ARTICLE

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# In Situ Electrochemistry inside the TEM with Controlled Mass Transport

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## A Development of the functionalized sample holder

A sample holder is required in order to bring the MEMS inside the TEM and begin with the analysis. Such holder acts as the interface between the user and the Nano-Cell. It enables the researcher to supply the different stimuli (bias, pressure, liquid) to the specimen inside the Nano-Cell. The electrolyte is introduced through the holder tip by PEEK tubing with an inner diameter of 0.15mm, which connects the Nano-Cell to the pressure-based liquid pump.

The tip of the holder, optimized for maximum tilting for EDS purposes, contains the electrical contacts (probe needles) which create ohmic contact with the contact pads of the Nano-Cell. Consequently, these needles enable the user to control the three electrodes via the potentiostat. Directly on the tip, as shown in Figure 1a, there is a precision slot over which the bottom chip fits, having two o-rings that prevent any liquid leakage around the inlet/outlet. Furthermore, there is an additional o-ring that fits inside a groove located on the top chip and seals completely the micro-chamber. The lid, when tightened, ensures the right compression of the o-ring and guarantees that the top chip will be in direct contact with the upper surface of the spacers located on the bottom chip, so that the microfluidic channel is well-sealed. In order to ensure easy cleaning of all holder tubing, tip and Nano-Cells, the holder has been developed to have a modular design. This means that all components can be detached from the holder..

## B Materials and methods

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### A Geometrical characterization

Scanning Electron Microscope (SEM) was used to measure the linewidth of the WE, RE & CE, the width of the microfluidic channel and the spacers, the size of the electron transparent windows and their level of cleanness. The latter was further inspected with TEM (scanning mode) to discard particle contamination that would have not been identified with SEM due to small feature sizes. The height of the spacer had also been inspected using a profilometer. Similarly, white light interferometry was used to inspect the groove profile (i.e. depth, width and smoothness of surface) of the top chips, to ensure the o-ring will be compressed in the appropriate way and that proper spacing will be achieved between top and bottom chip (i.e. that the top chip completely touches the upper surface of the spacers located on the bottom chip). Finally, the thicknesses of the suspended membranes (top and bottom) were measured with Ellipsometry and Electron Energy Loss Spectroscopy (EELS), respectively.

| **Relevant Dimensions** | | |
|---|---|---|
| ***Feature*** | ***Size*** | ***Tolerance*** |
| Electron transparent window, width & length | 20μm, 200μm | ±5μm |
| $Si_3N_4$ window thickness (top & bottom) | 50nm | ±5nm |
| Spacer thickness | 200nm | ±20nm |
| Spacer width | 150μm | ±3μm |
| Inlet/outlet, lateral size | 210μm | ±15μm |

Table S1. Geometrical dimensions of the Nano-Cell

### B Leak-tightness and pressure performance

Prior to start any in-situ electrochemical experiment, and to gain confidence that the designed chips would not represent any risk to the TEM, the top and bottom chips of the Nano-Cell

were tested for leak tightness and to assess their pressure performance. The windows of the top and bottom chips of the Nano-Cell were tested for their pressure performance, to ensure the membranes would survive at least 2.5 bars of pressure.

### C Typical workflow

As shown in **Figure S2**, the bottom and top chips should be aligned during the Nano-Cell assembling, making sure the working electrode can be observed through the top window. After loading the bottom chip in the tip pocket, the top chip with a lid is placed and roughly positioned. The lid is carefully moved to check that the working electrode can be visualized under an optical microscope. Once the working electrode appear, the lid is tightened carefully. Figure S2 shows typical scenarios of the aligned Nano-Cell.

After introducing the "Stream" holder into the TEM, the liquid is brought inside the Nano-Cell using the pressure-based pump. Experimental conditions such as inlet and outlet pressure of the Nano-Cell are digitally set and controlled through the software user-interface. The current/potential set by the potentiostat are also digitally controlled. As the electrolyte is introduced, real-time electrochemical reactions can be observed within the Nano-Cell's controlled microfluidic environment. During the experiment, the user can change at any moment the pressure, flow and applied currents. Any spontaneous bubble formed on the electrodes due to the intrinsic radiolysis process that is triggered during the liquid/e-beam interaction can be pushed away. If necessary, bubbles can also be intentionally introduced.

The pressure-based pump enable to control the pressures set at the inlet and outlet of the chip on the fly. The system manages to set pressures from 50 mbar up to 3000 mbar. When there is a force driving the liquid flow, e.g. an absolute pressure difference between the inlet and the outlet, the liquid can flow from the outside of the TEM to the Nano-Cell. Then, it can be evacuated from the viewing area to an exhaust reservoir outside of the TEM. The flow can be controlled from no flow, so-called static mode, to 1.5 µL/min.

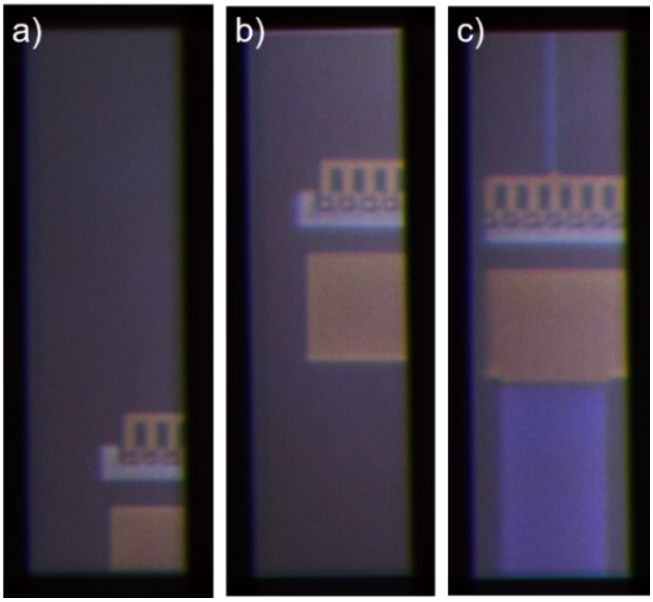


Figure S1. Optical microscope images of the Nano-Cell assembly: (a-c) Possible scenarios in aligning the top window with respect to the electrodes (WE and RE) on the bottom chip

## C Ex situ Copper deposition

### A Materials and methods

Ex situ experiments were performed within a mounted Nano-Cell outside a TEM, in order to identify any electron beam related effects on the electrochemical current measurements. The Nano-Cell was sealed without liquid or sample inside. A solution is flown into the holder and the Nano-Cell using a pumping system. The electrolyte solution was composed of 20 mM of CuSO4 and 10 mM of KH2PO4. Cyclic voltammetry measurements were carried out with a PalmSens4C$^{TM}$ potentiostat and a custom shielded cable to connect the electrode terminals of the potentiostat to the holder's.

### B Results and discussion

A series of tests have been carried out ex-situ. A solution composed of copper sulfate was flown into a Nano-Cell presented in **Figure S3**, outside of a TEM, thus eliminating any electron-beam influence. Cyclic voltammetry measurements were completed with a voltage window between -0.45 V and +0.15 V with respect to the platinum reference electrode. The resulting data show the oxidation and reduction of copper occurring at the working electrode. A couple of cycles were performed until the reference electrode's potential stabilizes, after which the cyclic voltammetry was recorded for 18 cycles and the results are presented in Figure S3. The shape of the copper oxidation peak (positive current) is centered at -0.12 V and a copper reduction (negative current) peak at -0.24 V. Even though a TEM compatible electrochemical Nano-Cell requires the use of a pseudo reference electrode, here made of platinum, we notice the stability of the electric potential measurement in liquid, with a drift limited to 2 mV over 18 cycles, which demonstrate the relevance of this tool for in-situ electroanalytical studies.

## Captions for ESI movies

**Movie S4** STEM movie showing flow from right to left, on the electron transparent window, as shown by debris being flushed out.

**Movie S5** STEM movie corresponding to Figure 3 showing a bubble being dissolved by setting a higher pressure in the Nano-Cell. At lower pressure the bubble size increases. At higher pressure the bubble size decreases until it disappears.

**Movie S6** STEM movie showing 5 cycles of copper growth and etching recorded during cyclic voltammetry at 0.1V.s$^{-1}$(Figure 7). Scalebar 500 nm.

**Movie S7** STEM movie showing side by side electrodeposition of copper at constant voltage with(left, flow direction bottom to top) and without flow(right), corresponding to Figure 8. Real time speed. For clarity, the electrode is highlighted in green.

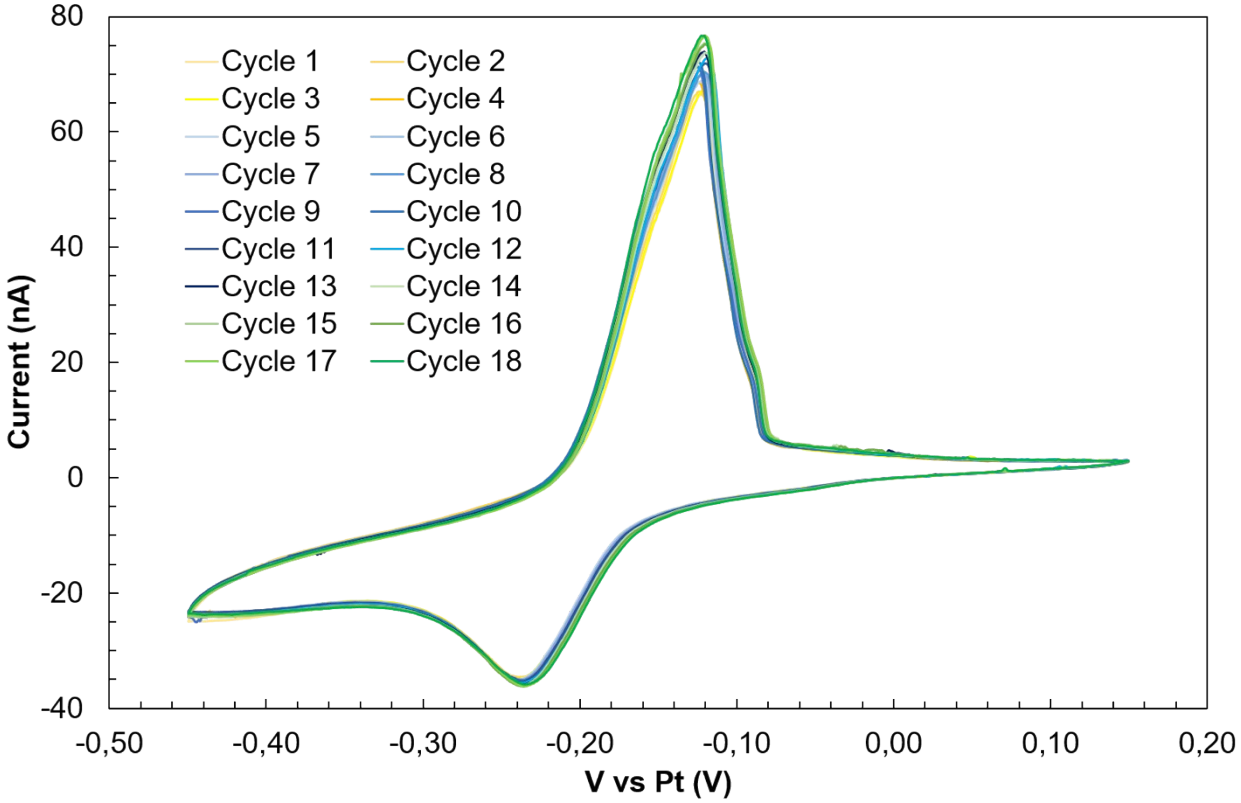


**Figure S2.** Cyclic voltammetry for an ex situ experiment in a Nano-Cell with the electrolyte 20 mM $CuSO_4$ + 10 mM of $KH_2PO_4$. Scan rate 100 mV/s. The potential is measured via an on-chip platinum pseudo reference electrode. The measurement shows reproducible (2 mV shift for oxidation and reduction peaks), overlapping cycles, showing reproducible potential control in liquid.