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Synthesis and electrochemical study of Pt-based nanoporous materials

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ABSTRACT

In the present work, a variety of Pt-based bimetallic nanostructured materials including nanoporous Pt, Pt–Ru, Pt–Ir, Pt–Pd and Pt–Pb networks have been directly grown on titanium substrates via a facile hydrothermal method. The as-fabricated electrodes were characterized by scanning electron microscopy, energy dispersive X-ray spectroscopy, X-ray photoelectron spectroscopy, X-ray diffraction and electrochemical methods. The active surface areas of these nanoporous Pt-based alloy catalysts are increased by over 68 (Pt–Pd), 69 (Pt–Ru) and 113 (Pt–Ir) fold compared to a polycrystalline Pt electrode. All these synthesized nanoporous electrodes exhibit superb electrocatalytic performance towards electrochemical oxidation of methanol and formic acid. Among the five nanoporous Pt-based electrodes, the Pt–Ir shows the highest peak current density at +0.50 V, with 68 times of enhancement compared to the polycrystalline Pt for methanol oxidation, and with 86 times of enhancement in formic acid oxidation; whereas the catalytic activity of the nanoporous Pt–Pb electrode outperforms the other materials in formic acid oxidation at the low potential regions, delivering an enhanced current density by 280-fold compared to the polycrystalline Pt at +0.15 V. The new approach described in this study is suitable for synthesizing a wide range of bi-metallic and tri-metallic nanoporous materials, desirable for electrochemical sensor design and potential application in fuel cells.

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1. Introduction

Platinum-based nanomaterials with high surface areas have been receiving increased attention due to their unique properties and a number of impressive applications in catalysis, fuel cells, and chemical sensors [1–4]. Driven by the increasing need for cleaner and more efficient engines in transportation applications, and by the longer lifetimes and higher energy densities achievable in compact power sources, polymer electrolyte membrane (PEM) fuel cells are being developed as the most attractive alternatives to combustion engines [5–7]. Of the common fuels generally considered, hydrogen is mechanistically the easiest to be oxidized and no CO_2 is produced. However, the commercialization of the hydrogen fuel cell still has considerable challenges related to production, purification, distribution and storage. There has been growing interest in studying the direct electrocatalytic oxidation of small organic molecules (SOMs), such as formic acid and methanol for potential use as fuels.

The electrochemical oxidation of fuels requires the use of a catalyst to achieve the current densities required for practical applications; Pt-based catalysts are some of the most efficient materials

for the oxidation of SOMs [8,9]. However, the performance of a pure Pt catalyst suffers considerable deterioration due to the formation of strongly adsorbed poison species. In particular, Pt is an excellent catalyst for the dehydrogenation of SOMs but, on the other hand, it is extremely susceptible to poisoning by CO, thiols and halides. These remain strongly adsorbed on the Pt surface and block the active sites from further catalysis, resulting in a dramatic decrease in efficiency and overall performance. Efforts to minimize this poisoning have been centered around the addition of co-catalysts such as Ru, Sn, Au, W, Mo, Os, Re, Rh, Pd, Pb, Bi and Ir to Pt to promote CO oxidation [9–18]. In particular, the incorporation of ruthenium into the Pt catalyst has yielded the best results, making the PtRu catalyst the industry and research standard [8-11,14]. Two mechanisms have been proposed to address the enhancement of Pt catalytic properties toward methanol oxidation by Ru. One is the bi-functional mechanism: Ru facilitates the generation of oxygenlike species on the catalyst surface which oxidize the poison species [19–21]. The other is the electronic ligand-effect mechanism: the modification of the electronic properties of Pt via a Pt-Ru orbital overlap [22,23].

In recent years, fabrication of Pt-based nanomaterials has been carried out via a variety of preparative strategies, such as the impregnation of metal precursors followed by chemical or physical reduction [24–32], electrodeposition [33–37], electroless deposition [38–40] and sol–gel derived process [41]. Given this extensive





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exploration into the synthesis of Pt-based electrocatalysts, it stands out that the electrocatalytic performance of the Pt-based catalysts is highly dependent on not only the nature of the metal elements, but also on a variety of surface conditions of the synthesized materials (i.e. surface composition, morphology, impurity contamination). Hence, an ideal synthesis method of Pt-based electrocatalysts should be facile, cost-effective, controllable, reproducible and free of surface contaminants.

Recently, we have directly grown three-dimensional (3D) nanoporous Pt networks on titanium substrates through a hydrothermal-assisted seed growth method and our study has shown that the active surface area of the formed nanoporous Pt network electrode is much larger than that of polycrystalline Pt [42]. Through a hydrothermal assisted precipitating process, the 3D nanoporous Pt networks were further decorated with Ru, producing well-defined 3D nanoporous Pt–Ru bimetallic networks. The Ru decoration significantly enhances the electrocatalytic activity of the nanoporous Pt networks not only by lowering the onset potential, but also by greatly increasing the current density for methanol oxidation [43]. In addition, we further developed this hydrothermal method and fabricated 3D nanoporous networks of Pt–Ru [44] and Pt–Ir [45,46].

In the present work, we report on the direct growth of nanoporous Pt and Pt-M networks (where M = Ru, Ir, Pb or Pd, with the atomic ratio of Pt:M close to 50:50) on Ti substrates using the novel one-step hydrothermal method and the systematic study of the electrocatalytic performance of the synthesized nanoporous Pt, Pt-Ru, Pt-Ir, Pt-Pb, Pt-Pd catalysts using the electrochemical oxidation of CO, methanol and formic acid as a probe. To the best of our knowledge, this is the first time to systemically compare the physical and electrochemical properties of Pt, Pt–Pb, Pt–Pd, Pt-Ru, and Pt-Ir nanomaterials fabricated by one universal synthesis method. The major advantages of the synthesis method we introduced here are that it is facile, reproducible and universal. Our study has shown that the innovative approach described in this study is suitable for synthesizing a wide range of bi-metallic and/or tri-metallic nanoporous materials with large active surface areas and high electrochemical performance.

2. Experimental

2.1. Materials

Titanium plates (99.2%) with a thickness of 0.5 mm were purchased from Alfa Aesar and cut into small pieces (1.25 cm \times 0.80 cm). Methanol (99.9%), H₂PtCl₆·6H₂O, Pb(NO₃)₂, RuCl₃, IrCl₃, PdCl₂, formaldehyde solution (37 wt.% in water), sulfuric acid (99.999%) and formic acid (96.0%) were used as received from Aldrich. Nanopure[®] water (18.2 M Ω cm) was used to prepare all solutions. All other chemicals were analytical grade and were used as received from commercial sources.

2.2. Synthesis of nanoporous Pt-based networks

The hydrothermal method used to fabricate the nanoporous Pt-based network electrodes is similar to that in our previous report [44]. Briefly, a Ti plate was washed in acetone followed by Nanopure[®] water, and then etched in an 18 wt.% HCl solution at 85 °C for 10 min. The etched Ti substrate was transferred into a teflon lined autoclave containing 10 ml of an aqueous mixture of inorganic metal precursors and an excess reducing agent. The precursors used in this study were H₂PtCl₆, Pb(NO₃)₂, RuCl₃, IrCl₃ and PdCl₂. Formaldehyde was used as the reducing agent. For comparison, the initial concentration of the H₂PtCl₆ precursor was kept the same (5.4 mM) in fabricating the nanoporous Pt and different Pt–M

networks. Then the autoclave was sealed and heated at $180 \degree C$ for 10 h. After cooling to room temperature, the coated Ti plate was annealed in a tube furnace at $250 \degree C$ under argon for 2 h; and then rinsed with pure water.

2.3. Instruments and electrochemical experiments

The surface morphology and composition of the synthesized samples were characterized using scanning electron microscopy (SEM) (JEOL JSM 5900LV) equipped with an energy dispersive X-ray spectrometer (EDS) (Oxford Links ISIS). Surface elemental compositions based on quantitative EDS analysis are reported in average values of readings taken at five different spots on each sample surface. The X-ray diffraction (XRD) patterns of the asprepared samples were recorded using a Philips PW 1050-3710 Diffractometer with Cu K α radiation. XRD patterns were compared and assigned according to the database of the International Centre for Diffraction Data (ICDD). The surface composition of the nanoporous Pt-Ir sample was further analyzed by X-ray photoelectron spectroscopy (XPS) (Omicron EA-125 energy analyzer and a multi-channel detector), using a monochromatic Mg K α X-ray source ($h\nu$ = 1253.6 eV). The X-ray source operated at an output of 220 W. All binding energies (BE) reported were corrected using the Cl 2p_{3/2} peak at 199 eV as an internal standard. Atomic sensitivity factors were employed for calculating the surface metallic compositions from the integrated peak areas.

Cyclic voltammetry (CV), chronoamperometry (CA) and electrochemical impedance spectroscopy (EIS) were carried out using the three-electrode cell system described in our previous studies [47,48]. In all cases a platinum coil was used as the counter electrode and was flame annealed before each experiment. The working electrode was the Ti-supported nanoporous Pt, Pt-Ru, Pt-Ir, Pt-Pb and Pt-Pd networks. For comparison, a smooth polycrystalline Pt wire with surface area 1.0 cm² was also used as a working electrode. A saturated calomel electrode (SCE) was used as the reference and was connected to the investigated electrolyte through a salt bridge. All potentials reported in this paper are referred to the SCE reference electrode. Data acquisition and analysis were performed with a Solartron 1287 Potentiostat and a Solartron 1252B Frequency Response Analyzer using the software CorrWare and ZPlot. Unless otherwise specified, the geometric surface area of each electrode was used to calculate the current density. The amplitude of modulation potential for the electrochemical impedance measurements was 10 mV and the frequency was varied from 40 kHz to 25 mHz. All solutions were de-aerated with ultra-pure argon (99.999%) before measurements and argon was passed over the top of the solution during the experiments. Carbon monoxide (PRAXAIR, 99.9%) was used for the CO-stripping study. Before scanning the applied potential, the working electrode was held at -0.1 V for 360 s while a stream of pure CO was bubbled into the solution during the first 180 s. Then the solution was purged with pure Ar for the remaining 3-min holding period. Immediately following the electrode pretreatment, two cycles of CV were recorded for each electrode. All measurements were conducted at room temperature $(22 \pm 2 \circ C)$.

3. Results and discussion

3.1. Surface characterization

The surface morphology and particle size of the as-synthesized Pt-based materials were examined by SEM at a magnification of 10,000. Fig. 1 shows five SEM images of the as-synthesized Pt (a) and the bimetallic Pt–M electrocatalysts, where M = Pb (b), Pd (c), Ru (d) and Ir (e). It is obvious that the Ti substrates are well covered by the catalyst networks and their surfaces consist of irregular



Fig. 1. SEM images recorded at a magnification of 10,000 for the as-synthesized Pt-containing catalysts: (a) nanoporous Pt; (b) Pt-Pb (50%); (c) Pt-Pd (50%); (d) Pt-Ru (50%); and (e) Pt-Ir (50%). (f) The corresponding EDS spectra of the samples as shown in (a-e).

pores ranging from tens of nanometers to several micrometers in diameter. The nanoporous Pt networks (Fig. 1a) are composed of Pt nanoparticles with several tens of nanometers in diameter; the Pt–Pb (Fig. 1b) and Pt–Pd (Fig. 1c) networks both have relatively uniform particle sizes of around 80–100 nm, whereas the Pt–Ru (Fig. 1d) and Pt–Ir (Fig. 1e) networks have relative larger particle size, ranging from tens of nanometers to hundreds of nanometers. All these SEM images reveal that the synthesized Pt-based materials possess particle-based nanoporous network morphology.

Our previous study has shown that the Pt-based bimetallic catalysts can be prepared with various bimetallic compositions by adjusting the ratio of the precursors [44–46]. It is well known that among most Pt-containing intermetallic phases, the one-to-one phase containing an equimolar ratio of Pt and the co-catalyst metal always exhibits the highest electrocatalytic activity [18,49]. Thus, in the present work, electrodes with only the equimolar ratio of Pt and each co-catalyst were fabricated and systematically studied. Fig. 1f presents the corresponding EDS spectra of these five Pt-based nanoporous electrodes. Quantitative EDS elemental analysis reveals that the surface compositions of the four bimetallic Pt-based nanoporous samples are all at a normalized atomic ratio of Pt:M close to 50:50 with a deviation less than 5%. Another important aspect in the EDS spectra is that there is no discernible carbon or oxygen signal, indicating that the synthesized nanoporous networks are free of surface organic impurities.

As seen in Fig. 1f, the Ir peak strongly overlaps with the Pt signal; we employed XPS to further analyze the composition of the nanoporous Pt-Ir sample. Fig. 2a shows the XP spectra in the Pt 4f region of the Pt-Ir (solid line) and nanoporous Pt samples (dashed line); and Fig. 2b presents the XP spectrum in the Ir 4f region of the synthesized Pt-Ir sample. The two 4f binding states of Pt in the nanoporous Pt sample are identified as $4f_{7/2}$ and $4f_{5/2}$ at 71.0 and 74.3 eV, which are consistent with previous studies [51-54]. Whereas the $4f_{7/2}$ and $4f_{5/2}$ doublets of Pt in the nanoporous Pt-Ir sample are found at 71.4 and 74.7 eV, respectively. As shown in Fig. 2b, the core level $4f_{7/2}$ and $4f_{5/2}$ doublets of Ir in the Pt-Ir sample appear at 60.6 and 63.6 eV, respectively; whereas the typical values of Ir metal 4f doublets are 60.9 and 63.9 eV [51,52]. Hence, a positive shift of 0.4 eV in binding energy occurs for the Pt $4f_{7/2}$ in the Pt-Ir sample, and a negative shift of 0.3 eV in binding energy occurs for the Ir $4f_{7/2}$. As the shift of binding energy of core-level orbital is closely correlated with a change of electron density, these results indicate an intra-atomic charge transfer from the Pt atom to the Ir atom. Similar Pt-Ir electronic interaction has also been



Fig. 2. XP spectra of the Pt 4f (a) and Ir 4f (b) regions for the nanoporous Pt (red dashed line) and Pt–Ir (solid black line) networks. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of the article.)

reported by other groups [16,54]. The surface atomic Pt/Ir ratio was determined based on the quantitative integration of Pt 4f and Ir 4f peak areas with consideration of the Pt and Ir atomic sensitivity factors [50]. The calculated Pt/Ir atomic ratio of the synthesized nanoporous Pt–Ir networks is 45:55, which is consistent with the EDS analysis.

Phase and structure characterization on the synthesized Ptbased nanoporous electrodes were achieved by XRD analysis. Fig. 3 shows the XRD patterns of a bare Ti substrate and all the five synthesized Pt-based nanoporous materials. All the diffraction patterns of the Ti substrate precisely matched the patterns of a hexagonal Ti crystal in the ICDD database (PDF No. 44-1294). These Ti diffraction patterns, with much less intensities, are also seen in the XRD spectra of the remaining five Pt-containing samples. The diffraction patterns of the nanoporous Pt, Pt-Pd, Pt-Ir and Pt-Ru all display the (111), (200) and (220) reflections, characteristic of the face centered cubic (fcc) crystal structure. However, the (111), (200) and (220) peaks of the Pt-Pd, Pt-Ir and Pt-Ru were found to have discernible positive shifts in 2θ values compared to the corresponding nanoporous Pt peaks. Such an increase in 2θ values of the (111), (200) and (220) peaks corresponds to decreased d-spacing values and decreased lattice constants due to the incorporations of Pd, Ir and Ru, respectively. This is confirmed by quantitative calculations on lattice constant (a) based on the diffraction angles of the (220) reflection peaks. Our results show that the synthesized Pt-Pd, Pt-Ir, and Pt-Ru materials have a values of 0.389, 0.388, and 0.388 nm, respectively, all of which are smaller than the *a* value of nanoporous Pt 0.392 nm. More importantly, the peak lines of Pt-Pd, Pt-Ir and Pt-Ru's patterns appear exactly between those



Fig. 3. XRD patterns recorded on the as-labeled Ti substrates and nanoporous Ptcontaining networks.

 2θ values for pure Pt and pure Pd/Ir/Ru; and there are no distinct (111), (200) and (220) reflections characteristic of pure Pd, Ir, Ru in each corresponding spectrum. All the evidence indicates that the Pt phase and the added co-catalyst Pd, Ru or Ir phase are partially or fully alloyed, rather than a simply physical mixture of the particles of the two metals [41,54–56]. As for the XRD patterns of the synthesized nanoporous Pt-Pb networks, all peaks, except those from Ti substrate, can be indexed to the PtPb hexagonal NiAs crystal structure. As there are no other distinct crystalline phases present in significant amount, the Pt and Pb components are considered fully alloyed [31,57,58]. The average crystallite size of each Pt-containing samples was further calculated using Scherrer formula [59], revealing that the nanoporous Pt, Pt-Pb, Pt-Pd, Pt-Ir, Pt-Ru networks possess average crystallite sizes of 24, 35, 18, 6 and 4 nm, respectively. Comparison of the XRD-derived grain sizes and the SEM-estimated particle sizes (Fig. 1) indicates that the synthesized Pt-containing nanocrystals are somewhat agglomerated, as is expected since no surfactants are used in their fabrication process.

3.2. Electrochemical oxidation of surface adsorbed CO

CO has been identified as an intermediate as well as the major poison species for Pt catalysts in the process of oxidation of most SOMs (e.g. formic acid, methanol). At low electrode potentials, CO remains strongly adsorbed, especially at the bridging and threefold hollow sites of Pt surfaces [18,47]. Therefore, one of the most important merits of an effective catalyst is its efficient removal of surface adsorbed CO. To compare the performance of the as-synthesized nanoporous electrodes towards CO poisoning, CO stripping experiments were carried out in a 0.1 M H₂SO₄ solution and the results are presented in Fig. 4. The most obvious common characteristics in Fig. 4a-c are: first, the hydrogen adsorption peaks of these electrodes are fully suppressed in the first positive-going scan due to pre-adsorbed CO blocking the active surface sites; second, a broad shoulder-like wave and a subsequent sharp current peak resulting from CO oxidation appear in the potential range from 0.0 to 0.6 V; third, the evidence (i) that the hydrogen desorption peaks appear in the first negative-going scan and (ii) that the second cyclic voltammogram resembles the CV in a CO free solution indicates the complete oxidation of adsorbed CO during the first forward scan. In particular, the nanoporous Pt-Ru electrode outperforms the other three electrodes (nanoporous Pt, Pt-Ir and Pt-Pd) in terms



Fig. 4. Cyclic voltammograms of CO stripping on the nanoporous Pt-containing electrodes: (a) Pt–Ru (blue) and nanoporous Pt (black); (b) Pt–Ir; (c) Pt–Pd; (d) Pt–Pb. Two cycles of the CV were recorded for each electrode in a $0.1 M H_2SO_4$ at a potential scan rate of 20 mV/s: the first sweep cycle is shown in solid line; and the second sweep cycle is drawn in dashed line. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of the article.)

of its very low onset and peak potential of CO oxidation, which are at about -0.03 and 0.30 V, respectively; while the nanoporous Pt, Pt-Ir and Pt-Pd electrodes have similar onset potentials at about 0.08 V and peak potentials centered around 0.41 V, both of which are more than 100 mV more positive than those of Pt–Ru. This can be explained by the bi-functional mechanism [19–21]: the Ru sites at the Pt–Ru boundaries facilitate the generation of oxygenated species thus oxidizing the adsorbed CO on Pt sites at a lower anode potential. It is also noteworthy that the nanoporous Pt–Ir electrode generated the highest peak current density upon CO oxidation.

As for the nanoporous Pt-Pb electrode, the onset potential of CO oxidation is difficult to discern due to the simultaneous onset of surface oxidation. The peak current density of the Pt-Pb electrode for CO oxidation is the lowest, but the peak potential is similar to that of the nanoporous Pt, except for its broader shape. In contrast to all the other Pt-based electrodes, the nanoporous Pt-Pb electrode (Fig. 4d) possesses an interesting feature, that is the hydrogen adsorption/desorption is still fully suppressed in the second cycle of CV, despite there being no more adsorbed CO present on the electrode surface. That Pt-Pb surface heavily suppresses the hydrogen adsorption/desorption and that it behaves less actively towards extrinsically adsorbed CO than the other Pt-containing electrodes should be considered as the consequence of the Pt-Pb's unique alloy structure. In the hexagonal NiAs type crystal structure, the surface Pt-Pt distance has been found to be dilated due to the incorporation of Pb atoms, which effectively prevents CO from binding at bridge or threefold hollow sites of Pt atoms [40,58].

Surface adsorbed CO monolayer oxidation has also been widely used as an effective method to evaluate the active surface area of Pt-based electrocatalysts [60]. Calculated from the peak areas associated with CO oxidation in Fig. 4a-c, the consumed charges upon CO stripping on nanoporous Pt, Pt-Pd, Pt-Ru and Pt-Ir surfaces are 20.4, 28.8, 29.3 and 47.8 mC, respectively. Assuming a charge to surface area value of $420 \,\mu\text{C/cm}^2$ used for CO stripping on a polycrystalline Pt surface [37,60], the electrodes' active surface areas were calculated to be 48.6 (nanoporous Pt), 68.6 (Pt-Pd), 69.8 (Pt-Ru) and 113.8 (Pt-Ir) cm², respectively. Due to the infeasibility of this method for the Pt-Pb surface, we are unable to quantitatively determine the active surface area of the fabricated Pt-Pb electrode at this point. However, after comparison of Pt-Pb with the other nanoporous Pt-containing electrodes in terms of the XRD-derived crystallite size. SEM-estimated particle size, and the observed porous morphology, the active surface area of the Pt-Pb network should be comparable to that of the nanoporous Pt and Pt-Pd networks. The control test of CO stripping shows that the smooth polycrystalline Pt electrode used in this study possesses an active surface area of 1.0 cm². These results indicate that, despite of the same geometric surface area for each electrode, the active surface areas of these 3D nanoporous Pt-containing electrodes are much larger than that of the smooth polycrystalline Pt electrode-the largest one (Pt-Ir) being over 113 times larger than that of the polycrystalline Pt.

3.3. Electrochemical oxidation of methanol

The electrocatalytic activity of the as-synthesized nanoporous Pt-based electrodes towards methanol oxidation was first studied by cyclic voltammetry. Fig. 5a presents the positive-going portions of the CV curves in a 0.1 M $H_2SO_4 + 0.1$ M CH_3OH solution at a potential scan rate of 20 mV/s. It is apparent that all the five nanoporous Pt-containing electrodes have significantly enhanced current densities compared to the bulk polycrystalline Pt. In particular, among these six Pt-containing electrodes, the peak current density, appearing at different potentials, increases in the order of bulk polycrystalline Pt (0.28 mA/cm² at +0.51 V) < nanoporous Pt (15.1 mA/cm² at +0.60 V) < Pt-Ru (17.5 mA/cm² at +0.50 V) < Pt-Pd (19.8 mA/cm² at +0.53 V) < Pt-Pb (48.3 mA/cm² at +0.69 V) < Pt-Ir (65.1 mA/cm² at +0.50 V). In terms of the onset potential of methanol oxidation, Pt-Ru outperforms the others at a potential



Fig. 5. (a) Positive-going portions of cyclic voltammograms of the nanoporous Ptcontaining electrodes in a solution of $0.1 \text{ M CH}_3\text{OH} + 0.1 \text{ M H}_2\text{SO}_4$ at a potential scan rate of 20 mV/s: Pt-lr (red); Pt-Ru (blue); Pt-Pd (pink); Pt-Pb (green); nanoporous Pt (black) and bulk polycrystalline Pt (brown). Positive-going portions of cyclic voltammograms shown in (a) are re-plotted in (b) for five selected electrodes with current densities shown as per active surface area. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of the article.)

of -0.05 V, while the rest of the nanoporous electrodes have a similar onset potential at around +0.10 V. In addition, it is interesting to note that the CV curves presented in Fig. 5a have their own characteristics. For instance, nanoporous Pt and Pt-Pd have shoulder-like waves at 100 mV negative to the large peak; Pt-Ru and Pt-Pb exhibit a single yet very broad peak during the methanol oxidation; Pt-Ir, unlike the other electrodes, has a relatively sharp and large peak.

Although these as-synthesized nanoporous electrodes all have the same geometric area, their active surface areas are quite different as seen from the previous discussion. Hence the methanol oxidation curves of the five selected Pt-containing electrodes were re-plotted in Fig. 5b, with current densities shown per their active surface areas. The nanoporous Pt, Pt–Ru and Pt–Pd electrodes have approximately similar peak current densities to the polycrystalline Pt, indicating the much higher current densities of the those nanoporous electrodes seen in Fig. 5a are mainly due to their much larger active surface areas. The nanoporous Pt–Ir once again surpasses the other electrodes with respect to the peak current density, showing that the incorporation of Ir into Pt greatly enhances the electrode's intrinsic electrocatalytic activity towards methanol oxidation.

We further measured the steady-state current of the nanoporous Pt-based electrodes at different electrode potentials. The chronoamperometric plots recorded in a $0.1 \text{ M CH}_3\text{OH}+0.1 \text{ M}$ H₂SO₄ solution are presented in Fig. 6. The electrode potential was first held at -0.10 V for 60 s, then stepped up to +0.30 V (Fig. 6a), +0.50 V (Fig. 6b) and +0.80 V (Fig. 6c) for 500 s. The steady-state current densities are summarized in Table 1. It is clearly shown that the nanoporous Pt-based electrodes have much higher current densities than the bulk polycrystalline Pt under all the three inves-



Fig. 6. Chronoamperometry of the nanoporous Pt-containing electrodes in a solution of 0.1 M CH₃OH + 0.1 M H₂SO₄. The electrode potentials was first held at -0.10 V for 60 s, then stepped up to +0.30 V (a), +0.50 V (b) and +0.80 V (c), respectively. In all cases, line a, b, c, d, e and f represent the CA curves of nanoporous Pt (black), Pt–Pb (green), Pt–Pd (pink), Pt–Ru (blue), Pt–Ir (red) and bulk polycrystalline Pt (brown), respectively. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of the article.)

tigated electrode potentials. Suggested by the positive-going CV curves of each electrode shown in Fig. 5a, 0.30 V is where the onset of methanol oxidation occurs on the electrodes. At this relatively low anode potential, the nanoporous Pt–Ru electrode exhibits the highest current density. This is attributed to the Pt–Ru "bi-functional" catalytic activity [19–21]. The current density of Pt–Ir

Table 1

Steady-state current densities (mA/cm^2) at three applied potential values for methanol oxidation at the nanoporous Pt-based electrodes in 0.1 M CH₃OH+0.1 M H₂SO₄

	+ 0.30 V vs. SCE	+0.50 V vs. SCE	+0.80 V vs. SCE
Pt	0.1	0.4	0.1
NP–Pt	2.6	13.2	1.1
Pt–Ru	7.2	15.7	1.1
Pt–Ir	4.8	27.4	1.6
Pt–Pb	0.9	24.5	3.9
Pt–Pd	1.7	15.6	0.8



Fig. 7. Nyquist plots from electrochemical impedance spectroscopy at the potential of +0.3 V in a solution of 0.1 M CH₃OH + 0.1 M H₂SO₄, recorded for each Pt-containing electrode: (a) nanoporous Pt (black); (b) Pt–Pb (green); (c) Pt–Pd (pink); (d) Pt–Ru (blue); (e) Pt–Ir (red); (f) bulk polycrystalline Pt (brown). The amplitude of modulation potential is 10 mV. The frequency changes from 40 kHz to 25 mHz. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of the article.)

ranks the second, indicating that the incorporation of Ir to the Pt surface also significantly promotes methanol oxidation at the low electrode potential. The nanoporous Pt-Pd and Pt-Pb electrodes both exhibit much lower current densities than the nanoporous Pt-Ru electrode. This may be due to a lower performance in the dehydrogenation of methanol at this low potential. Under 0.50 V (Fig. 6b), the steady-state current density decreases in the order of nanoporous Pt-Ir > Pt-Pb > Pt-Pd \approx Pt-Ru > nanoporous $Pt \gg polycrystalline Pt$, indicating that under this near-peak potential, the catalytic activities of all the bimetallic materials are significantly enhanced compared to pure Pt materials. Especially in the case of Pt-Ir. its steady-state current density reached a value over 68 times larger than that of the polycrystalline Pt. When these electrodes were tested under the potential of 0.80 V, their current densities all dramatically dropped due to the oxide formation under this high electrode potential.

Fig. 7 compares the Nyquist plots of all the Pt-containing electrodes at 0.30 V in a solution of 0.1 M $CH_3OH+0.1$ M H_2SO_4 . The inset is the Nyquist plot of the polycrystalline Pt as both its imaginary and real components of impedance are extremely high. The frequency was changed from 40 kHz to 25 mHz. It can be seen from Fig. 7 that the electrochemical impedance increases as follows: Pt-Ru < Pt-Ir < nanoporous Pt < Pt-Pd < Pt-Pb \ll polycrystalline Pt. This order exactly matches the results of chronoamperometry shown in Fig. 6a, suggesting that the significantly enhanced catalytic activity of Pt-Ru and Pt-Ir electrodes at low anode potential may be associated with their much lower charge transfer resistance compared to the rest of the nanoporous electrodes [44,45].

From a mechanistic point of view, our electrochemical results on the oxidation of CO and methanol at the nanoporous Pt–Ru electrode are well supported by the "bi-functional" mechanism [43,44]. Nevertheless, it is important to point out that the exact bimetallic composition of the Pt–Ru system also plays a vital role in determining the best catalytic effect. For example, Pt–Ru alloys with an equimolar ratio of Pt and Ru have been found to yield the best performance for CO and HCOOH oxidation [49,61]. In the case of methanol, it has been reported that Pt–Ru alloys with 10–30% Ru are more suitable for the dissociative chemisorption and oxidation of methanol fuel [61,62]. In addition, the nanoporous Pt–Ir mate-



Fig. 8. Positive-going portions of the cyclic voltammograms of the nanoporous Ptcontaining electrodes in a solution of 0.1 M HCOOH + 0.1 M H₂SO₄ at a potential scan rate of 20 mV/s: Pt–Ir (red); Pt–Ru (blue); Pt–Pd (pink); Pt–Pb (green); nanoporous Pt (black) and bulk polycrystalline Pt (brown). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of the article.)

rials exhibit the strongest catalytic activity towards the oxidation of CO and methanol in terms of peak current density. This is consistent with recent findings, which show positive effects brought on by the addition of Ir to a Pt catalyst on the electrochemical oxidation of methanol, carbon monoxide and hydrogen oxidation [16,28,41,45,47,63]. It has been suggested that the incorporated Ir, similar to the role of Ru in Pt-Ru systems, likely stabilizes the adsorbed surface OH group, thus assisting in the oxidation of CO or other adsorbed intermediates [28,54]. In the case of Pt-Pb, on the one hand, Pb cannot provide adsorbed oxygenated species for CO and methanol oxidation [64]; on the other hand, as discussed earlier, the Pt-Pb surface is poisoned by the CO_{ads} to a lesser extent than a pure Pt surface, a process which is promoted by the "third body effect" [40,65] wherein the addition of Pb to Pt surfaces dilates the Pt-Pt distance and reduces the number of adsorption sites for CO due to geometrical hindrance. Therefore, the nanoporous Pt-Pb electrode exhibits a compromised performance towards methanol oxidation: behaving inertly at lower potential regions; and producing remarkable high current densities in the high potential regions.

3.4. Electrochemical oxidation of formic acid

We further investigated the electrocatalytic activity of the synthesized nanoporous Pt-based electrodes towards formic acid oxidation. Despite a lower theoretical energy density than methanol, formic acid has its own advantages as a fuel for fuel cells, such as ease in transportation and storage, low fuel crossover through the membrane and high theoretical open circuit potential [46]. Fig. 8 presents forward-scanning CV curves of the nanoporous Pt-containing electrodes and the polycrystalline Pt electrode recorded in a 0.1 M $H_2SO_4 + 0.1$ M HCOOH solution. All the nanoporous Pt-based electrodes exhibit much higher current than the polycrystalline Pt electrode. Two anodic waves

Table 2

Steady-state current densities (mA/cm²) at three applied potential values for formic acid oxidation at the nanoporous Pt-based electrodes in 0.1 M HCOOH + 0.1 M H_2SO_4

	+ 0.15 V vs. SCE	+0.30 V vs. SCE	+0.50 V vs. SCE
Pt	0.1	0.7	0.4
NP–Pt	4.6	11.1	14.6
Pt–Ru	5.9	22.8	28.3
Pt–Ir	9.8	24.6	34.4
Pt–Pb	28.3	29.1	25.2
Pt–Pd	14.1	33.6	19.6

are observed in each curve and the peak potentials are strongly dependant on the nature of each co-catalyst. The onset potential of formic acid oxidation increases in the following order: $Pt-Pb < Pt-Pd < Pt-Ir \approx Pt-Ru \approx$ nanoporous Pt < polycrystalline Pt. The mechanism of formic acid oxidation on platinum electrodes has been well studied, involving the so-called dual pathways which are dehydrogenation and dehydration, represented by the following equations [7,29,39,66–71]:

$$HCOOH \rightarrow CO_2 + 2H^+ + 2e^-$$
 dehydrogenation path (1)

$$HCOOH \rightarrow CO_{ads} + H_2O \rightarrow CO_2 + 2H^+ + 2e^-$$

dehydration path (2)

The preferred reaction for the complete oxidation of formic acid is the dehydrogenation reaction Eq. (1), in which CO_2 is directly formed through the formation of adsorbed active intermediates (-COOH_{ads}). In contrast, formic acid oxidation via a dehydration



Fig. 9. Chronoamperometry of the nanoporous Pt-containing electrodes in a solution of 0.1 M HCOOH + 0.1 M H₂SO₄. The electrode potentials were first held at -0.10V for 60 s, then stepped up to +0.15 V (a), +0.30 V (b) and +0.50 V (c), respectively. In all cases, line a, b, c, d, e and f represent the CA curves of nanoporous Pt (black), Pt–Pb (green), Pt–Pd (pink), Pt–Ru (blue), Pt–Ir (red) and bulk polycrystalline Pt (brown), respectively. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of the article.)

reaction Eq. (2) produces adsorbed carbon monoxide $(-CO_{ads})$ which acts as a poison intermediate and requires a higher electrode potential to be further oxidized into CO₂. In the case of the polycrystalline Pt electrode, the electrochemical oxidation of formic acid occurs mainly through the dehydration pathway. This is why the current is very small at the low electrode potentials. In contrast, a significantly enhanced current is seen in the CV curve of the nanoporous Pt-Pb electrode at the low electrode potential region and is attributed to the direct oxidation of formic acid, indicating that the electrochemical oxidation of formic acid on the nanoporous Pt-Pb electrode is mainly through the dehydrogenation path. The electrochemical oxidation of formic acid on the other four nanoporous electrodes takes place through both the dehydrogenation and the dehydration paths. All these results show that by changing the composition of the Pt-based nanoporous electrode. one can easily tune the mechanisms of the electrochemical oxidation of formic acid.

Chronoamperometry was employed to further measure the steady-state current densities of the nanoporous Pt-containing electrodes at different electrode potentials in formic acid oxidation. Due to the high electrocatalytic activities of the Pt-Pb and Pt-Pd electrodes in the low potential region indicated by Fig. 8, chronoamperometric plots were compared at +0.15 V (Fig. 9a), +0.30 V (Fig. 9b) and +0.50 V (Fig. 9c). The steady-state current densities are summarized in Table 2. It can be clearly seen that the nanoporous Pt-Pb electrode possesses the highest steady-state current density-over 280 times of that of polycrystalline Pt. Pt-Pd electrode, ranking only second to Pb at this potential, surpassing the remaining four electrodes in current density. In the case of +0.30 V, Pt-Pd and Pt-Pb exchanged their ranks in current density, while still outperforming the remaining 4 electrodes. As suggested by other researchers [39,58,72], this can be explained by the preferred dehydrogenation pathway adopted by Pt-Pb and Pt-Pd at low potential regions. As the applied potential was raised to +0.50 V, Pt-Ir and Pt-Ru took over the first and second places in steady-state current density. At this intermediate potential. Pt-Ir and Pt-Ru electrodes showed a much higher activity than pure Pt due to the rapid enhancement in CO₂ production rate by the effective removal of CO_{ads} formed in the dehydration reaction, which is referred to a bifunctional mechanism analogous to methanol oxidation [46,70]. In all cases, the Pt-Pb electrode is able to retain very large current densities (25-29 mA/cm²) from low to intermediate potentials; the Pt-Pd electrode can only offer its largest current density at +0.30 V; whereas the Pt-Ru, Pt-Ir and nanoporous Pt electrodes are capable of delivering much larger current densities at +0.50 V than those at lower potentials. In the case of Pt-Ir, its current density at +0.50 V is 86 times of that of polycrystalline Pt electrode.

4. Conclusions

In summary, novel 3D nanoporous bimetallic Pt–Ru, Pt–Ir, Pt–Pb and Pt–Pd networks have been fabricated by a one-step facile hydrothermal method that allows controllable variation of the bimetallic compositions. For ease of comparison, these nanoporous Pt-based electrodes were prepared at an equimolar ratio of Pt to the co-catalyst. XRD results indicate that the Pt atoms are alloyed with the co-catalyst components, resulting in a hexagonal crystal structure for Pt–Pb, and fcc crystal structures with contracted lattice constants for Pt–Pd, Pt–Ru and Pt–Ir materials. XRD-derived crystallite sizes, together with particle sizes observed in SEM images indicate particle agglomeration during the hydrothermal reduction process. The nanoporous Pt–Ir surface was further characterized by XPS, results of which showed a positive shift of 0.4 eV in binding energy for the It $4f_{7/2}$, indicating a unique

electronic interaction between Pt and Ir atoms. The electrocatalytic performance of these nanoporous Pt-based electrodes was investigated towards methanol and formic acid oxidation. It is difficult to quantitatively compare our electrochemical results with those yet published as our electrodes are Ti-supported catalysts, which were formed onsite in one single step without extra additives, whereas a large fraction of fuel cell catalysts reported in most electrochemistry journals were prepared with the addition of Nafion, polymer binder and carbon black, and applied onto glassy carbon substrate; in light of providing a standard point, we specifically included a bulk polycrystalline Pt electrode as a comparable target. The adsorbed CO monolayer stripping experiment reveals that the active surface areas of the nanoporous Pt-containing electrodes are much larger than that of the polycrystalline Pt electrode. It also demonstrated enhanced catalytic activities towards CO oxidation on the nanoporous Pt-Ru electrode. Moreover, our electrochemical results show that for methanol oxidation, the Pt-Ru electrode outperforms the other electrodes in having a low onset potential of -0.05 V, and the Pt-Ir electrode delivers a substantially enhanced current density at +0.50 V with 68 times of enhancement compared to polycrystalline Pt, whereas the nanoporous Pt-Pb electrode exhibits low activity at the low potential regions and is very active in delivering a remarkable high current density at the higher potential regions; for formic acid oxidation, the nanoporous Pt-containing electrodes distinguished themselves by favoring different reaction pathways, by virtue of which the Pt-Pb electrode at +0.15 V, and the Pt-Ir electrode at +0.50 V produced current densities over 280 times and 86 times larger than that of polycrystalline Pt. The approach described in this study is suitable for synthesizing a wide range of bi-metallic and tri-metallic nanoporous materials with large active surface areas and high electrocatalytic activity, desirable for novel electrochemical sensor

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