



	Experiment title: Operando study of alloy formation in Au-Pd Nanoparticle catalysts for Formic Acid Oxidation	Experiment number: CH6610
Beamline: SNBL/BM31	Date of experiment: from: 02.05.2023 to: 07.05.2023	Date of report: 18.09.2023
Shifts: 12	Local contact(s): Dragos Stoian, Kenneth Marshall	<i>Received at ESRF:</i>
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Report:

1. Abstract

PdAu alloys are promising catalysts for direct formic acid fuel cells (DFAFCs). With this project, we aim to understand the formation of surface alloys from Au-Pd/C nanocomposite catalysts. Comparing different Pd-Au alloy nanoparticles prepared by a laser ablation method, we investigate the effect of the formic acid oxidation reaction (FAOR) on the structure of the alloy. A row of PdAu nanoparticles with different compositions was exposed to formic acid-containing electrolytes and different FAOR protocols, while X-ray total scattering data were collected. To complete the structural characterization X-ray absorption spectroscopy data (XANES and EXAFS) were collected at both the Au L₃- and the Pd K-edge.

2. Experimental Details

In the experiment, we used our home-developed *operando* electrochemical flow-cell set-up optimized for X-ray scattering was used. The catalyst layers were prepared by vacuum filtration of the catalyst particles (PdAu supported on Carbon) onto a gas diffusion layer in our home lab. They were used as working electrodes in the electrochemical cell, with a platinum counter electrode and an Ag/AgCl reference electrode. The 0.1M HClO₄ electrolyte containing 0.2M HCOOH was flown through the cell during the experiment. A series of potential steps were applied, gradually stepping from the open circuit potential (OCP) to oxidizing potentials where FAOR significant currents were measured. The potential was then gradually stepped back to OCP, to observe if the changes under applied potential were reversible or not. At each potential, total scattering data were collected, at different depths of the catalyst layer. In the following, a row of cyclic voltammograms was collected during FAOR to analyze the stability of different PdAu alloy nanoparticles as FAOR catalysts.

Background subtraction is necessary to treat the total scattering data. This was performed based on the different scans through the cell, where the carbon background was collected. In that way, it was possible to subtract both the contributions from the cell and electrolyte as well as from the carbon-based gas-diffusion layer. As the carbon changes as a function of applied potential, background data were recorded and subtracted for each potential step.

3. Results

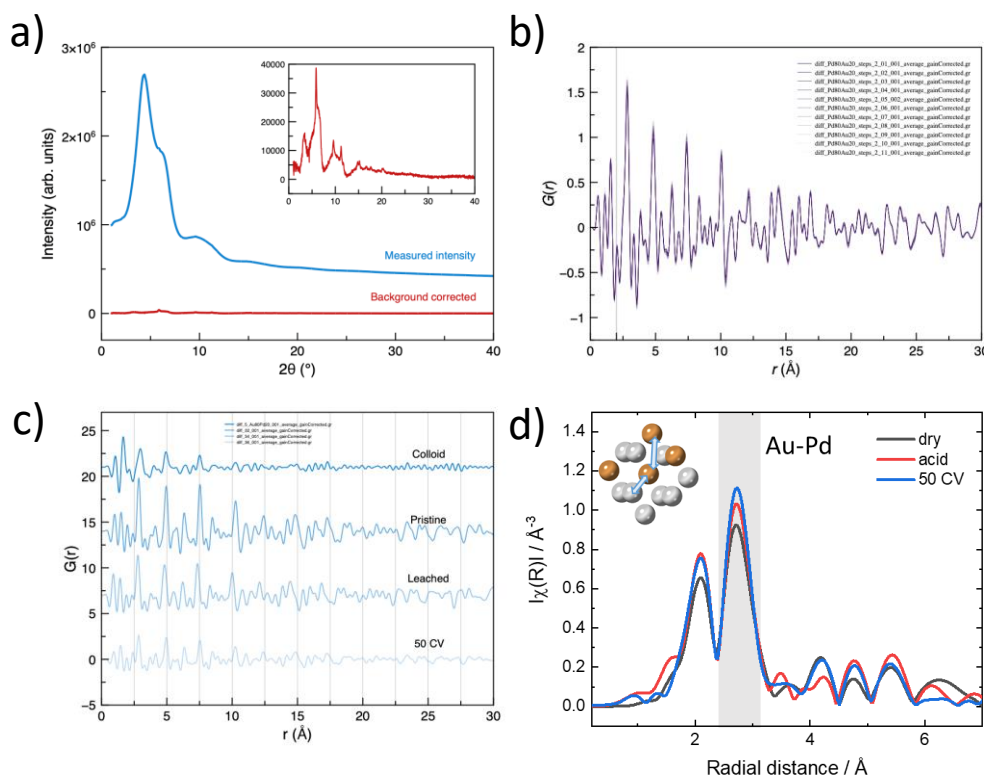


Figure 1 a) X-ray total scattering data before and after background subtraction b) PDFs of the Pd₈₀Au₂₀ catalyst as a function of applied potential c) PDFs when going from the colloid to the pristine, acid-leached and FAOR treated catalyst and d) EXAFS of Au L₃-edge of dry, acid-leached and FAOR treated catalyst

different across different length scales. We have begun to investigate core-shell behavior and Pd migration as a potential cause for this. Our initial analysis of the collected PDFs from the *operando* experiment, indicates that the catalyst is stable under operating conditions and exhibits only very little structural changes, as shown exemplarily in Fig. 1b. We found more noticeable structural changes to occur during the preparation of the electrode and the immersion in the electrolyte (Fig 1c). These structural changes that can occur during electrode preparation are often overlooked and thus these results are very interesting. We combine this fit analysis of the XAS data collected ex-situ, where we observe small changes in Pd-Au coordination for the different treatment steps as illustrated in Figure 1d.

4. Conclusions and future work

The beamtime has been a success in demonstrating the possibility of collecting total scattering data during FAOR electrochemistry. The data can be analyzed if a very careful background subtraction is performed. The quality of background data measured is, therefore, of utmost importance. With this, it was possible to obtain analyzable PDF data that showed structural changes in the PdAu alloy catalysts. We are now in the process of analyzing the data and combining the PDF analysis with the results obtained from the ex-situ X-ray absorption spectroscopy. As we were not able to collect XAS data in our scattering electrochemical cell, we are now in the process of building a synchrotron *operando* cell suitable for both X-ray total scattering and X-ray absorption spectroscopy. The results from this beamtime have shown that a crucial step is the catalyst preparation from the colloid and its conditioning in the acidic electrolyte. The catalysts obtained from the conditioning then appear to be stable in FAOR.

5. Publications resulting from the work

We expect to publish the results once the data analysis from both TS-PDF and XAS (EXAFS and XANES) is finished.

We have analyzed the total scattering data and the PDFs that could be obtained after careful background subtraction. Due to scattering from the cell, the background scattering can account for ~95 % of the total intensity, therefore careful background subtraction is required (see Fig 1 a). We were able to successfully subtract a suitable background and extract small Bragg peaks. The small Bragg features observed in the X-ray total scattering data correspond to the FCC structure type of the PdAu alloy. The PDF data can be fit using small-box modeling so that lattice parameters and crystallite sizes can be extracted. Furthermore, a box-car approach has suggested that changes in the structure are