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DELIVERABLE REPORT

WP15 JA5-Correlative Nano-Spectroscopy and Nano-Diffraction

D15.4

Tested liquid cells

Due date

M42

This initiative has received funding from the EU's H2020 framework program
for research and innovation under grant agreement n. 101007417, NFFA-Europe Pilot Project

PROJECT DETAILS

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WORK PACKAGE LEADER
Dr. Thomas Keller (DESY)

DELIVERABLE DETAILS

DELIVERABLE ID	DELIVERABLE TITLE
D – D15.4	Tested liquid cells - Liquid cell for X-ray nano-spectroscopy available for users

DELIVERABLE DESCRIPTION

Liquid cells equipped with on-purpose microfabricated thin silicon nitride membranes, with thickness in the 15-25 nm range, have been successfully tested at the HAXPES endstation of the GALAXIES beamline at the SOLEIL synchrotron radiation facility. Low stress membranes have been fabricated from 100 mm silicon wafers using standard lithography techniques and platinum alignment marks have been added to facilitate the positioning of the X-ray beam on the membrane. Two types of liquid cells have been used, a static one built on an Omicron-type sample holder with the liquid confined in the cell container, and a circulating liquid cell, in which the liquid can flow to mitigate the effects due to beam damage. The membranes are mechanically robust and withstand 1 bar pressure difference between the liquid inside the cell and vacuum and the intense synchrotron radiation beam during data acquisition, opening new opportunities for spectroscopic studies of liquids and dispersions of nanoparticles.

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AUTHORS

Dr. Jordi Fraxedas (ICN2), Dr. María José Esplandiu (ICN2), Olga Muntada (CSIC), Prof. Francesc Pérez-Murano (CSIC)

PERSON RESPONSIBLE FOR THE DELIVERABLE

Dr. Jordi Fraxedas (ICN2)

NATURE

☐ R - Report

☐ P - Prototype

☐ DEC - Websites, Patent filing, Press & media actions, Videos, etc

☒ O – Other (Demonstrator)

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FOR MORE INFO PLEASE CONTACT

Jordi Fraxedas
ICN2
UAB Campus, Bellaterra
Barcelona
08193, Spain

email: jordi.fraxedas@icn2.cat

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INTRODUCTION

Workpackage JA5, Correlative Nano-Spectroscopy and Nano-Diffraction, aims to establish a user platform for routine experiments at Nanolabs and analytical large-scale facilities (ALSFs) permitting to collect structural and chemical information from a statistically relevant number of distinct nanoscale objects.

One of the objectives of JA5 is to provide dedicated sample environments to investigate the dynamical behavior of nanoscale objects in situ during e.g., catalytic, electrochemical or corrosion experiments in liquid or gaseous environments. Task 15.3 (Sample environments for in situ correlative analysis) centralizes the work for the design, test and offer of a dedicated micro/nano fabrication platform for in situ sample environment.

The present report summarizes first exploratory HAXPES (Hard X-ray Photoelectron Spectroscopy) results obtained at the GALAXIES beamline at the SOLEIL synchrotron radiation facility of aqueous solutions and dispersions of nanoparticles using on-purpose microfabricated thin silicon nitride membranes (15-25 nm thickness) using both static and circulating liquid cells. The membranes, microfabricated on silicon chips at IMB-CNM-CSIC (Barcelona) and adapted to the size of the monochromatic synchrotron radiation beam (nominally 30 μm × 100 μm), are mechanically robust and withstand the 1 bar pressure difference between the liquid cell and vacuum and the intense synchrotron radiation beam during data acquisition and are ready for public use under the established NEP terms.

A detailed description of the liquid cells together with first HAXPES results has been submitted to the Journal of Synchrotron Radiation (Open Access). The revised version is currently under consideration (minor revisions). The results will be also presented at 50th International Micro and Nano Engineering Conference (MNE 2024) in September in Montpellier (France).

TESTED LIQUID CELLS

The tested liquid cells correspond to advanced versions of the prototypes described in Deliverable D15.1 (approved in M12) and Milestone MS21 (approved in M24). The cell consists of a cell body, that hosts the liquid, and a silicon chip containing a thin silicon nitride membrane. The assembly of both components provides a vacuum tight cell that can be used in HV/UHV environments.

Description of liquid cells

Static liquid cells

The static liquid cells (see Fig. 1) consist of three main pieces: (i) an Omicron-type stainless steel sample holder plate, (ii) a spacer made from polyether ether ketone (PEEK) that defines the available volume of the liquid (about 30 μL) and holds the grooves for two Viton O-rings and (iii) a 1 mm thick stainless steel cover piece with a centered 3.5 mm hole. In the simplest configuration, the bottom plate and the top cover piece are in electrical contact with stainless steel screws and grounded through the sample manipulator. Thus, the liquid inside the container is in electrical contact with the holder plate which is grounded. In a second configuration, the cells are adapted for electrochemistry experiments. In this case, the bottom and top parts of the cell are electrically isolated using PEEK

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screws building a conventional coin-cell assembly but with smaller electrode diameters (about 4 mm). A parking specifically designed for this cell is available at GALAXIES on the manipulator of the analysis chamber that allows to apply potential/current with an external potentiostat.

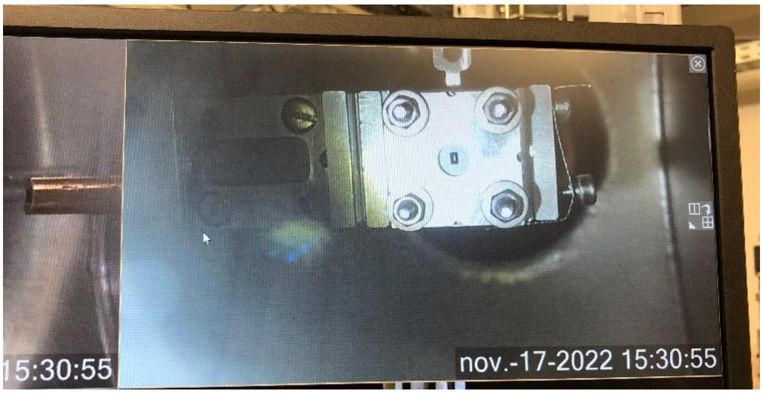

Figure 1: Picture of an assembled static liquid cell containing water in the fast-entry lock of the HAXPES endstation at the GALAXIES beamline in SOLEIL before its transfer to the analysis chamber showing the membrane (small bright rectangle in the center of the cell).

Circulating liquid cells

A prototype of a liquid cell with circulating liquid used for the HAXPES experiments was based on an existing electrochemical cell at the LUCIA beamline at the SOLEIL synchrotron facility [1]. Figure 2(left) shows a picture of the cell, made from PEEK, mounted on a motor stage fixed to a DN100CF flange with sub-D feedthroughs. Two polytetrafluoroethylene (PTFE) tubes (1/16″ OD, 1 mm ID) are shown which are used for the liquid inlet and outlet.

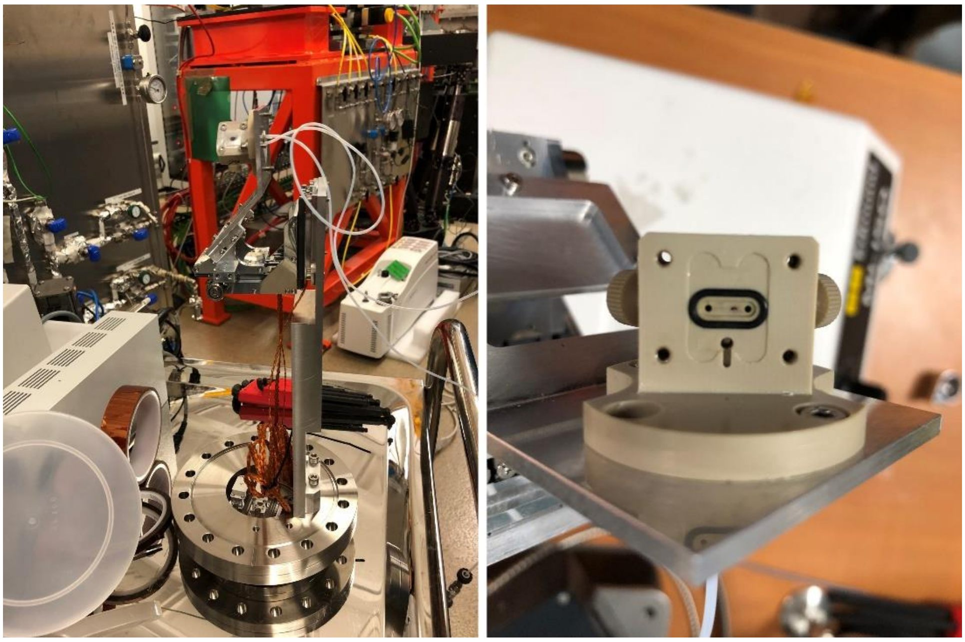

Figure 2: (left) Picture of the circulating liquid cell mounted in a DN100CF flange, showing the motors stage and cabling and PTFE tubing and the PEEK cell hosting the chip with the membrane. The used liquid flux during the experiments was 0.2 ml/min and the pressure in the analysis chamber was in the 10^{-6} mbar range during measurements. (right) Detail of the cell before assembly of the chip with the membrane showing the O-ring and the inlet/outlet holes.

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Silicon nitride membranes

Silicon nitride membranes have been microfabricated in silicon chips and designed on purpose for the HAXPES experiments at the GALAXIES beamline. SiNx films have been deposited by low-pressure physical vapor deposition (LPCVD). The nominal thicknesses of the membranes were 15, 20 and 25 nm, which guarantee sufficient photoelectron signal in the electron analyser arising from the liquid [2]. Details of the fabrication process are shown below in Fig. 3. In order to achieve an optimal balance between having a large enough membrane for the measurements, ensuring mechanical stability as well as conforming to the elliptical shape of the synchrotron radiation beam, rectangular membranes were chosen since in this case the strain depends mainly on the short dimension of the rectangle [3]. This allows to substantially increase the large dimension of the rectangle without affecting its mechanical response.

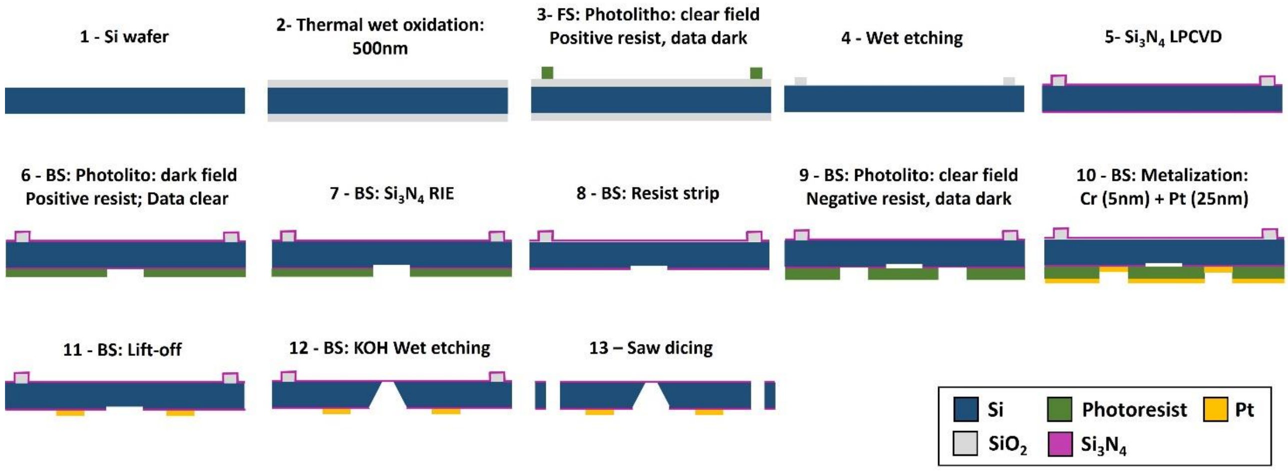

Figure 3: Fabrication process flow for the membrane-containing chips. Steps 1- 4 correspond to the fabrication of alignment and sawing marks by silicon oxide grow, photolithography and wet etching. Step 5 is the deposition of silicon nitride that will constitute the membrane material and also serves as a mask during wet etching in step 12. Steps 6-8 define by means of photolithography and dry etching the front side aperture of the cavity to obtain the suspended membrane. Steps 9-11 illustrate the fabrication of the Pt alignment marks for beam positioning. Step 12 is the anisotropic etching of the bulk silicon that frees the membrane. Finally, in step 13 the wafer is diced into chips of the size required to fit into the liquid cell.

Figure 4 shows schemes and pictures of the two different geometries adapted to the used cells. The dimensions of the silicon chips were set to 10 mm × 10 mm. For the static cell [Fig. 4(a)], the membrane is aligned diagonally while for the circulating cell the membrane lies orthogonal/parallel to the chip edges [Fig. 4(b)]. Platinum stripes as alignment marks [orange color in Fig. 4(c)] are included to facilitate the positioning of the X-ray beam on the membrane [purple color in Fig. 4(c)] Dimensions of the membranes vary across designs and are in the 20-50 μm range for the short dimension (a) and 500-600 μm for the long dimension (b). A schematic cross-section of the silicon chip is shown in Fig. 4(d) and pictures of a chip are shown in Fig. 4(e). The front and back sides of the membranes are in contact with the vacuum and liquid, respectively. Note that the etching process of silicon imposes the morphology of the cavity, with an angle of 54.7º.

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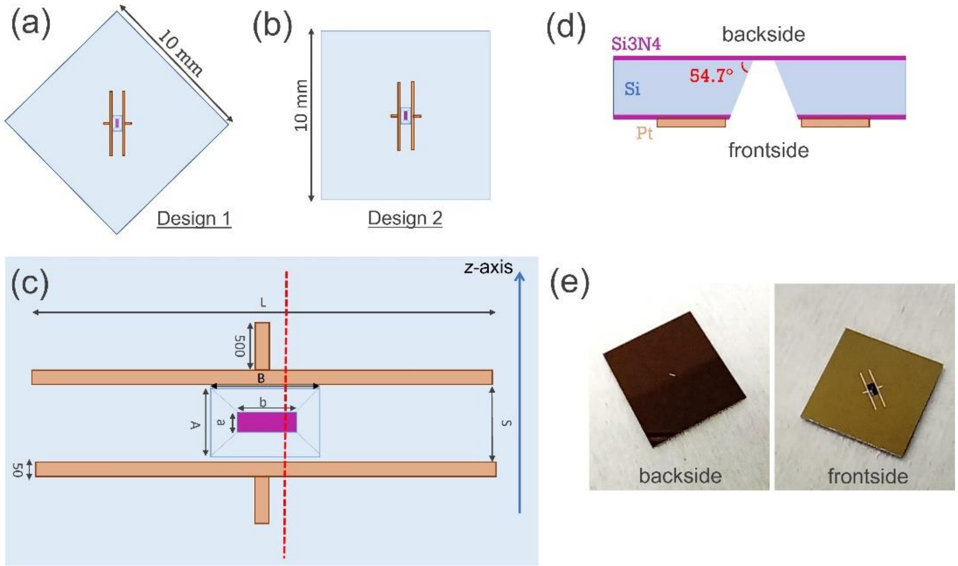

Figure 4: Design of the chips with a silicon nitride suspended membrane (not to scale). (a) Overview of the first chip design with the membrane placed diagonally about the chip edges. (b) Overview of the second chip design, the membrane is orthogonal/parallel to the chip edges. (c) Detailed scheme of the platinum alignment marks (orange) and the silicon nitride membrane (purple). (d) Schematic cross-section of the silicon chip (not to scale) and (e) images of the frontside (right) and backside (left) of the chip.

PRELIMINARY RESULTS

We highligth here the first experimental HAXPES results using 20 nm thick silicon nitride membranes in a static cell and 15 nm thick membranes using the circulating liquid cell, respectively. The results have been obtained during the following beamtimes at SOLEIL: 20220156 (M21), 99230005 (M26) and 20230319 (M36).

Static liquid cells with 20 nm membranes

Figure 5 shows the C 1s (left) and F 1s (right) lines, respectively, corresponding to four different membranes in the cell filled with: air (blue), vacuum (red), with air but with a ca. 5 nm thick amorphous carbon coating deposited in the inner part (back side) of the membrane (black) and with 60 µl of a LP57 conventional Li-ion battery electrolyte (1M $LiPF_6$ in EC:EMC 3:7) and with the ca. 5 nm thick carbon coating (green line). The C 1s spectra corresponding to the membranes capped with carbon coating (black and green lines), show extra contributions towards higher kinetic energies that are ascribed to the carbon coating while the lower kinetic energy lines arise from surface contamination.

Figure 5(right) shows the F 1s line, that corresponds to the used electrolyte. The peak can be fitted with two components that can be ascribed to the fluorine in the dissolved $LiPF_6$ salt (dominant blue component) and to LiF (red component), a common reaction product of this salt found at the interfaces in these systems. The kinetic energy difference between the two signals is in agreement with what is commonly observed in Li-ion batteries [4].

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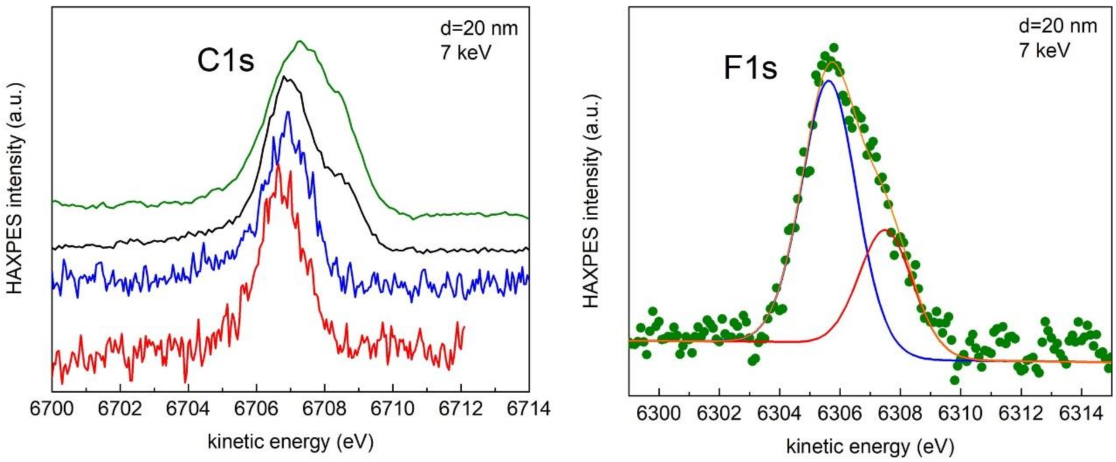

Figure 5: Normalized HAXPES spectra obtained with 7 keV photons of the (left) C 1s and (right) F 1s lines corresponding to four different membranes in the electrochemical cell filled with: air (blue line), vacuum (red), with air and with a ca. 5 nm thick amorphous carbon coating deposited in the inner part of the membrane (black) and with 60 µl of the LP57 electrolyte (1M $LiPF_6$ in EC:EMC 3:7) and with the ca. 5 nm thick carbon coating (green).

Circulating liquid cells with 15 nm membranes

First experiments using 15 nm thick membranes were performed with concentrated aqueous solutions of CsCl (2.6 M) with the liquid circulating with a flux of 0.2 ml/min. The measured Cs 3d (left) and Cs 4d (right) core lines are shown in Fig. 6. These results can be compared to previous similar experiments performed in a laboratory XPS system using environmental cells with commercial microchips with 5 nm thick and 30 µm × 30 µm wide silicon nitride membranes and a conventional Al Kα excitation source in normal emission [5]. In that case the acquisition time was more than 200 minutes while in our case the acquisition time was about 5 min/spectra.

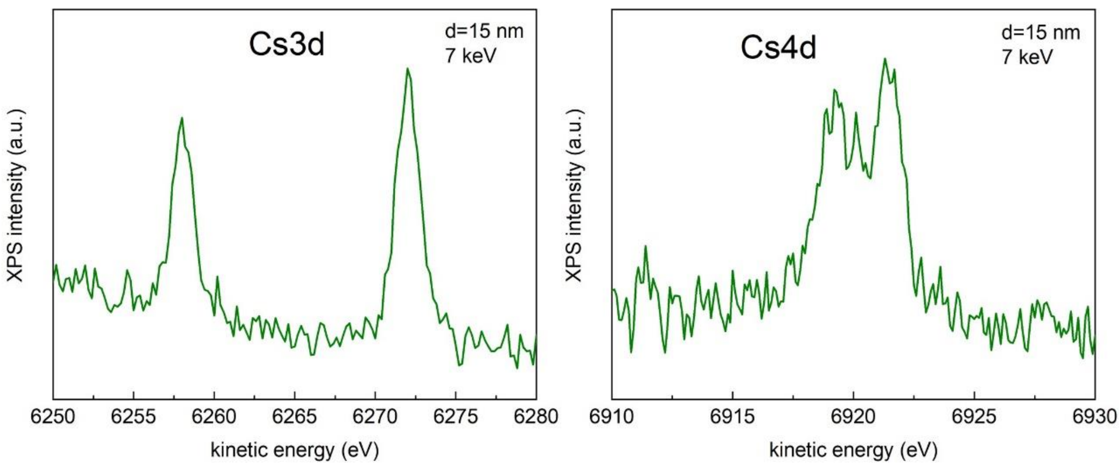

Fig. 6. HAXPES spectra of (left) Cs 3d and (right) Cs 4d lines of a 2.6 M aqueous solution of CsCl obtained with 7 keV photons and using 15 nm membranes.

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CONCLUSIONS AND OUTLOOK

- New environmental liquid cells for HAXPES using specially designed thin low-stress silicon nitride membranes (15 to 25 nm thickness) have been developed. The cells have been successfully tested with aqueous solutions of salts, dispersions of gold nanoparticles and in electrochemical experiments.
- The nominal dimensions of the beam (30 µm × 100 µm) sets the smaller dimensions of rectangular membranes. The geometry of the HAXPES endstation of the SOLEIL facility (horizontal polarization parallel to the analyser axis) together with the intrinsic 54.7 degrees angle arising from the etching of silicon for the fabrication of the membranes impose an incidence angle of about 45 degrees.
- The strategy of defining Pt alignment marks on the back of the chip to easily locate the membrane has been validated and can be used for the future correlative platforms.
- When the membranes are carefully inspected and handled, the lifetime of the membranes is beyond the time scale of the performed experiments, which amount to more than 6 hours.
- Our results open the door to regular HAXPES studies of liquids under circulation and potentially to other techniques using synchrotron radiation.
- The selected users for subtask 15.3.3 have been Dr. R. Dedryvère (University of Pau and CNRS, France) for electrochemical studies of Li-batteries and Dr. Pawin Iamprasertkun (Thammasat University, Thailand) for decoration of the silicon nitride membranes with molybdenum sulfide (on-going collaborations).
- A detailed description of the fabrication of the cells and membranes and first HAXPES results have been submitted to the Journal of Synchrotron Radiation (in Open Access) and the revised version is currently under evaluation. The results will be also presented at 50th International Micro and Nano Engineering Conference (MNE 2024) in September (16-19) in Montpellier (France).
- A new proposal for beamtime will be submitted to SOLEIL in the next call (deadline 16/9, M43) to further explore the use of the silicon nitrides membranes in the cells under circulation of liquid.
- With the upgrade of most synchrotron facilities to the 4th generation, with the reduction of the horizontal beam size, we envisage to reduce the long dimension of the membranes, which should allow the use of membranes thinner than 15 nm, an improvement for HAXPES as well as for XPS using soft X-rays.

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