

## Dynamics of Surface Species on Pt Electrode Induced by Laser Pulse Irradiation

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### Introduction

It is consequently essential to understand the reaction mechanisms behind these reactions through the investigation of adsorbates behavior. Time-resolved (TR) IR spectroscopy is a powerful tool for observing the dynamics of adsorbates, particularly when combined with the surface-enhanced IR spectroscopy (SEIRA). [1] The high sensitivity of SEIRA enables us to observe short-lived reaction intermediates.

In this study, we observed the change of the electrochemical interface induced by laser irradiation of the surface. The laser irradiation rapidly increases the surface temperature. The rapid temperature increase put the system non-equilibrium state which can induce some reactions. The behavior of molecules in the non-equilibrium state determines the reaction. To study the transient states, we constructed a picosecond and a nanosecond TR-IR spectrometer. First, we observed the CO dynamics on Pt electrode.

### Experimental

The electrode was irradiated by a 532 nm pulse of 5 mJ/cm<sup>2</sup>, 10 ns duration, and a 10 Hz repetition rate. Transient current and IR absorption were measured using an EG&G 263A potentiostat and the home-built TR-IR spectrometers, respectively. A picosecond TR-IR system is based on a mid-IR pulse generated by OPG/OPA and DFG. A nanosecond TR-IR system is constructed with a dispersive spectrometer. These apparatus allow the observation of dynamics between 35 ps to 1 s.

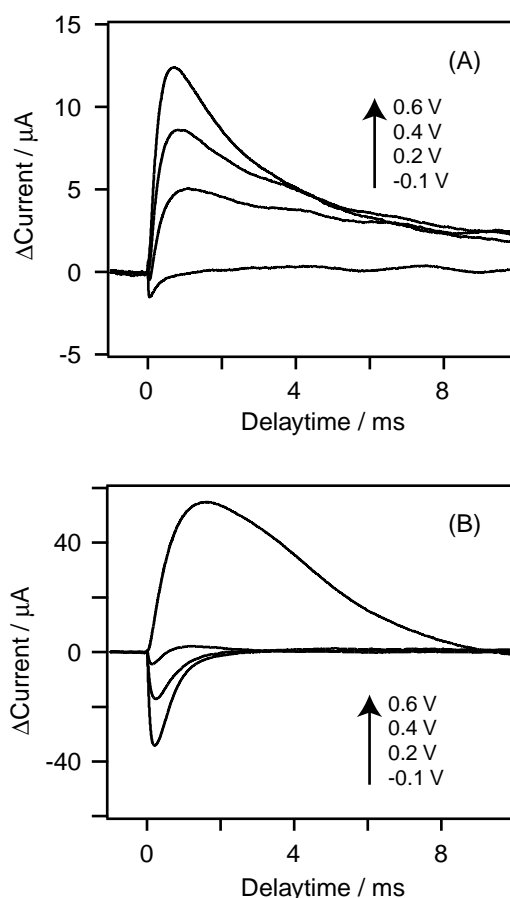
The working electrode was prepared by electroless deposition of Pt on hemicyrindical Si prism. A saturated calomel electrode (SCE) was used as the reference. The electrolyte solution was 0.1 M HClO<sub>4</sub>.

### Results and Discussion

Figure 1A shows the transient current induced by a 532 nm laser pulse irradiation. When the electrode is irradiated in the electrolyte solution without the presence of CO, a cathodic current flows after laser irradiation at -0.1 V. This amplitude became smaller and the current direction changed to anodic with increasing applied potential. Similar results have been reported by Climent et al. [2] and Brennan et al. [3], and explained by the change in double layer capacitance induced by the laser heating, as follows. When the temperature rises, the capacitance is reduced resulting in extra charge flow. As the surface cools down, the capacitance returns to its original value and current flows to recharge the double layer. The current direction is changed around the potential zero point (~ 0.1 V). The first rapid discharging process in a microsecond time-scale was not observed in our experiments, probably due to the slow response of our potentiostat.

The same experiment was carried out in CO-saturated solution. The results are shown in Figure 1B. When the surface is irradiated by a laser pulse at -0.1 V, a cathodic current is observed. This cathodic current is about 20 times larger than in the absence of CO. The cathodic current gradually decreases with increasing applied potential. At 0.6 V, a large anodic current flows. This is about 5 times larger than in the absence of CO.

The enhanced current will be induced by the adsorbed CO. One possible explanation at < 0.6 V is that due to CO desorption. At this potential, the preadsorbed CO inhibits proton adsorption. CO desorption makes this adsorption possible resulting in a cathodic current. On the other hand, laser heating accelerates the CO oxidation at 0.6 V which leads to an enhanced anodic current. These hypotheses will be discussed based on TR-SEIRA spectra acquired simultaneously with the current-time measurements



**Figure 1** Transient current induced by a 532-nm laser pulse irradiation on Pt electrode in 0.1 M HClO<sub>4</sub> solution. The applied potential vs. SCE is indicated in the figure. (A) and (B) are measured in the absence and presence of CO bubbling, respectively.

### References

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