

# ELECTROCHEMISTRY AND MICROFLUIDIC ENVIRONMENTS FOR THE TARUMÃ STATION AT THE CARNAÚBA BEAMLINE AT SIRIUS/LNLS

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## Abstract

TARUMÃ is a multi-technique sub-microprobe experimental station of the CARNAÚBA (Coherent X-Ray Nanoprobe Beamline) beamline at Sirius, the 4th-generation synchrotron light source at the Brazilian Synchrotron Light Laboratory (LNLS). This work describes two related setups that have been developed in-house for TARUMÃ: a small-volume electrochemical cell, and another multifunctional liquid environment that can be used both as a microfluidic device and as an electrochemistry cell that allows for fluid control over electrodes. The mechanical design of the devices, as well as the architecture for the fluid and electrical supply systems are described in detail.

## INTRODUCTION

CARNAÚBA (Coherent X-Ray Nanoprobe Beamline) [1] is a state-of-the-art multi-technique beamline of Sirius [2], the 4th-generation Light Source at the Brazilian Synchrotron Light Laboratory (LNLS) at the Brazilian Center for Research in Energy and Materials (CNPEM), with achromatic optics and fully-coherent X-ray beam in the energy range between 2.05 and 15 keV. It is equipped with two in-line experimental stations, namely: TARUMÃ [3], a sub-microprobe station in an advanced commissioning phase, for which the sample environments presented here were specially designed; and SAPOTI, a nanoprobe station still in design phase.

At the TARUMÃ station, the in-vacuum KB focusing system has been designed with a large working distance of 440 mm, allowing for a broad range of independent sample environments to be developed in open atmosphere to benefit from the spot size between 550 and 120 nm, with a flux in the order of  $1e11$  ph/s/100mA. Hence, together with a number of detectors that can be simultaneously used, as shown in Fig. 1, a wide variety of studies of organic and inorganic materials and systems are possible using cutting-edge X-ray-based techniques in the micro and nanoscale, including: coherent diffractive imaging (CDI), fluorescence (XRF), optical luminescence (XEOL), absorption spectroscopy (XAS), and diffraction (XRD). Even though samples over the centimeter range can be taken at TARUMÃ, the small beam and relatively low energies point towards optimized and small sample setups for in situ experiments. Indeed, reduced-size geometry and light materials allow lighter sample environments, helping with fast flyscan mapping and the final stability of the sample positioning system, which is composed of commercial stages for up to 6 degrees of freedom (DoF) (see [3]).

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To explore the resolution and the multi-techniques available at TARUMÃ for studies in the fields of electro-chemistry (electrocatalysis) [4] and microfluidic (in situ reactions and in vivo studies) [5], two sample environments for *in situ* experiments were especially designed following the precision engineering concepts required for nanopositioning performance. The first setup is a small-volume electrochemical cell with working, counter and reference electrodes, and the machined parts made of light and non-reactive polymeric materials. The second one is a multifunctional glass-based device that can be used both as a microfluidic device only, or an electrochemical cell, by controlling fluids over embedded electrodes. This work presents the details of the mechanical designs of the two sample environments developed in-house, and the architecture for the electrical and hydraulic supply system.

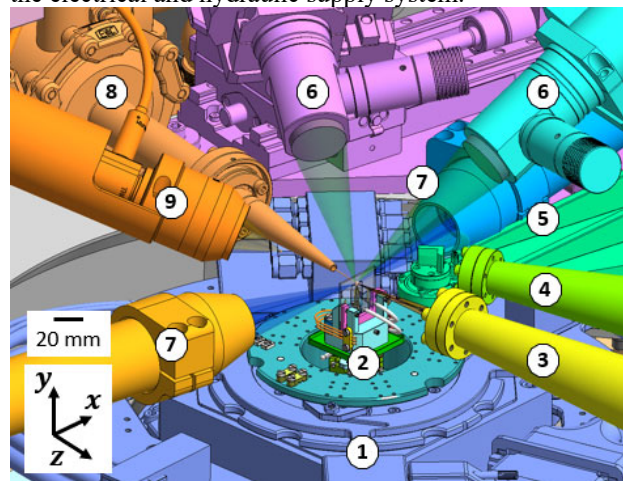


Figure 1: Sample region at TARUMÃ, with the several detectors that allow for multi-technique experiments: sample positioning stages (1), sample environment setup (2), flying paths for transmission (3) and diffraction (4) area detectors, crystal analyser spectrometer (5), optical microscopes (6), fluorescence detectors (7), exit vacuum nipple of KB chamber (8) and luminescence detector (9).

## ELECTROCHEMICAL SETUP

The setup depicted in Fig. 2 was designed for in situ experiments in electrochemistry and electrocatalysis at TARUMÃ, according to the infrastructure capabilities and interfaces at the station. It is a versatile small-volume oxidation-reduction reaction cell with external dimensions of  $45 \times 33 \times 45$  mm<sup>3</sup>. The electrolyte, with a static volume of 1 ml, as well as the working, counter and reference electrodes, may be suitably selected according to the scientific

cases. The parts in contact with the electrolyte are manufactured in PEEK, due to its inert condition and chemical resistance, whereas the remaining parts can be manufactured of a more cost-effective polymer, such as POM (Polyoxymethylene), which still has some resistance to reactions. The cell main elements are detailed below:

*Main frame (1)* – it is the main structural part of the cell, with the electrolyte container and the fittings for coupling the electrodes. Two auxiliary access points (2) at the top are used to manage the electrolyte and two nuts at the rear (3) allow for fine position adjustment and locking of the working and counter electrodes. The sealing of the electrolyte container is made with a 12.5  $\mu\text{m}$  thick Mylar® film (4) (for about 50% beam transmission at 2.05 keV), which is clamped via a Viton® o’ring (5) that is fitted into a groove on the outer cylindrical surface.

*Working electrode (6)* – it consists of a solid cylinder, typically of gold or platinum, with diameter of 1 mm and length of 15 mm, that is hermetically inserted into a PEEK threaded housing, which is sealed via a double layer of Viton o’rings and has an opening for the electrical connector (detailed below). Only the reaction surface of the electrode, with 0.785 mm<sup>2</sup>, is exposed to the electrolyte, while facing the film for the X-ray probing in reflection mode.

*Counter electrode (7)* – it is a disk with an outside diameter of 17 mm and thickness of 0.5 mm that fixed to the bottom of the electrolyte container by a nut (8). A gold-plated stainless-steel cylinder hermetically fitted into another PEEK threaded housing, also with a complementary double-layered Viton o’ring sealing and an opening for the electrical connector, is put in contact with the electrode disc to for electrical connection.

*Reference electrode (9)* – as the working electrode, it is also a solid cylinder with diameter of 1mm and length of 15mm, inserted in a polymeric housing that allows the coupling of the electrical connector. Yet, as it currently implemented as a commercial silver chloride (Ag/AgCl) electrode [6], which is fragile and prone to damage, a clamping system with manual force control was designed, in which two Viton o’rings are compressed by a nut (10) to make pressure on the cylindrical surface of the electrode.

*Electrical connectors (11)* – they are customized parts that electrically connect the solid electrodes to the control hardware. They consist essentially of a cylindrical piece of copper that is soldered to a 24-AWG cable at one side and fitted with a spring-loaded probe [7] making contact with the electrode at the other. This set is inserted into a POM housing with a pin (12), for a locking mechanism.

*Interface frame (13)* – it is the part responsible for the interface with the TARUMÃ sample positioning system, which is achieved via a magnetically-preloaded kinematic mount. Since it is made of POM, three stainless steel spheres are glued in recesses in the bottom face for Hertz contact with three V-grooves in the coupling part, whereas a magnetic piece in the center of the contact triangle is used to increase the preloading loading force and, thus, the contact stiffness for superior dynamic performance. Also regarding dynamics, the wider footprint was made to increase the mounting lever-arms as much as possible and to

shift the center of mass of the assembly, both downwards and to the center of the kinematic mount in the  $xz$  plane. Finally, to passively minimize drifts in the region of interest in the sample due to thermal expansion effects, the reaction surface of the working electrode was aligned over the thermal center of the assembly, lying on the center of the kinematic mount in the  $xz$  plane. Anticipating that sealing failures could occur, the interface base has high borders to contain the leaked solution before it reaches (and possibly damages) the stages located just below the cell.

To conclude, some clamps are fixed to the sides of the main and interface frames for routing and fixing the cables according to predictable dynamic links with respect to the sample stage, both preventing tensions forces and/or fatigue from damaging the connectors, and managing disturbance forces in the cell due to sample positioning.

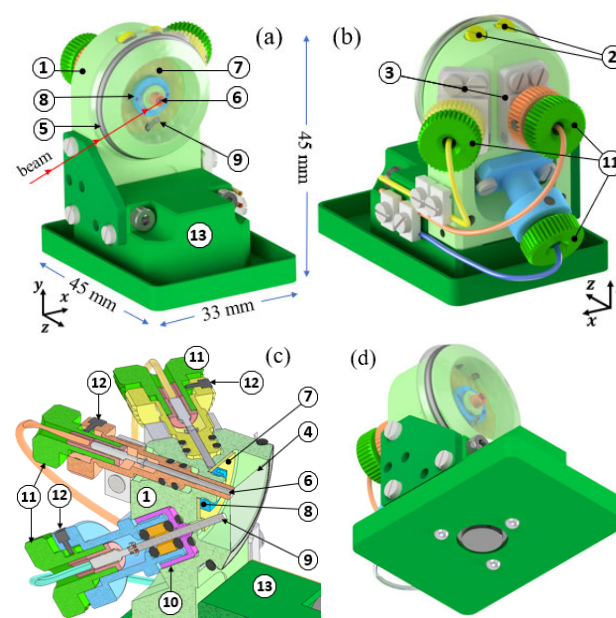


Figure 2: The electrochemical setup seen from the front (a) and back (b) sides, in quarter-section view (c) and also from below (d) (with the kinematic mount).

## MICROFLUIDIC SETUP

The setup shown in Fig. 3 has been designed to be the microfluidics platform at TARUMÃ, with volumes in the order of  $\mu\text{l}$  and a precise flow control. Optionally, embedded metallic electrodes can be prepared via photolithography and deposition processes to allow for in situ experiments of electrochemistry [8], as in the previous cell, but at a different scale. It can be broken down into 3 main parts, as described below:

*Microfluidic device (1)* – it is the core component in the setup, manufactured with in-house technology in the Microfabrication Laboratory (LMF) at LNNano/CNPem. Although different geometries and features may be considered in the future, the first device (see [8]) consists of a 30 x 26 x 1 mm<sup>3</sup> glass substrate with a micro-reservoir connected to one inlet and one outlet microchannels. Bridging from the micro-reservoir to a macroscopic connection re-

gion, three 100 $\mu$ m-thick gold electrodes are deposited on the glass via a lithographic process. Finally, two small flexible silicone tubes (6) are connected to the microchannels via a PDMS (5) pad. In this case, the regions of interest for the sub-micrometer X-ray probe are the electrodes within the micro-reservoir volume, where the reaction occurs.

*Main frame (2)* – made of aluminum, it is the part responsible for holding the microfluidic device in place via fastening screws (9) and making the interface with the TARUMÁ sample positioning system. As in the interface frame of the electrochemical cell, coupling is made via a magnetically-preloaded kinematic mount. Also, equivalently to the interface frame, a complementary tray (4) is included to contain any leaks and prevent damage to the stages. The same care regarding precision engineering concepts for dynamics, thermal drift and cable/tubing management with clamps (7 e 8) are applied here.

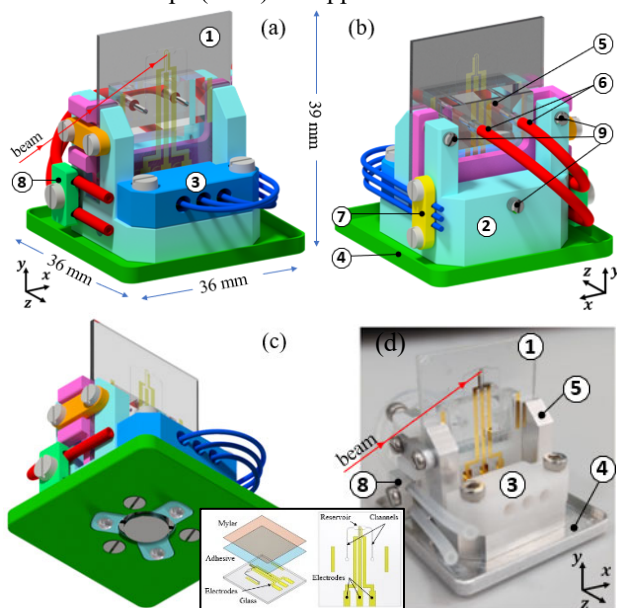


Figure 3: Drawing of the microfluidic setup seen from the front (a) and back (b) sides, and the bottom view, with of the kinematic mount (c). Prototype fully made in house (d).

*Electrical connector (3)* – for devices with electrodes, it is used to connect them to the control hardware. It consists of an insulating housing made of POM with contact sets based on spring-loaded probes, as in the connectors of the electrochemical cell. Here the spring probes help compensating small dimensional variations in the glass or assembly errors, ensuring electrical contact while preserving the glass substrate.

## SUPPLY SYSTEM

Both special sample setups require complementary functional resources, i.e., either a control hardware for current/voltage, or pumps for the fluids. Due to the tight volume constraints in the surroundings of the sample and the dynamic-oriented architecture of the station, the standard solution is installing the large pieces of equipment on auxiliary stands around the station. Hence, a permanent set of cables and tube guides – with deterministic links between

the precise air-bearing rotary stage of sample stack and a synchronized auxiliary rotary stage dedicated to cable management – should be used. Indeed, as illustrated in Fig. 4, this concept allows for rotations of  $\pm 110^\circ$  for tomography experiments, while preventing unknown and uncontrolled force disturbances at the sample.

Thus, the electrodes of the cells can be connected via a short cable to an electrical patch panel on the top frame of the sample stage, while the cables exiting the cable chain are connected to the control hardware, such as the SRS EC301 potentiostat, to be used in day 1 at TARUMÁ. Similarly, short tubes leaving the microfluid cell can be connected to a manifold on the sample stage, while independent tubes are connected to a syringe pump, for example. Still, for small volumes, a local embedded reservoir for the outlet fluid can also be considered.

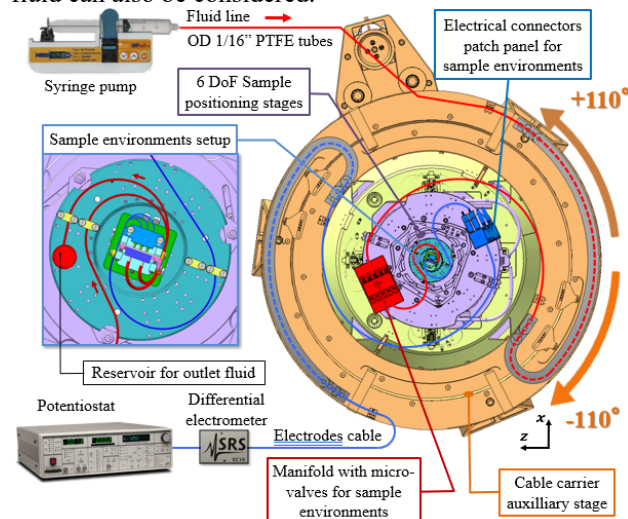


Figure 4: The supply system architecture at TARUMÁ.

## CONCLUSION

Two sample environments for in situ experiments in electrochemistry with static fluid and microfluidics have been designed in-house for compatibility with the multiple X-ray techniques at the TARUMÁ station. They are based on previous experience in the field and follow precision engineering concepts, not only for stability with respect to the nanometric beam and but also for flyscan compatibility. After validating assembling and sealing concepts via preliminary prototypes, the microfluidic cell has just been manufactured and the electrochemical cell is in procurement. They are expected to be finalized and fully commissioned soon, becoming part of the station experiments portfolio in the second half of 2021.

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