Au as an efficient promoter for electrocatalytic oxidation of formic acid and carbon monoxide: a comparison between Pt-on-Au and PtAu alloy catalysts

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Abstract The absence of unpaired d-electrons of gold leads to its lack of reactivity and paucity of catalytic activity. Synergistic activity of bimetallic PtAu has been proved, and its structure greatly influences on the electrocatalytic activity toward formic acid and carbon monoxide oxidation. Here, a comparison between Pt-modified Au (designated as Pt-on-Au) and PtAu alloy catalysts has been studied. The Pt-on-Au catalyst was prepared by electrodeposition of Pt on the pre-prepared Au, while PtAu alloy was obtained by co-electrodeposition. As a whole, both types of PtAu catalysts were found to be more active toward formic acid electrooxidation compared to pure Pt, exhibiting maximum activity on Pt-on-Au catalyst with Pt to Au atomic ratio of 1:10.22. Moreover, the Pt/Au atomic ratio directly relates to the oxidation pathway of formic acid and carbon monoxide oxidation. The results may be ascribed to much less CO_{ads} on the surface than single Pt catalyst due to the effect of Au nanoparticles. CO stripping voltammograms present the obvious variation between Pt-on-Au and PtAu alloy catalysts. Meanwhile, the electrocatalytic activities of bimetallic PtAu are evaluated by electrochemical impedance spectroscopy and Tafel analysis.

Keywords Pt-on-Au catalyst · PtAu alloy · Electrocatalytic activity · Formic acid · CO stripping voltammograms

Introduction

In order to solve the problems of air pollution, increasing energy demands, as well as limited fuel reserves caused by

traditional fuel consuming, energy storage devices including fuel cells become more and more concerned [1–7]. In particular, direct formic acid fuel cell (DFAFC) has attracted great attention with its advantages of nontoxicity and low fuel crossover as compared to methanol, which makes DFAFC a promising candidate for power source in portable electronic devices [8, 9]. As we have known, a catalyst is a very important part of fuel cells, and platinum is the most common anode catalyst for formic acid (FA) oxidation. However, Pt is prone to poisoning by CO-like intermediates, leading to a significant decrease of catalytic performance [10–12]. It is due to the fact that the indirect pathway by dehydration is predominant in the oxidation reaction of FA on pure Pt, but not by the dehydrogenation pathway [13].

In order to improve the catalytic performance of FA oxidation by dehydrogenation pathway, the development of bimetallic Pt–M (M = Au, Pd, Ru, Bi, etc.) catalysts has been recognized as one of the most effective strategies. The facts show that a Pt-based catalyst has improved the catalytic performance of FA oxidation compared with pure Pt [14–19]. Among various Pt-based catalysts, bimetallic Pt–Au is one of the best catalysts for formic acid oxidation, which is attributed to its enhanced activity [11, 20, 21] and stability against dissolution by raising the Pt oxidation potential [20, 22–26]. Moreover, the incorporation of Au into Pt could lead to the segregation of Pt sites and further reduce the number of adsorption sites for CO, thereby yielding an improvement in the activity of FA oxidation [13, 20, 27].

Recently, various bimetallic Pt–Au catalysts with different structures, such as PtAu alloy [21, 28], Pt-modified Au (Pt-on-Au) [29, 30], and Au@Pt [31, 32], show excellent catalytic activity toward FA oxidation. Park et al. [33] found that the uniform Pt-on-Au nanoparticles showed higher electrocatalytic activities than the pure Pt electrocatalyst in the area- and mass-specific current densities. It is attributed to the enhancement effect of Au atoms and the high Pt utilization in the FA electrooxidation reaction. Ding et al. [29]

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Table 1 Preparation variables and composition of Pt-on-Au catalysts

Catalysts	Precursor concentration/mmol L ⁻¹		Q_{dep}/C		Atomic ratio ^a
	HAuCl ₄	H ₂ PtCl ₆	Au	Pt	
M-1:20.01	3.0	0.77	5×10^{-2}	5×10^{-5}	1:20.01
M-1:10.22	3.0	0.77	5×10^{-2}	1×10^{-4}	1:10.22
M-1:7.16	3.0	0.77	5×10^{-2}	2×10^{-4}	1:7.16
M-1:5.28	3.0	0.77	5×10^{-2}	5×10^{-4}	1:5.28
M-1:2.19	3.0	0.77	5×10^{-2}	1×10^{-3}	1:2.19
Pure Pt	–	0.77	–	1×10^{-2}	–

^a The atomic ratio on the surface of catalyst obtained by EDX

fabricated the monolayer Pt-modified nanoporous Au catalyst with ultralow Pt loading, great tolerance to poisoning, and high stability for FA electrooxidation. They suggested that the outmost Au layer may not only inhibit Pt oxidation but also hold a thermodynamic stabilization effect. Xu and co-workers [21] studied the electrocatalytic activity of PtAu alloy nanoparticles with 1:1 atomic ratio and demonstrated that the PtAu/C catalyst exhibited a higher activity for FA oxidation reaction than commercial Pt/C. Liu et al. [34] developed a 3D porous AuPt alloy foam film catalyst with superior electrocatalytic activity toward FA oxidation. Huang et al. [35] prepared a PtAu alloy catalyst by electrodeposition method for FA electrooxidation with the dehydration pathway. Additionally, the surface composition of atomic Pt/Au ratio and the preparation method are significantly related to the electrocatalytic activity of bimetallic PtAu catalyst for FA oxidation reaction [13, 34–36]. In general, the high electrocatalytic activity of bimetallic PtAu catalyst has been ascribed to the special electronic effect [29, 36, 37], ensemble effect [11, 20, 30], and synergistic effect [34, 38, 39]. Many research findings have revealed that both Pt-on-Au and PtAu alloy catalysts exhibited high electrocatalytic activity toward FA oxidation with much less CO_{ads} than that

on Pt catalyst surface. However, to the best of our knowledge, there are no reports on the comparison of electrocatalytic activity of Pt-on-Au and PtAu alloy obtained by electrodeposition toward FA and CO oxidation.

In this work, we synthesized two types of bimetallic PtAu catalysts by electrodeposition of Pt on pre-prepared Au nanoparticle (designated as Pt-on-Au) and co-deposition of Pt and Au (designated as PtAu alloy). The electrocatalytic activities of bimetallic PtAu catalysts with a different Pt/Au ratio toward FA and CO oxidation were investigated systematically by cyclic voltammetry, Tafel plots, and electrochemical impedance spectroscopy (EIS).

Materials and methods

Materials

H₂PtCl₆ and HAuCl₄ were purchased from Sinopharm Chemicals Reagent Co., Ltd., China. All chemicals (HCOOH and H₂SO₄) were of analytical grade. All aqueous solutions were prepared with double-distilled water.

Table 2 Preparation variables and composition of PtAu alloy catalysts

Catalysts	Precursor concentration ^a /mmol L ⁻¹		Q_{dep}/C	Atomic ratio ^b
	HAuCl ₄	H ₂ PtCl ₆		
A-5.08 :1	2.5	0.5	5×10^{-3}	5.08:1
A-3.44 :1	2.25	0.75	5×10^{-3}	3.44:1
A-0.94 :1	1.5	1.5	5×10^{-3}	0.94:1
A-1:2.04	1.0	2.0	5×10^{-3}	1:2.04
A-1:2.70	1.0	2.0	5×10^{-3}	1:2.07
A-1:3.85	0.75	2.25	5×10^{-3}	1:3.85

^a A mixed solution containing HAuCl₄ and H₂PtCl₆

^b The atomic ratio on the surface of catalyst obtained by EDX

^c The total deposited charge for PtAu alloy

Fig. 1 SEM images of M-1:10.22 (a) and A-1:2.04 (b)

Apparatus

The electrochemical experiments were carried out in a conventional three-electrode cell using a CHI660B electrochemical workstation (Shanghai Chenhua Instrumental Co., Ltd., China). A glassy carbon electrode (GCE, 3 mm in diameter) was used as the working electrode. Before use, GCE surface was polished with 0.3 μm alumina slurry and then rinsed with doubly distilled water in ultrasonic bath. The counter electrode and the reference electrode were platinum wire and saturated calomel electrode, respectively, which were carefully cleared before the experiment. Electrolyte solutions were deaerated by a dry nitrogen stream and maintained with a slight overpressure of nitrogen during the electrochemical measurements. All of the electrochemical measurements were carried out at room temperature. Scanning electron microscope (SEM, S-4700, Japan) equipped with an energy-dispersive X-ray analyzer (EDX, S-4700, Japan) was used to determine the morphology and composition of catalysts. X-ray diffraction (XRD) measurements and X-ray photoelectron spectroscopy (XPS) were performed on an X'Pert-Pro MPD X-ray diffractometer using CuK α radiation (50 kV) and on an ESCALab220i-XL electron spectrometer from VG Scientific using 300-W AlK α radiation, respectively.

Preparation of the catalysts

The procedures of Pt-on-Au nanoparticles were prepared by a two-step electrodeposition. First, the Au-modified GCE (Au/GCE) were obtained by the electrodeposition of Au on GCE at -0.2 V in a solution consisting of 3.0 mM HAuCl $_4$ and 0.5 M H $_2$ SO $_4$ and then was rinsed with double-distilled water for the following experiment use. The pre-prepared Au/GCE as working electrode was immersed into 0.5 M H $_2$ SO $_4$ solution containing 0.77 mM H $_2$ PtCl $_6$ for the electrodeposition of Pt. Pt nanoparticles were deposited under an applied potential of -0.2 V by a potentiostatic method. The resultant Pt-modified Au/GCE (Pt-on-Au) was rinsed thoroughly with double-distilled water several times. The Pt-Au catalysts with different atomic ratios on the surface of catalysts by controlling the deposited charge of Pt are designated as M-1:20.01, M-1:10.22, M-1:7.16, M-1:5.28, and M-1:2.19 in Table 1. For the preparation of PtAu alloy catalysts, it was completed by co-deposition at a constant applied potential of -0.2 V in a mixed H $_2$ PtCl $_6$ /HAuCl $_4$ solution containing 0.5 M H $_2$ SO $_4$. The different atomic ratios of PtAu alloy were prepared by changing the concentration of H $_2$ PtCl $_6$ and HAuCl $_4$, and the corresponding samples were designed as A-5.08:1, A-3.44:1, A-0.94:1, A-1:2.04, A-

Fig. 2 XRD patterns of Pt-on-Au and PtAu alloy nanoparticles: **a** Pt-on-Au nanoparticles, **b** PtAu alloy nanoparticles

Fig. 3 XPS spectra of Pt_{4f} and Au_{4f} for the M-1:10.22 and A-1:2.04

1:3.27, and A-1:3.85 in Table 2, respectively. For a comparison of voltammetric features and electrocatalytic activities, the pure Pt catalyst on GCE (Pt/GCE) was also prepared under similar conditions as stated earlier.

Pt or Au loading was evaluated by the charge integrated during the deposition process (Q_{dep}) with an assumption of 100 % current efficiency according to Eq. (1):

$$W = \frac{\eta Q_{\text{dep}} M}{FZ} \quad (1)$$

Here, W is the mass of deposited Pt or Au, η is current efficiency (assuming 100 % current efficiency here), Q_{dep} is the total charge passed through the electrodes during the deposition process, M is the molecular weight, F is the Faraday constant (96,485 C mol⁻¹), and Z is the number of electrons transferred (taken as four for the Pt and three for the Au formation).

Results and discussion

Morphology and structure characterization

The morphology and structural features of the two types of PtAu catalysts were investigated by SEM and XRD. Figure 1 shows a SEM micrograph for the M-1:10.22(A) and A-1:2.04(B) on GC electrode. As can be seen from Fig. 1a, the M-1:10.22 catalyst formed with Pt particles growing layer by layer on the surface of pre-deposited Au substrate exhibits rough surface morphology and coral-like structure. However, the A-1:2.04 shown in Fig. 1b displays a quasi-spherical particle structure with small pricks uniformly dispersing on the surface, which is the nucleation site for the alloy deposition. Figure 2 shows the XRD patterns of the two types of as-prepared PtAu catalysts. As is known, the peaks of pure gold nanoparticles ($2\theta=38.2^\circ$, 44.4° , and 64.6°) and pure platinum nanoparticles ($2\theta=39.8^\circ$, 46.2° , and 67.5°) are assigned to the (111), (200), and (220) planes, respectively, indicating the typical face-centered-cubic crystal structure. As shown in Fig. 2a, besides the diffraction peaks of Au, no obvious reflection peaks of Pt can be observed due to the low loading of Pt on the Au surface, also indicating that the Pt nanoparticles are uniformly deposited on Au surface without agglomeration. In Fig. 2b, it is worth noting that the (111) peaks of PtAu alloy occur between (111) peaks of pure Au and Pt nanoparticles, which move to a lower 2θ value tending towards the corresponding peak of pure Au as the Pt/Au ratio decreases. It suggests that a single-phase alloy of PtAu has been formed by electrochemical co-deposition. In addition, the EDX analysis in Tables 1 and 2 has also confirmed the presence of Pt and Au in the as-prepared Pt-on-Au and PtAu alloy catalysts.

To investigate the atomic composition and properties of M-1:10.22 and A-1:2.04, XPS was then used to characterize

Fig. 4 a CVs of Pt/GC and Pt-on-Au electrodes and b Pt/GC and PtAu alloy electrodes recorded in 0.5 M H₂SO₄ aqueous solution. Scan rate, 50 mV s⁻¹

Fig. 5 **a** CVs of Pt/GC and Pt-on-Au electrodes. **b** PtAu alloy and Pt/GC electrodes in 0.5 M HCOOH + 0.5 M H₂SO₄ solution only the positive-going potential scans at 50 mV s⁻¹ and current densities of

peak O₁ and the peak O₂ in HCOOH oxidation on Pt-on-Au electrodes (**c**) and on PtAu alloy electrodes (**d**) as a function of sample compositions

these samples. As shown in Fig. 3, for M-1:10.22, the peaks at 74.1 and 70.9 eV correspond to the 4f_{5/2} and 4f_{7/2} of

metallic Pt, which shift slightly to lower binding energy as compared to bulk Pt (74.5 and 71.2 eV) [40], indicating that

Table 3 Parameters of FA oxidation and CO stripping voltammograms on the Pt-on-Au and PtAu catalysts, respectively

Catalysts	FA oxidation			CO stripping		
	j_{O1} mA cm ⁻²	j_{O2} mA cm ⁻²	j_{O1}/j_{O2}	E_I V	E_{II} V	Q_{CO} C
M-1:20.01	8.82	1.30	6.78	0.671	0.84	0.013
M-1:10.22	15.76	4.33	3.64	0.682	—	0.062
M-1:7.16	12.44	5.10	2.44	0.688	—	0.052
M-1:5.28	6.67	8.59	0.78	0.693	—	0.043
M-1:2.19	4.86	9.29	0.52	0.689	1.10	0.067
A-5.08 :1	1.57	3.67	0.43	0.71	—	0.097
A-3.44 :1	1.87	2.25	0.83	0.73	1.10	0.034
A-0.94 :1	4.71	1.19	3.97	0.76	1.07	0.010
A-1:2.04	6.94	1.48	4.69	0.84	1.04	0.008
A-1:2.70	0.13	0.18	0.72	—	1.01	—
A-1:3.85	—	—	—	—	1.01	—
Pure Pt	1.13	5.56	0.20	0.660	0.97	0.136

Fig. 6 Quasi-steady-state polarization curves for the oxidation of HCOOH in 0.5 M HCOOH + 0.5 M H₂SO₄ electrolyte recorded on **a** Pt-on-Au and Pt electrodes, **b** PtAu alloy, and Pt electrodes (**c**) area-specific current densities at 0.1 V. Scan rate, 1.0 mV s⁻¹

the electronic structure of Pt is modified by Au [41]. While for Au in M-1:10.22, its 4f_{7/2} and 4f_{5/2} peaks can be observed at 84.00 and 87.70 eV, the same as that of bulk Au due to the scattering dispersion of Pt nanoparticles on the Au substrate [40]. However, as exhibited in Fig. 3, both the peaks of Au_{4f} and of Pt_{4f} in A-1:2.04 shift to lower binding energies as compared to those of bulk Au and Pt, which indicates that the PtAu in A-1:2.04 catalyst is an alloy [42].

Voltammetric analysis

Figure 4 shows the cyclic voltammograms (CVs) of pure Pt, Pt-on-Au (Fig. 4a), and PtAu alloy (Fig. 4b) on GCE in

deaerated 0.5 M H₂SO₄ solution under a scan rate of 50 mV s⁻¹. For Pt/GCE, the curve presents a well-defined hydrogen adsorption/desorption ($H_{\text{ads/des}}$), the broad double layer, and the cathodic reduction peak of Pt oxide in the potential region of -0.2~0.1, 0.1~0.28, and 0.28~0.9 V, respectively. The CVs of Pt-on-Au and PtAu alloy show the shapes similar to the pure Pt. Moreover, the peaks of $H_{\text{ads/des}}$ are smaller than that on pure Pt and gradually increase with the increase of Pt loadings. It can be observed that the reduction peaks of Pt oxide on both PtAu catalysts shift to a lower potential as the decrease of Pt loading ascribed to the size effect of Pt islands [43]. Additionally, it is noted that the reduction peak of Pt oxide on Pt-on-Au consists of two overlapping peaks when the ratio of Pt:Au is larger than 1:5.28, indicating the formation of two different Pt particles/structures/agglomerates [44, 45]. A similar phenomenon can be seen on the PtAu alloy catalysts with the Pt/Au ratio exceeding 0.94:1. When the Pt composition on/in Au becomes larger, the $H_{\text{ads/des}}$ peaks and the reduction peaks of Pt oxide markedly increase. Kristian [46] pointed out that the Pt entities on the Au surface have more negative potential for the reduction of Pt oxide at lower Pt/Au ratios since it makes obtaining electrons more difficult for Pt atoms compared to higher Pt/Au ratios and pure Pt.

Electrooxidation of formic acid

Figure 5a presents the positive scan CVs of Pt/GCE and Pt-on-Au catalysts toward FA oxidation in a mixed solution of 0.5 M HCOOH and 0.5 M H₂SO₄. For Pt/GCE, the typical feature of the FA electrooxidation is observed according to the dual-pathway mechanism. As can be seen, a weak peak (O₁) current density at about 0.3 V is related to the direct oxidation of FA via the dehydrogenation mechanism, while the other peak (O₂) at 0.70 V is due to the oxidation of intermediate CO generated from the dehydration of FA [47]. Obviously, the peak current density at O₁ (j_{O1}) on Pt-on-Au is larger, and the peak current density at O₂ (j_{O2}) relatively becomes lower than that on pure Pt toward FA oxidation (in Fig. 5a and Table 3), which is in agreement with the results of previous reports [29, 30]. Especially, the M-1:10.22 catalyst of Pt-on-Au shows the highest j_{O1} (15.76 mA cm⁻²), which is ~14 times higher than that of Pt/GCE. With further decrease of the Pt/Au ratios to 1:20.01, the first anodic peak (O₁) decreases drastically and the second peak (O₂) almost vanishes. It indicates that FA electrooxidation mainly follows the dehydrogenation pathway on the M-1:10.22 and M-1:20.01 Pt-on-Au catalysts.

The ratio of $j_{\text{O1}}/j_{\text{O2}}$ (in Table 3) was further used to evaluate the effect of Pt/Au composition on FA oxidation pathway. The $j_{\text{O1}}/j_{\text{O2}}$ on Pt-on-Au is larger than that on pure Pt (0.20) and gradually increases as the Pt loadings on Au surface decrease. It is due to the dehydration pathway on pure

Fig. 7 **a** CO_{ads} stripping voltammograms on M-1:20.01, M-1:10.22, M-1:7.16, M-1:5.28, M-1:2.19, and pure Pt, respectively. **b** CO_{ads} stripping voltammograms on pure Pt, A-5.08:1, A-3.44:1, A-0.94:1, A-1:2.04, A-1:2.70, and A-1:3.85, respectively, recorded in 0.5 M H_2SO_4 at a scan rate of 20 mV s^{-1}

Pt or Pt-rich catalyst, leading to the formation of CO intermediates. When the Pt/Au ratio is below 1:7.16, the pathway of FA oxidation transforms into dehydrogenation. It is in agreement with the observation by Kristian et al. [30] who attributed such to a proposed ensemble effect for Pt-on-Au.

For comparison, Fig. 5b shows the positive scan CVs of PtAu alloy catalysts for the electrooxidation of FA. A similar phenomenon for FA electrooxidation can be observed on PtAu alloy. Interestingly, the highest j_{O_1} and $j_{\text{O}_1}/j_{\text{O}_2}$ were obtained on the A-1:2.04 PtAu alloy (6.94 mA cm^{-2}) (Fig. 5b and Table 3), which is different from Pt-on-Au. However, on A-1:2.70 and A-1:3.85, the FA oxidation peak at both O_1 and O_2 almost vanishes due to the increase of Au. Although a similar dehydrogenation pathway for FA oxidation can be observed on Pt-on-Au (M-1:10.22) and PtAu alloy (A-1:2.04) catalysts, the different Pt/Au composition suggests that the electronic structure of PtAu has a significant influence for the FA oxidation pathway, which needs more and further work to study.

As explained earlier, the height of the peak O_1 and O_2 and their ratio give an indication along which path the reaction is dominant during the electrooxidation of formic acid on the catalyst. Figure 5c, d shows a systematic dependence of these two peaks on the surface composition of Pt-on-Au and PtAu alloy, respectively. At Pt-on-Au surface, peak O_1 is the highest at the ratio of Pt/Au 1:10.22 and decreases with an increase in the ratio of Pt/Au, while peak O_2 height ascends with further increase of Pt loading. For PtAu alloy catalyst, the trend of peak O_1 is similar to that of Pt-on-Au catalyst; however, the height of peak O_2 starts to descend and would probably reach zero with a decrease in the ratio of Pt/Au.

To further investigate the kinetics of FA oxidation, Tafel measurements were performed under a steady-state condition. As seen from Fig. 6a, b, the slope of Tafel plots for the Pt-on-Au and PtAu alloy shows a much lower value than that

of Pt/GCE (145 mV dec^{-1}). Moreover, the M-1:10.22 Pt-on-Au and A-1:2.04 PtAu alloy catalysts show the lowest values of 102 and 114 mV dec^{-1} , respectively. As we have known, the Tafel slope is related to the CO coverage on catalyst, and a lower CO coverage means a lower Tafel slope value [10, 33]. In addition, Fig. 6c shows the area-specific current densities at 0.1 V based on the Tafel plots. The activities of Pt-on-Au and PtAu alloy catalysts are much higher than Pt/GC. Also, the current density for FA oxidation on M-1:10.22 Pt-on-Au is about two times higher than that of A-1:2.04 PtAu alloy. Compared with Pt/GCE, the lower slopes and the higher current density of both PtAu catalysts are attributed to the low amount of adsorbed CO or intermediates on the Pt sites. Meanwhile, this result indicates that the Au atoms of Pt-on-Au nanoparticles are more powerful in improving the electrocatalytic activity toward FA oxidation than those of PtAu alloy particles [33].

CO_{ads} stripping voltammetry

The CO_{ads} stripping voltammetry measurements were performed on Pt-on-Au (Fig. 7a) and PtAu alloy catalysts on GCE (Fig. 7b) in 0.5 M H_2SO_4 solution. As shown in Fig. 7, the pure Pt on GCE presents a typical CO_{ads} oxidation peak at $\sim 0.65 \text{ V}$ [43]. For the Pt-on-Au catalysts, the CO stripping peak shifts positively to a higher potential and becomes narrower compared with that on pure Pt. The CO stripping curve of M-1:20.01 Pt-on-Au evolves into a small and broad peak consisting of two poorly separated peaks (a peak at 0.67 V and a shoulder at 0.83 V), indicating that two types of Pt sites exist on the Au substrate [48]. With the increase of Pt loading on Au surface, the CO stripping peaks appear at a lower potential (at $\sim 0.7 \text{ V}$) and becomes larger. Yu and co-workers [49] reported similar results and illustrated that the ratio of the isolated single Pt atom within the Pt adatom population decided the CO adsorption on the Pt-modified

Fig. 8 Nyquist plots of HCOOH electrooxidation on M-1:10.22 (**a–c**) and on A-1:2.04 (**d–f**) electrodes in 0.5 M HCOOH + 0.5 M H₂SO₄ solution at electrode potentials from –0.2 V to 1.0 V

Au surface. The Pt atoms on the Au surface are isolated with lower coverage of Pt, and consequently, the CO stripping peak shifts negatively owing to the weak Pt–CO bond energy compared with pure Pt. Conversely, Pt–Pt neighboring atoms gradually increase with increasing Pt coverage; accordingly, the adsorption of CO is much stronger than that on bulk Pt, leading the CO stripping peak to shift positively.

The CO_{ads} stripping voltammograms of PtAu alloy (Fig. 7b) are somewhat different from those on Pt-on-Au catalysts. As can be seen from Fig. 7b, the CO stripping peak appears at 0.71 V (peak I) at the Pt/Au ratio of 5.08:1, which is 60 mV higher than that of pure Pt. With the ratio of Pt/Au up to 3.44:1,

the current density of peak I decreases; however, a new peak (peak II) appears at a more positive potential. Peak I becomes smaller and finally vanishes at a lower Pt/Au ratio, indicating a less or no poisoning on PtAu alloy catalyst by CO_{ads} with the increasing Au composition [46]. It can be clearly observed that peaks I and II lose their intensity rapidly on the PtAu alloy catalysts (Pt/Au=0.94:1 and 1:2.04). However, upon further decreasing the ratio of Pt/Au to 1:2.70 and 1:3.85, peak I was not observed, while the intensity of peak II obviously becomes larger. Kristian and co-workers [46] has pointed out that the up-shift in the d-band center of the Pt atoms results in increasing Pt–CO bond strength.

EIS studies for the composite catalysts

Electrochemical impedance spectroscopy as a sensitive and powerful technique has been used to test the catalytic activity of electrocatalyst for FA oxidation. Figure 8 presents the Nyquist plots of formic acid electrooxidation on M-1:10.22 Pt-on-Au and A-1:2.04 PtAu alloy catalysts at various potentials in 0.5 M HCOOH + 0.5 M H₂SO₄ at 0.3 V. When the applied potential is below 0.1 V, the impedance arcs of M-1:10 Pt-on-Au are located in the first quadrant, and the diameter of the arcs decreases with increasing electrode potential, as shown in Fig. 8a. This indicates that more active sites are available for formic acid oxidation [50], which coincidentally increases the oxidation current density of formic acid with increasing potential, as shown in Fig. 5. However, with the electrode potential increasing further, the arc diameter increases correspondingly, and interestingly, the arc reverses to the second quadrant (Fig. 8b, c). Such interesting impedance behaviors have also been reported in the studies of methanol or formic acid electrooxidation on Pt or Pt-based alloy electrodes [50–52]. At a positive potential more than 0.95 V, the impedance curves return to normal behaviors in the first quadrant and the arc diameter decreases with the potentials. At these positive potentials, surface-adsorbed CO was almost removed completely, which is indicative of the diminishing charge transfer resistance (R_{ct}). From Fig. 8d–f, similar features can be also found on A-1:2.04 PtAu alloy, except that the arc diameter is substantially larger than that on M-1:10.22 Pt-on-Au catalyst, indicating a higher R_{ct} for formic acid oxidation on A-1:2.04 PtAu alloy catalyst. This coincides with the results of the aforementioned CV in Fig. 5 wherein the catalytic activity of M-1:10.22 is higher than that of A-1:2.04 for formic acid electrooxidation.

Conclusions

In the present work, PtAu catalysts with various Pt/Au ratios obtained by electrodeposition of Pt precursor on pre-prepared Au nanoparticles (Pt-on-Au) and by simultaneous co-electrodeposition of Au and Pt (PtAu alloy) have been investigated as an anodic electrocatalyst toward formic acid and carbon monoxide oxidation. The two types of PtAu catalysts show a higher electrocatalytic activity toward formic acid oxidation compared to pure Pt on GCE. The Au atoms in PtAu catalysts promote the activity of formic acid electrooxidation. The highest activities under potentiodynamic and quasi-steady-state condition were obtained on M-1:10.22 Pt-on-Au and on A-1:2.04 PtAu alloy, respectively. The results of CO_{ads} stripping experiment show that the CO stripping peak position shifts positively on the two types of PtAu nanoparticles compared with that of the Pt catalyst. Moreover, EIS data indicate that the performance of M-1:10.22 Pt-on-Au

for formic acid electrooxidation is much better than that of A-1:2.04 PtAu alloy.

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