



	Experiment title: Combined high energy surface x-ray diffraction and infrared reflection absorption spectroscopy study of carbon monoxide adsorption at the Pt(111)/electrolyte interface	Experiment number: CH6228
Beamline: ID31	Date of experiment: from: 05.07.2022 to: 10.07.2022	Date of report: 01.03.2023
Shifts: 15	Local contact(s): Andrea Sartori	<i>Received at ESRF:</i>
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Report:

The aim of this proposal is to map the CO / Pt(111) surface phase diagram as a function of the potential and time under electrochemical conditions. The adsorption site of CO will be identified by EC-IRRAS, while the corresponding structural information of CO/Pt(111), such as the surface rod of CO induced reconstructions and the crystal truncation rods (CTRs) of Pt single crystal, can be extracted by HE-SXRD simultaneously. Most recently, we developed a unique instrument to investigate the surface structure and the surface chemistry under in situ/operando conditions combining these two methods, which we plan to employ here for the first time. The combined use of electrochemical infrared reflection absorption spectroscopy (EC-IRRAS) and high energy surface x-ray diffraction (HE-SXRD) will serve as a benchmark for other electrocatalytic investigations.

Set-up

Our IR spectrometer was shipped to the ESRF and built up at the beamline in the days before the experiment. In short: a special frame is built around the HEMD onto which the spectrometer is mounted. The IR and X-ray beams pass through a hemispherical CaF₂ crystal. Onto the flat side of this crystal, the Pt111 sample is pressed and the electrolyte is let in (a special sealing is also present). The sample and IR-window sit on the end of an aluminium hollow cylinder, which is mounted on an L-shaped arm on the diffractometer and is hanging through an open port inside the spectrometer. The spectrometer is thus fixed in space and the sample can be rotated around its surface normal by using the diffractometer angles.

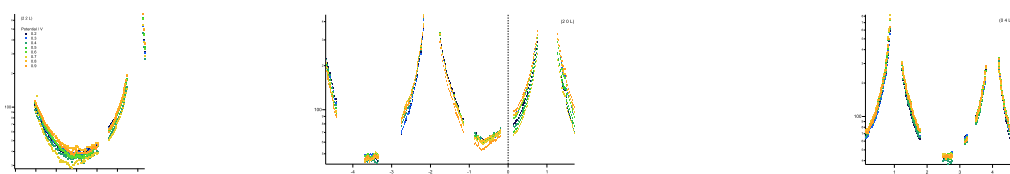


Fig 1. Extracted structure factors along several CTRs for different voltages during CO exposure.

Results

Extensive measurements were taken for different conditions. Figure 1 shows CTR data taken during CO exposure and subsequent lifting while gradually changing the voltage to 0.9 V. Around 0.7 V, the CO starts desorbing. This is seen in the IR spectra, shown in Figure 2. Increasing the voltage even further (beyond 0.9 V) results in oxidation of the Pt. The results of these measurements are completely in agreement with previous results [1].

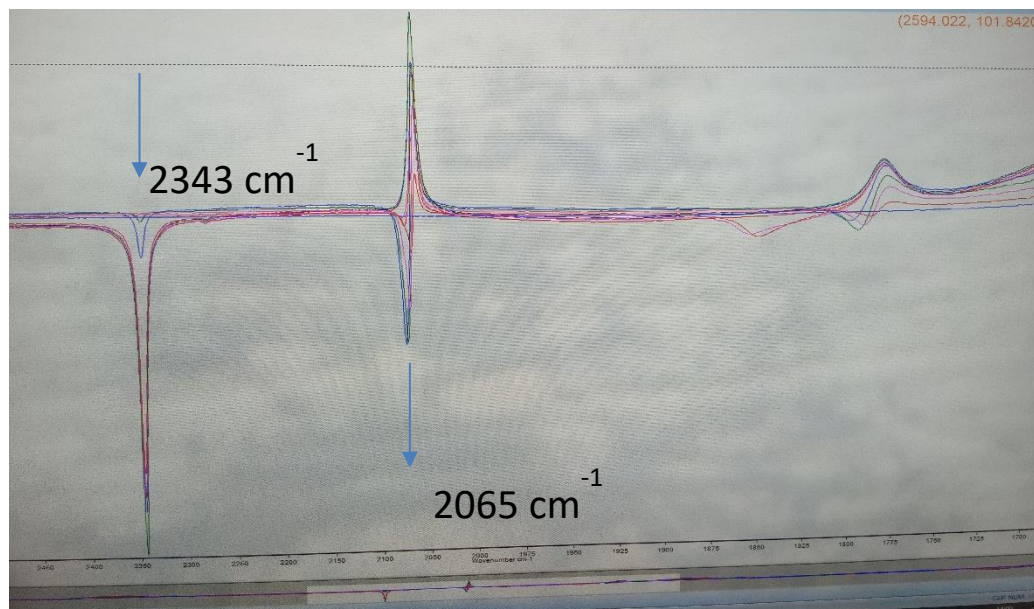


Fig 2. IR spectra recorded after CO adsorption and subsequent oxidation by gradual increase of the voltage. Clearly visible are the two bands at 2065 cm⁻¹ (CO_t) and 2343 cm⁻¹ (CO₂), where the former is vanishing and the latter is increasing.

Conclusion

A dedicated set-up was brought to and built up at ID31. The experiment showed the feasibility of the method. In particular, the influence of CO on the CTR signal is extremely weak, but is very well visible with IR. These measurements show the compatibility of the two methods and this constitutes a large break-through in the field of electro-catalysis, where the challenge remains to obtain an atomic-scale insight into the mechanisms occurring at the buried interface.

The results are currently being worked out further to arrive a more quantitative and solid conclusions.

[1] Jacobse, L. Vonk, V. ; Mccrum, I. ; Seitz, C. ; Koper, M. ; Rost, M. ; Stierle, A. Electrochemical oxidation of Pt(111) beyond the place-exchange model *Electrochimica acta* 407, 139881 (2022) [10.1016/j.electacta.2022.139881]