Chemical sensor project
Pierre-A. GROSS, Tom LARSEN and Frederic LOIZEAU
Thomas JARAMILLO, Beth PRUITT and Denis SPITZER

Development of a micro-chemical gas sensor.

The goal is to detect trace amount of VOCs (Volatile Organic Compounds) in the gas phase with the highest possible selectivity and/or sensitivity.

Introduction
The electrochemical gas sensor project is now at a state were the results of the first test pointed out the different needs for improvement and optimization both of the fabrication process and the testing. This report will focus on this sensor, detail the obtained results for CO sensing, and list the different feedbacks obtained. All those information will help building a second generation of electrochemical gas sensors.

Design and process
All the tests presented in this report were performed on the sensors obtained on the first of the three wafers that came out of the micro-fabrication run in August. The sensors of the two last wafers being completely nonfunctioning. The reason of this nonfunctioning is unclear since the process was kept similar for all wafers. Nevertheless, the main issues being related to the Nafion layer, it is more than probable that this is related to too thin and non-homogeneous layer of Nafion. The design and fabrication process of the sensor is presented on Figure 1.

Results
The experiments presented in this report were proposed in order to confirm that the previously observed redox peaks on figure 2, in the gas phase experiment were indeed CO oxidation. The absence of reference electrode in this experiment and the position of the observed peak on the potential scale raises some questions about what electrochemical process is in fact occurring on the surface of the Pt electrodes. To do that a set of simple experiments, presented in Figure 3, were conducted. The first one is a three electrodes experiment in H₂SO₄ with CO bubbling in the electrolyte. The CO oxidation peak on Pt is located at 0.8 V vs RHE on the anodic branch. Then, the second experiment will be done in the same conditions (H₂SO₄) but in a two electrode setup, to mimic the situation of the experiment in the gas flow. In this second experiment, the signal should be shifted on the potential scale, but it will give the information of the location on the CO oxidation peak without the reference electrode. Then this location can be compared with the location of the peak observed during the experiment done in the gas

![Figure 1](image1.png)
![Figure 2](image2.png)
phase (Figure 2). If the positions match, it means that the observed redox peaks in the gas phase might indeed be CO oxidation.

The first experiment is presented on Figure 4. The obtained curve is typical for Pt in acidic medium and exhibits the classically observed redox peaks of H ads/des, Pt oxides formation and reduction and a capacitive region. The black curve is obtained under N₂ flow and constitutes a reference curve. No particular signal is observed besides the normal ones for Pt. Then CO is bubbled in the electrolyte, on cycles 37 to 40, one can see the apparition of an oxidation peak at 0.15 V vs MSE. This peak corresponds to the oxidation of CO in CO₂ on Pt, and the potential converted to the RHE scale is ≈ 0.8 V vs RHE, confirming the nature of the oxidation process. In addition, one can also see a small decrease in the H ads/des peaks as the CO oxidation peak increases. This is due to the adsorption competition between H and CO, since they adsorb on the same sites on Pt. The presence of this oxidation peak indicated that the sensor is capable of detecting CO in “normal” electrochemical conditions.

The second experiment is presented on Figure 5. It is composed of two sets of curves. The first set (black, red, blue and green curves) are obtained in H₂SO₄ in the 2 electrodes configuration, and then the purple curve is just the cycle 8 of the Figure 2 superimposed for interpretation. In H₂SO₄ in the 2 electrodes configuration, the curve is symmetric with respect to the 0 voltage and 0 current point. This shape is expected for this type of configuration, since each electrode is
alternatively polarized positively and then negatively by the same absolute value. The black curve is obtained under N\textsubscript{2} flow, and does not exhibit any particular redox signal and the shape looks like the capacitive region observed on Pt CVs. However, cycles 2 to 4 are obtained under CO flow and one can see the apparition of a symmetrical couple of peaks located at 0.2 and -0.2 V. In the present experiment, this peak can only be CO oxidation.

The position of the observed peaks can then be compared to the one observed in the gas phase experiment (purple curve) and one can see that the position of the peaks match really well. This peak matching constitutes a first proof that the signal observed during the gas phase experiment might indeed be CO oxidation in CO\textsubscript{2} and that the micro electrochemical sensor can indeed be used to detect CO.

**Discussion**

Working with the electrochemical sensors for a little more than 2 months has pointed out different problems and questions which have to be addressed in order to fabricate an improved second generation. Most of the encountered issues concern the Nafion layer, which appears to be too thin and inhomogeneous. This leads to poor stability of the Pt electrodes sitting on top of it, that’s why we could consider working with Nafion membranes directly. It will be necessary to immobilize such a membrane on a wafer in order to be able to perform all the micro-fabrication processes, but the membranes could be cleaned with H\textsubscript{2}O\textsubscript{2} prior to all remaining process and then be rehydrated with the steam protocol.

Some new design of the Pt electrodes should also be proposed, since the actual interdigitated seems to induce a lot of stress in the Pt, leading to cracks which might participate to its delamination during experiments in the liquid phase.

Other materials for the electrodes should be considered, since certain metals have enhance electrocatalytic properties toward specific species, and both electrodes could be in different metal.

Of course, the implementation of a reference electrode into the device would add particular value, especially in the eventuality of patent filling. Even a quasi-reference electrode composed of a Ag layer would suffice for first tests. Ideally the Ag layer should expend on the full size of the device and be located underneath the Nafion if the current type of design would be kept.

**Conclusion & Outlook**

Some complementary experiments will be conducted as soon as possible, and especially new experiments in the gas phase under different conditions. In particular, obtaining a curve of the sensor under hydrated N\textsubscript{2} flow will definitely confirm the identity of the peak observed on Figure 2.

In parallel, calibration experiments for the capacitor sensor must be made prior to any testing in CO detection. In particular, the heater must be calibrated against the applied voltage in order to be able to do CO detection experiments at different temperatures. To do that, an infrared laser thermometer will be used.

**References**