



	Experiment title: In-situ XAS of a Pt anode for Kolbe electro-oxidation of carboxylic acids to alkanes	Experiment number: CH-6436
Beamline: BM23	Date of experiment: from: 8 November 2022 to: 14 November 2022	Date of report: 20 February 2023
Shifts: 18	Local contact(s): Cesare Atzori	<i>Received at ESRF:</i>
Names and affiliations of applicants (* indicates experimentalists): Prof. Bastian Mei* Dr. Marco Altomare Dr. Viktoriia Seveleva Dr. Alessandro Minguzzi Prof. Paolo Ghigna Margot Olde Nordkamp* Talal Ashraf*		

Report:

After system alignment and explanation on how to operate the system, we started Tuesday afternoon in-situ measurements of Kolbe electrolysis of acetic acid on Pt. For these measurements, we brought an electrochemical cell designed within ESRF suitable for low-incidence angle fluorescence measurements. Unfortunately, the extensive formation of bubbles caused by oxygen, ethane and CO₂ evolution disturbed the XAS spectra severely (see Figure 1 for an example)

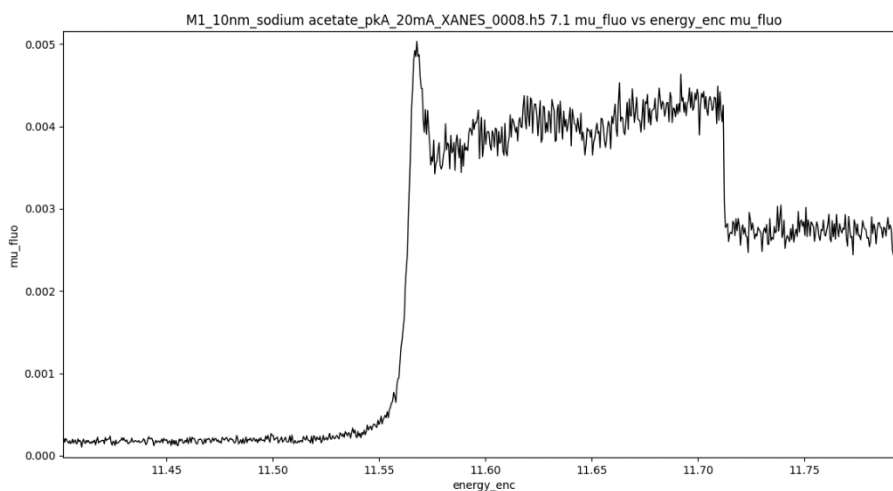


Figure 1 In situ XAS spectrum of Pt sample in 1M sodium acetate under applied current of 20 mA in ESRF cell design

A few attempts were made to minimize the effect of bubble formation, for example by adjusting the applied current density or the pump speed. Unfortunately, the bubbles continued to affect the quality of the XAS spectra. Therefore, we decided to shorten the measurement time of an XAS spectra, so that the chance of a bubble disrupting the spectra was reduced. Still, many of the obtained spectra were of bad quality. So, we decided to continue with a different cell designing prior to the beamtime referred to in the following as the gravity flow cell.

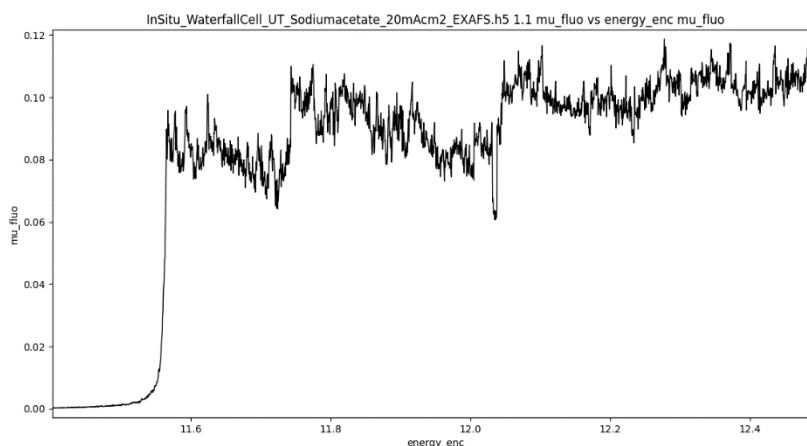


Figure 2 In situ XAS spectrum of Pt sample in 1M sodium acetate under applied current of 20 mA in gravity flow cell design

This new cell had an electrolyte flow based on gravity flow. We hoped that with this design, the formed bubbles were effectively transported away from the electrode. Unfortunately, this was not the case and we ended up with another set of low quality XAS spectra (see Figure 2 for an example) due to excessive bubble formation.

Considering the severe limitations caused by bubble evolution, ex situ X-ray absorption spectroscopy was applied to analyze the electronic and structural changes of the platinum oxide layer formed under polarization at high anodic potentials in blank and acetic acid electrolyte. The XAS experiments were performed on thin film (10 or 25 nm) platinized titanium samples (Ti foil, 0.5mm, 99%) produced by sputtering. After polarization of the Pt anode in an ex-situ operated electrochemical cell, the Pt was removed from the electrolyte to measure XANES and EXAFS spectra in fluorescence mode. Table 1 provides a summary of all ex situ measurements performed. In the following the experimental data refer to measurements performed with 10 nm thick Pt films only. Figure 2 shows the XANES spectra of an unpolarized Pt foil and a PtO₂ pellet (references), and the Pt electrodes (10 nm thick Pt films) polarized at 100 mA cm⁻² until a charge of 70 C has passed the cell using the blank electrolyte and actual Kolbe conditions, ie acetic acid containing electrolyte, with the corresponding EXAFS data summarized in Figure 3.

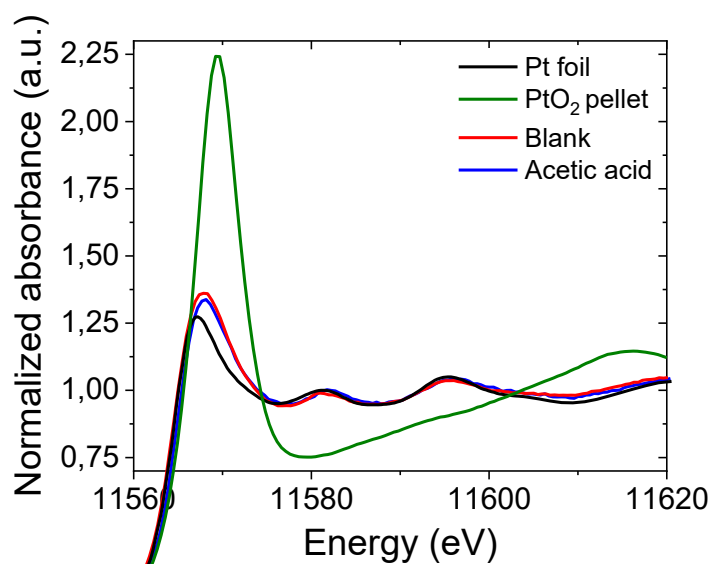


Figure 2 Pt LIII-edge normalized XANES of a Pt foil reference (black), PtO₂ pellet reference (green), Pt polarized in blank electrolyte (red) Pt after polarization in acetic acid electrolyte (blue). The platinum electrode (10 nm thick Pt film on Ti substrates) was polarized in blank and acetic acid electrolyte at 100 mA/cm² until 70 C of charge was reached.

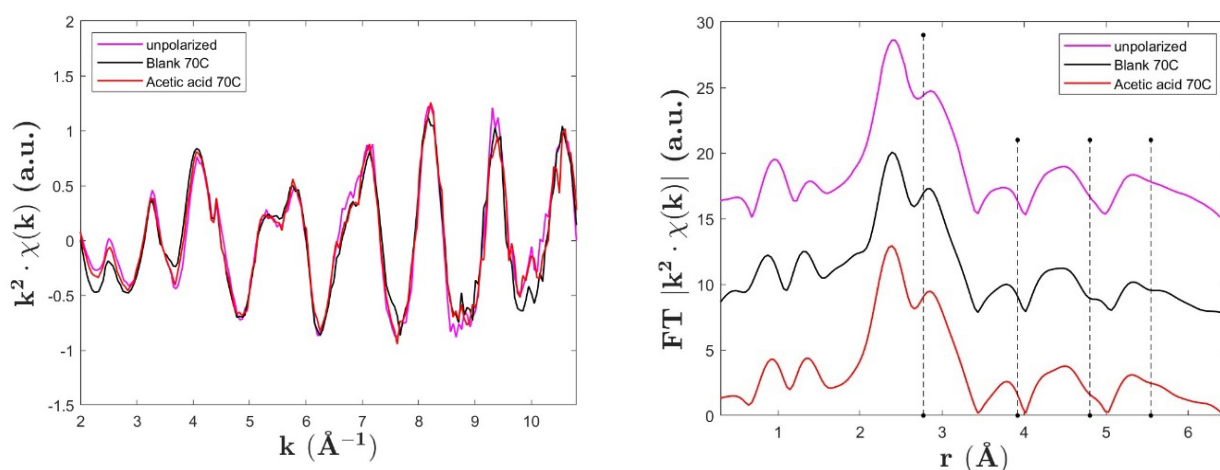


Figure 3 (a) EXAFS and (b) Fourier Transform (FT) of unpolished Pt and of Pt polarized at 100 mA/cm² in blank and acetic acid electrolyte after 70 C.

After polarization (in either blank electrolyte or acetic acid electrolyte), clear changes occur in the XANES spectra of the Pt electrode. The location of the adsorption edge increased to higher energy, the white-line has a higher peak intensity and a “dip” occurs in the post-edge region. The stronger white-line intensity and the dip in the post-edge region at high potentials are characteristic spectral features of platinum oxides as also revealed by the reference PtO₂ data. These changes are more prominent in the blank electrolyte, which implies that the platinum surface after polarization in blank electrolyte is more oxidized compared to polarization in acetic acid electrolyte, confirming the research hypothesis that under Kolbe condition a surface layer is formed inhibiting oxidation of the electrode surface. It should be noted that though already thin film Pt electrodes have been used, the surface sensitivity is still compromised by the surface to bulk Pt ratio.

In summary, it was not possible to obtain good quality in-situ XAS spectra during Kolbe oxidation of acetic acid due to the extensive formation of bubbles on the Pt electrode during our beamtime. For future in-situ XAS experiments, it is important that a cell is designed which can effectively transport bubbles away from the electrode surface. Ex-situ XAS spectra were successfully collected and changes in the electronic properties of

the Pt could be observed. These observations will be incorporated in a manuscript which is drafted at the time of writing.

Table1. List of all measurements performed using ex situ XAS.

#	Electrolyte	Thickness Pt coating (nm)	Polarization current density (mA/cm ²)	Polarization duration (Coulombs)
1	1 M Acetic acid/sodium acetate	10	100	70
2	1 M Acetic acid/sodium acetate	10	1	1
3	1 M Acetic acid/sodium acetate	10	20	1
4	1 M Acetic acid/sodium acetate	25	100	10
5	1 M Acetic acid/sodium acetate	10	100	10
6	1 M Acetic acid/sodium acetate	25	100	70
7	1 M Acetic acid/sodium acetate	10	100	70
8	1 M Acetic acid/sodium acetate, for reproducibility	10	100	70
9	0.5 M Sodium acetate, 0.5 M Sodium perchlorate	10	100	70
10	0.5 M Sodium acetate, 0.5 M Sodium perchlorate	10	100	10
11	1M Sodium acetate + 0.1 M Sodium bicarbonate	25	100	70
12	1 M Sodium perchlorate	25	1	1
13	1 M Sodium perchlorate	25	20	1
14	1 M Sodium perchlorate	25	100	1
15	1 M Sodium perchlorate	25	100	10
16	1 M Sodium perchlorate	10	100	70
17	0.75 M Sodium perchlorate + 0.25 M Sodium acetate	10	100	70
18	Unpolarized	10	-	-