A Review of Pd Based Multimetallic Anode Electrocatalysts for Direct Formic Acid Fuel Cells

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Abstract Due to the increasing population and developing industry, the energy demand in the world is increasing. Fuel cells are technologies that can meet this need without a negative impact on the environment. However, for the commercialization of fuel cells, their costs must be reduced and their efficiency increased. An important way to reduce cost is to reduce the amount of Pd, a precious metal used as an anode catalyst, by adding a second metal. The aim of this study is to explain how Pd increases the activity when used as an anode catalyst with a second metal for the formic acid electrooxidation.

Keywords palladium, formic acid, electrooxidation, alloy

Introduction

It is known that 28% of total greenhouse gas emissions are transport-related.^[1] Due to the increasing number of cars, this problem is expected to grow further in the coming years. Fossil fuels, which occupy a large part in today's automobile technology, have significant environmental impacts such as climate change and global warming.^[2] For these reasons, it is vital to investigate alternative energy sources. Renewable energy sources can be listed as sunlight, rain, waves, wind, tides, hydrogen, and geothermal energy, among which hydrogen energy provides effective solutions for environmental problems caused by fossil fuels.^[3]

Fuel cells are eco-friendly energy conversion systems since they produce electrical energy utilizing hydrogen. Fuel cells can be classified as phosphoric acid, solid oxide, polymer exchange membrane, molten carbonate and alkali fuel cells based on the electrolyte type employed in the system.^[4] Among these, polymer exchange membrane fuel cell is the closest fuel cell type to commercialization. However, researchers have turned their research to look for safer direct liquid fuel cells (DLFCs) due to the cost and danger associated with the storage and transportation of hydrogen.

With their own advantages and drawbacks, the applications of various alcohols and non-alcohol fuels in different DLFC systems have been reported in the literature. The most commonly investigated DLFCs are direct methanol (DMFC), direct ethanol (DEFC), direct ethylene glycol (DEGFC), direct hydrazine (DHFC), direct dimethyl ether (DDMEFC), direct NaBH₄ (DBFC), direct formate (DFFC), direct glucose (DGFC), and direct formic acid (DFAFC) fuel cells. Various studies related to these fuel cells are summarized in Table 1. Toxicity and membrane crossover problems of DMFCs, slow oxidation of ethanol at anode, formation of side products and need for high operating temperature in DEFCs and incomplete oxidation of ethylene glycol due to the release of unwanted by-products in DEGFCs are some of the obstacles encountered within these studies.^[5] Hence, further work is needed to improve the performance of abovementioned systems and there is still an increasing interest for other liquid fuel alternatives.^[6]

The use of formic acid in fuel cells as a small organic molecule offers many advantages such as low operating

Table 1 Fuel cell types and their anode catalysts

Fuel Cell Type	Anode Catalyst	Ref.
DMFC	Pt@Ru/C	[10]
DEFC	Pt/C	[11]
DMFC	PtRu/C	[12]
DMFC	PtCo/SBA-15	[13]
DEFC	PtIr@C	[14]
DEFC	PtRu/C	[15]
DEFC	PtSn/CNT	[16]
DEFC	PdAu/CNT	[17]
DEGFC	Pt/CNT	[18]
DEGFC	PdAuCo/CNT	[6]
DHFC	Pd	[19]
DDMEFC	PtRuPd/C	[20]
DGFC	Graphene/ITO	[21]
DGFC	B doped graphene/ITO	[22]
DBFC	PtZn/C	[23]
DFAFC	PdZn/CNT	[24]

temperature, minimal crossover, high theoretical open circuit potential, high energy density, and low adverse effects on nature.^[7,8] Low toxicity, non-flammability, ready availability, and high electrooxidation rate strengthens the potential use of formic acid as an alternative fuel in DLFCs.^[5] Being a natural biomass and a CO₂ reduction product made formic acid an alternative in many DLFC studies.^[9]

Anode catalysts for DLFCs are being investigated extensively. Table 1 represents the variation of anode catalyst types and their usage in different fuel cell systems. Since fuel cell performance tests of anode catalysts have not been performed in most of the studies in the literature, it is not possible to thoroughly compare the performance of fuel cells with each other.

The decomposition of formic acid on an anode catalyst follows either direct or indirect pathway. In the latter, dehydration of HCOOH to surface poisoner CO occurs.^[25] In other words, the dehydrogenation reaction (direct pathway) is the desired pathway for formic acid electrooxidation.^[26] Reactions of dehydrogenation and dehydration pathways are given in Eqs. (1) and (2), respectively.

Figure 1 shows a schematic representation for the working principle of a DFAFC. DFAFCs consist of an anode, cathode, and proton exchange membrane. Formic acid, which is used as fuel, is subjected to dehydrogenation reaction in the anode catalyst layer to form protons and electrons. While protons are transferred to the cathode side through the proton exchange membrane, electrons pass through the external circuit to generate electricity. On the cathode side, supplied O_2 , electrons coming from the outer circuit and protons passing through the membrane react, and water is released. The anode, cathode and overall reactions taking place in a DFAFC are shown in Eqs. (3), (4) and (5), respectively.

Figure 1 Schematic representation for working principle of DFAFC.

Pt and Pd are the two main electrocatalysts, on which electrooxidation of formic acid has been investigated since 1960's.^[9] In several studies, higher tendency of Pt and Pt-based catalysts to poisoning rather than Pd-based catalysts was reported. Additionally, oxidation of formic acid to CO_2 through dehydrogenation pathway takes place on Pd-based catalysts without any intermediate formation.^[27,28] Pd and Pt have the same number of electrons at their outer shell and their physicochemical properties are quite parallel to each other. On the other hand, Pd is much more cost-effective, its abundance on earth is about fifty times higher than Pt^[29] and higher resistance of Pd to CO poisoning is reported in the literature.^[30,31] Additionally, Pd-based electrocatalysts show high activity in alkaline media for the oxidation of numerous substrates.^[32] Pd shows a high initial activity during formic acid electrooxidation, while it loses this activity during long term performance. This result is mostly explained by the poisoning of Pd majorly by CO and some anions of the electrolyte. Additionally, high dissolution rate at acidic conditions weakens the durability and stability of the Pd based catalysts.^[33] Therefore, numerous studies searching for different strategies to improve the catalytic performance of Pd have been conducted. Alloying of Pd with different metals reduces the cost of the catalyst while maintaining its oxidizing activity. Enhanced performance of alloys is often explained by the coupling of ligand and ensemble effects. Ensemble effects are described as changes in the electronic state and catalytic properties of the surface, while ligand effects generally represent changes in the chemical properties of surface atoms.^[34,35]

Palladium based nanoparticles have been synthesized by several techniques, namely electrodeposition,^[36] chemical reduction,^[37] ion exchange,^[38] solvothermal,^[39] sol-gel,^[40]

colloidal,^[41] and polyol^[42] methods. To the best of our knowledge, colloidal methods have been reported most frequently in the literature. In order to synthesize Pd nanoparticle by colloidal method, a reducing agent and stabilizer are required. A reducing agent provides reduction of metal salt to Pd^0 , while stabilizer prevents agglomeration of the synthesized particles.^[43,44] In this method, Pd salt and reducing agent concentration significantly affect the shape and size of the nanoparticles.^[45] Furthermore, the ratio of the amount of Pd salt to reducing agent is the main cause of by-products formed subsequent to synthesis. X-ray photoelectron spectroscopy (XPS) is the most commonly used technique for the detection of by-products.

Structure Sensitivity

Catalytic reactions can be classified according to many criteria. One of these classifications is made using the relation of turnover rate with particle size. Accordingly, alteration in turnover rate with the change in particle size is called structure sensitivity while catalysts that exhibit otherwise are classified as structure insensitivity.^[46]

Metal catalysts are classified as structure sensitivity catalysts and are generally used in nanoscale. Because the reactions take place only on the surface and the catalysts in nanoscale have a wider surface than the larger particle size.^[47] Therefore, the efficiency of the nanoscale catalysts is higher than the others.^[48,49]

It is very important to adjust the particle size, which directly affects the activity of the metal catalysts. The main factors affecting particle size are synthesis parameters, namely precursor type, synthesis temperature, reduction time of metal salt, and precursor concentration.^[50]

The effect of Pd morphology at the nanoscale is an intensively investigated issue. Its significant effect on the electrocatalytic performance was emphasized by many authors.^[51,52] Zhang *et al.* have used one-pot synthesis method to produce Pd-Zn nanocrystals (Pd-Zn NCs) by reducing transition metal ions in the existence of ascorbic acid and noble metals. High activity and stability for formic acid electrooxidation with the catalytic activity of 1945 mA/mg Pd were reported. High tolerance of the catalysts to CO poisoning was attributed to the synergistic effect between Pd and Zn in the structure of Pd-Zn NCs.^[53] In another study of the same research group, PdCo nanodots (PdCo Nds) were synthesized on graphene as an anode catalyst using *in situ* adsorption-reduction method. Oxidation peak current density for formic acid electrooxidation was reported to be 1362.1 mA/mg Pd, which is the highest value among the PdCo based alloy catalysts.^[54]

Huang *et al.* used galvanic displacement electrochemical reaction to prepare PdAg@Pd core-shell nanotubes with high electrocatalytic activity for formic acid electrooxidation. They compared the potential of PdAg@Pd core-shell nanotubes to that of PdAg nanotubes and reported the mass activity and specific activity values as 1930 mA/mg_{Pd} and 2.67 mA/cm².^[55]

Unsupported Pd Based Alloy Electrocatalysts

Major disadvantages of Pd are reported to be the dissolution and corrosion problems encountered especially in acidic conditions. Formation of Pd-based alloys by the addition of a second metal is one of the frequently used strategy in order to modify the outer electronic structure of Pd and hence increase its catalytic activity.^[28] Performance of binary and ternary Pd-based alloys such as PdPt, Pd-Au, Pd-Ru, Pd-Pb, PdCo, PdNi, PdCu, PdIr, PdRh, PtBi, PdAg and PdAuCu, AuPdPt, PdSnPt have been frequently studied in the literature

Table 2 Recent studies on unsupported Pd based catalysts for formic acid electrooxidation

Catalysts	Preparation Method	Mass Activity/ (mA/mg _{Pd})	Used Solution	Ref.
PdZn	One-pot synthesis process in dimethylformamide	1945	0.1 M HClO ₄ + 0.5 M HCOOH	[97]
PdCu	Staged thermal treatment route	1108.2	0.5 M H ₂ SO ₄ + 0.5 M HCOOH	[67]
Pd	One-pot synthesis with tannic acid	304	0.5 M H ₂ SO ₄ + 0.5 M HCOOH	[68]
PtPdCu	One-pot liquid phase chemical reduction	–	0.5 M H ₂ SO ₄ + 1 M HCOOH	[69]
PdRu	Polyol reduction method	850	0.5 M HClO ₄ + 0.5 M HCOOH	[70]
PdBi	Wet-chemical method	1628.5	0.5 M H ₂ SO ₄ + 0.5 M HCOOH	[71]
PdCu	One-pot method with AA	986.1	0.5 M H ₂ SO ₄ + 0.5 M HCOOH	[98]
PtPd	Co-chemical reduction method	960	0.5 M H ₂ SO ₄ + 0.5 M HCOOH	[74]
PdPt	Electrodeposition	1200	0.3 M HCOOH	[72]
PdAg	Galvanic replacement	ca. 550	0.1 M HClO ₄ + 0.1 M HCOOH	[99]
PdPt	Polyol method	–	0.5 M H ₂ SO ₄ + 0.5 M HCOOH	[75]
CuO _x -Pd	Electrodeposition	–	0.3 M HCOOH	[73]

for formic acid electrooxidation.^[56–61] Table 2 summarizes recent studies on formic acid electrooxidation with unsupported Pd-based catalyst.

Pd loading can be reduced and electrocatalytic performance can be improved by the application of alloy catalysts.^[62–65] Behind the alloying strategy, three main effects namely ligand effect, geometric effect and ensemble effect are being discussed.^[66]

Using staged thermal treatment route, Zhang *et al.* synthesized twisted PdCu nanochains that resulted with many catalytic active sites and modified electronic effects. Compared to previously reported PdCu alloy catalysts, a relatively high catalytic activity and stability with 1108.2 and 30.7 mA/mg Pd were obtained for formic acid electrooxidation. A possible effect of Cu precursors on the reduction rate of Pd species was discussed in the related study. The researchers suggested that the main reasons for the increase in electrocatalytic properties were the twisted nanochain structure of the catalyst and its very small size. However, it is thought that the defects shown in TEM images have also contributed to the improved activity and stability.^[67] Wang *et al.* have employed tanning acid both as the reagent and the stabilizer at the same time and developed an eco-friendly synthesis method for the production of polycrystalline palladium nanoparticles. Developed catalyst has improved the efficiency and durability for formic acid electrooxidation thanks to its large electrochemical surface area and resulted in 304.00 mA/mg_{Pd} of mass activity value. This increased performance of the catalysts has been attributed to their increased poisoning tolerance. In particular, the effect of average particle sizes of Pd catalyst on activity and stability was emphasized. As in the study conducted by Zhang *et al.*, formic acid electrooxidation activity was reported to decrease with increasing Pd size. With the smallest particle size (12 nm), this trend is disrupted due to the agglomeration of small Pd nanoparticles. Investigating this very important result of the study for multimetal catalysts would be very useful for the future of electrocatalysts.^[68] The study conducted by Zhang *et al.*

focused on the metal ratios of the Pd-Zn alloy catalysts, and it was emphasized that the formic acid electrooxidation activity changed significantly with varying metal ratios. All synthesized Pd-Zn alloy catalysts showed higher mass activity and durability in 4000 s than that of Pd/C. In addition, the stability of all Zn containing catalysts has increased compared to that of Pd/C, indicating the ability of Zn to prevent CO poisoning. The researchers explained the increased activity to the nanostructure of the Pd-Zn alloy and the synergistic effect between the metals. The researchers reported that ZnO accumulation occurs at a high zinc amount while the reaction proceeds on the dehydration pathway at low Zn amount. Therefore, they emphasize the importance of the optimum Pd: Zn ratio for the highest catalytic activity and durability. It has been proved that only the metal ratio optimization can increase the mass activity of PdZn catalysts by about 3 times. On the other hand, the chemical reasons for the positive contribution of molar ratios of metals to activity and stability have not been studied in detail.^[53] PdPtCu truncated-octahedral morphology was investigated by Lv *et al.* They reported that trimetallic catalyst shows better performance than Pt. Although the catalyst in the trimetallic octahedral structure is promising, researchers have not extensively reported the cause of improved activity and stability. Improved activity and stability were attributed to Pd and Cu that change the electronic structure of Pt, but they did not report the details of this change.^[69] Kang *et al.* stressed that there is a volcano shape dependence between the size of the PdRu alloy and the activity of formic acid electrooxidation. The low activity values observed with small particle size have been explained by the formation of palladium hydride. Wang *et al.*^[68] reported similar results for the relationship between electrochemical activity and particle size of Pd. They attributed the decrease in the electrochemical activity of Pd with particle size less than 12 nm to agglomeration, while Kang *et al.* subjected to the formation of palladium hydride.^[70] Although the CA results for the highest activity PtRu catalyst indicate that the catalyst was poisoned by

CO and other undetectable structures, this catalyst still has higher stability than that of commercial Pd/C.^[70] Xu *et al.* synthesized PdBi nanodots by controlling the size of the catalyst. The PdBi catalyst was prepared by the wet chemical method, and the particle size (2.5 nm) was controlled by changing the synthesis time. It has been clearly demonstrated that particle size affects the formic acid electrooxidation activity significantly. One of the important reason why PdBi catalyst exhibits a high mass activity such as 1628.5 mA/mg_{Pd} is the very homogeneous dispersion of the nanodots. The stability of PdBi nanodots has also been reported to be higher than Pd/C. This suggests that the effect of Bi addition on stability is greater than the catalyst size impact.^[71] PtPd core-shell catalysts were prepared by Al-Akrra *et al.* via electrodeposition method, and the core-shell structure is clearly shown with TEM images. In particular, the loading of Pd on Pt is optimized for maximum formic acid electrooxidation performance. Possible CO poisoning of Pt was prevented by the Pd shell, thereby improving stability and activity was observed. Formic acid electrooxidation proceeds predominantly by dehydrogenation on the Pd surface and by dehydration on the Pt surface. The authors emphasized this by using Pt in both the core and shell. In addition, maximum electrocatalytic activity was obtained with 6 Pd monolayer. The unique aspect of this study is the optimization of the number of Pd layer on the Pt core for maximum electrocatalytic activity with the optimum Pd amount.^[72] The same research group also investigated the formic acid electrooxidation activity of CuO_x-Pd prepared by the electrodeposition method. In this study, researchers used CuO_x instead of Pt and optimized CuO_x quantity was loaded on Pd. According to their previous studies, CuO_x-Pd exhibited much higher specific activity compared to that of core-shell PdPt (6.5 > 2.54 mA/cm⁻²) despite the use of less precious metal content.^[73] The PdPt bimetallic catalyst was also investigated by other groups. For example, Qian *et al.* synthesized PtPd NPs with an average particle size of 6.5 nm using octa-maleamic acid silsesquioxanes (OM-POSS) as a stabilizing agent and optimized the metal precursor/OM-POSS ratio to achieve the highest dispersion value. The higher electrocatalytic activity of PdPt NPs compared to Pt/C was attributed to the very good dispersion of PdPt NPs. This strategy was proposed so that the catalyst was not exposed to CO poisoning. The stability of PtPd NPs is 1.7 and 5.6 times higher than Pt NPs and Pt/C, respectively. The researchers explained this with OM-POSS presence, which prevents the agglomeration of nanoparticles. Furthermore, the isolation of Pt atoms using a second metal is the main reason for alloy catalysts with high activity and stability. Using this strategy, Qian *et al.* developed a promising catalyst system.^[74] Gralec *et al.* prepared PdPt nanocatalyst with polyol method with very low Pt ratio. According to the results of the characterization, Pt enters the Pd lattice structure, thereby changing the electronic properties of Pd and improved the formic acid electrooxidation performance. Although the researchers reported similar results to other PdPt catalyst results, they did not investigate the stability properties of the catalyst.^[75]

Supported Pd Based Alloy Electrocatalysts

It is known that the formation of small crystals with high uniformity promotes active sites and catalytic activity due to its enhancement effect on accessible surface area, which in the end increases the utilization ratio of Pd.^[76] Another strategy to improve the catalytic activity of Pd-based catalysts is to utilize surfactants, polymers and ligands. This strategy mostly results with decreased active areas because of the unwanted adsorption of organic species.^[51] In order to overcome this situation, support materials with high surface area and

anchoring sites are being investigated. Carbon nanotubes (CNTs) with their high electrical conductivity and chemical stability are one of these support materials.^[77] Table 3 summarizes recent studies on formic acid electrooxidation with supported Pd-based catalysts.

The electrooxidation of HCOOH on Pd takes place by the following reaction:

In this reaction, HCOO is adsorbed onto the Pd surface as an intermediate. The strength of the bond between Pd-O is the primary determinant for the catalytic activity. This bond weakens as the difference between Pd's d-band center and Fermi level increases, whereas in the opposite case it becomes stronger. The d-band center position affecting the bond strength between HCOO-Pd should be optimized to obtain high electrocatalytic activity.^[78] Recently, it has become more common to optimize the d-band center position by adding early transition metals onto the Pd. The addition of a second early transition metal to the Pd catalyst causes the Pd-Pd bond to be compressed, thereby changing the electronic structure of the surface.^[79]

The studies carried out by our research group also benefited from the mentioned features of CNT. The most important motivation in our studies is to determine the optimum d-band center value by modifying the Pd surface with other metals and thereby increasing the electrocatalytic activity of Pd. Caglar *et al.* used NaBH₄ reduction method to synthesize CNT supported Pd catalysts. Several synthesis parameters were optimized by using Central Composite Design in order to obtain maximum mass activity toward formic acid electro-oxidation. Reported values were 974.80 mA/mg_{Pd} theoretically and 920 mA/mg_{Pd} experimentally. Optimized parameters were applied in formic acid fuel cell measurements and better results were obtained for Pd/CNT compared to commercial Pd black catalysts.^[18] In the study of Ulas *et al.*, the molar ratio of Pd and Ni was optimized to maximize the potential of CNT supported PdNi alloy catalysts towards formic acid electrooxidation for the first time in the related literature. NaBH₄ reduction was the method of choice to produce catalysts with at desired molar composition. The reported maximum mass activity value was 613.9 mA/mg_{Pd} for PdNi/CNT with 90 : 10 molar ratio. PdNi/CNT with 90 : 10 molar ratio exhibited the highest stability at the end of 1000 s, while all Ni containing catalysts showed higher stability than that of Pd/C. As previously reported many times, the increased activity and stability with the presence of Ni have been attributed to the synergy between Pd and Ni. In addition, the change in the electronic properties of Pd with the addition of Ni is the main component of this synergy.^[80] Ulas *et al.* investigated the effect of molar atomic ratio on the potential of carbon supported Pd based binary and ternary alloy catalysts, which are synthesized by using NaBH₄ reduction method. They reported maximum mass activity as 428.3 mA/mg Pd for ternary alloy catalyst PdAgNi (70 : 20 : 10). It was also observed that the catalytic activity decreased with the addition of Ni to the PdAg/CNT catalyst, while the stability of the catalyst increased. The synergistic effect and electronic promotion effect, as well as the optimization of the molar composition, were emphasized in the related study as an explanation of the enhanced performance compared to that of Pd/C. The PdAgNi catalyst showed lower electrochemical activity than that of PdNi/CNT. The main reason for this is thought to be the agglomeration of the PdAgNi/CNT nanoparticles and partial reduction of the Nickel salt.^[81] Xu *et al.* optimized the atomic ratio between Pd

Table 3 Recent studies on supported Pd based catalysts for formic acid electrooxidation

Catalysts	Preparation Method	Mass Activity (mA/mg _{Pd})	Used Solution	Ref.
Pd/CNT	NaBH ₄ reduction method	974.8	0.5 M H ₂ SO ₄ + 1.0 M HCOOH	[100]
PdIrCu/C	One-pot solvothermal reduction	4559	0.5 M H ₂ SO ₄ + 0.5 M HCOOH	[101]
PdCo/graphene	<i>In-situ</i> adsorption-reduction method	1362.1	0.5 M H ₂ SO ₄ + 0.5 M HCOOH	[54]
PdGa/OCNTs	One-pot synthesis process in ethanol	1321	0.5 M H ₂ SO ₄ + 0.5 M HCOOH	[28]
PdAgNi/C	NaBH ₄ reduction method	428.3	0.5 M H ₂ SO ₄ + 1 M HCOOH	[81]
Pt/Pd/PDAN	Repeated potential cycling	1825	0.5 M H ₂ SO ₄ + 0.01 M HCOOH	[102]
PtPd/rGO-TiO ₂	Electrodeposition	–	0.5 M H ₂ SO ₄ + 0.5 M HCOOH	[85]
Pt-Pd /C	Electrodeposition	363.09	0.5 M H ₂ SO ₄ + 1 M HCOOH	[87]
Pd/CNT	NaBH ₄ reduction method	–	–	[84]
PdCuCo/C	One-pot liquid phase chemical reduction	2142.9	0.5 M H ₂ SO ₄ + 0.5 M HCOOH	[103]
Pd ₃ Fe/C	Chemical reduction	696.4	0.5 M H ₂ SO ₄ + 0.5 M HCOOH	[104]
Pd/NP-Coal-CFs	Electrospinning	536.6	0.5 M H ₂ SO ₄ + 0.5 M HCOOH	[88]
PdAgCu/CNTs	Wet chemical route	443.6	0.5 M H ₂ SO ₄ + 0.5 M HCOOH	[30]
Pd/TiO ₂ -Gr	Solvothermal method	ca. 150	0.5 M H ₂ SO ₄ + 0.5 M HCOOH	[105]
PdRu/CNT	Polyol reduction method	850	0.5 M HClO ₄ + 0.5 M HCOOH	[70]
PdCo/C	Impregnation method	–	0.5 M H ₂ SO ₄ + 2 M HCOOH	[106]
PdNiIr/C	Ethylene glycol-assisted NaBH ₄ reduction	2830	0.5 M H ₂ SO ₄ + 0.5 M HCOOH	[107]
PdAg@ Pd/CNT	Galvanic displacement	1930	0.5 M HClO ₄ + 0.5 M HCOOH	[108]
PdNi/C	NaBH ₄ reduction method	613.9	0.5 M H ₂ SO ₄ + 1 M HCOOH	[42]
PdAgCr/MWCNT	NaBH ₄ reduction method	–	5 M H ₂ SO ₄ + 5.5 M HCOOH	[109]

and Ga on functionalized carbon nanotubes for formic acid electrooxidation. The highest mass activity (1321 mA/mg_{Pd}) and the long term stability were reported for PdGa (3.9 : 1). The researchers attributed this result to the positive contribution of functionalized CNT and to the weakening of the adsorption of formate intermediate on the Ga modified Pd surface.^[28] In addition, the carbon supported Pd catalyst was modified with Au, V, Co, Mn, Zn in other studies carried out by our research group. All PdAu/C catalysts at different metal ratio showed higher electrocatalytic activity than Pd/C. It was observed from CO stripping voltammograms of PdAu/C that the stability and poisoning tolerance of the catalyst increased with the addition of Au.^[82] In other studies, this similar synergy between Pd and Au has been observed between Pd and Co. Despite the sudden drop in initial current, PdCo/C has the highest current density at the end of 1000 s. This improvement in stability is due to the introduction of Co atoms into the lattice structure of Pd, thereby changing its surface properties.^[83]

Mazurkiewicz-Pawlicka *et al.* used the ammonia solution to increase the catalytic activity of Pd deposited on CNTs. Ammonia solution was used for the removal of polynuclear aromatic compounds, which are formed subsequent to the oxidation of multiwall CNTs and likely to be adsorbed on the metal active sites. The maximum specific power density reported in the related study was 216 mW/mg Pd.^[64] Promsawan *et al.* utilized titanium dioxide (TiO₂) modified reduced graphene oxide as the support material for the electro-

deposition of Pt and PtPd catalysts. The improved electrocatalytic activity was referred to Pd and TiO₂, as well as high electrochemically active surface area. Researchers have explained the high stability and low CO poisoning of the PtPd/rGO-TiO₂ catalyst by the charge transfer between rGO and TiO₂. In addition, the blocking of the interaction between CO and Pt by Pd atoms was observed in CO stripping tests. The improvement in the stability of the catalyst has been attributed to this behavior of Pd.^[85] In the study of Li *et al.*, PdAgCu NPs were constructed on MWCNTs support using a wet chemical route and its electrocatalytic activity through formic acid electrooxidation was studied. Catalytic performance was reported with mass activity value as 443.64 mA/mg Pd. The contribution of Cu on the increased electrocatalytic activity was explained by the induced geometric effect and improved electronic interaction between Pd, Ag, and Cu. Furthermore, researchers reported that changing the d-band center of Pd using an appropriate amount of Ag and further defect formation by Cu leaching are also among the main reasons for the good stability and improved activity values of the PdAgCu/MWCNT. However, this catalyst has lower electrocatalytic activity than other anode catalysts in the literature. The researchers have not reported the reason for this, but it can be said according to CV curves that the electrochemical activity of PdAgCu/MWCNT may have decreased due to CO poisoning.^[30]

A significant increase in mass activity value for formic acid electrooxidation was obtained in the study of An *et al.* Potential

of ternary metal elements alloy has been investigated through the synthesis of a three dimensional Ir-alloyed ultrathin ternary PdIrCu nanosheets-composed flower structure (PdIrCu/C NCF) by one-pot solvothermal reduction method. Enhancement in the electrocatalytic properties obtained through Ir and Cu addition was explained by the prevention of CO poisoning, increasing the active sites by modifying the electronic structure of Pd and by facilitating charge transfer rate and mass transport. Utilization of Ir in this study was due to its high redox potential that provides high stability in acidic media as well as its ability to produce hydroxyl groups at low potentials, which prevents CO poisoning. Moreover, the stability of PtIrCu/C NCF catalyst is 9.56 times higher than Pd/C due to its superior CO tolerance.^[86] Muthukumar *et al.* used electrodeposition technique and by changing the lower potential limit they produced Pt-Pd bimetallic catalysts with leaf-like and flower-like dendritic structures on carbon black coated carbon paper. The maximum power density values of the prepared catalysts were 49 mW/cm² and 20 mW/cm², respectively. The relatively low mass activity (363.1 mA/mg_{Pd}) reported in this study may be caused by poisoning of the PtPd catalyst. In this study, the peak pointing to the total electrooxidation on the clean electrode surface in the reverse scan is approximately 3 times the peak indicating HCOOH dehydrogenation in the forward scan. It is emphasized from the researchers that nano leaf like PtPd possesses the highest long term stability (181.78 for 3600 s) due to the high surface concentration of Pt.^[87] A similar situation was reported a study conducted by Lou *et al.*^[88] In this study, a shoulder peak of about 0.4 V was detected and in our opinion, this peak was caused by carbonaceous compounds.

Taking the advantage of their high surface area and porous structure, conducting polymers were also utilized as the support materials of catalysts. It is known that conducting polymers facilitate the flow of electronic charges and improves the efficiency of formic acid electrooxidation.^[89]

Pd Based Thin Film Electrocatalysts

Synthesis of thin films is a novel method for preparing metal coatings, in which the surface of less precious metal is replaced with a noble metal through different techniques like immersion, sputtering, electrodeposition, *etc.*^[90] Thin film method minimizes the total amount of metal required while enabling the control of metal nanostructure, cluster size and dispersion. Type of the deposition technique and the related experimental parameters, as well as the surface properties of the substrate materials, are the other factors affecting the electrochemical characteristics and morphology of the synthesized thin film catalysts.^[91,92]

In the very detailed study of Baldauf and Kolb, the effect of substrate material and film thickness on oxidation of formic acid was investigated. Based on these parameters, significant changes were observed in the catalytic properties of Pd. They used the electrodeposition technique to produce ultrathin Pd overlayers. The highest catalytic activity and resistance to CO poisoning were obtained for Pd overlayers with (100) orientation. Different atomic spacings of different substrates, namely Au, Pt, and native Pd, have caused the differences in the electronic properties of the surfaces.^[93] Obradovic and Gojkovic has also used electrodeposition technique to prepare Pd thin films on polycrystalline Au substrates and investigated their potential for formic acid electrooxidation. Obtained electronic modification has resulted in high oxidation rate as well as rapid poisoning by CO.^[94] Unlike to the study of Baldauf and Kolb, no XPS result was given in this study. Hu *et al.* used vapor deposition technique to prepare layered Pd-Cu bimetallic thin films surfaces on glassy carbon. They have eliminated the obstacles encountered during electronic and electrochemical

analyses of bimetallic nanoparticles. As the Pd film thickness decreases, D-band center is positioned away from the Fermi level and a positive binding energy shift arising from the charge transfer from Pd to Cu has observed. These changes indicates a significant modification in surface electronic structure that resulted with higher peak current density, lower onset potential, and enhanced stability for formic acid electrooxidation.^[95] In the study of Kibler *et al.*, Pd monolayers were prepared on different substrates namely, Au (111), Pt (111), PtRu (111), Rh (111), Ir (111), Ru (0001), Re (0001) and Pd (111). It is reported in the study that shifting of the d-band center down resulted with an increase in the catalytic activity of palladium monolayer.^[96]

Conclusions and Perspectives

The Pd-based catalysts have been extensively studied in the literature. However, the effect of Pd molar ratio and second metal on formic acid electrocatalytic activity was not investigated in many of these studies. In other words, the optimum d-band center has not been determined in many studies as a result of Pd surface modification with another metal. Thus, the maximum mass activity of the electrocatalysts used for formic acid electrooxidation cannot be achieved. In the future studies, the relationship between d-band center value and the electro- catalytic activity of the catalyst should be emphasized.

The electrooxidation of formic acid on Pd is predominantly carried out direct pathway. However, the large particle size of Pd-based catalysts may result in lower activity than these of Pt-based catalysts. In our opinions, comprehensive studies on the synthesis methods of Pd-based catalysts are required. In most studies, electrochemical activity was increased by alloying Pd with a second metal and this increase was generally attributed to the possible bifunctional effect, electronic effect, synergistic effect and ligand effect. However, systematic studies examining these effects are very limited. We believe that electrocatalysts with higher activity and stability can be designed by illuminating these effects.

Author Contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

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