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Mass-transport-limited oxidation of formic acid on a $Pd_{ML}Pt(100)$ electrode in perchloric acid

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ABSTRACT

In this communication, we study the electrocatalytic formic acid oxidation process on an epitaxially grown Pd monolayer on a Pt(100) single crystal in perchloric acid. The formic acid oxidation activity on this $Pd_{ML}Pt(100)$ electrode in perchloric acid is significantly enhanced compared to the same electrode in sulfuric acid and compared to unmodified Pt(100), with a low onset potential of around 0.14 V_{RHE}. The absence of hysteresis between the positive and negative scan during formic acid oxidation indicates the remarkable resistance to CO poisoning of the Pd monolayer surface. Most importantly, we report, for the first time, a mass-transport-limited formic acid oxidation rate on the $Pd_{ML}Pt(100)$ rotating electrode in perchlorate acid, setting a catalytic benchmark for future electrocatalysts for formic acid oxidation.

1. Introduction

Direct alcohol fuel cells are attracting attention as new-generation power sources to replace fossil fuel-based energy sources. Formic acid oxidation occupies an important role in fuel cell technology both as a potential fuel and as a model reaction for providing a simple example of more complex organic molecules that can also be applied as fuels [1]. The successful development of this advanced energy-conversion system depends critically on the understanding of the fundamental oxidation mechanism at electrified metal-liquid interfaces. The fundamental mechanistic study of formic acid oxidation has focused mainly on noble metal electrodes, especially platinum and gold. The classical dual pathway [2,3] process has been widely accepted as mechanism. In this mechanism, the direct oxidation pathway leads directly to the formation of CO_2 through a reactive intermediate (presumably some form of adsorbed formate [4]). In the indirect pathway, formic acid dehydrates to form strongly adsorbed CO_{ads} [5,6], which acts as a poison blocking the surface and impedes further oxidation of formic acid. Studies of formic acid oxidation on Au show that Au is not poisoned by CO but the activity is an order of magnitude lower compared to Pt [7,8]. Palladium shows high activity towards formic acid oxidation and the remarkable difference with Pt is the absence of CO poisoning on Pd surfaces [9,10]. As a result, Pd-based catalysts have attracted increasing attention and are regarded as the best catalysts for formic acid oxidation [11,12]. It has been established from single crystal studies that formic acid oxidation on Pd is structure sensitive and that the oxidation peak current density follows the order Pd(110) < Pd(111) < Pd(100) in perchlorate acid [13]. Interestingly, previous studies by Kolb's [8] and Feliu's [14] group on epitaxially grown Pd overlayer on Pt single crystals (Pd and Pt have the roughly same lattice constant) showed a similar high activity on Pd/Pt(100). Therefore, Pd(100) appears to be the most active basal plane for the oxidation of formic acid in acidic electrolyte.

Given the high activity of Pd(100), many high-surface-area high-performance electrocatalysts towards formic acid oxidation have been synthesized through controlling the Pd(100) facets [15,16]. Still, the nature of the high activity of Pd, and its low tendency to poison, is not fully clarified [11]. This may come from very practical reasons including the difficulty to prepare Pd single crystals and to keep them clean. Epitaxially grown Pd layers on a foreign metal, especially Pt, are a promising alternative and have attracted significant attention, especially Pd layers on Pt(111) single crystals [8,17]. Although the activity of Pd sub/multi-layers on Pt(100) substrate for formic acid oxidation has been reported, however, only few studies are found in the literature for a Pd monolayer [8,18,19].

In this paper, we investigate formic acid oxidation on an epitaxially grown Pd monolayer on Pt(100) single crystal with a rotating electrode and demonstrate, for the first time, that formic acid oxidation on $Pd_{ML}Pt(100)$ in perchlorate acid is a mass-transport-limited process in a wide potential window. Such Levich behavior in formic acid oxidation has not been reported before although several research groups have used Pt [20–22] and Au [23] rotating disk electrodes to investigate the contribution of mass transport effect. Hoshi et al. [13] concluded that the oxidation of formic acid on Pd single crystal electrodes was not

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controlled by diffusion from performing experiments in the solution stirred at 400 rpm. The finding presented in this Communication is significant, because it shows that the combination of a well-defined Pd surface structure with perchloric acid, i.e. absence of specific anion adsorption, results a very high catalytic performance, to the extent that the oxidation activity becomes mass transport limited in a wide potential window. We believe that our result may provide a benchmark for future formic acid oxidation studies.

2. Experimental

Cyclic voltammetric measurements were carried out in standard electrochemical cells using a three-electrode assembly at room temperature. A bead-type single crystal electrode of Pt(100), with a diameter of 2.56 mm, was used as the working electrode. Prior to every experiment, the working electrode was prepared according to the Clavilier method [24]. A platinum wire was used as counter electrode and a reversible hydrogen electrode (RHE) was employed as the reference electrode in a separate compartment filled with the same electrolyte, at the same pH as the electrolyte in the electrochemical cell. The electrochemical measurements were performed with the single-crystal electrode in the hanging meniscus configuration. Mass-transport controlled measurements were performed with the AFMSRCE (Pine Research Instrumentation) rotator using a homemade rotating Pt single crystal electrode as working electrode. The potential was controlled with an Autolab PGSTAT302N potentiostat. The current density shown in the manuscript represents the measured current normalized to the geometric area of the working electrode.

The $Pd_{ML}Pt(100)$ in this study was prepared using method similar to the one reported before [19]. Briefly, the freshly prepared Pt(100) electrode was immersed into the Pd^{2+} containing solution at 0.85 V_{RHE}, where no Pd deposition occurred, and the potential was continuously cycled between 0.07 and 0.85 V_{RHE} at 50 mV s^{-1}. Then the electrode was taken from the cell and immersed in a nitric oxide (NO) saturated solution at open circuit. Afterwards, the crystal was thoroughly rinsed with ultrapure water to avoid any contamination from the solution and was transferred to the electrochemical cell at 0.85 V_{RHE} and the adsorbed NO was reductively stripped. The NO procedure is a sort of electrochemical annealing which enables the possibility to prepare Pt(100) electrode fully covered by a Pd monolayer.

Electrolytes were made from ultrapure water (Merck Millipore, 18.2 MΩ cm, TOC $<$ 3 ppb), high purity reagents $HClO_4$ and H_2SO_4 from Merck Suprapur, $PdSO_4$ (99.99%) and HCOOH (99.99%) from Sigma-Aldrich Ultrapure. Before each experiment, the electrolytes were first purged with argon (Air Products, 5.7) for at least 30 min to remove air from the solution.

3. Results and discussion

Fig. 1 shows the voltammetry of the $Pd_{ML}Pt(100)$ electrode giving well-defined and reversible responses in both H_2SO_4 and $HClO_4$, compared to the same curves for an unmodified Pt(100) electrode. In Fig. 1a, the reversible pair of adsorption/desorption peaks around 0.17 V_{RHE} has been ascribed to the reversible desorption/adsorption of hydrogen/anion (bi)sulfate on the Pd monolayer [19,25]. The blank voltammogram of the $Pd_{ML}Pt(100)$ in H_2SO_4 is in very good agreement with the cyclic voltammogram reported before [19]. Hydrogen desorption and anion adsorption does not take place significantly on Pt(100) at potentials lower than 0.25 V_{RHE}, as shown by the voltammograms of Pt(100) in $HClO_4$ and H_2SO_4. In the 0.1 M $HClO_4$ electrolyte (Fig. 1b), the broad peak between 0.10 and 0.25 V_{RHE} is assumed to be related to the desorption of adsorbed H and the formation of adsorbed OH (from water oxidation) on the Pd monolayer (with the reverse happening in the negative-going scan). In both electrolytes, the reversible voltammetric profiles obtained in the presence of the Pd monolayer remain unchanged upon successive cycles in the potential range as shown in Fig. 1, indicating the stability of the monolayer system.

Previous studies on the oxidation of formic acid on well-defined Pd layers on Pt were performed in H_2SO_4, showing interference by (bi) sulfate, which can strongly adsorb on Pd surfaces [26]. Adsorbed anions change the activity of formic acid oxidation on noble-metal electrodes due to site blocking and competitive adsorption [16,23,27]. Here, the voltammetric profiles for the oxidation of formic acid on Pt(100) and $Pd_{ML}Pt(100)$ are recorded in 0.1 M $HClO_4$ containing 50 mM HCOOH, in which the effect of anion adsorption can be neglected. As shown in Fig. 2a, no current is measured on Pt(100) during the positive scan until 0.80 V_{RHE} since the surface is almost completely blocked by CO formed at low potential. The current rises as the potential is scanned to lower potentials in the negative scan because the CO adlayer started to be oxidatively stripped at potentials above 0.80 V_{RHE}. The current in the negative-going scan is due to direct formic acid oxidation. In contrast to Pt(100), for the $Pd_{ML}Pt(100)$ electrode a high peak current density at 0.20 V_{RHE} is observed along with a very low onset potential at around 0.14 V_{RHE}. Comparison of the blank voltammogram of $Pd_{ML}Pt(100)$ in Fig. 1b with the curve in Fig. 2a shows that the onset of formic acid oxidation appears to coincide with hydrogen desorption, suggesting that the adsorbed hydrogen inhibits the formic acid oxidation.

The voltammogram in Fig.2a shows a peak current at 0.20 V_{RHE} which could mean that the reaction is diffusion controlled. To control the mass transport conditions, further experiments were performed using a $Pd_{ML}Pt(100)$ rotating electrode as demonstrated in Fig. 2b. Specifically, the voltammograms observed during positive-going as well as negative-going scan show relatively little hysteresis and strongly depend on the rotation speed. In case of mass transport limitations, the plateau current densities follow the Levich equation as a function of rotation rate ω:

$$J_L = 0.620nFD^{2/3}\upsilon^{-1/6}C\square^{1/2} = B\omega^{1/2}$$

where n is the number of electrons in the formic acid oxidation reaction ($n = 2$), F is the Faraday constant (96,485 C mol^{-1}), v is the kinematic viscosity of the electrolyte (1.01×10^{-2} cm^2 s^{-1}), C is the reactant concentration (5×10^{-5} mol cm^{-3}), ω is the angular rotation rate of the electrode (rad/s) and D is the diffusion coefficient of formic acid in 0.1 M $HClO_4$ [28].

As illustrated in Fig. 2c, a plot of the limiting current density j as a function of square root of the electrode rotation rate ω indeed reveals a clear linear behavior as expected from the Levich equation. The straight line yields a slope of $B = 6.32 \times 10^{-3}$ mA cm^{-2} rad $s^{-1/2}$, implying a formic acid diffusion coefficient of 1.1×10^{-5} cm^2 s^{-1}, in reasonable agreement with the reported value of 1.5×10^{-5} cm^2 s^{-1} [28,29]. Fig. 2d also shows the voltammograms obtained in 0.1 M H_2SO_4 containing 50 mM HCOOH. The $Pd_{ML}Pt(100)$ electrode shows a peak current density at 0.24 V_{RHE} along with a very low onset potential at around 0.13 V_{RHE}, which is quite similar with the behavior in 0.1 M $HClO_4$. It is noticed that the peak current density in 0.1 M H_2SO_4 is lower than that of 0.1 M $HClO_4$, due to the strong anion adsorption [16,26]. The oxidation currents in the positive- and the negative-going scan suggest the absence of significant CO poisoning on the $Pd_{ML}Pt$ (100) electrode, in agreement with the cyclic voltammograms from previous studies [16]. In the presence of strongly adsorbed (bi)sulfate, enhancing mass transport through increasing the rotation rate barely affects the current values as compared to measurement performed in quiescent conditions.

Recently, Osawa et al. [26] observed the adsorption of formate on Pd during formic acid oxidation in sulfuric acid by using surface-enhanced infrared absorption spectroscopy (SEIRAS) in the attenuated total reflection (ATR) mode. On the other hand, formate was not observed on Pd in perchloric acid, in which larger formic acid oxidation currents were obtained compared to sulfuric acid. They proposed that the lifetime of formate is shorter because of the increased reaction rate in perchloric acid, resulting in the absence of observable formate adsorption in perchloric acid.

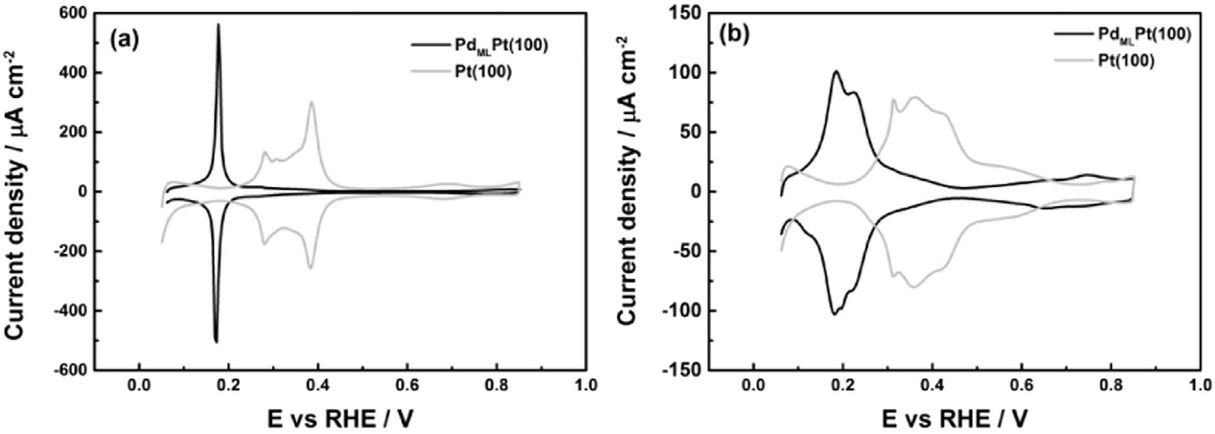

Fig. 1. Cyclic voltammograms of the Pd$_{ML}$Pt(100) electrode in (a) 0.1 M H_2SO_4 and (b) 0.1 M $HClO_4$ recorded at 50 mV s^{-1}. The blank voltammograms for the Pt(100) electrode recorded under identical conditions are shown for comparison.

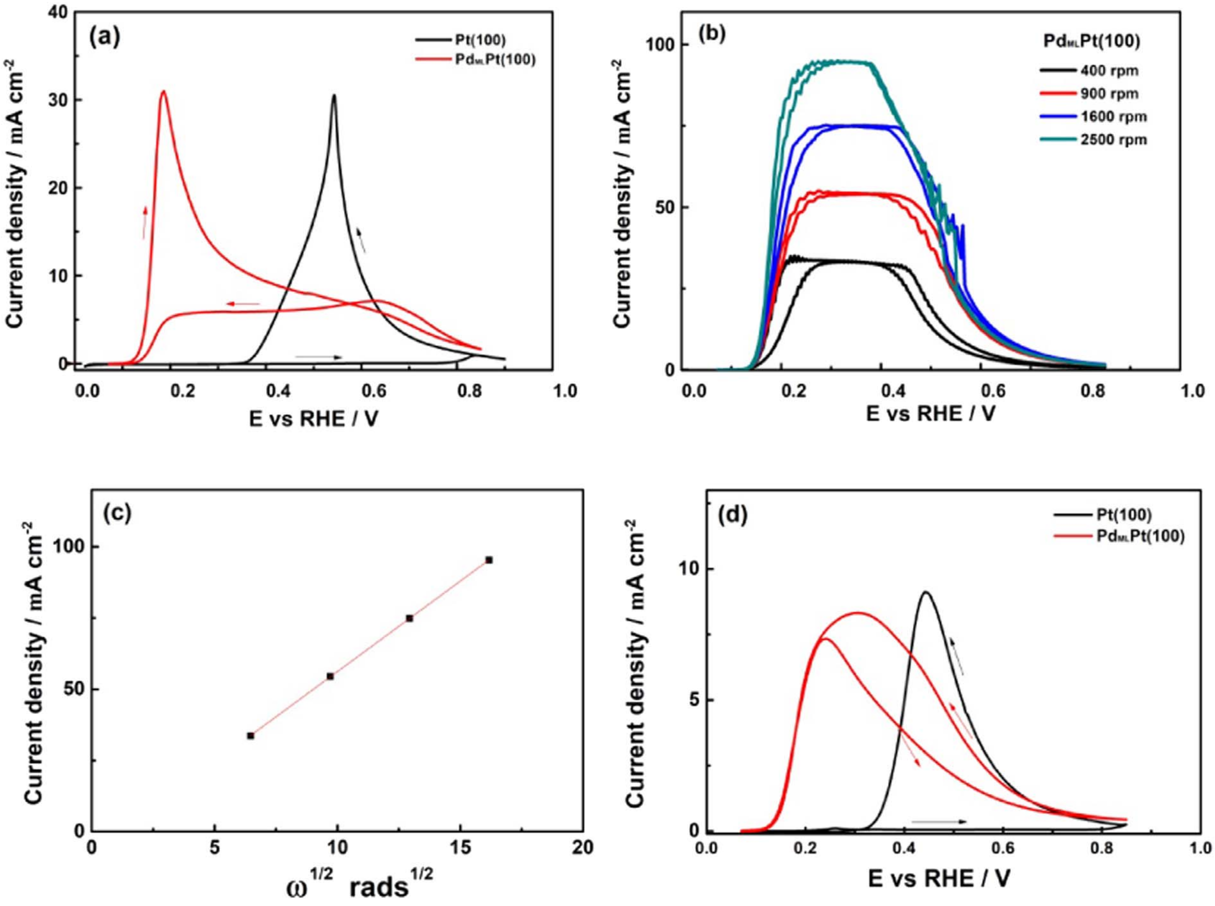

Fig. 2. Voltammetric profiles for the oxidation of 50 mM HCOOH on (a) Pt(100) and Pd$_{ML}$Pt(100) in 0.1 M $HClO_4$ without rotation, (b) Pd$_{ML}$Pt(100) at various rotation rates in 0.1 M $HClO_4$ and (c) Levich plot (the limiting current density J_L versus square root of rotation rate ω) calculated from 2b and (d) Pt(100) and Pd$_{ML}$Pt(100) in 0.1 M H_2SO_4. Scan rate: 50 mV s^{-1}.

These results clearly demonstrate that the combination of a Pd$_{ML}$Pt (100) electrode and an electrolyte without adsorbing anions yields a very high activity for electrocatalytic formic acid oxidation, even reaching diffusion limitation in a wide potential window. This system therefore sets a benchmark for high-rate formic acid oxidation electrocatalysts.

4. Conclusion

In conclusion, we have shown here that a well-defined Pd monolayer on Pt(100) single crystal has unique catalytic properties with respect to formic acid oxidation in perchlorate acid. The Pd$_{ML}$Pt(100) electrode exhibits high activity without CO poisoning at low potentials and reaches mass transport controlled conditions in a wide potential window, an observation which to the best of our knowledge has not been made before.

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