

## The Pt(111) Electrode Surface in the Acid Solutions Containing Methanol and CO: Current and Structural Oscillations

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**Introduction:** Direct methanol oxidation fuel cells are attractive because they do not need to store hydrogen as fuel or to generate it from hydrocarbons via reforming chemistry. The major problem causing unacceptable performance of Pt catalysts for methanol oxidation is the self-poisoning by CO adsorption. As an intermediate of the methanol oxidation, CO has been found by IR spectroscopy to be adsorbed on Pt. Thus, adsorbed OH at high potential is needed for oxidative removal of CO in order to have sustained activity. To reveal the state of CO adsorption and role of surface diffusion/reaction in the kinetics of CH<sub>3</sub>OH oxidation, we carried out a surface x-ray diffraction study to investigate the Pt(111) surface in acid solutions containing CH<sub>3</sub>OH in the absence and in the presence of gaseous CO.

**Methods and Materials:** A single crystal Pt(111) electrode was prepared by flame annealing and cooling in Ar gas flow. The electrochemical cell was sealed by a Prolene x-ray film (Chemplex Industries, Inc.), which acts as the x-ray window and allows CO gas in the outer chamber to diffuse through into the solution.

### Results and Discussion:

In the absence of CO gas, no ordered phase was found on Pt(111) in 0.1 M H<sub>2</sub>SO<sub>4</sub> solution containing 0.5 M CH<sub>3</sub>OH, while the diffractions from the (2×2)-3CO phase were observed when CO gas was introduced. The lack of CH<sub>3</sub>OH-related ordered adlayer suggests that the CO coverage resulting from the reaction intermediate of CH<sub>3</sub>OH oxidation is too low to form the (2×2)-3CO phase. Adsorbed CO molecules probably have a stronger poisoning effect on oxidation of CH<sub>3</sub>OH than H<sub>2</sub> because, unlike H<sub>2</sub>, the oxidative adsorption of methanol in the first reaction step requires multiple Pt sites. The strong inhibition, in turn, limits the amount of CO generated by the CH<sub>3</sub>OH dehydrogenation.

With an additional CO in the solution, the formation and oxidative removal of the (2×2)-3CO phase were observed by measuring the diffraction intensity at the (1/2,1/2,0.13) position during potential cycles. The major effect of the coexistence of CH<sub>3</sub>OH with CO on the phase behavior of CO adsorption and the observed current is the oscillatory behavior in negative potential sweeps. As shown in Fig. 1, sharp peaks appear in both the (1/2,1/2) diffraction intensity and the current curves. Although the peak potentials and heights vary with the positive potential limit, these peaks always occur at the same time in the two curves, indicating a strong correlation between the current spike and the temporal formation of the (2×2)-3CO phase.

Fig. 2 shows the oscillatory peaks observed at -2 mV/s sweep rate started at 1.1, 1.0, and 0.9 V, and the cyclic voltammetry for Pt(111) in 0.1 M H<sub>2</sub>SO<sub>4</sub> solution. Apparently, the oscillation pattern varies with the positive potential limit and the sweep rate, suggesting that the oscillatory behavior is dynamic in nature. This can be proved by the observation of the oscillatory peaks in time dependent intensity curve after a step change of potential (not shown). Note that the Pt surface oxidation current increases (Fig. 2, lower panel) above 0.9 V, and the Pt-O place exchange may occur causing a roughening of the Pt(111) surface. During the negative sweep, the competition for adsorption sites among CO, OH, and CH<sub>3</sub>OH and the interdependence of multiple surface reaction steps, coupled with the slow recovery of the surface morphology, may lead to the temporal formation of the (2×2)-3CO phase.

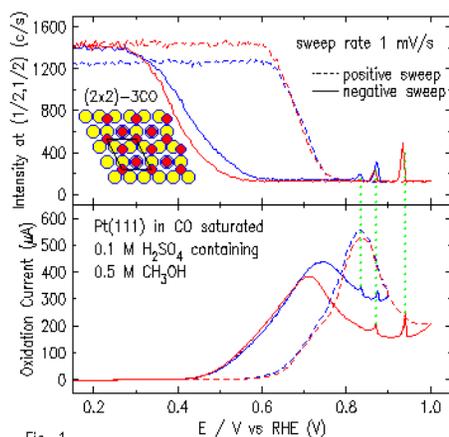


Fig. 1.

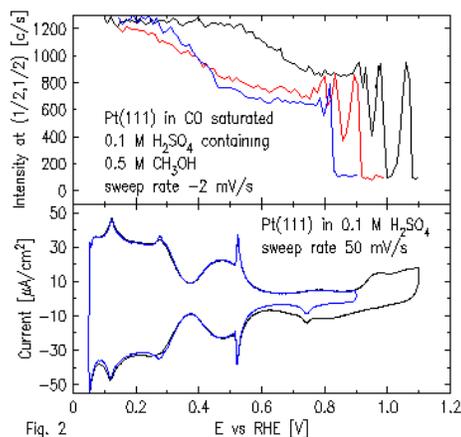


Fig. 2