membranes. *Journal of Power Sources* 117: 35-38.
50. Uhm S, Chung ST, Lee J (2008) Characterization of direct formic acid fuel cells by Impedance Studies: In comparison of direct methanol fuel cells. *Journal of Power Sources* 178: 34-43.
51. Zhou Y, Liu J, Ye J, Zou Z, Gu J, et al. (2010) Poisoning and regeneration of Pd catalyst in direct formic acid fuel cell. *Electrochimica Acta* 55: 5024-5027.
52. Chen F, Chang MH, Lin MK (2007) Analysis of membraneless formic acid microfuel cell using a planar microchannel. *Electrochimica Acta* 52: 2506-2514.
53. Chen YX, Heinen M, Jusys Z, Behm RJ (2006) Bridge-bonded formate: active intermediate or spectator species in formic acid oxidation on a Pt film electrode. *Langmuir* 22: 10399-10408.
54. Chen YX, Heinen M, Jusys Z, Behm RJ (2007) Kinetic Isotope Effects in Complex Reaction Networks: Formic Acid Electro-Oxidation. *Chem Phys Chem* 8: 380-385.
55. Lipkowsky J, Ross PN (1998) *Electrocatalysis* 3. John Wiley & Sons.
56. Sun S, Clavilier J, Bewick A (1988) The mechanism of electrocatalytic oxidation of formic acid on Pt (100) and Pt (111) in sulphuric acid solution: an emirs study. *Journal of Electroanalytical Chemistry and Interfacial Electrochemistry* 240: 47-159.
57. Miki A, Ye S, Osawa M (2002) Surface-enhanced IR absorption on platinum nanoparticles: an application to real-time monitoring of electrocatalytic reactions. *Chemical Communications* 14: 1500-1501.
58. Miyake H, Okada T, Samjeske G, Osawa M (2008) Formic acid electrooxidation on Pd in acidic solutions studied by surface-enhanced infrared absorption spectroscopy. *Physical Chemistry Chemical Physics* 10: 3662-3669.
59. Cuesta A, Cabello G, Gutiérrez C, Osawa M (2011) Adsorbed formate: the key intermediate in the oxidation of formic acid on platinum electrodes. *Physical Chemistry Chemical Physics* 13: 20091-20095.
60. Cuesta A, Cabello G, Gutiérrez C, Osawa M (2012) Mechanism of the electrocatalytic oxidation of formic acid on metals. *ACS Catalysis* 2: 728-738.
61. Grozovski V, Vidal-Iglesias FJ, Herrero E, Feliu JM (2011) Adsorption of formate and its role as intermediate in formic acid oxidation on platinum electrodes. *ChemPhysChem* 12: 1641-1644.
62. Neurock M, Janik M, Wieckowski A (2009) A first principles comparison of the mechanism and site requirements for the electrocatalytic oxidation of methanol and formic acid over Pt. *Faraday discussions* 140: 363-378.
63. Wang HF, Liu ZP (2009) Formic acid oxidation at Pt/H₂O interface from periodic DFT calculations integrated with a continuum solvation model. *The Journal of Physical Chemistry C* 113: 7502-7508.
64. Mei D, He ZD, Jiang DC, Cai J, Chen YX (2014) Modeling of potential oscillation during galvanostatic electrooxidation of formic acid at platinum electrode. *The Journal of Physical Chemistry C* 118: 6335-6343.
65. Campbell CT, Campbell JM, Dalton PJ, Henn FC, Rodriguez JA, et al. (1989) Probing ensemble effects in surface reactions. 1. Site-size requirements for the dehydrogenation of cyclic hydrocarbons on platinum (111) revealed by bismuth site blocking. *The Journal of Physical Chemistry* 93: 806-814.
66. Marković N, Ross PN (2002) Surface science studies of model fuel cell electrocatalysts. *Surface Science Reports* 45: 117-229.
67. Jung WS, Han J, Ha S (2007) Analysis of palladium-based anode electrode using electrochemical impedance spectra in direct formic acid fuel cells. *Journal of Power Sources* 173: 53-59.
68. Mikolajczuk A, Borodzinski A, Kedzierzawski P, Stobinski L, Mierzwa B, et al. (2011) Deactivation of carbon supported palladium catalyst in direct formic acid fuel cell. *Applied Surface Science* 257: 8211-8214.
69. Capon A and Parsons R (1973) The oxidation of formic acid on noble metal electrodes: II. A comparison of the behaviour of pure electrodes. *Journal of Electroanalytical Chemistry and Interfacial Electrochemistry* 44: 239-254.
70. Solis V, Iwasita T, Pavese A, Vielstich W (1988) Investigation of formic acid oxidation on palladium in acidic solutions by on-line mass spectroscopy. *Journal of electroanalytical chemistry and interfacial electrochemistry* 255: 155-162.
71. Zhou W, Lee JY (2008) Particle size effects in Pd-catalyzed electrooxidation of formic acid. *The Journal of Physical Chemistry C* 112: 3789-3793.
72. Ren M, Kang Y, He W, Zou Z, Xue X, et al. (2011) Origin of performance degradation of palladium-based direct formic acid fuel cells. *Applied Catalysis B: Environmental* 104: 49-53.
73. Zhu Y, Khan Z, Masel R (2005) The behaviour of palladium catalysts in direct formic acid fuel cells. *Journal of Power Sources* 139: 15-20.
74. Arenz M, Stamenkovic V, Schmidt TJ, Wandelt K, Rossa PN et al (2003) The electro-oxidation of formic acid on Pt-Pd single crystal bimetallic surfaces. *Physical Chemistry Chemical Physics* 5: 4242-4251.
75. Pronkin S, Hara M, Wandlowski T (2006) Electrocatalytic properties of Au (111)-Pd quasi-single-crystal film electrodes as probed by ATR-SEIRAS. *Russian Journal of Electrochemistry* 42: 1177-1192.
76. Weber M, Wang JT, Wasmus S, Savinell RF (1996) Formic Acid Oxidation in a Polymer Electrolyte Fuel Cell A Real-Time Mass-Spectrometry Study. *Journal of the Electrochemical Society* 143: L158-L160.
77. Waszczuk P, Crown A, Mitrovski S, Wieckowski A (2003) Methanol and formic acid oxidation on ad-metal modified electrodes. *Handbook of Fuel Cells*.
78. Ha S, Rice CA, Masel RI, Wieckowski A (2002) Methanol conditioning for improved performance of formic acid fuel cells. *Journal of power sources* 112: 655-659.
79. Choi JH, Jeong KJ, Dong Y, Sung YE (2006) Electro-oxidation of methanol and formic acid on PtRu and PtAu for direct liquid fuel cells. *Journal of Power Sources* 163: 71-75.

80. Zhou X, Xing W, Liu C, Lu T (2007) Platinum-macrocyclic co-catalyst for electro-oxidation of formic acid. *Electrochemistry communications* 9: 1469-1473.
81. Uhm S, Chung ST, Lee J (2007) Activity of Pt anode catalyst modified by underpotential deposited Pb in a direct formic acid fuel cell. *Electrochemistry Communications* 9: 2027-2031.
82. Waszczuk P, Barnard TM, Rice C, Wieckowski A (2002) A nanoparticle catalyst with superior activity for electrooxidation of formic acid. *Electrochemistry Communications* 4: 599-603.
83. Thomas FS, Masel RI (2004) Formic acid decomposition on palladium-coated Pt (110). *Surface science* 573: 169-175.
84. Casado-Rivera E, Volpe DJ, Alden L, Lind C, Downie C, Vázquez-Alvarez T et al. (2004) Electrocatalytic activity of ordered intermetallic phases for fuel cell applications. *Journal of the American Chemical Society* 126: 4043-4049.
85. Alden LR, Han DK, Matsumoto F, Abruña HD, DiSalvo FJ et al. (2006) Intermetallic PtPb nanoparticles prepared by sodium naphthalide reduction of metal-organic precursors: electrocatalytic oxidation of formic acid. *Chemistry of materials* 18: 5591-5596.
86. Alden LR, Roychowdhury C, Futoshi Matsumoto, Han DK, Zeldovich VB et al. (2006) Synthesis, characterization, and electrocatalytic activity of PtPb nanoparticles prepared by two synthetic approaches. *Langmuir* 22: 10465-10471.
87. Tripkovic AV, Gojkovic SL, Popovic KD, Lovic JD, Kowal A et al. (2007) Study of the kinetics and the influence of Bi_{irr} on formic acid oxidation at Pt 2 Ru 3/C. *Electrochimica Acta* 53: 887-893.
88. Zhang LJ, Wang ZY, Xia DG (2006) Bimetallic PtPb for formic acid electro-oxidation. *Journal of alloys and compounds* 426: 268-271.
89. Herrero E, Vega F, Feliu JM, Aldaz A (1993) Poison formation reaction from formic acid and methanol on Pt (111) electrodes modified by irreversibly adsorbed Bi and As. *Journal of Electroanalytical Chemistry* 350: 73-88.
90. Xia X, Iwasita T (1993) Influence of underpotential deposited lead upon the oxidation of HCOOH in HClO₄ at platinum electrodes. *Journal of the Electrochemical Society* 140: 2559-2565.
91. Macia, M, Herrero E, Feliu J (2003) Formic acid oxidation on Pure Bi-Pt (111) electrode in perchloric acid media. A kinetic study. *Journal of Electroanalytical Chemistry* 554: 25-34.
92. Arenz M, Stamenkovic V, Ross PN, Markovic NM (2004) Surface (electro-) chemistry on Pt (111) modified by a Pseudomorphic Pd monolayer. *Surface science* 573: 57-66.
93. Gojković SL, Tripkovic AV, Stevanovic RM (2007) High activity of Pt₄Mo alloy for the electrochemical oxidation of formic acid. *Langmuir* 23: 12760-12764.
94. Demirci UB (2007) Theoretical means for searching bimetallic alloys as anode electrocatalysts for direct liquid-feed fuel cells. *Journal of Power Sources* 173: 11-18.
95. Baldauf, M, D. Kolb (1996) Formic acid oxidation on ultrathin Pd films on Au (hkl) and Pt (hkl) electrodes. *J. Phys. Chem* 100: 11375-11381.
96. Tian M, Conway BE (2005) Phenomenology of oscillatory electro-oxidation of formic acid at Pd: role of surface oxide films studied by voltammetry, impedance spectroscopy and nanogravimetry. *Journal of Electroanalytical Chemistry* 581: 176-189.
97. Hoshi N, Kida K, Nakamura M, Nakada M, Osada K (2006) Structural effects of electrochemical oxidation of formic acid on single crystal electrodes of palladium. *The Journal of Physical Chemistry B* 110: 12480-12484.
98. Ha S, Larsen R, Zhu Y, Masel RI (2004) Direct formic acid fuel cells with 600 mA cm⁻² at 0.4 V and 22°C. *Fuel Cells* 4: 337-343.
99. Liu H, Song C, Zhang L, Zhang J, Wang H ,et al. (2006) A review of anode catalysis in the direct methanol fuel cell. *Journal of Power Sources* 155: 95-110.
100. Park IS, Kug-Seung L, Jong-Ho C, Hee-Young P, Yung-Eun S, et al. (2007) Surface structure of Pt-modified Au nanoparticles and electrocatalytic activity in formic acid electro-oxidation. *The Journal of Physical Chemistry C* 111: 19126-19133.
101. Zhang L, Tang Y, Bao J, Lu T, Li C (2006) A carbon-supported Pd-P catalyst as the anodic catalyst in a direct formic acid fuel cell. *Journal of Power Sources* 162: 177-179.
102. Li X, Hsing IM (2006) Electrooxidation of formic acid on carbon supported Pt x Pd 1-x (x= 0-1) nanocatalysts. *Electrochimica Acta* 51: 3477-3483.
103. Yin M, Li Q, Jensen JO, Huang Y, Cleeman LN, et al. (2012) Tungsten carbide promoted Pd and Pd-Co electrocatalysts for formic acid electrooxidation. *Journal of Power Sources* 219: 106-111.