Improving the electrocatalytic activity for formic acid oxidation of bimetallic Ir–Zn nanoparticles decorated on graphene nanoplatelets

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Abstract
A graphene nanoplatelet (GNP)-supported Ir–Zn catalyst (Ir–Zn/GNP) was fabricated by H₂ reduction to discover an alternative for non-platinum and non-palladium catalysts as an anode catalyst in direct formic acid fuel cell (DFAFC). The obtained Ir–Zn/GNP catalyst with ratio of Ir:Zn = 50:50 (Ir50Zn50/GNP) exhibited better electrocatalytic activity than GNP-supported iridium catalyst (Ir/GNP) for formic acid oxidation. Although the oxidation peak current density of Ir50Zn50/GNP was slightly lower than that of Ir/GNP, the oxidation peak potential shifted more negatively (193 mV) than Ir/GNP with higher value of the ratio of forward scan to reverse scan peak current (If/Ilb). The presence of Zn also enhanced the power density and current generation with increased performance stability in a passive DFAFC cell tests. The improvement of the electrochemical performance was ascribed to the ensemble effect where the addition of Zn could modify the Ir atom arrangement, thereby promoting the oxidation through dehydrogenation pathway. However, extremely high Zn content would inhibit oxidation capability because Zn atoms might reduce the Ir catalytic sites. A new alternative for non-Pt and non-Pd anode catalysts for DFAFC applications was successfully achieved.

1. Introduction
In recent years, fuel cell technology has been considered one of the promising alternatives to batteries for portable power sources. Fuel cells generate electricity through electrochemical reactions in which the reactant in the form of fuel reacts at the anode and oxidant converted at the cathode [1]. The advantages of fuel cells compared with batteries are longer operating times, wider temperature range, reduced environmental issues associated with disposal, the capability to work on different fuels, and instantaneous recharging capability [2, 3].

Direct formic acid fuel cells (DFAFCs) have attracted increasing attention as a potential power source for portable electronic devices due to the fuel properties that are non-toxic and non-flammable [4, 5]. The theoretical open-circuit voltage (OCV) of DFAFC (1.45 V) is higher than that of proton exchange membrane fuel cell (PEMFC) (1.23 V) and direct methanol fuel cell (DMFC) (1.21 V) [6, 7]. Formic acid exhibits lower fuel crossover through the Nafion membrane, which allows the use at higher fuel concentration up to 20 M, compared with only 2 M in methanol [8, 9]. The reduction of fuel crossover is caused by the repulsion between formate ions in formic acid and sulfonic group in the surface of Nafion membrane [10]. The main disadvantage of formic acid is its lower theoretical energy density (2086 W h l⁻¹) than methanol (4690 W h l⁻¹), although its power density is higher [4, 11]. Under ambient temperature (30 °C), the DFAFC power density value of 110 mW cm⁻² outperformed DMFC with 67 mW cm⁻² as reported by Zhu et al [12].
A generalized anode–cathode structure of a fuel cell is shown in figure 1. Fuel and other reactants are supplied to the prevailing section where the reaction occurs. DFAFCs show a great advantage compared with other fuel cell types because of their relatively high electromotive force (theoretical OCV of 1.45 V). Formic acid fuel cell systems generally exhibit higher cell voltages compared with other popular fuel cell systems.

Another supplementary advantage is the limited fuel crossover and relatively high power densities. However, the main disadvantage is the low volumetric energy density, which can be remedied by the use of high-concentration formic acid feed. The electrooxidation of formic acid has been reported via dual pathway, direct pathway (dehydrogenation), and indirect pathway (dehydration) [6, 10, 13, 14]. The electrode and cell reactions in the formic acid fuel cell occur as follows.

Anode reaction: HCOOH → CO2 + 2e− + 2H+ (1)

Cathode reaction: 1/2O2 + 2H+ + 2e− → H2O (2)

Cell reaction: HCOOH + 1/2O2 + H+ → CO2 + H2O (3)

The formation of CO intermediates in equation (1) can cause poisoning on the catalyst surface, which will disrupt the oxidation at equation (2). Thus, the ideal oxidation pathway is the direct pathway to increase overall cell efficiency [15].

The selection of anode catalyst is vital to direct formic acid oxidation toward the direct pathway. Bimetallic catalysts have been extensively studied for DFAFC to solve the poisoning and stability problems in Pt and Pd catalysts. The addition of a second metal in Pt- and Pd-based catalysts, such as Ir [8], Zn [5, 16, 17], Co [2, 14], Sn [18, 19], and V [20] at a suitable ratio, can increase the electrochemical performance toward formic acid oxidation compared with Pt and Pd monometallic catalysts. Zhang et al [19] found that the addition of Sn could modify Pd catalyst by electronic effect. On the basis of d-band theory, the presence of a second metal will lower the Pd d-band center position, thereby weakening the bonds between the metal surface and CO intermediates. The Pd/C–V catalyst synthesized by Ge et al [20] showed the ensemble effect by the adsorption of vanadium ions on the Pd surface. Given that formic acid oxidation requires at least three continuous catalyst atoms to proceed through the indirect pathway, this pathway is hindered given that vanadium ions separate the catalyst atoms through ensemble effect. In addition, Zhang et al [5] explained the synergistic effect of Zn and Pd. The addition of Zn to Pd-based catalyst can improve the selectivity of CO adsorption and increase the tolerance capability to poisoning of Pd–Zn nanocrystals due to the weakening of CO adsorptive bond on Pd active sites.

Aside from Pt and Pd catalysts, Ir can be considered one of the alternatives for the anode catalyst in DFAFC. Ir-based catalysts have been studied as an anode catalyst in PEMFC and DEFC. Li et al [21] reported that Ir–Co/C catalyst exhibits 74% higher H2 oxidation reaction than Pt/C in PEMFC. Cao et al [22] investigated the performance of Ir–Sn/C catalyst toward ethanol oxidation, and comparable OCV value with Pt–Sn/C makes it as an alternative choice as anode catalyst in DEFC.

In general, the catalyst support has an influence on the performance of electrocatalyst in terms of efficiency, durability and lifetime. Carbon materials have been widely used as electrocatalyst support for PEMFC electrodes because of their large specific surface areas, large pore volumes and high electrical conductivity [23]. Graphene, the 2D monolayer of carbon atoms, has been attracted a significant interest in electrochemical applications due to excellent electronic conductivity and corrosion resistance properties [24]. Graphene nanoplatelets (GNPs) as support for Pt nanoparticles have demonstrated high electrochemical activity and performance durability compared to commercial Pt/C catalyst [25, 26].

In the present study, graphene nanoplatelets supported Ir–Zn catalysts were synthesized by H2 reduction with different Ir:Zn atomic ratios. The catalysts were then characterized by x-ray diffraction (XRD), transmission electron microscopy (TEM), and x-ray photoelectron spectroscopy (XPS), whereas the electrochemical performances were investigated by cyclic voltammetry (CV) and chronoamperometry (CA).
2. Materials and methods

The metal precursor salts IrCl₃ and Zn(NO₃)₂·6H₂O were purchased from Sigma-Aldrich and Arcos Organics, respectively. Catalyst support GnP xGnP® was purchased from XG Sciences with an average surface area of 750 m² g⁻¹.

2.1. Preparation of catalysts

Ir–Zn/GNP catalysts were synthesized by H₂ reduction. First, calculated amounts of IrCl₃, Zn(NO₃)₂·6H₂O, and GNPs were mixed with 20 ml of distilled water, followed by ultrasonication at room temperature for 30 min. After the solution was stirred by magnetic stirrer for 30 min, 3.0 M KOH was added to the solution to adjust the pH to ca. 10. The solution was then heated in a microwave for 1 min before washing with distilled water, ethanol, and acetone. The slurry was dried in an oven at 100 °C for 12 h. Finally, the resultant powder underwent H₂ reduction by flowing H₂ in a heated tube furnace at 550 °C for 2 h. All Ir–Zn/GNP catalysts obtained with 30 wt% metal loading (Ir and Zn) on the GNP support and the atomic ratios Ir:Zn of 30:50, 25:75, and 16.7:83.3 were denoted as Ir₃₀Zn₅₀/GNP, Ir₂₅Zn₇₅/GNP, and Ir₁₆.₇Zn₈₃.₃/GNP, respectively. For comparison, GNP-supported iridium catalyst (Ir/GNP) of 30 wt% Ir loading was prepared by the same method.

2.2. Physical characterization

The XRD patterns of the catalyst were obtained using a Bruker D8 Advance x-ray diffractometer using Ni filtered Cu Kα (λ = 0.15406 nm) radiation source and operating at 40 kV and 40 mA. XRD patterns were recorded between 2θ = 10° and 80° with a scan rate of 0.25° s⁻¹. TEM was performed with a Philips CM12 microscope operating at 100 kV. The sample for TEM analysis was prepared as follows. The mixture of catalyst and ethanol was ultrasonicated for 5 min to obtain a uniform catalyst ink and dropped onto copper grids covered with carbon film. The surface chemical composition and the binding energy of Ir and Zn were analyzed using XPS (KRATOS Axis Ultra DLD) with Al Kα (1486 eV) monochromatic x-ray as the excitation source.

2.3. Electrochemical measurements

All electrochemical measurements were conducted with potentiostat/galvanostat PGSTAT204 and standard 3-compartment electrochemical cell. Pt wire and Ag/AgCl electrode were used as counter and reference electrodes, respectively. All potentials were referred to Ag/AgCl electrode. The working electrode was prepared as follows. A glassy carbon electrode with alumina was washed before use. The catalyst of 2.5 mg was mixed with 66.7 μl of isopropyl alcohol, 20.8 μl of Nafion, and 66.7 μl of distilled water and dispersed ultrasonically for 30 min at 25 °C. The resultant catalyst ink was spread on the surface of glassy carbon electrode before drying at room temperature for 1 h. Finally, the electrode was dried in the oven at 80 °C for 30 min. The surface area of glassy carbon electrode was 0.0707 cm², and catalyst loading on the electrode was 0.172 mg cm⁻². The electrode was washed before use. The catalyst of 2.5 mg was mixed with 3.0 M KOH solution in 0.5 M H₂SO₄ and 1.0 M HCOOH for 10 min to remove any O₂ dissolved in the solution. All electrochemical experiments were performed at 25 °C.

2.4. Passive DFAFC: membrane electrode assembly (MEA) preparation and pre-treatment

The membrane electrode assembly (MEA) consisted of a catalyst layer of Ir/GNP and Ir₃₀Zn₅₀/GNP on the anode and Pt on the cathode with a loading of 8 mg cm⁻² on both sides. The active area of the cell on the anode and cathode was 4 cm². Pre-treatment was performed to activate MEA. The MEA was sandwiched between the anode and cathode current collectors of fuel cell. A single cell was used to conduct all parametric studies in this work. The cell was filled with formic acid at the anode and incubated for 8 h to activate the MEA. The setup of the experiment is shown in figures 2(a) and (b).

3. Results

3.1. Characterization of the catalysts

Figure 3 shows the XRD patterns of Ir–Zn/GNP and Ir/GNP catalysts. The broad diffraction peak at ca. 26° for all catalysts was attributed to the (002) of GNP support, whereas the peaks at ca. 40°, 47°, and 69° corresponded to the (111), (200), and (220) planes of face-centered cubic (fcc) crystalline structure of Ir, respectively. With the introduction of Zn in the Ir fcc structure, the diffraction peaks of Ir were shifted to increased 2θ values, thereby showing the lattice contraction and Ir–Zn alloy formation. Furthermore, the diffraction patterns of Ir₁₆.₇Zn₈₃.₃/GNP and Ir₁₂₅Zn₇₅/GNP catalysts showed the diffraction peaks of ZnO; the patterns indicated that in Ir–Zn/GNP catalysts with high Zn content, only Ir and Zn atoms were partially alloyed, whereas the
remaining Zn atom was oxidized. In addition, no peaks related to Zn in Ir–Zn/GNP catalyst were observed. This result was probably caused by the entry of Zn into the Ir lattice and formation of Ir–Zn alloy. The average crystallite size $d$ can be calculated on the basis of the Ir\((220)\) peak based on Scherrer formula, as shown as follows [27]:

$$d = \frac{0.9 \lambda_K}{B_{2 \theta} \cdot \cos \theta_{\max}} \quad (4)$$

where $\lambda_K$ is the x-ray wavelength at 0.15406 nm, $B_{2 \theta}$ is the full width at half maximum peak in radian, and $\theta_{\max}$ is the Bragg angle at maximum peak. Lattice parameter is evaluated at Ir\((220)\) peak using Bragg formula, as shown as follows:

$$a_{fcc} = \frac{\sqrt{2} \lambda_K}{\sin \theta_{\max}} \quad (5)$$

On the basis of the average crystallite size shown in table 1, Ir/GNP displayed the smallest crystallite size at 8.85 nm, followed by Ir$_{50}$Zn$_{50}$/GNP, Ir$_{16.7}$Zn$_{83.3}$/GNP, and Ir$_{25}$Zn$_{75}$/GNP at 9.87, 10.61, and 11.33 nm, respectively. The calculated lattice parameter of Ir/GNP, Ir$_{50}$Zn$_{50}$/GNP, Ir$_{25}$Zn$_{75}$/GNP, and Ir$_{16.7}$Zn$_{83.3}$/GNP was 0.3828, 0.3826, 0.3824, and 0.3830, respectively. This result indicated that the addition of Zn to Ir may slightly reduce the lattice distance of Ir, which could be due to the atomic size of Zn (1.42 Å) being smaller than that of Ir (1.80 Å).

The TEM images of Ir–Zn/GNP and Ir/GNP catalysts are shown in figures 4(a)–(d). The particles in the Ir/GNP catalyst dispersed more evenly in the GNP support than in the Ir–Zn/GNP catalysts, although some
agglomeration remained. In the Ir–Zn/GNP catalysts, the particle dispersion improved and less agglomerated when Zn content decreased. The average particle sizes for Ir16.7Zn83.3/GNP, Ir25Zn75/GNP, and Ir16.7Zn83.3/GNP were estimated to be 4.01, 5.30, 6.23, and 8.78 nm, respectively, which indicated that the small ratio of Zn in the Ir catalyst could reduce the particle size.

XPS analyses were performed to investigate the surface composition and analyze the valence state of metals in the catalyst. The XPS spectra of Ir 4f and Zn 2p in the Ir50Zn50/GNP catalyst are shown in the figures 5(a) and (b), respectively. As shown in figure 5(a), the most intense set of doublets (Ir 4f7/2 and Ir 4f5/2 at approximately at 61.13 eV and 64.15 eV, respectively) was attributed to Ir0, which indicated the successful formation of fresh iridium surface. Two relative peaks at approximately 61.70 eV and 64.73 eV correspond to IrO2 4f7/2 and IrO2 4f5/2, respectively [28]. In addition, a formation of a set of doublets (at approximately 62.55 eV and 65.76 eV) assigned for IrCl3 was observed. The spectrum of Zn 2p in figure 5(b) was deconvoluted into two components. The first set of peaks was observed at around 1022.28 eV and 1045.43 eV, which was attributed to the presence of Zn0, thereby indicating that the majority of metallic Zn was present at the catalyst surface. The other set of peaks located at around 1023.30 eV and 1046.33 eV corresponded to the ZnO formation. The XPS result showed that the present Ir and Zn were mainly in their metallic states at the surface of the Ir50Zn50/GNP catalyst.

Table 1. Average crystallite size and lattice parameter for Ir–Zn/GNP and Ir/GNP catalysts.

| Catalyst         | Average Crystallite Size (nm) | Lattice Parameter |
|------------------|-------------------------------|------------------|
| Ir/GNP           | 8.85                          | 0.3828           |
| Ir16.7Zn83.3/GNP | 9.87                          | 0.3826           |
| Ir25Zn75/GNP     | 11.33                         | 0.3824           |
| Ir16.7Zn83.3/GNP | 10.61                         | 0.3830           |

Figure 4. TEM images of (a) Ir/GNP, (b) Ir50Zn50/GNP, (c) Ir25Zn75/GNP, and (d) Ir16.7Zn83.3/GNP catalysts.
3.2. Electrochemical studies

3.2.1. Cyclic voltammetry

Figure 6(a) shows the cyclic voltammetry (CV) curves of the catalysts in 0.5 M H$_2$SO$_4$. The peaks at −0.2 V to 0 V corresponded to the adsorption/desorption of H$_2$. Through these peaks, electrochemical surface area (ECSA) could be evaluated using the following equation [29]:

$$\text{ECSA} = \frac{Q_H}{m \cdot q_h}$$  

where $Q_H$ (C) is the charge transfer from the catalyst in the H$_2$ adsorption region, $q_h$ (μC cm$^{-2}$) is the charge transfer for the monolayer H$_2$ adsorption on the Ir surface, and $m$ (g) is the catalyst loading on the electrode. The calculation of $Q_H$ involves the integration of area under H$_2$ adsorption peak, whereas $q_h$ is the constant value from reference 220 μC cm$^{-2}$ [30]. As shown in table 2, the highest value of ECSA was of the Ir–GNP catalyst, whereas Ir–Zn–GNP catalysts showed decreased values. This result was possibly caused by the addition of Zn, which could modify the elemental composition and agglomeration level, thereby influencing the activity of catalyst material in electrochemical oxidation.

Formic acid oxidation activities of Ir–Zn–GNP and Ir–GNP catalysts were evaluated in CV with 0.5 M H$_2$SO$_4$ and 1.0 M HCOOH (figure 6(b)). On the Ir$_{50}$Zn$_{50}$/GNP catalyst, two anodic peaks, one at 0.537 V in the forward scan and another at 0.261 V in the reverse scan, showed similar shape with the Ir–GNP catalyst. Ir$_{16.7}$Zn$_{83.3}$/GNP and Ir$_{25}$Zn$_{75}$/GNP catalysts showed low peak current density values of 1.69 mA cm$^{-2}$ and 1.66 mA cm$^{-2}$, respectively.
In terms of peak potential, Ir–Zn/GNP catalysts displayed lower values than Ir/GNP catalysts, in which the peak of the Ir50Zn50/GNP catalyst exhibited the lowest negative shift at 193 mV compared with the Ir/GNP peak potential. This value could be explained by the reduced overpotential for formic acid oxidation by alloying Ir with Zn. In addition, the reverse anodic peak could be attributed to the elimination of incompletely oxidized carbonaceous species adsorbed on the catalyst metal sites \([32–34]\). Thus, the calculation of the ratio of forward scan to reverse the scan peak current \((I_f/I_b)\) could determine the poisoning rate of oxidation. On the basis of the \(I_f/I_b\) values in table 2, the Ir50Zn50/GNP catalyst showed increased \(I_f/I_b\) value, which demonstrated that the presence of Zn in the catalyst could reduce the accumulation of CO intermediates as the oxidation pathway mainly through the direct pathway.

### 3.2.2. Chronoamperometry

The catalytic activities and stability were investigated in chronoamperometry (CA) experiment in 0.5 M H\(_2\)SO\(_4\) and 1.0 M HCOOH at 0.4 V (figure 7). The current densities of all catalysts decayed rapidly at the beginning and then slowly decayed until a constant state was reached. The increased initial current density indicated additional active sites available for oxidation. The Ir/GNP catalyst showed the highest initial current density at 1.80 mA cm\(^{-2}\), which was 1.4 times higher than that of the Ir50Zn50/GNP catalyst at 1.33 mA cm\(^{-2}\). Ir16.7Zn83.3/GNP and Ir25Zn75/GNP showed extremely low current densities at 0.22 mA cm\(^{-2}\) and 0.17 mA cm\(^{-2}\), respectively. The presence of unwashed KCl phase in Ir/GNP catalyst, confirmed by XRD results, assisted in increasing the conductivity of the catalyst and subsequently enhanced its current density \([35]\). Furthermore, the current density of the Ir/GNP catalyst decayed slower and reached a higher current density at 1000s in comparison with Ir–Zn/GNP catalysts, which showed high durability and stability. Among Ir–Zn/GNP catalysts, Ir50Zn50/GNP showed the highest catalytic activity and the most stable, followed by Ir16.7Zn83.3/GNP and Ir25Zn75/GNP.

### 3.3. Performance of the catalysts in passive DFAFC

The single-cell cell tests were performed with passive DFAFC at room temperature using Ir/GNP and Ir50Zn50/GNP and Pt as anode (8 mg metal cm\(^{-2}\)) and cathode catalysts (8 mg Pt cm\(^{-2}\)), respectively. The fuel reservoir in the anode was filled with 5 ml of 5.0 M formic acid solution for each experiment. The results were discussed into two parts, that ism the polarization curves and the fuel cell performance for 1 h.

### Table 2. Summary of cyclic voltammetry (CV) results.

| Catalyst     | ECSA (m\(^2\) g\(^{-1}\)) | Scan Rate (mV s\(^{-1}\)) | Peak Potential (V versus Ag/AgCl) | Peak Current Density, \(j\) (mA cm\(^{-2}\)) | \(I_f/I_b\) | References |
|--------------|-----------------------------|---------------------------|---------------------------------|---------------------------------|------------|------------|
| Ir/GNP       | 21.01                       | 50                        | 0.730                           | 4.20                            | 1.71       | This Work  |
| Ir50Zn50/GNP | 5.70                        | 50                        | 0.537                           | 3.98                            | 2.78       | This Work  |
| Ir25Zn75/GNP | 0.23                        | 50                        | 0.562                           | 1.66                            | —          | This Work  |
| Ir16.7Zn83.3/GNP | 0.09                    | 50                        | 0.583                           | 1.69                            | —          | This Work  |
| PtRu         | —                           | 100                       | —                               | 1.35                            | —          | [31]       |
| Ir50Pt50     | —                           | 100                       | —                               | 2.30                            | —          | [31]       |

Figure 7. CA of formic oxidation in 0.5 M H\(_2\)SO\(_4\) and 1.0 M HCOOH at potential 0.4 V versus Ag/AgCl.
Figure 8(a) and shows the fuel cell polarization for Ir/GNP and Ir$_{50}$Zn$_{50}$/GNP catalysts. The OCV of DFAFCs with different catalyst layers were variable around 0.46 V and 0.37 V for Ir/GNP and Ir$_{50}$Zn$_{50}$/GNP anode catalysts, respectively, which showed a slight decrease of OCV in Ir–Zn bimetallic catalyst. Interestingly, the performance Ir$_{50}$Zn$_{50}$/GNP started to exceed the Ir/GNP at higher current value (lower applied potential).

At 0.1 V the current density outputs for Ir/GNP and Ir$_{50}$Zn$_{50}$/GNP are 13.8 and 16.1 mA cm$^{-2}$ respectively. Figure 8(b) illustrates the power density curves of the catalysts. Increased maximum power density of 2.65 mW cm$^{-2}$ was obtained at a current density of 11.6 mA cm$^{-2}$ when using the Ir$_{50}$Zn$_{50}$/GNP as an anode catalyst in comparison with Ir/GNP of 1.95 mW cm$^{-2}$ at 8.76 mA cm$^{-2}$. Bimetallic Ir$_{50}$Zn$_{50}$/GNP catalyst could produce higher power output for DFAFC compared with monometallic Ir/GNP. By contrast, the Ir$_{50}$Zn$_{50}$/GNP anode catalyst performance of a single DFAFC was compared with reported works, such as PtBi/C [36] and PdSb/C [37], and showed comparable performance.

The 1-hour performance of passive DFAFC for Ir/GNP and Ir$_{50}$Zn$_{50}$/GNP anode catalysts is presented in figure 9. Generally, both catalyst layers showed good stability throughout the duration. The power density increased sharply, followed by a slow decrease along 1 h operation for each catalyst layer. High power densities were achieved by the cell at the first 60 s because the MEA was free of impurities that were attached at the active site of the catalyst layer at the beginning of the operation. The power densities were decreasing slowly with time as the formic acid solution was consumed for the electro-oxidation reaction at the anode.
4. Discussions on the promoting effect of zinc metal

On the basis of the electrochemical experiments results, although Ir_{50}Zn_{50}/GNP catalyst showed lower ECSA value than Ir/GNP catalyst, an enhancement of peak potential to reduced value and comparable peak current density to Ir/GNP were observed. The presence of Zn in the catalyst also reduced the poisoning, as shown by the I_p/I_s value of the Ir_{50}Zn_{50}/GNP catalyst. The considerable improvement of the electrochemical performance may be attributed to the ensemble effect by the addition of Zn to the Ir catalyst [38, 39]. The ensemble effect could be described by the adsorption of the Zn atoms to Ir sites, which promoted the formic acid oxidation through the direct pathway. Ge et al [20] explained that formic acid oxidation via indirect pathway requires at least three continuous Pd atoms to occur; the case may be the same for Ir-based catalysts. However, in Ir_{16.7}Zn_{83.3}/GNP and Ir_{25}Zn_{75}/GNP catalysts, the performances were reduced because excessive Zn content would block Ir active sites.

5. Conclusions

In the present work, GNP-supported Ir–Zn catalysts were prepared by H_2 reduction method with varied atomic ratios. With reduced content of Zn in the Ir catalyst, the particles were dispersed better on GNP with small particle size in comparison with Ir/GNP. Among the Ir–Zn/GNP catalysts, the ratio of Ir:Zn = 50:50 exhibited the best electrochemical performance for formic acid oxidation in comparison with Ir/GNP. The enhancement of electrochemical performance may be attributed to the adsorption of Zn atoms at the Ir sites, which promoted the ensemble effect as the formic acid oxidation was mainly through the direct pathway. However, when the content of Zn was extremely high, the electrocatalytic activity of Ir–Zn/GNP catalyst was decreased because Zn atoms blocked the Ir active sites. From the passive cell tests, the presence of Zn enhanced the power density and current generation of DFAFC with increased performance stability. This study successfully presented a new alternative for non-Pt and non-Pd anode catalysts for DFAFC applications.

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