

Article

Sb Surface Modification of Pd by Mimetic Underpotential Deposition for Formic Acid Oxidation

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Academic Editor: Minhua Shao

Received: 13 May 2015 / Accepted: 22 July 2015 / Published: 28 July 2015

Abstract: The newly proposed mimetic underpotential deposition (MUPD) technique was extended to modify Pd surfaces with Sb through immersing a Pd film electrode or dispersing Pd/C powder in a Sb(III)-containing solution blended with ascorbic acid (AA). The introduction of AA shifts down the open circuit potential of Pd substrate available to achieve suitable Sb modification. The electrocatalytic activity and long-term stability towards HCOOH electrooxidation of the Sb modified Pd surfaces (film electrode or powder catalyst) by MUPD is superior than that of unmodified Pd and Sb modified Pd surfaces by conventional UPD method. The enhancement of electrocatalytic performance is due to the third body effect and electronic effect, as well as bi-functional mechanism induced by Sb modification which result in increased resistance against CO poisoning.

Keywords: formic acid oxidation; palladium; Sb modification; mimetic underpotential deposition

1. Introduction

Direct formic acid fuel cells (DFAFCs) are considered promising power sources of clean and environment-friendly energy for miniature and portable electronic devices because of excellent

performance, such as high power density [1,2]. The direct formic acid fuel cell has a theoretical open circuit potential of 1.48 V, higher than that of direct methanol fuel cell (1.18 V) [3]. The improvement of performance of DFAFCs depends on fabrication of high-efficient electrocatalysts. The commonly-used anodic catalyst for DFAFCs is platinum black, on which the formic acid electrooxidation occurs via a dual pathway [4,5], which consists of the direct pathway without CO poison and the indirect pathway with the formation of CO as poisonous intermediates. The resulting CO intermediates are strongly adsorbed on the Pt surface and block the active sites, then decrease the activity. In this regards, platinum is not so favorable for practical formic acid fuel cell application because of the CO intermediates build-up, poisoning the catalysts, and degenerating the fuel cell performance gradually [3,6].

Many studies have confirmed that palladium is a more efficient catalyst with higher catalytic activity for the electrooxidation of formic acid [6–11]. The excellent property derives from the extraordinary formic acid oxidation mechanism on Pd which is different from the dual pathway mechanism on Pt. Briefly, on the Pd surface, the electrooxidation of formic acid occurs via a dominantly direct pathway with a minimized buildup of CO on the surface (The formation of CO_{ad} on a Pd electrode in formic acid solutions at the OCP and practical working potentials has been confirmed by Wang *et al.*, using *in situ* high-sensitivity attenuated-total-reflection surface-enhanced infrared absorption spectroscopy (ATR-SEIRAS), proposing that the reduction of the FA dehydrogenation product CO₂ should be mainly responsible for the above CO_{ad} formation [12]). Unfortunately, the activity of Pd is unstable and deactivation exists during formic acid oxidation due to gas build-up on the anodic side of a fuel cell [13,14], catalyst leaching or impurities in the formic acid or intermediate species [15]. However, a majority of literature proved that it is mainly CO-like intermediates accumulated on Pd surface that degenerate the activity of Pd, and it reached a consensus among most research workers [16,17]. On this issue, much effort has been made to improve the catalytic activity and stability through alloying or surface modification with metallic adatoms, such as Sb. Yu *et al.* [18] fabricated carbon supported PdSb alloy catalysts which show much better resistance to poisoning (deactivation) and decrease the accumulation of CO on the catalyst surface during formic acid oxidation. Masel *et al.* [19] have studied the effects of Sb adatoms on the performance of a DFAFC. They showed that electrochemical surface modification of Pd by Sb adatoms enhances the oxidation of formic acid by more than two-fold in an electrochemical cell. For Sb modification, previous approaches, such as irreversible adsorption (IRA) and traditional UPD method required external potential controlled desorption of partial Sb, which were not suitable for scaled synthesis or upgrading of practical powder catalysts [20–22]. Among the known Sb surface modification method, mimetic underpotential deposition (MUPD) technique was a newly proposed electroless approach to achieve sufficient surface modification [23]. Compared with underpotential deposition followed by potential controlled desorption of partial Sb adatoms usually applied in Sb modification on Pt, MUPD requires no external potential control and is a versatile electroless approach extended for surface nanoengineering of electrocatalysts [24].

In this work, we extended the MUPD strategy to the modification of Sb on Pd surface of film electrode and Pd/C powder by introducing ascorbic acid (AA) as a mild reductant to Sb(III)-containing modification solution. Besides, for comparison, Pd film substrate was also modified by Sb UPD. We studied the influence of Sb modification on Pd surface for the electro-oxidation of formic acid by cyclic voltammetry and chronoamperometry together with anodic stripping voltammetry of pre-adsorbed CO.

2. Results and Discussion

2.1. Sb UPD on Pd Film Electrodes

Different from Sb UPD on Pt surfaces [20,25], coverage of Sb (θ_{Sb} , a coefficient based on the ratio of Pd sites filled and not filled) on Pd surface was tuned by controlling the UPD time. In this paper, Sb UPD on fresh Pd films was performed for 10 s, 20 s, 30 s, respectively. The modified Pd film electrodes were marked as Sb/Pd(UPD). Figure 1a depicts cyclic voltammograms of unmodified Pd film and Sb/Pd(UPD) electrodes in 0.5 M H_2SO_4 . It can be seen that the hydrogen adsorption/desorption region was restrained for Sb modified Pd film electrodes. A conspicuous peak near 0.66 V in positive scan is due to the oxidative dissolution of Sb modifiers on Pd surface. The peak of negative scan in high potential is ascribed to reduction of oxygenous species formed on positive scan. Based on hydrogen adsorption-desorption charge with or without Sb modifiers, θ_{Sb} on Pd surface can be evaluated through the following equation [22]:

$$\theta_{\text{Sb}} = (Q_{\text{O-H}} - Q_{\text{Sb-H}}) / Q_{\text{O-H}} \quad (1)$$

where $Q_{\text{O-H}}$ and $Q_{\text{Sb-H}}$ is the charge for oxidation of adsorbed hydrogen on unmodified and Sb modified Pd, respectively. By calculating, it is found that the Pd electrodes through UPD for 10 s, 20 s, 30 s enable θ_{Sb} to reach a value of 0.52, 0.62 and 0.66, respectively. This revealed that coverage of Sb on Pd surface increased with UPD time. Formic acid oxidation was chose as a probe reaction to compare the catalytic activity of Sb/Pd(UPD) electrodes with various θ_{Sb} . Figure 1b showed that peak current density of HCOOH electrooxidation on Sb/Pd(UPD) increased with θ_{Sb} from 0.52 to 0.62 and then dropped down with θ_{Sb} from 0.62 to 0.66, which might follow a volcano-like relationship between θ_{Sb} and electrocatalytic activity of Sb/Pd(UPD) (seen from inset in Figure 1b).

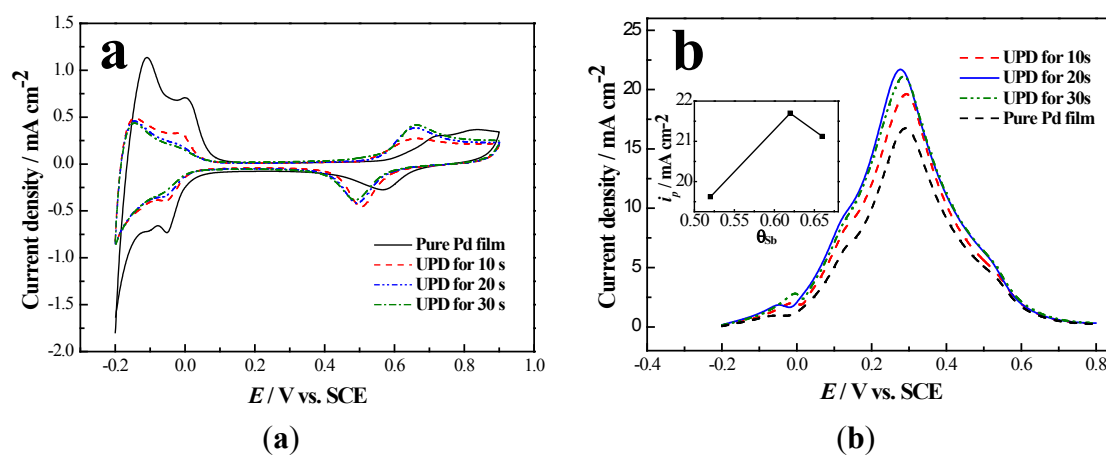


Figure 1. (a) CV curves of Sb/Pd(UPD) electrodes with various θ_{Sb} in 0.5 mol L^{-1} H_2SO_4 at 50 mV s^{-1} ; (b) The comparison of catalytic activity of Sb/Pd(UPD) electrodes with various θ_{Sb} towards HCOOH electrooxidation in 0.5 mol L^{-1} H_2SO_4 + 0.5 mol L^{-1} HCOOH at 50 mV s^{-1} . The inset presents a plot showing the direct relation between catalytic activity and θ_{Sb} .

2.2. Sb MUPD on Pd Film Electrodes

Figure 2 compared the open circuit potential recorded on the Pd film electrode in 0.1 mM APT solution with or without 20 mM AA. A high open circuit potential of *ca.* 0.29 V at 30 s was seen in

single 0.1 mM APT (curve a) due to the oxygen-containing species that spontaneously formed on Pd surface, thus limited effective modification of Sb on Pd. With addition of 20 mM AA to 0.1 mM APT aqueous solution (curve b), the OCP negatively shifted to 0.12 V at 30 s because the ascorbic acid served as mild reductant removed the oxygen-containing species to ensure freshly reduced Pd surfaces for better Sb modification [23]. Upon this, Sb MUPD was carried out through immersing Pd film electrode into modification solution for 30 s which was the optimal MUPD time reported by Cai *et al.* [23] when modifying bulk Pt electrode and powder catalyst by MUPD.

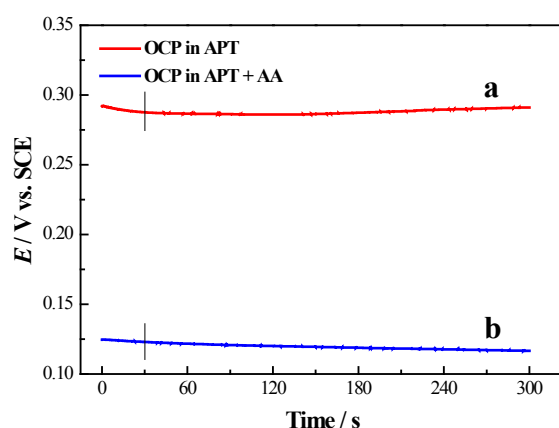


Figure 2. Open circuit potential (OCP) curves recorded on a Pd film electrode in 0.1 mM APT aqueous solution without (a) or with (b) 20 mM AA.

Hydrogen region properties of Sb/Pd(MUPD) electrode were studied by cyclic voltammetry in 0.5 mol L⁻¹ H₂SO₄. Observed in Figure 3a, after pure Pd film electrode was immersed in Sb containing solution for just 30 s, the area of hydrogen region was severely shrunk due to Sb coverage on Pd surface, thus leading to restriction of hydrogen adsorption/desorption, and, therefore, θ_{Sb} herein reached 0.67.

To compare the electrocatalytic activity of modified and unmodified Pd film electrodes, linear sweep voltammograms for formic acid oxidation are recorded on pure Pd film, optimal Sb/Pd(UPD) with UPD time for 20 s and Sb/Pd(MUPD) in 0.5 M H₂SO₄ containing 0.5 M HCOOH. As can be seen in Figure 3b, the formic acid oxidation current density in low potential was weak on unmodified pure Pd film. A small anodic peak was observed below 0 V which might be assigned to oxidative desorption of hydrogen produced in decomposition of formic acid over Pd surface at open circuit [26] and the main larger peak centered at 0.3 V was attributed to the direct oxidation of formic acid to CO₂ (black curve). For Sb/Pd(UPD), the shape of LSV was all the same except that the current density of formic acid oxidation was higher than that of unmodified Pd film (red curve). In the case of Sb/Pd(MUPD), not only the peak current density was further increased, but the main peak potential and onset potential of formic acid oxidation shifted negatively by 100 mV and 80 mV, respectively (blue curve). It indicated that the electrocatalysis of formic acid oxidation was significantly enhanced at low potentials on Sb/Pd(MUPD) compared with unmodified Pd and Sb/Pd(UPD).

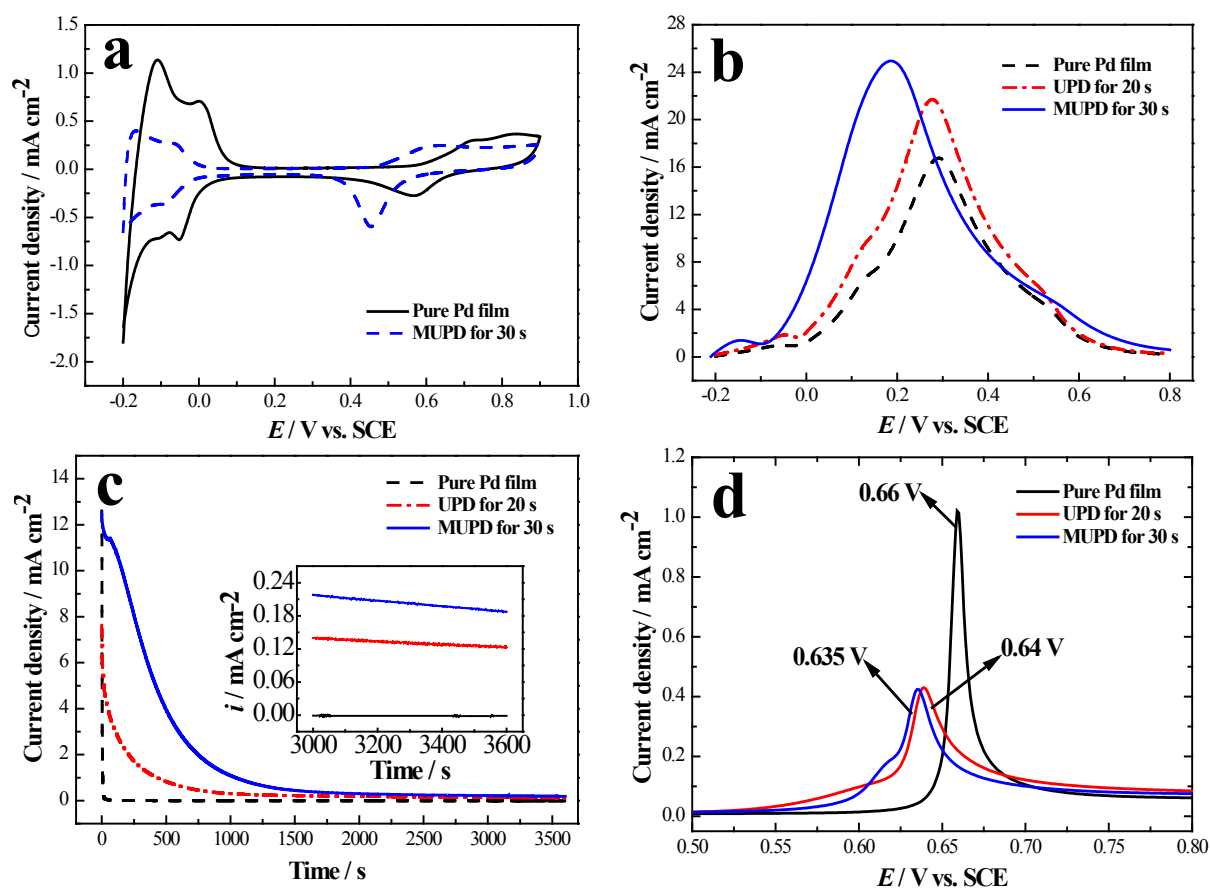


Figure 3. (a) CVs of pure Pd film and Sb/Pd(MUPD) electrodes in 0.5 mol L⁻¹ H₂SO₄ at 50 mV s⁻¹; (b) Linear sweep voltammograms and (c) chronoamperometric *i* vs. *t* curves of HCOOH oxidation at the constant potential of 0.2 V on pure Pd film, Sb/Pd(UPD) and Sb/Pd(MUPD) electrodes in 0.5 mol L⁻¹ H₂SO₄ + 0.5 mol L⁻¹ HCOOH; (d) Pre-adsorbed CO stripping voltammograms on pure Pd film, Sb/Pd(UPD) and Sb/Pd(MUPD) in 0.5 mol L⁻¹ H₂SO₄ at 10 mV s⁻¹. The inset in (c) is partial enlarged image.

The long-term electrocatalytic activities of the modified or unmodified Pd film electrodes are explored by polarizing pure Pd film, Sb/Pd(UPD) and Sb/Pd(MUPD) electrodes at 0.2 V in 0.5 M H₂SO₄ + 0.5 M HCOOH for 3600 s. Figure 3c showed the corresponding *i* vs. *t* curves. The current density on pure Pd film was intensively decayed in the initial stage (black curve) because of Pd surface poisoning by CO intermediates produced in self-decomposition of formic acid. For Sb/Pd(UPD) and Sb/Pd(MUPD), the current density for HCOOH electrooxidation was enhanced maximally and the decay became weak. During the whole testing (3600 s), the current density followed the order of Sb/Pd(MUPD) > Sb/Pd(UPD) > unmodified Pd which was consistent with the results in Figure 3b. Namely, the electrocatalytic performances were improved on Pd film electrodes by Sb modification due to the so-called third body effect, which accelerated formic acid oxidation through direct pathway [19,23]. Specifically, Sb modification can break adjacent Pd active sites which is favorable to dehydration of formic acid molecules to produce water and CO, thus CO poisoning on Pd surfaces were inhibited to some extent.

To further explore the poisoning resistant effect after Sb modification, pre-adsorbed CO stripping voltammetry was performed. Figure 3d showed CO stripping voltammograms for pure Pd film,

Sb/Pd(UPD) and Sb/Pd(MUPD) in 0.5 mol L⁻¹ H₂SO₄. It can be observed that on pure Pd film, the oxidative stripping peak was normally sharp and located at 0.66 V. Otherwise, both the onset and the peak potential of CO oxidation were significantly shifted to lower potentials on Sb/Pd(UPD) and Sb/Pd(MUPD) compared to unmodified pure Pd film. Therefore, the presence of Sb promoted the oxidation of CO adsorbed on Pd [18]. Seen from Figure 3d, the promotion can be explained by electronic effect or bi-functional mechanism induced by Sb. The electronic effect leads to a weakening of the CO-Pd interaction [27] and makes the direct pathway of formic acid oxidation being predominant [23]. In bi-functional mechanism, Sb adatoms provide active sites for –OH formation at lower potentials than on pure Pd, and –OH promotes the oxidative removal of adsorbed poisoning intermediates during formic acid oxidation [18,20,28].

2.3. Sb MUPD on Pd/C Powder Catalyst

The MUPD approach was further applied to modify 40 wt. % Pd/C(BASF) powder catalyst. Figure 4a shows XRD patterns of Pd/C before or after Sb modification by MUPD. The main diffraction peaks at 40.06°, 46.68°, 68.08°, 82.08°, 86.60° are characteristic peaks of Pd(111), (200), (220), (311), (222) plane which suggest face-centered cubic structure of metallic Pd. The peak located at 33.92° is attributed to palladium oxide on Pd/C (BASF), but the peak disappeared after immersed in the MUPD modification solution, which may be attributed to reduction of PdO by ascorbic acid. Any peak was observed for Sb or PdSb alloy among the XRD peaks because the Sb content is extremely low, as well as Sb is highly dispersed in active structure on Pd surface or Sb exists as amorphous structure.

Figure 4b shows cyclic voltammograms within hydrogen adsorption/desorption region on unmodified Pd/C and Sb modified Pd/C by MUPD. It was found that the hydrogen region was partially restrained, as well on Pd/C(MUPD) with a relatively small θ_{Sb} of 0.26, which was far below optimal θ_{Sb} value around 0.6. This may be due to partial adsorption of Sb on active carbon supports leading to limited Sb modification on Pd and less higher electrocatalytic activity for Pd/C(MUPD) (seen from Figure 4c). Despite of this, Figure 4d showed that the catalytic stability was enhanced further. CO anodic stripping voltammograms (Figure 4e) revealed negative shift of both peak potential and onset potential of CO oxidation by 70 mV and 50 mV, respectively. It is suggested that the resistance against CO poisoning was enhanced on Pd/C after Sb MUPD modification.

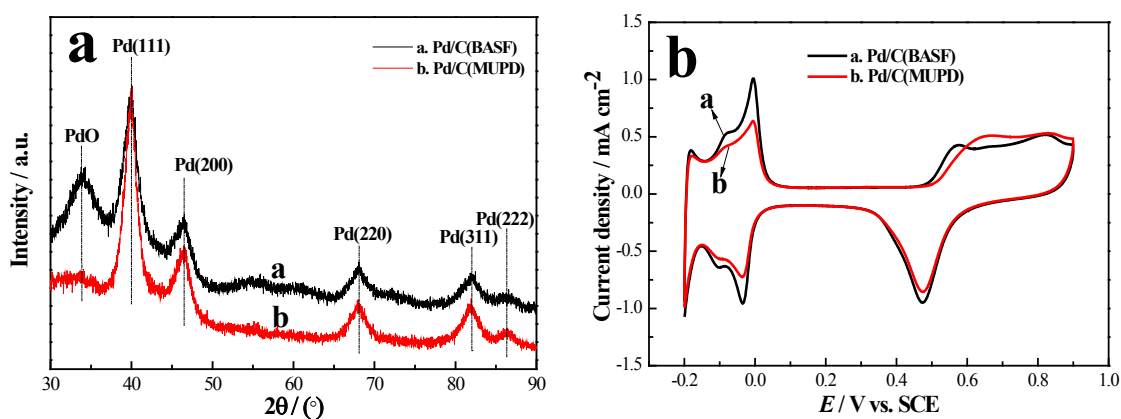


Figure 4. Cont.

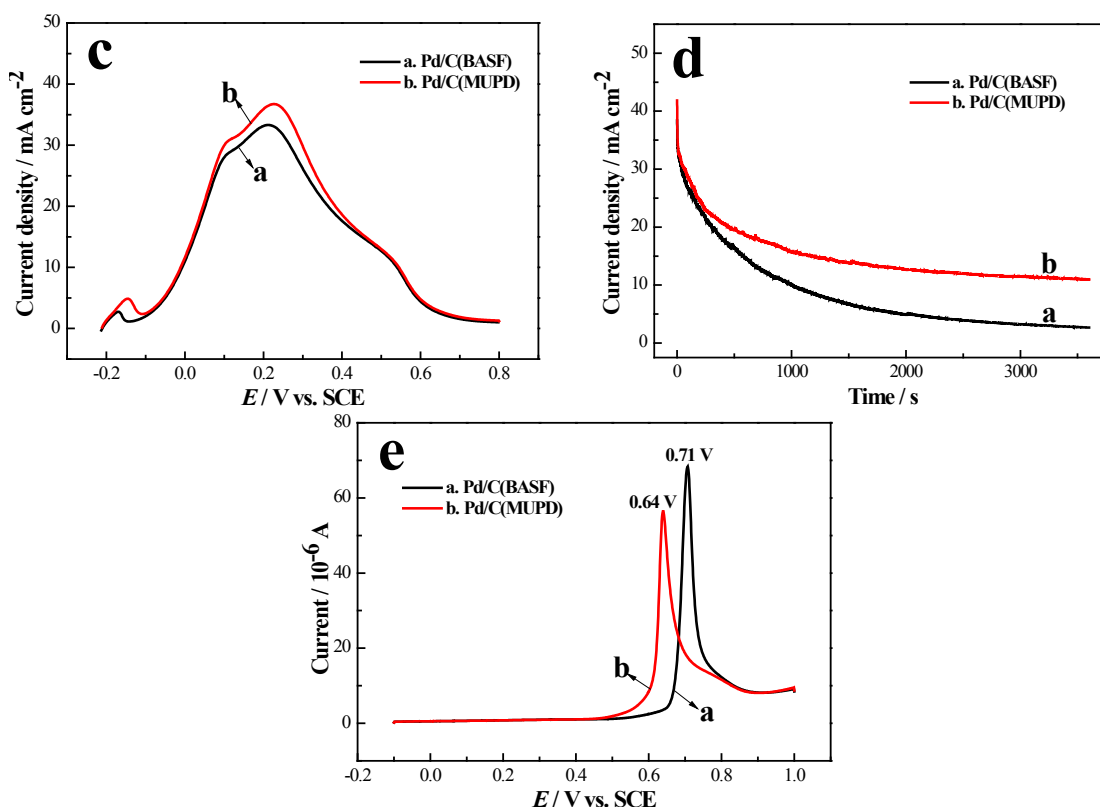


Figure 4. XRD patterns (a), cyclic voltammograms (b) in 0.5 mol L⁻¹ H₂SO₄ scanned at 50 mV s⁻¹, anodic linear sweep voltammograms (c) and chronoamperometric *i-t* curves (d) in 0.5 mol L⁻¹ H₂SO₄ + 0.5 mol L⁻¹ HCOOH scanned at 50 mV s⁻¹, anodic stripping voltammograms (e) of pre-adsorbed CO monolayer in 0.5 mol L⁻¹ H₂SO₄ scanned at 10 mV s⁻¹ on Pd/C before (a) and after (b) Sb modification by MUPD.

3. Experimental Section

3.1. Modification of Pd Surfaces

Palladium chloride (PdCl₂, analytical reagent), formic acid (analytical reagent) were obtained from Sinopharm Chemical Reagent Co. Ltd (SCRC, Shanghai, China). Perchloric acid (HClO₄, analytical reagent), sulfuric acid (H₂SO₄, analytical reagent), antimony potassium tartrate (analytical reagent) and ascorbic acid (analytical reagent) were obtained from Aladdin. Pd/C (40 wt. %) and 5 wt. % Nafion solution were purchased from BASF (Ludwigshafen, Germany) and Cabot Co. (Boston, MA, USA), respectively.

The Sb modification on Pd surface was carried out by the recently proposed MUPD method. For the film substrate, Pd thin film was first electrodeposited on a electrochemically cleaned glass carbon (GC, $\Phi = 3$ mm) electrode by cyclic voltammetric scanning in the potential range between -0.15 V and 0.42 V vs. SCE in the electrolyte of 0.1 M HClO₄ and 5 mM PdCl₂. Then, to achieve Sb MUPD, the Pd film electrode was immersed in the aqueous solution containing 0.1 mM antimony potassium tartrate (APT) and 20 mM ascorbic acid (AA) for 30 s, rinsed with ultrapure Milli-Q water. To make a comparison, the fresh Pd film was modified via Sb UPD process in which the electrode was modified in 0.5 M H₂SO₄ containing 0.1 mM APT at the UPD potential of 0.25 V vs. SCE for certain time. For

the powder catalyst, catalyst ink was prepared by dispersing 2 mg of Pd/C (40 wt. %, BASF) in 1 mL of ethanol with 120 μL of Nafion (5 wt. %) under sonication. An aliquot of the catalyst ink was transferred onto GC electrode with a Pd loading of 28 $\mu\text{g cm}^{-2}$. After the ink was dried in air, the catalyst coating was modified with the same procedure as Pd film substrate for MUPD.

3.2. X-ray Diffraction

X-ray diffraction (XRD) for Sb modified Pd/C was performed using a Bruker D8-Advance X-ray diffractometer (Karlsruhe, Germany) equipped with Cu $\text{k}\alpha$ radiation ($\lambda = 0.15406 \text{ nm}$), employing a scanning rate of $0.02^\circ \text{ s}^{-1}$ in the 2θ range from 20° to 90° .

3.3. Electrochemical Measurements

Electrochemical measurements were performed in a conventional three-electrode cell with a CHI 660E workstation (CH Instruments, Shanghai Chenhua, Shanghai, China) in 0.5 M H_2SO_4 without or with 0.5 M HCOOH solution deaerated by bubbling pure nitrogen (99.999%). The unmodified or modified Pd film electrode or powder catalyst covered GC electrode served as the working electrodes. A platinum gauze was used as the counter electrode, a saturated calomel electrode (SCE) as the reference electrode. For CO anodic stripping voltammetry, CO was pre-adsorbed on the Pd surface at the potential of -0.1 V in CO saturated 0.5 M H_2SO_4 and then oxidized (stripped) with an anodic potential scan. The values of current density in this paper are normalized by electrode geometric surface area (0.07065 cm^2). All electrochemical measurements were performed at room temperature.

4. Conclusions

The facile electroless MUPD method has been extended to the modification of Sb on Pd surfaces by immersing Pd film substrate and dispersing Pd/C powder into modification aqueous solution containing Sb(III) and ascorbic acid. As a mild reducing agent, ascorbic acid removed oxygenous species to shift down the open circuit potential of Pd substrate for achieving a sub-monolayer of Sb. The Sb/Pd(MUPD) exhibited enhanced electrocatalytic activity towards formic acid oxidation compared to unmodified pure Pd film and Sb modified Pd film by conventional UPD method. As for Pd/C powder catalyst, the electrocatalytic activity was improved by Sb MUPD. These improvements or enhancements derive from the third body effect, electronic effect and bi-functional mechanism resulting in stronger resistance against poisoning by CO poisons.

Acknowledgments

This work was financially supported by the Natural Science Foundation of China (21103107), Key Project of Shanghai Committee of Science and Technology, China (10160502300), Science and Technology Commission of Shanghai Municipality (No: 14DZ2261000).

Author Contributions

Long-Long Wang and Qiao-Xia Li conceived and designed the experiments; Long-Long Wang performed the experiments; all authors analyzed the data; Long-Long Wang and Qiao-Xia Li wrote the paper. All authors read and approved the final manuscript.

Conflicts of Interest

The authors declare no conflict of interest.

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