

On the origin of oscillations in the electrocatalytic oxidation of HCOOH

포름산 산화시 전극촉매의 비선형적 반응특성연구

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서론

The electrocatalytic oxidation of HCOOH on Pt in the presence of foreign adatoms to be explained in this chapter is one of the most studied subjects experimentally and theoretically in electrocatalysis of organic oxidations. This reaction may be considered as a model to understand the oxidation of more complex organic species (*e.g.*, methanol) on a Pt electrode, since it produces carbon dioxide and interfacial electrons that are of great interest in direct fuel cell applications.

In this study, we try to elucidate the mechanistic origin of current oscillations in the electro-oxidation of formic acid on a Pt electrode modified by bismuth deposition.

실험방법

Figure 1 shows the schematic experimental setup for monitoring of the local potential distributions at electrochemical interfaces studied. The electrochemical cell body consisted of a glass cylinder capped with a Teflon lid holding all electrodes. A smooth polycrystalline Pt ring with inner diameter of 34.5 mm and with outer diameter of 40.5 mm was used as working electrode (WE). The geometric area of the WE was 7 cm². A concentric platinized Pt wire ring of 70 mm diameter was used as counter electrode (CE). The tip of a Luggin-Haber capillary hosting a Hg/Hg₂SO₄, saturated K₂SO₄ reference electrode (RE) was placed in the centre of the ring WE. A home-built potentiostat (ELAB of Fritz-Haber-Institut) was used for all cyclic voltammetry (CV) experiments.

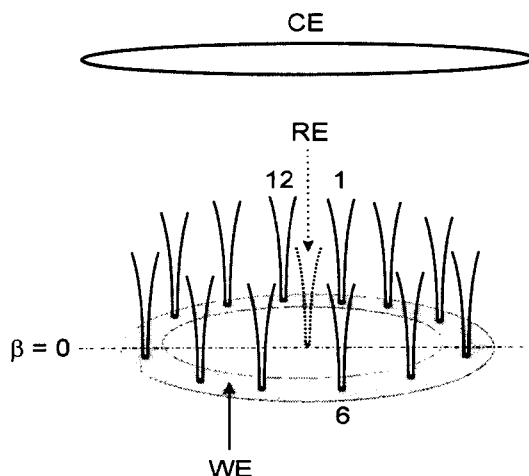


Figure 1. Schematic diagram of experimental setup for the measurements of HCOOH oxidation on a Pt ring electrode.

All solutions were prepared with ultrapure water (Millipore Milli(Q) water, 18 M Ω cm). Prior to the experiment, the Pt ring WE was first subjected to cleaning with acetone and pure water in an ultrasonic bath followed by chemical cleaning in a mixture of conc. H₂SO₄ (Merck, suprapur) : 30 % H₂O₂ (1 : 1). For all experiments involving formic acid oxidation, a deaerated solution mixture of 0.1 M HCOONa (Merck, p.a.) and 0.033 M H₂SO₄ (Merck, suprapur) was employed as the electrolyte. The formic acid buffer solution has a constant bulk pH value of 2.85 and a resistivity of 107 Ω cm. After the experiments, the WE was treated in conc. HClO₄ (Merck, suprapur) and conc. HNO₃ (Merck, suprapur) in order to completely remove Bi complex residuals.

Bi deposition modifications of the Pt WE in this work was done with under potential deposition of Bi. In other words, Bi ions were present in the bulk electrolyte throughout the entire experiment. A 1×10^{-3} M Bi³⁺ containing solution was prepared by dissolution of high-purity Bi (III) oxide (Bi₂O₃, Strem Chemicals Inc., 99.9998 %) in 0.5 M HClO₄ (Merck, suprapur). Appropriate amounts of the 1×10^{-3} M Bi³⁺ solution were added to the electrolyte to obtain final concentrations of Bi³⁺.

결과 및 결론

Figure 2 illustrates the effect of Bi adatoms on the formic acid oxidation on a Pt electrode. Figure 2 shows the typical cyclic voltammetry profile (dotted line) on an pure Pt electrode, while an about five times higher electro-oxidation current of HCOOH on the Bi-modified Pt electrode is observed (solid line). According to previous studies, this

higher electrocatalytic activity of Bi/Pt for HCOOH oxidation can be due to two modification effects of Bi adatoms such as a third-body effect on a Pt (100) and an electronic effect on a Pt(111). In this work, polycrystalline Pt was used, and thus one can speculate that the enhanced current may be the result of both steric hindrance of the formation of poisoning species (CO) and intrinsic kinetic enhancement. The value of the oscillatory current related with HCOOH oxidation is significantly higher than that on pure Pt. This oscillation is observed over a broad potential region between +110 mV to +280 mV and it indicates periodic activating and passivating processes of the electrode. This result is in good agreement with previous studies that the current for HCOOH oxidation may increase by up to a factor of 50. The oscillatory cyclic voltammetry was found to be reproducible for many successive voltammetric cycles.

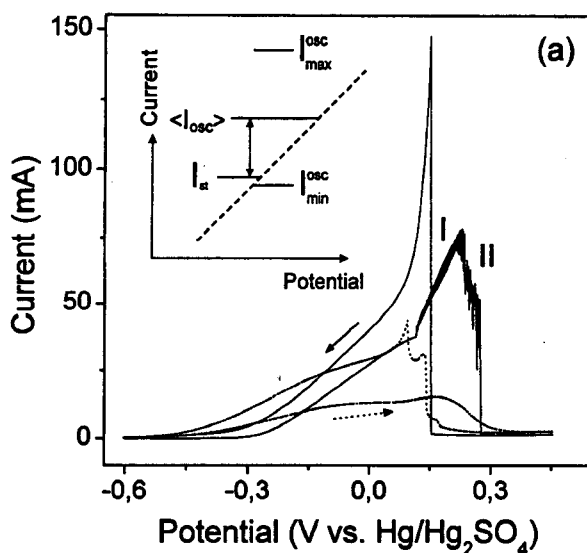


Figure 2. Cyclic voltammetry of electro-oxidation of formic acid in the absence of Bi^{3+} (dotted line) and in the presence of Bi ions of $1 \times 10^{-6} \text{ M Bi}^{3+}$ (solid line). Electrolyte is $0.1 \text{ M HCOONa}/0.033 \text{ M H}_2\text{SO}_4$ and scan rate is 5 mV/s . The inset schematically shows that oscillatory systems can exhibit an advantage in the current yield. Extrapolation of the stationary current suggests that this may be the case in the present system.

The potential parameter dependence of the current oscillations exhibits the following interesting features. Current oscillations with high frequency and small amplitude abruptly set in on the left flank of the peak on the anodic scan. At the onset of

oscillations, a stationary current-potential curve with positive slope (Figure 2-I) is obtained, while at higher anodic overpotential, an current-potential profile with negative slope (negative differential resistance) shows higher amplitude and smaller frequency oscillation (Figure 2-II). Analysis of Figure 2 suggests that the formation of Bi surface oxides leads to a relatively rapid decline in the high currents between +220 mV and +280 mV. On the other hand, a very high coverage of metallic Bi (below -200 mV) decreases the oxidation current, since Bi on the Pt electrode inhibits the adsorption of HCOOH. Interestingly, as sketched in Figure 2 (see inset), the average value ($\langle I_{osc} \rangle$) of the oscillatory current during HCOOH oxidation on Bi/Pt electrode is higher than that of the (extrapolated) stationary operation points at the same applied potential. Accordingly, direct formic acid or methanol oxidation under autonomous oscillatory conditions and/or by applying external pulses can lead to an increased power output.

참고문헌

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