



Formic acid electro-catalytic oxidation at high temperature in supporting electrolyte free system: Mechanism study and catalyst stability



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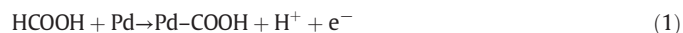
ABSTRACT

As a potential fuel for proton exchange membrane fuel cell, formic acid (FA) is easily decomposed on palladium (Pd) based catalysts, which are also the most effective and commonly used FA electro-oxidation catalysts in the direct formic acid fuel cell (DFAFC). Here we try to study the interaction between these two reactions in a supporting electrolyte free electrochemical cell. Considering the operation condition in the anode of DFAFC, influence of FA decomposition on FA electro-oxidation is detected and confirmed by mechanistic study. By doping platinum (Pt) into Pd, stability of the FA electro-oxidation can be extremely improved at fuel cell operation temperature.

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1. Introduction

Direct formic acid fuel cells (DFAFCs) have achieved significant improvements on both key material development and manufacturing technologies [1–6] and have shown great potential as power sources for the portable electronic applications. The DFAFC has relatively great theoretical open circuit voltage (approximately 1.45 V at 25 °C) [7,8] brought by the high kinetic rate of formic acid (FA) oxidation on noble metal catalysts. Except for the Pt based FA electro-oxidation catalysts [9–17], i.e. Pt with ad-atoms (Pb, Bi, Sn, Sb) on the surface and inter-metallic PtM (M: Bi, Pb, Pd, Au) catalysts, the Pd based catalysts, which performed excellent for FA electro-oxidation, were extensively studied [18–22]. However, FA oxidation mechanism on Pd is less studied compared with that on Pt surface [23–29]. By using a real-time high-sensitivity surface-enhanced IR absorption spectroscopy, Wang et al. [30] confirmed that CO detected on Pd surface was attributed to the reduction of CO₂ product and the mechanism for FA electro-oxidation on Pd surface can be expressed as follows:



FA molecule firstly adsorbs on Pd active site before the first proton is generated as addressed in Eq. (1). –COOH group adsorbed on Pd active site is then directly oxidized to generate CO₂, H⁺ and electron (Eq. (2)). The accumulated CO₂ on Pd surface may be reduced to CO (Eq. (3)), which is considered as the poison species. This FA electro-oxidation mechanism on Pd surface is defined as “direct-pathway” mechanism. However, the “direct-pathway” mechanism may not be accurate in an operating DFAFC since the calculations and experiments for the mechanism proposed were mostly based on room temperatures (20–25 °C), while temperature of an operating DFAFC (stack) can reach 60–80 °C.

At such high temperatures, catalytic decomposition of FA [31–35] will occur on the surface of Pd-based catalysts to generate hydrogen and carbon dioxide:

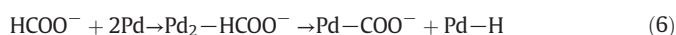


The decomposition of FA on Pd surface would not only reduce the fuel utilization in DFAFCs, but also alter the mechanism of FA electro-oxidation at high temperatures. A “micro-battery” mechanism (Eqs. (5)–(9)) for the catalytic FA decomposition can be therefore proposed according to the results in literature [33,36]:



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After ionization of FA molecule in the aqueous solution (Eq. (5)), the HCOO^- ion subsequently dehydrogenates with the help of two Pd active sites to form an adsorbed COO^- ion and an H atom (Eq. (6)). As the key of the “micro-battery” mechanism, the COO^- is oxidized to CO_2 by losing an electron (Eq. (7)) and the ionized H^+ in Eq. (5) is simultaneously reduced by the electron to generate an H atom (Eq. (8)). This COO^- oxidation (Eq. (7)) is the anodic reaction while the proton reduction (Eq. (8)) acts as the cathodic reaction of the “micro-battery”. Two adjacent adsorbed H atoms finally form a hydrogen molecule (Eq. (9)).

Interaction between the “micro-battery” and “direct-pathway” mechanisms is in detail discussed in the present work *via* electrochemical methods. The FA decomposition occurring on the Pd surface through “micro-battery” mechanism at high temperature may decrease the efficiency of FA as the fuel of DFAFC. For the purpose of enhancing the catalyst and fuel utilization of DFAFC, Pt was doped into Pd to form an alloyed catalyst to reduce FA catalytic decomposition on Pd surface in the anode of DFAFC during the operation. The influence of “micro-battery” mechanism on FA electro-oxidation can be successfully inhibited due to the third-body effect. The stability of FA electro-oxidation at the operation temperature of DFAFC was also therefore improved by adding Pt in the catalyst.

2. Experimental

2.1. Preparation of catalysts

20 wt.% carbon black supported Pd (Pd/C) catalyst was prepared using a pre-precipitation method as previously reported [37]. As an alternative catalyst of Pd/C for FA electro-oxidation, a 20 wt.% PdPt/C with a PdPt atom ratio 1:1 was also prepared according to the same method.

2.2. Electrochemical measurements

The electrochemical measurements were carried out in a conventional three-electrode electrochemical cell at 25 °C and 60 °C using cyclic voltammetry (CV) on a EG&G Potentiostat/Galvanostat Model 273A (Princeton Applied Research Co., US). A glassy-carbon working electrode ($\Phi 3$, surface area 7.0 mm^2) was used as substrate and the catalyst loading was controlled to be 0.357 mg cm^{-2} , meaning 0.025 mg Pd/C catalyst or PdPt/C catalyst on every working electrode. A platinum electrode and a saturated calomel electrode (SCE) were used as the counter electrode and the reference electrode, respectively. All potentials reported in this work are referred to the SCE. Prior to CV measurements, the electrolytes were saturated by ultra-pure argon. The 0.5 mol L^{-1} (M) HCOOH solutions both with and without supporting electrolyte ($0.5 \text{ M H}_2\text{SO}_4$) was freshly made. The potential was varied between -0.2 and 1.0 V at a scan rate of 50 mV s^{-1} and the 5th cycle of the CV test was recorded. Electrochemical Impedance Spectroscopy (EIS) testing was conducted before every CV measurement to obtain the solution resistance for the iR correction. Chronoamperometry was also measured in the same system by setting the potential at 0.2 V .

3. Results and discussion

3.1. Feasibility of supporting electrolyte free system

In order to eliminate the influence of supporting electrolyte on FA electro-oxidation study, supporting electrolyte free system was used in this work since the protons generated from the FA ionization can play the function of the supporting electrolyte. CV tests of Pd/C were respectively performed in H_2SO_4 solution and $\text{HCOOH} + \text{H}_2\text{SO}_4$ mixture at 25 °C to attest the influence of supporting electrolyte (H_2SO_4) on FA electro-oxidation (Fig. 1). Fig. 1a displays the forward sweeps of these two CV curves. The only peak at about -0.1 V in the H_2SO_4 sweep is attributed to the oxidation of adsorbed hydrogen atom on Pd surface. In the curve of $\text{HCOOH} + \text{H}_2\text{SO}_4$, the maximum current density of HCOOH oxidation is above 40 mA cm^{-2} , which is about 4 times of that of the hydrogen oxidation peak in the same curve. It can also be found from Fig. 1a that the hydrogen oxidation peaks in these two curves do not overlap with each other due to that H^+ can be reduced by HCOOH at potentials lower than -0.2 V in the $\text{HCOOH} + \text{H}_2\text{SO}_4$ solution.

CV curve of H_2SO_4 (black line in Fig. 1a) was therefore deduced from that of $\text{HCOOH} + \text{H}_2\text{SO}_4$ (red line in Fig. 1a) to obtain a “net” CV curve of HCOOH (Fig. 1b). Since HCOOH is electro-oxidized on Pd surface *via* the “direct-pathway” mechanism, peak II and shoulder III in Fig. 1b can be attributed to the oxidation of HCOOH to $-\text{COOH}$ (Eq. (1)) and adsorbed $-\text{COOH}$ to CO_2 (Eq. (2)), respectively. Moreover, it can be implied from peak I, which can be attributed to H oxidation, that H_2SO_4 in the electrolyte may affect the HCOOH oxidation during the electrochemical measurements.

Therefore, CV measurements in the supporting electrolyte free HCOOH solution were carried out at room temperature (25 °C). According to the EIS measurement before the CV testing, solution resistance of the supporting electrolyte free is *ca.* 10 times higher than that of the H_2SO_4 HCOOH solution. iR correction was therefore made on the CV curves as shown in Fig. 2. It can be found that the electrochemical signal of HCOOH oxidation can be recorded in the system without supporting electrolyte and only one peak is detected in the forward sweeps of the CV curves, which is different from the “net” CV curve in Fig. 1b. We attributed this difference to that the HCOOH oxidation rate on Pd surface is controlled by the H^+ migration in the supporting electrolyte free system since H^+ concentration is very low in this system due to the incomplete ionization of HCOOH. The shoulder II in Fig. 1b is therefore not reflected in the curves. However, two peaks at 0.2 and 0.4 V in the backward sweep ascribing to Eqs. (1) and (2) can be detected. Moreover, the small peak appeared at *ca.* 0.65 V can be attributed to the oxidation of CO formed from the Eq. (3). As a result, it can be concluded that performing the HCOOH electrochemical measurements in the supporting electrolyte free system is feasible.

3.2. Effect of temperature

Rapid catalytic decomposition of HCOOH will occur on Pd surface according to the “micro-cell” mechanism at high temperature. Therefore, it is necessary to study the high temperature electrochemical performance of Pd/C in HCOOH solution to investigate the interaction between electro-oxidation and catalytic decomposition of HCOOH in the anode of DFAFC. Temperature of the supporting electrolyte free system was set at 60 °C to simulate the real DFAFC operation. iR corrected CV curves measured at 60 °C were compared in Fig. 3a with those recorded at 25 °C in the supporting electrolyte free system. In the initial section of the forward sweep, oxidation current density at 60 °C is higher than that measured at 25 °C, which was caused by numerous H^+ generated from HCOOH ionization at higher temperature. This viewpoint can be proved by the 25% reduced solution resistance of the 0.5 M HCOOH solution at 60 °C. There were hence more adsorbed H atoms oxidized at the low potential on Pd surface at 60 °C. However,

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