

Influence of Bi Modification of Pt Anode Catalyst in Direct Formic Acid Fuel Cells

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The influence of Bi modification of Pt anode catalyst on the performance of direct formic acid fuel cells was investigated. Compared with the unmodified Pt anode, the Bi modified Pt (PtBi_m) electrode prepared by under-potential deposition (UPD) caused faster electrocatalytic oxidation of formic acid at the same value of the overpotential, and thus, PtBi_m resulted in an increase in the power performance of direct formic acid fuel cells. Electrochemical impedance spectra helped to explain the difference of performance between the unmodified Pt and Bi modified Pt electrodes. Solution conductivity and dehydration phenomena occurring in highly concentrated formic acid solutions can also explain the higher power performance of PtBi_m.

1. Introduction

In the last three decades, the elementary step in the electrocatalytic oxidation of small organic molecules (C₁) on Pt and its alloys has been studied in detail both experimentally and theoretically in more than 1000 papers. The role of Pt remains central to electrocatalysis in fuel cell applications. Small organic molecules (SOM) such as formate, formaldehyde, formic acid, and methanol have potential as possible fuels in direct small organic fuel cells.^{1–5} In particular, the electrocatalytic oxidation of HCOOH on Pt in the presence of foreign adatoms is one of the most studied subjects of organic oxidations.^{1,2,6} This reaction may be considered as a model to understand the oxidation of more complex organic species on a Pt electrode, since it produces carbon dioxide and interfacial electrons that are of great interest in direct small organic fuel cell applications.

Even if formic acid has only about half the energy density (2086 Wh/L) of methanol (4690 Wh/L), a formic acid fuel cell has a higher power density compared with the direct methanol fuel cell (DMFC) due to its lower fuel crossover and the faster oxidation kinetics of anode catalysts. Of late, several groups characterized different anode catalysts, mostly noble metal and alloys, which demonstrated better performance than DMFC.^{7–12}

In our previous studies,^{13–20} a higher activity of Bi modified Pt electrode in the electrocatalytic oxidation of formic acid was observed. It was explained as resulting from the modifying effect on the Pt electrode, i.e., the electronic and third-body effect of Bi species on the Pt surface. However, as yet, no one has tried to study Bi modified Pt as anode catalyst in direct small organic fuel cells. Therefore, we investigated the influence of Bi modification of Pt in the operation of direct formic acid fuel cells, and it was compared with half cell results. Cyclic voltammetry, galvanostatic current-potential polarization and electrochemical impedance spectroscopic (EIS) techniques were the tools of choice.

2. Experimental Section

2.1. Catalyst ink preparation. Catalyst inks were prepared by dispersing 3 mg/cm² of unsupported Pt catalyst powder

(Johnson Matthey, HISPEC 1000) in the mixture of (1) deionized water and (2) isopropyl alcohol with five times the amount of catalyst loading after 5% Nafion solution (1100 EW, DuPont) with 5% of catalyst loading was added. The anode catalysts used for the formic acid electro-oxidation were unmodified and Bi modified Pt electrodes. The cathode catalyst was Pt black (Johnson Matthey, HISPEC 1000).

2.2. Half-Cell Test. We used conventional experimental apparatus with three electrodes (see Figure 1a). Catalyst ink was coated on a gas diffusion layer/carbon paper (SIGRACET GDL 31BC) with a geometric area of 0.2 cm². The working electrode (WE) was pure Pt and Bi modified Pt electrode, and the reference electrode (RE) was Hg/Hg₂SO₄, saturated K₂SO₄ (+0.64 V vs. NHE). The counter electrode (CE) was a Pt wire (99.999%).

All solutions were prepared with ultrapure water (Millipore Milli-Q water, 18 MΩ cm) and kept at room temperature. Prior to all experiments, a preliminary cyclic voltammetric (CV) curve between –0.65 V and +0.85 V was recorded in 0.5 M H₂SO₄ in order to confirm the absence of any residual impurities. In this work, modification of the Pt WE by underpotential deposition (UPD) was performed in a 1.0 mM Bi³⁺ containing solution prepared by dissolution of high-purity Bi (III) oxide (Bi₂O₃, Strem Chemicals Inc., 99.9998%) in 0.5 M HClO₄ (Merck, Suprapur). The WE potential was kept at –0.32 V for 30 min in order to establish the homogeneous Bi coverage of ca. 0.20 on the Pt electrode and the coverage of Bi on the Pt was calculated according to previous studies.^{17,18} A potentiostat/galvanostat (EG&G PAR 273A) was used for the CV experiments.

2.3. Single Cell Test. Pt catalyst ink was coated on a gas diffusion layer/carbon paper (SIGRACET GDL 31BC) with a cell geometric area of 9.0 cm². Then, additional ionomer solution was sprayed onto the catalyst layer of each electrode in order to decrease the contact resistance with polymer electrolyte membrane (Nafion 115, DuPont). Cathode and anode were placed on both sides of Nafion 115 and was hot-pressed at a temperature of 140 °C and with a pressure of 160 kgf/cm² for 300 s (CARVER Model CH). The operating temperature was 60 °C and various concentration of formic acid and oxygen were

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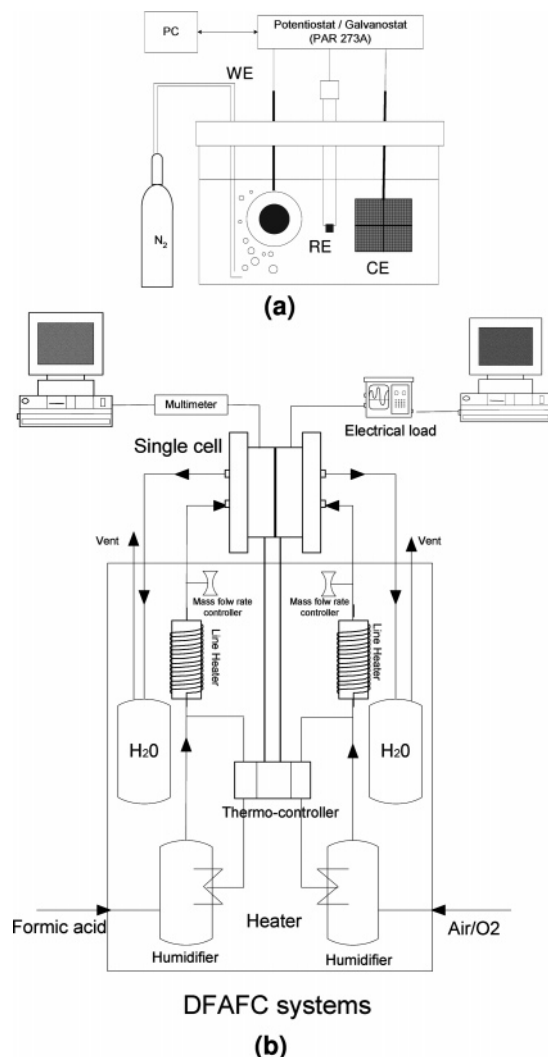


Figure 1. Schematic diagram of experimental setup for (a) half-cell experiments and (b) single cell measurements.

applied with flow rate of 15 cm³/min and 250 cm³/min, respectively (see Figure 1b).

All experiments including electrochemical measurements were conducted with cells which consisted of MEAs sandwiched between two graphite flow field plates. Current–potential transients were measured galvanostatically using an electronic load (carbon and fuel cells). Impedance spectra were measured at different constant outer potentials using a potentiostat and galvanostat/log-in amplifier (Zahner IM6). The frequency range investigated ranged from 10 kHz to 20 mHz with 15 points per decade. Solution conductivity and pH of formic acid were measured using a pH/conductivity benchtop meter (ORION). Surface morphology, crystallinity and binding energy of the unmodified and the Bi modified Pt electrode were observed using a scanning electron microscope (SEM, Hitachi S-4300), X-ray diffraction (XRD, Phillips DY616), X-ray photoelectron spectroscopy (XPS, AG ESCALAB 250), respectively.

Results and Discussion

The effect of underpotential deposition of Bi during cyclic voltammetry (CV) of the Pt electrode in 0.5 M H₂SO₄ is shown in Figure 2. The underpotential deposition of Bi was used to modify Pt electrode and total cathodic charge for Bi modification is about 13 ± 0.5 mC/cm² (see inset in Figure 2). CVs show the hydrogen adsorption/desorption and oxidation/reduction of

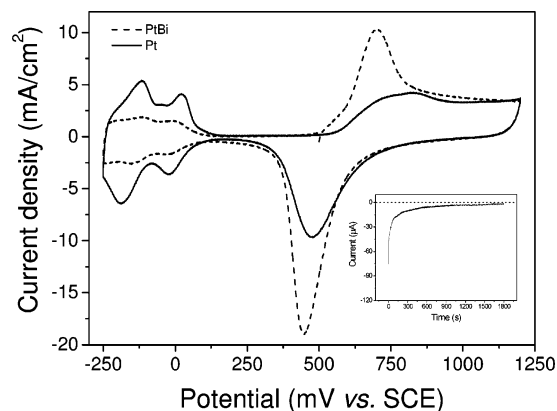


Figure 2. Cyclic voltammogram of (a) Pt and (b) PtBi_m in 0.5 M H₂SO₄. Scan rate = 50 mV/s. Inset is current–time profile of underpotential deposition of Bi at −0.32 V for 30 min.

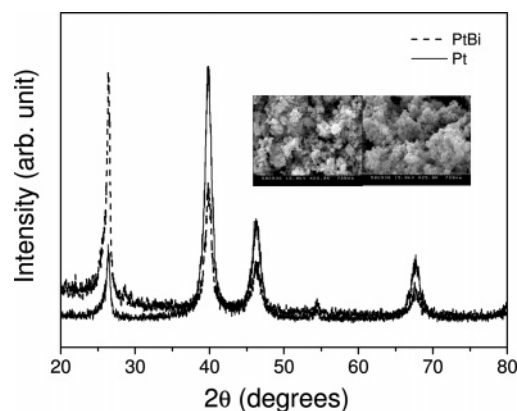


Figure 3. XRD observations of (a) modified and (b) unmodified Pt anode. Insets are SEM images of different anode surfaces.

the unmodified Pt and the Bi modified Pt electrode. The Pt electrode modified by bismuth suppresses the electrochemical characteristics of hydrogen (adsorption) and increases the oxidation current of PtBi, and we assumed that the lower onset overpotential of oxidation could increase cell potential/power density in the operation of direct formic acid fuel cells.

To analyze the structural changes in the Pt electrode induced by bismuth modification, XRD and XPS measurements were performed. In Figure 3, after Bi modification of Pt electrode, the crystal peaks of Pt and C alter their relative intensities. The carbon peak at 26.6° becomes dominant, whereas all Pt peaks become relatively smaller. Considering the XRD peak and surface modification, we assume that Bi selectively adsorbs on the Pt surface. However, the average size of the nanoparticles does not change, according to the Debye–Scherrer calculations. In XRD analysis, the Bi peak is not detected and it might be due to the highly active structure of the catalyst layer and/or the fact that the deposited Bi is amorphous structure. The Bi 4f and Pt 4f XPS spectra of Bi on a Pt surface are shown in Figure 4. Signals in the spectrum of the electrode correspond to metallic Bi and Bi complex species and, compared with the unmodified Pt anode, only a small increase of Pt binding energy is observed.

Figure 5 illustrates the effect of Bi adatoms on the formic acid oxidation on a Pt electrode. Figure 5a shows the typical CV profile on an unmodified pure Pt electrode, while an about five times higher electrocatalytic oxidation current of HCOOH at 900 mV on the Bi modified Pt electrode is observed as expected in Figure 2. In addition, the difference between Pt and PtBi_m at low outer potential of 300 mV is about 100 mA/cm². This result resembles the pattern of oxidation/reduction of

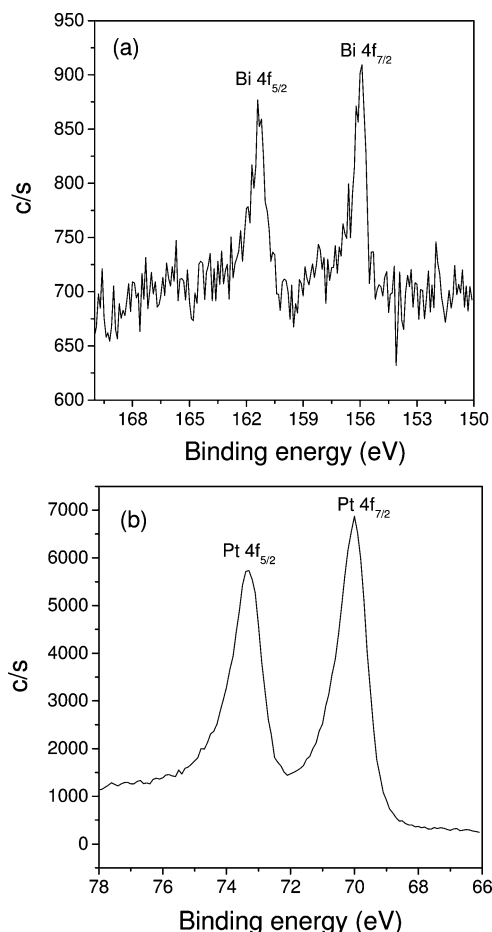


Figure 4. XPS data of (a) Bi and (b) Pt elements of Bi modified Pt anode.

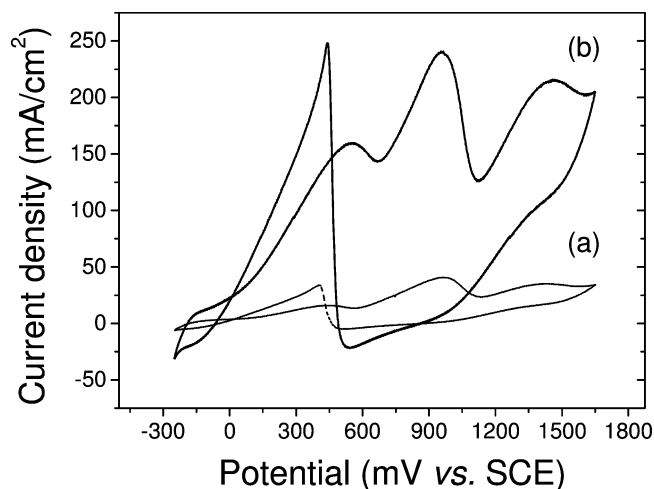


Figure 5. Cyclic voltammogram of (a) Pt and (b) PtBi_m in 1.0M HCOOH/0.5M H₂SO₄. Scan rate = 50mV/s.

in Figure 2b. Referring to previous studies,^{1,13} this higher electrocatalytic activity of PtBi_m for HCOOH oxidation is due to two modifying effects of Bi adatoms: (i) the third-body effect and (ii) an electronic effect on a single crystalline Pt surface. As mentioned in a previous study,¹² as polycrystalline Pt is used in this work, one could speculate that the enhanced current might be the result of both steric hindrance of the formation of poisoning species (CO) and intrinsic kinetic enhancement.¹

Figure 6 shows the voltage–current curve and power density of unmodified Pt anode and Pt cathode with various concentrations of formic acid. We observe that the open-circuit voltage

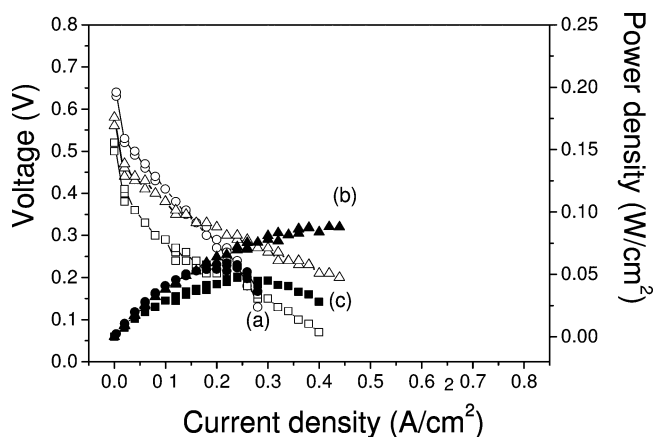


Figure 6. Single cell current–potential performance of unmodified Pt anode at 60°C. (a) 6.0M, (b) 9.0M, and (c) 15.0 M. Formic acid flow rate = 15 cm³/min, Humidified oxygen (50%) flow rate = 250 cm³/min.

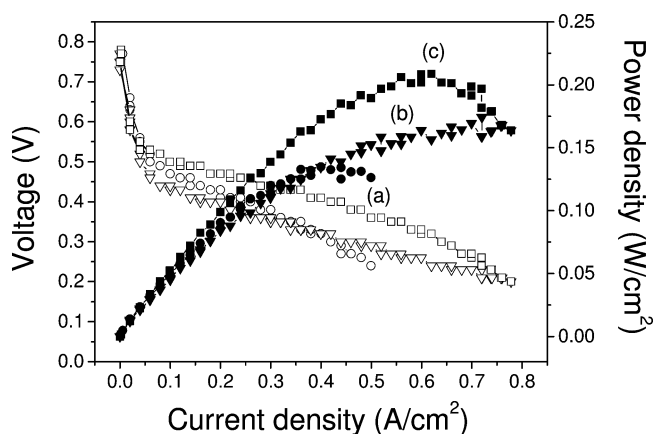


Figure 7. Single cell current–potential performance of PtBi_m anode at 60°C. (a) 6.0 M, (b) 9.0 M, and (c) 15.0 M. Formic acid flow rate = 15 cm³/min, Humidified oxygen (50%) flow rate = 250 cm³/min.

(OCV) is strongly dependent on the formic acid concentration. Using formic acid of 6.0 M, OCV is 0.64 V and it decreases to 0.53 V at 15.0 M. The OCV is strongly dependent on the amount and rate of fuel crossover. More formic acid can be electrochemically oxidized and, to compensate for the electrochemical oxidation of formic acid on the Pt cathode, a reduction reaction is initiated, which induces cathodic overpotential under OCV conditions. At the beginning of load application (very low current density applied), a similar potential drop caused by the initiation of formic acid oxidation, i.e., similar onset overpotential, is observed in all concentration formic acid ranges. The maximum power density of unmodified Pt anode in direct formic acid fuel cells is about 85 mW/cm² using 9.0 M. Even if OCV using 9.0 M is lower than OCV of 6.0 M, the IR drop is less and is similar to 15.0 M. The observations can be interpreted as the mass transfer limitation of active species.

Figure 7 shows the voltage–current curves and power density plots of bismuth modified Pt anode and Pt cathode with various concentrations of formic acid. Unlike the unmodified Pt anode, the OCV of PtBi_m is 0.75 V, and there is little difference between 6.0M and 15.0M. At low current densities, the cell voltage drops by ca. 0.6 V and it is due to the initial activation loss of anode and cathode catalyst. On the other hand, due to the slower IR drop at 15.0 M, the power density reaches 210 mW/cm². The relationship between the solution conductivity/pH value and the activity of catalyst and membrane induces different IR drop, i.e., power profile.

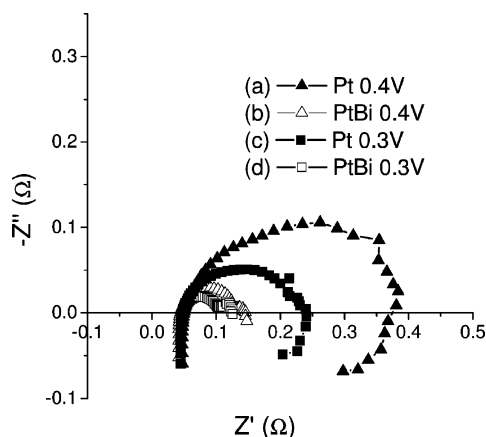


Figure 8. Impedance of (a) Pt and (b) PtBi_m anode at 0.4V. (c) and (d) are impedance data of Pt and PtBi_m anode at 0.3V, respectively. Formic acid flow rate = 4.0 cm³/min, hydrogen flow rate = 500 cm³/min.

In our previous RRDE study,¹³ we reported dissolution/desorption of Bi metal and/or its (hydro) oxides at the Pt oxidation overpotential. Redeposition of Bi onto the Pt surface could be accomplished by a cathodic scan of an electrolyte containing Bi ions. After repetitive CVs, the Bi modification by UPD could not be recovered due to the low concentration of Bi ions. However, the constant coverage of Bi on the Pt anode can be maintained during application in direct formic acid fuel cells, because the applied anodic overpotential of the cell is below the Bi oxidation overpotential.

To understand the difference between Figures 6 and 7, the electrochemical impedance spectra of the cell were measured. Figure 8 shows comparative impedance spectra of direct formic acid fuel cell systems using unmodified/modified Pt anode catalyst. The impedance plots exhibit a clock-wise loop indicating a dynamically stable stationary mode. At OCV, we observe a similar impedance value, because it reflects simply the membrane (cell) resistance (not shown in this work). Loading low current density range, i.e., at a cell voltage of 0.4 V, the theoretical stability (the value of mixed potential at the cathode) of the unmodified/modified electrode is different and comparable data is observed. Bi modified Pt anode decrease the resistance from 0.37 to 0.15 Ω. A lower cell potential of 0.3V causes the impedance to decrease due to the faster oxidation kinetics at high anodic overpotential. In all potential ranges, the unmodified Pt anode has a higher impedance. This is in good agreement with the lower cell performance.

In a performance measurement of direct formic acid fuel cells using the Bi modified Pt anode, the maximum power is obtained using 15.0 M acid. The conductivity and pH value of the formic acid solution is strongly dependent on the amount of water, i.e., the concentration of "free" formate ions. It can be understood by considering of the dissociation of HCOOH by water (see reaction 1). In Figure 9, the conductivity of formic acid has a



maximum value between 6.0 and 12.0 M; below 6.0 M and above 12.0 M, the conductivity is reduced. The pH value decreases with increasing formic acid concentration. According to Figure 9, we understood that an appropriate concentration of formic acid could cause a decrease in IR between 6.0 and 12.0 M resulting in the generation of maximum power. However, maximum power of about 210 mW/cm² is observed using 15.0 M acid. We interpret this as meaning there is less

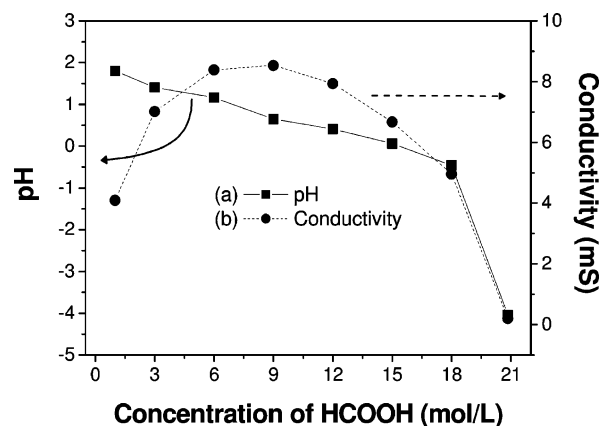


Figure 9. Conductivity and pH value of formic acid as a function of concentration.

water flooding phenomena at the cathode and perhaps enhanced dehydration of membrane, as previously reported.¹¹ Even if 15.0 M formic acid has lower conductivity and more crossover of formic acid from anode to cathode occurs, the dehydration by concentrated formic acid could induce appropriate operating conditions. Above 15.0 M, the conductivity of formic acid solution dramatically falls and its low value brings about the much smaller power performance of ca. 60 mW/cm². In a previous studies,^{22,23} proton spin-spin relaxation measurements and the solvation parameters, calculated using Kirkwood-Buff's integrals for HCOOH-H₂O, indicated that a hydrophobic interaction due to the formation of (HCOOH)_m(H₂O)_n hetero-solvates dominates in the region up to 0.8 mole fractions (i.e., ca. 16 M) of HCOOH destroying the structure of liquid water and producing H⁺ ions. Less fuel crossover, due to the repulsion between formate ions and sulfonic acid groups and the lower performance at concentrations > 15.0 M can thus be understood.

In addition, previous studies by Masel et al.¹¹ demonstrated that high concentrations of formic acid and/or high cell temperatures caused dehydration and the decrease of the partial pressure of oxygen at the cathode when dry air only was used. Below 10.0 M, the dehydration of the MEA had only little influence of the performance, but the membrane conductivity was decreased when using > 10.0 M acid due to the severe dehydration. Our results, i.e., better performance using higher concentration of 15.0 M, are different with Masel's observations and interpretation, because excess water produced in this study using humidified oxygen might be dehydrated at a usage of 15.0 M formic acid. The difference between the two studies might be due to the differing activities of the anode catalysts.

Conclusions

We investigated the influence of Bi modification of Pt anode catalyst in the operation of direct formic acid fuel cells and compared them with the unmodified Pt anode. Due to the faster oxidation of formic acid, the Bi-Pt electrode (PtBi_m) prepared by under-potential deposition (UPD), increased power performance up to 210mW/cm², that is, about double that using a Pt anode electrode alone. Impedance data and solution conductivity can explain the higher power performance of PtBi_m. Using concentrated formic acid (> 15 M), the performance was lower than that of the unmodified Pt anode. Pure formic acid solution has a very low conductivity, since its ionization is not possible. In this work, the UPD modification method using bismuth as dopant is the key feature of the results.

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