Abs. 234, 206th Meeting, © 2004 The Electrochemical Society, Inc.

Structural Effects on the Oxidation of Formic Acid on the Low and the High Index Planes of Palladium

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The oxidation of formic acid has been widely studied on single crystal electrodes of Pt (1). Formic acid is dissociated to adsorbed CO on Pt electrodes (2), and the adsorbed CO prevents the oxidation of formic acid at lower potentials. On the other hand, no adsorbed CO is produced on Pd electrodes during the formic acid oxidation (3). The oxidation currents of formic acid on poly-crystal electrodes of Pd are higher than those of Pt (4). There have been, however, few reports on the oxidation of formic acid using single crystal electrodes of Pd (5). We have studied the oxidation on the low index planes and kinked stepped surfaces of Pd in 0.1 M $HClO_4$.

Single crystal electrodes of Pd were prepared according to the method reported previously (6). Crystals examined were Pd(111), Pd(100), Pd(110) and Pd(S)-[*n*(100)×(110)] (*n* = 2~9). Electrolytic solution was prepared with suprapure grade chemicals (Merck) and ultrapure water. Potential was scanned at 0.020 V s^{-1}. All potentials were referred to RHE.

We measured the voltammograms of the Pd electrodes in 0.5 M H_2SO_4 for the confirmation of the crystal orientation. The voltammograms were identical with those reported previously (6,7), thus we judged that the crystals were oriented correctly.

The oxidation of formic acid was studied in 0.1 M $HClO_4$ in which no anion is strongly adsorbed on the Pd surfaces. **Fig. 1** shows the results of the low index planes. High anodic currents due to the formic acid oxidation are observed at lower potentials (between 0.1 and 0.6 V). The oxidation of formic acid is inhibited completely by the formation of oxide film above 1.0 V. Formic acid gets oxidized again with the oxide film reduced in the negative scan. We estimated the activity of the formic acid oxidation using the maximum current density in the positive scans; the surfaces may be roughened owing to the formation of the oxide film in the negative scan. The rate for the formic acid oxidation gives the following order: Pd(110) < Pd(111) < Pd(100). This order differs from that of Pt remarkably: Pt(111) < Pt(100) < Pt(110) (8). This difference may be attributed to the different oxidation mechanism between Pt and Pd: reaction proceeds via adsorbed CO on Pt, whereas no CO is formed on Pd. The rate of the formic acid oxidation on Pd(100) is higher than that on Pt(110). The maxima of the anodic currents on Pd appear at lower potentials than those on Pt electrodes. The potential of the peak shows the following order: Pd(110) ~ Pd(111) < Pd(100).

The effects of the kink structure on the reaction was studied using kinked stepped surfaces of Pd(S)-[*n*(100)×(110)]. The kinked stepped surfaces have high activity for CO_2 reduction on Pt electrodes (9). The voltammograms are shown in **Fig. 2**. The peak current density was plotted against the kink atom density in **Fig. 3**. The kink structure does not affect the oxidation of formic acid down to terrace atomic rows 3. The oxidation current drops significantly on Pd(210) (*n*=2) on which no (100) terrace exists in the first layer. From these results, (100) terrace of Pd is the most active structure for the oxidation of formic acid.

References

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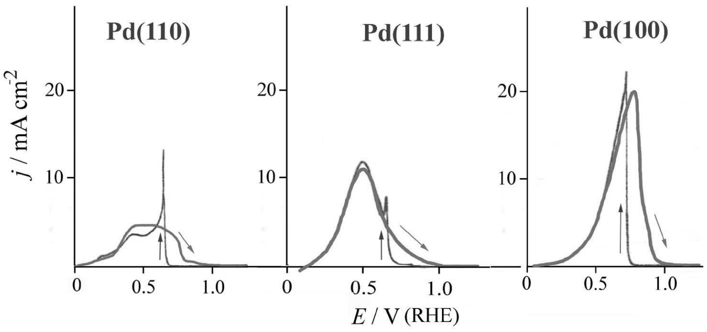

Fig. 1 Voltammograms of the formic acid oxidation on the low index planes of palladium in 0.1 M $HClO_4$ containing 0.1 M HCOOH.

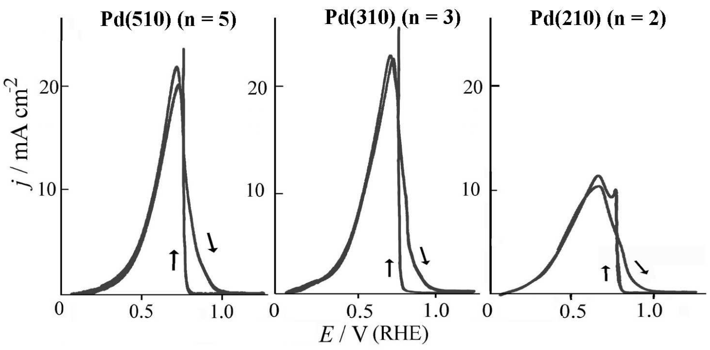

Fig. 2 Representative voltammograms of the formic acid oxidation on Pd(S)-[*n*(100)×(110)] electrodes in 0.1 M $HClO_4$ containing 0.1 M HCOOH.

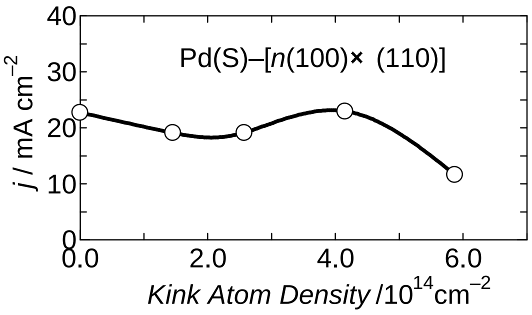

Fig. 3 Maximum currents of the formic acid oxidation in the positive scan plotted against the kink atom density.