A CATALYTIC STUDY OF FORMIC ACID OXIDATION ON PREFERENTIALLY ORIENTED PLATINUM ELECTRODES

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The oxidation of formic acid was examined by cyclic voltammetry and chronoamperometry in order to determine the rate of catalytic activity (reaction turnover) as a function of surface crystallography on preferentially oriented (electrochemically modified) platinum electrodes. The resulting turnover rates indicated a maximum fourfold current enhancement for an approximately 60% (111)-oriented surface versus a polycrystalline surface, suggesting that preferentially oriented electrodes are of potential practical significance.

1. Introduction

The study of the catalytic oxidation of formic acid has been active over the last three decades and a number of comprehensive reviews indicating the practical importance of this process have been published [1–6]. The oxidation of formic acid shows pronounced structure sensitivity at low index metal surfaces [7–13]. However, the use of single crystals in real-life electrocatalytic applications is impractical due to their high manufacturing costs. More recently, a procedure for the preparation of preferentially oriented surfaces that approximate the characteristics of single crystals has been pioneered by Arvia et al. [14–17]. The objective of this work was to assess the influence of surface crystallography on the rate of formic acid oxidation at such preferentially oriented Pt surfaces.

2. Experimental details

Oxygen-free nitrogen (Linde), reagent grade formic acid (Fischer) and reagent grade sulfuric and perchloric acids (Fischer) were used in this study. All electrochemistry experiments (orientation, voltammetry, and chronoamperometry) were
carried out using a three-compartment glass cell equipped with a Luggin capillary. All potentials are given with respect to Ag/AgCl, [Cl\(^{-}\)] = 1.0 M NaCl. The working electrode was a 1 mm diameter round platinum wire (Johnson Matthey, purity = 99.95%), the prepared working face (geometric area = 0.785 mm\(^2\)) contacting the solutions via a meniscus arrangement. The small area electrode was chosen to minimize the capacitive component of the current passes, thus reducing the cell time constant, \(R_uC_d\), and preventing significant lag in the potential at the working interface. The working surface was prepared by polishing with diamond past down to 0.25 \(\mu\)m, degreasing in warm sulfuric acid, soaking in concentrated hydrofluoric acid to remove any carbonaceous residue, and hydrogen annealing followed by quenching. A final step in the preparation involved electrochemically stepping the surface between the \(O_2\) and \(H_2\) evolution threshold potential limits to remove any remaining surface impurities. Cyclic voltammetry was used as a check for surface cleanliness.

In preparing the preferentially oriented surfaces the working electrode was immersed ~ 2 mm into 0.5 M \(H_2SO_4\) electrolyte, chosen for its voltammetric enhancement of the hydrogen adsorption-desorption peaks used in assessing the degree of orientation achieved. Electrochemical orientation involves the selective redistribution of a polycrystalline surface to a desired crystallographic orientation by applying a fast periodic square wave potential perturbation between the potential limits characterizing the underpotential decomposition of water [14–17]. The square wave potential perturbation was applied with the signal generated using a function generator (Dynascan Model 310), fed into the external input of the potentiostat (PAR model 273) and monitored using an oscilloscope. The (100) orientation parameters were: lower potential \((E_l) = -0.15\) V, upper potential \((E_u) = 1.2\) V, frequency \((f) = 2.5\) kHz, time = 10 hours. The (111) orientation parameters were: \((E_l) = 0.50\) V, \((E_u) = 1.20\) V, \((f) = 2.0\) kHz, time = 2.5 hours.

Scanning electron micrographs and corresponding electron channeling (backscatter) patterns were obtained using a JEOL model JSM-35C scanning electron microscope modified for channeling applications. In obtaining the backscatter patterns, an ~ 30 \(\mu\)m disc of least confusion (spot size) was utilized.

Chronoamperometric data were collected for 0.1 M formic acid in 0.5 M perchloric acid (chosen for its non-affinity towards platinum). A prestep from 0.0 V to 1.2 V was initiated to ensure a clean starting surface free of any adsorbed species or poisons. A potential step from 1.2 V to an intermediate potential in the range covering the double-layer and species oxidation threshold region (0.10 V to 0.45 V) was then applied in order to monitor the steady-state kinetics of formic acid electrooxidation. The duration of the potential program was determined by the time needed for the current to decay to negligible values after reaching the intermediate potential. The current response of the electrolyte was subtracted point-by-point from the current values of the formic acid current component to obtain the final background-corrected current-time decay profiles.