

IN SITU OPTICAL STUDIES OF INTERFACIAL DYNAMICS IN THE SUBMICROSECOND REGIME

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INTRODUCTION

In situ, time-resolved second harmonic generation (SHG) has been used to monitor changes in the coverage of CO adsorbed on Pt(111) microfacets in perchloric acid solutions induced by potential steps to values high enough for CO oxidation to ensue. Several factors make our methodology especially suited for this type of study:

- the size of spontaneously formed microfacets exceeds the diffraction limit allowing the laser to be focused within one facet, allowing its interfacial optical response to be isolated from the rest of the electrode.
- the interfacial capacity is directly proportional to the electrode area, hence, small spheres of only a few tens of μm in diameter grown using commercially available wires will lead to short cell RC time constant, enabling access to faster interfacial events¹.

As with any relaxation method, the perturbation must be applied within times shorter than the time constant of the process being investigated, i.e. the potential, in our case, must settle at the desired value before the onset of CO oxidation.

EXPERIMENTAL

All experiments were performed in a quartz cuvette using a three-electrode arrangement, with the microsphere being the working electrode.² Potentials control was provided by a universal programmer and potentiostat. All potentials were measured and reported against reversible hydrogen electrode (RHE). A cavity dumped dye laser pumped by mode locked Nd:YLF laser and a single focusing lens were used to deliver a 10 MHz train of 3 ps 600 nm light pulses focused onto single crystal facet surface. Light polarization was controlled by polarizers, all experiments were done in p-in p-out polarization. Second harmonic signals, $I_{p,p}(2\omega)$ were detected by a photomultiplier and recorded with a multichannel scaler (Stanford Research Systems SR 430).

RESULTS AND DISCUSSION

Shown in Fig 1 are a series of experiments in which the potential E was stepped from $E_i = 0.4$ V, to final values $E_f > 0.9$ V while monitoring $I_{p,p}(2\omega)$ signals. As shown therein, a drop in $I_{p,p}(2\omega)$, signaling the onset of adsorbed CO oxidation, was observed only after a certain period of time or induction period, τ , had elapsed.

From a strictly qualitative viewpoint, these results cannot be accounted for by the kinetic model employed by Love and Lipkowski³. If one forces such a model to fit the data, the agreement with the experiment is very poor. Excellent fits could be obtained, however, by introducing τ in an ad hoc fashion, i.e. by replacing t by $(t-\tau)$ in the equation that governs the temporal dependence of the coverage $S(t) = \exp[-t^2/2t_{\text{max}}^2]$.

A comparison between values of t_{max} vs E_f obtained in this work (see scattered points in Panel A in this figure, where open and solid circles represent two different runs), with those from the data of Love and Lipkowski are shown in Fig. 2.

Induction times are often found for consecutive reactions in which the first step acts as a “bottleneck”. In this, τ could represent the probability that a nucleus will be formed, multiplied by its (potential dependent) initial rate of growth. It is tantalizing to suggest that oxidation of the compact $c(2 \times 2)$ CO adlayer must be preceded by formation of available oxygen donor adsorption sites generated via at least a partial phase transformation to the less dense or reactive superstructure⁵. Also consistent with our data, **without introducing τ** , is the mean field model invoked by Lebedeva⁴ to explain the results of their chronocoulometric experiments involving oxidation of CO on Pt(111). In fact, plots of the rate constant for oxidation of adsorbed CO obtained in our study based on mean field theory are shown in Panel B, Fig. 2.

ACKNOWLEDGMENTS

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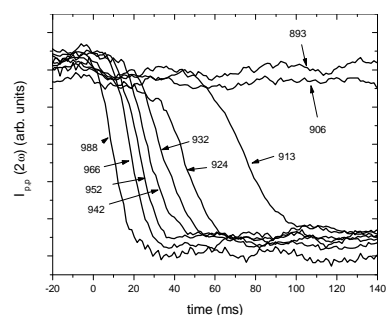


Fig. 1. Plots of $I_{p,p}(2\omega)$ vs time for potential step experiments between $E_i = 0.40$ V and E_f values in the range 0.893 – 0.988 V vs RHE.

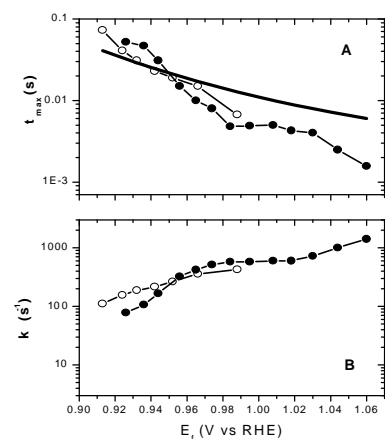


Fig. 2. Plots of t_{max} vs E_f (Panel A) and k vs E_f (Panel B)