

**A Combined Surface-enhanced Infrared Spectroscopy and
First-Principles Study on Electro-oxidation of Formic Acid at
Sb-Modified Pt Electrodes**

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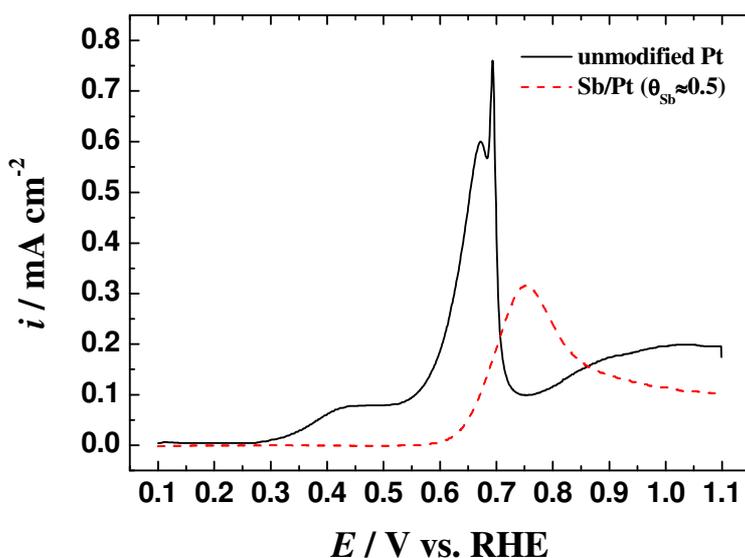


Figure S1. CO stripping curves on unmodified Pt and Sb/Pt ($\theta_{\text{Sb}} \approx 0.5$) in 0.1 M HClO_4 with the scan rate of 25 mV s^{-1} . CO-predosing was achieved by keeping the electrode at 0.1 V (RHE) in 0.1 M HClO_4 with initial CO (99.9%) bubbling for 15 min and subsequent Ar bubbling for 60 min.

Although Sb modification inhibits “indirect pathway” in which HCOOH first

dehydrates to form CO on Pt, it does not necessarily mean that the stripping of a predosed CO adlayer on Sb/Pt electrode should occur at a more negative potential as compared to that on Pt electrode, since the electrooxidation of CO adlayer depends not only on the CO adsorption strength but also on the coverage and structure of CO adlayer as well as on the availability of the reactive oxygen-containing species.¹ Figure S1 compares the anodic stripping curves of predosed CO adlayer on Pt and on Sb/Pt electrode. The oxidation of CO proceeds after the stripping of Sb occurring at ca. 0.66 V (vs. RHE),² similar to the report by Kizhakevariam et al.³ Given that both the prepeak and main peak for CO oxidation at Pt electrode require the adsorption of OH (Langmuir-Hinshelwood mechanism),¹ the hindered CO oxidation on Sb/Pt is therefore ascribed to the inhibited OH adsorption and/or CO diffusion on Sb-modified Pt electrode surface. In fact, Waszczuk et al. also reported that a higher potential was required to remove CO adlayer on a Pd modified Pt (Pd/Pt) electrode as compared to that on a Pt electrode,⁴ while the Pd/Pt electrode presented a much higher electrocatalytic activity towards HCOOH oxidation than the Pt electrode.

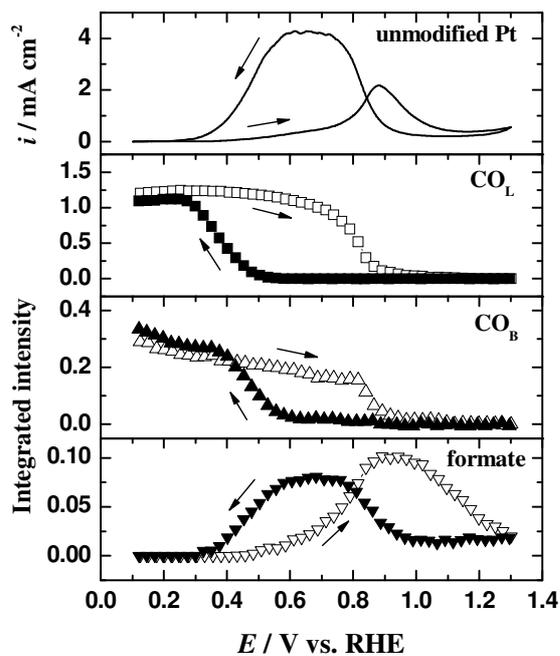
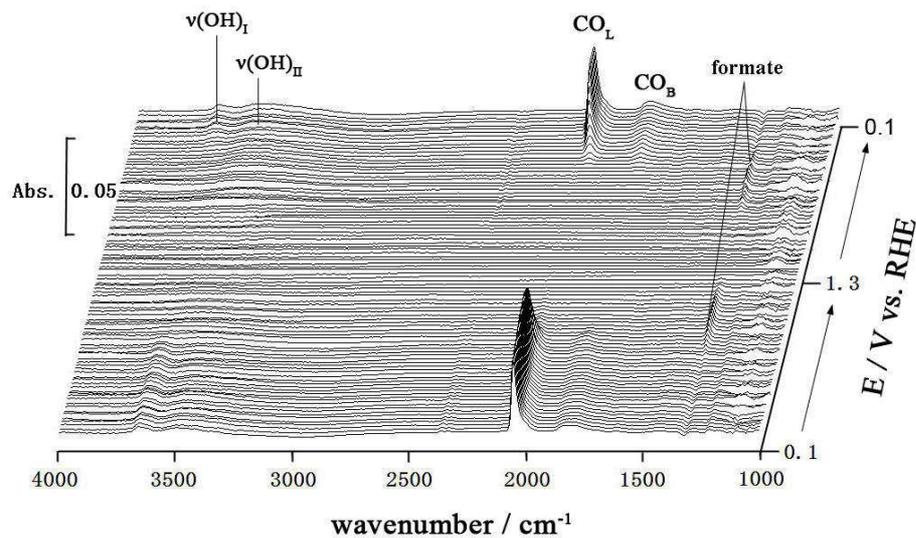


Figure S2. Series of time-resolved SEIRAS spectra and selected integrated intensities of CO_L , CO_B and formate on unmodified Pt electrode acquired during the cyclic voltammetry at 10 mV s^{-1} in $0.5 \text{ M HClO}_4 + 0.1 \text{ M HCOOH}$ solution. The reference spectrum was taken at 1.3 V .

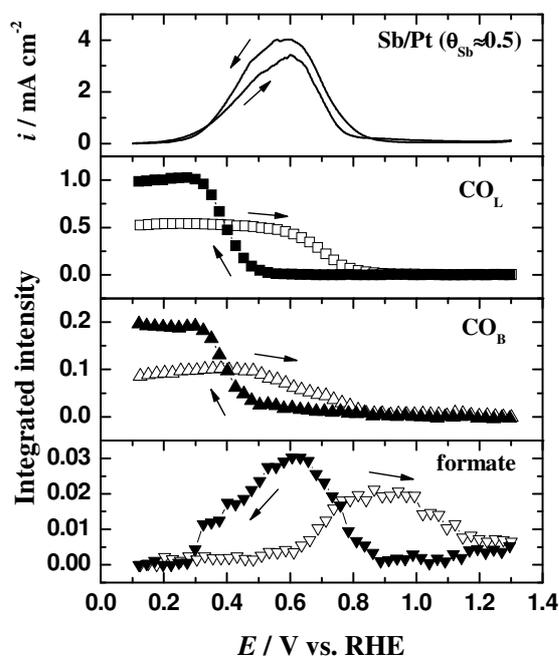
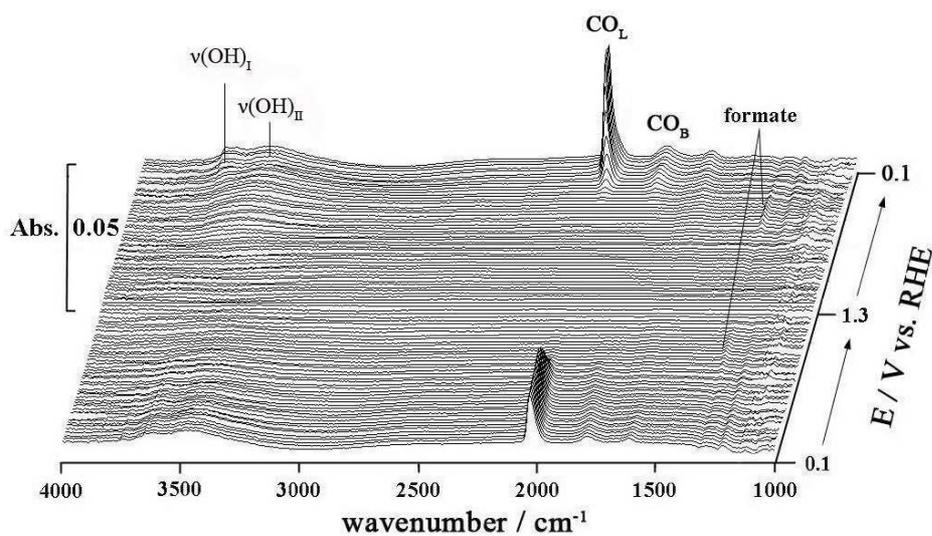


Figure S3. Series of time-resolved SEIRAS spectra and selected integrated intensities of CO_L , CO_B and formate on the $\text{Sb/Pt}(\theta_{\text{Sb}} \approx 0.5)$ electrode acquired during the cyclic voltammetry at 10 mV s^{-1} in $0.5 \text{ M HClO}_4 + 0.1 \text{ M HCOOH}$ solution. The reference spectrum was taken at 1.3 V .

Figures S2 and S3 show the EC-SEIRAS spectra for Pt and Sb/Pt electrodes in a solution containing 0.1 M HCOOH and 0.5 M HClO_4 , respectively. The results

obtained here are in general similar to those obtained in 0.5 M H₂SO₄ + 0.1 M HCOOH, especially for the main oxidation of HCOOH in the positive scan (see Figures 1-4 of the manuscript), indicating that the electro-oxidation of HCOOH as well as the adsorption of the possible intermediate formate on Pt or Sb/Pt electrode as a function of potential is least affected in the potential range of interest (<0.6 V) during the positive scan. This can be understood, given that the chemically adsorbed CO species on Pt and Sb/Pt electrodes owing to the self-dissociation of formic acid prevents the adsorption of ClO₄⁻ or SO₄²⁻, and thus mitigating the effect of the anion effect. Even on Pd electrode in the same solutions (CO adsorption is far less significant), Osawa and his coworkers proposed that adsorbed SO₄²⁻ does not suppress formate adsorption.⁵

Nevertheless, the main HCOOH oxidation peak in the negative scan (corresponding to the direct oxidation of HCOOH) turns narrower in H₂SO₄ than in HClO₄, which may be ascribed to the suppressed oxidation of HCOOH by more effective adsorption of SO₄²⁻ (than ClO₄⁻) on open Pt sites released from CO and Sb oxidative desorption during the previous anodic excursion. Notably, due to the negligible CO adsorption in the initially positive scan, similar oxidation peak expansion was also observed on a Pd electrode when HClO₄ instead of H₂SO₄ was used as the supporting electrolyte.⁵

Based on the above results, it may be concluded that the current strategy of combined SEIRAS and DFT calculation study is valid in understanding the enhanced electrocatalysis on Sb/Pt electrode.

References

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