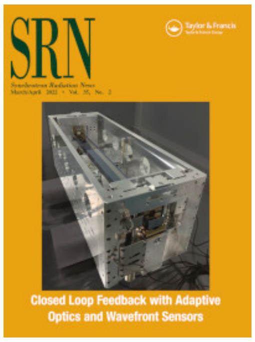

Synchrotron Radiation News

ISSN: (Print) (Online) Journal homepage: https://www.tandfonline.com/loi/gsrn20

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Technical Report

The Berlin Joint Lab for Electrochemical Interfaces, BElChem: A Facility for In-situ and Operando NAP-XPS and NAP-HAXPES Studies of Electrochemical Interfaces at BESSY II

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Introduction

The Berlin Joint Lab for Electrochemical Interfaces (BElChem) is located at the BESSY II synchrotron in Berlin, Germany, and co-run by the Fritz-Haber-Institut, the Max-Planck-Institut of Chemical Energy Conversion and the Helmholtz-Zentrum Berlin. BElChem focuses on providing a molecular-level description of (photo)electrochemical interfaces that are of high relevance for solar fuel production and renewable energy storage. The CO_2 reduction reaction (CO2RR) and the oxygen evolution reaction (OER) are of particular current interest. In BElChem, near-ambient pressure X-ray photoelectron spectroscopy (NAP-XPS) and near-ambient pressure hard X-ray photoelectron spectroscopy (NAP-HAXPES) will be used for the in-situ and operando interrogation of the electronic structure and chemical composition of catalytically active solid/gas and solid/liquid interfaces. BElChem will also enable heterogeneous catalytic reactions, such as oxidation and hydrogenation reactions, to be investigated.

The BElChem facility consists of two beamlines with two endstations in two separate hutches and an additional sample preparation/chemical lab. One beamline, the undulator beamline U49/2 PGM (plane grating monochromator), covers the soft X-ray energy range, whereas the other dipole magnet sourced beamline, BElChem-DCM, with a double crystal monochromator (DCM), covers the tender X-ray energy range. Combined, the BElChem beamlines cover a photon energy range nominally from 90 eV to 10 keV. Each endstation has its own electron spectrometer. The endstation frame is composed of two separate parts. On one part, the electron spectrometer is mounted and, on the other, the analysis chamber is mounted. This allows the easy exchange of experimental modules and the ability for users of BElChem to provide tailor-made modules targeting the sample environment relevant for their in-situ or operando measurement.

The BElChem facility provides the opportunity to study electrochemical interfaces with two general approaches. Due to the high surface sensitivity and short mean free paths of low kinetic energy photoelectrons generated with soft X-rays, a suitable method to explore the electrode/electrolyte interface with XPS during a (photo)electrochemical reaction is needed. At BElChem, these types of measurements are carried out using dedicated electrochemical cells or setups, and generally make use of thin membranes with arrays of holes that are either open or covered with graphene, to separate the electrochemical cell from the vacuum environment. Different types of cells are available, and which cell is most appropriate will be determined by the properties of the sample and the desired experimental conditions [1]. Using tender X-rays can produce photoelectrons with higher kinetic energies than soft X-rays, facilitating the investigation of buried interfaces. At the BElChem-DCM beamline, two approaches are used to study electrified solid/liquid interfaces. With the dip-and-pull method, thin electrolyte films, on the order of a few tens of nanometers, cover the electrode surface, and tender X-ray photoemission is used to study the buried solid/electrolyte interface [1, 2]. (Photo)electrochemical reactions can also be investigated in situ using a 3-electrode H-cell [3]. The NAP-HAXPES measurements are carried out such that both the X-ray excitation and electron detection occur through a thin electrolyte film. In both cases, the simultaneous detection of the activity of the electrode, product analysis, and measurement of the electrode's chemical composition and electronic structure enables structure-function relationships to be established.

Beamlines

BElChem-DCM

The BElChem-DCM beamline is currently under design and construction. The source for the BElChem-DCM is the dipole bending magnet 4.2. As shown in Figure 1A, the beamline is composed of two cylindrical mirrors (M_1, M_2) and a double crystal monochromator containing a Si(111) crystal pair. The M1 mirror will collimate the white beam onto the first crystal of the DCM. Horizontal focusing of the beam will be achieved by the second (bendable) crystal of the DCM. The M2 mirror will be used for vertical focusing of the beam and for directing it to the experimental position. The usable photon energy

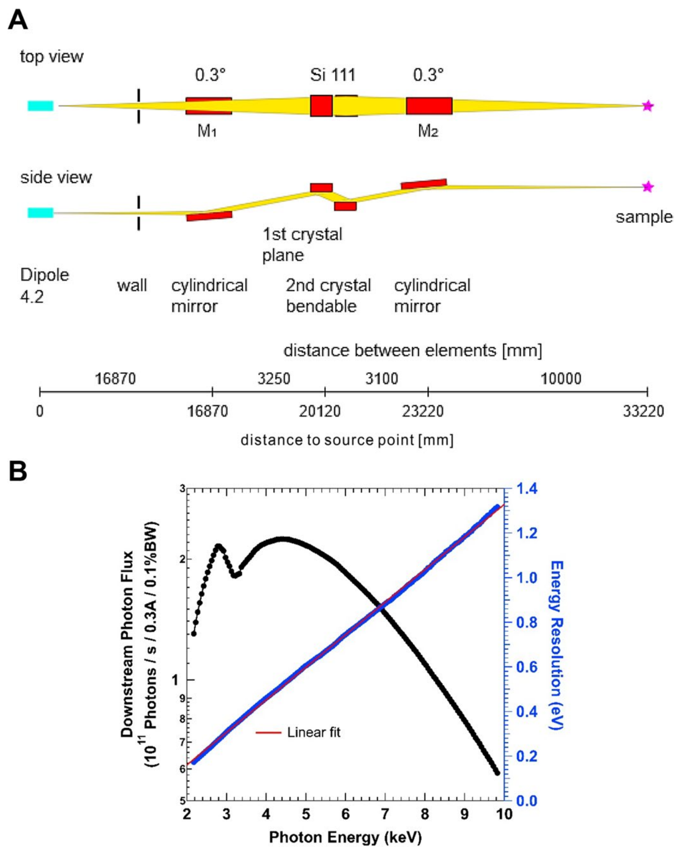

Figure 1: *(A) Optical layout (top and side views) of the future BElChem Double Crystal Monochromator (DCM) beamline, providing photons in the tender X-ray range and currently under development at the BESSY II synchrotron facility. (B) Results of the X-ray tracing simulations showing the DCM beamline performance. Downstream photon flux (left) and beamline resolution (i.e., transmitted bandwidth).*

range will be approximately from 2.4 to 10 keV. Figure 1B shows the results of X-ray tracing simulations performed with Ray-UI [4, 5]. This shows that the downstream photon flux will remain above 10^{11} photons$\cdot$s$^{-1}\cdot$0.3A^{-1}/0.1%BW for photon energies up to 8 keV. The beamline resolution will range from about 0.2 eV at 2.4 keV to 1.3 at 10 keV. In addition, the simulations predict a beam dimension of about 400 (vertical) × 200 (horizontal) μm^2, irrespective of the photon energy at the location of the experiment.

BElChem-PGM

The BElChem-PGM beamline will cover the soft X-ray energy range from approximately 90 eV to 2000 eV with a plane grating monochromator. The source for the BElChem-PGM beamline is a planar undulator with a period length of 49.4 mm (U49-2) and minimum gap of 16 mm. The layout of the BElChem-PGM beamline is shown in Figure 2A. The optical elements and layout of the beamline have been optimized to deliver a high photon flux over a broad energy range, in particular at energies above 800 eV, with moderate spectral resolution. This high flux in the high photon energy range helps to facilitate in-situ and operando experiments that are conducted at elevated gas pressures or in liquids, since it produces a sufficiently high number of photoelectrons with high kinetic energies that have increased mean free paths through gases and liquids. The beamline is composed of three mirrors with an included angle of 177°. The small incident angle of 1.5° ensures high reflectivity even at photon energies above 1000 eV. The entire photon energy range is covered by a single, optimized blazed grating with a line density of 600 l/mm. This makes the BElChem-PGM beamline very user friendly since experiments can be conducted without the need to switch gratings and adapt beamline settings to different gratings. The expected photon flux and spectral resolution as obtained by Ray-UI tracing [4, 5] is displayed in Figure 2B for an exit slit setting of 20 μm. While the high efficiency of the 600 l/mm grating is the best choice for most applications, two additional gratings with 400 l/mm (optimized for low photon energies) and a 1200 l/mm grating (optimized for very high spectral resolution, not shown) are available for the users if needed. The X-rays are focused by a toroidal mirror M4 to the endstation. The spot size as obtained by ray tracing simulations is around 100 μm × 20 μm (horizontal × vertical) with a 20 μm exit slit for most photon energies and a fixed focus constant of cff = 2.25. This focus size is suitable for

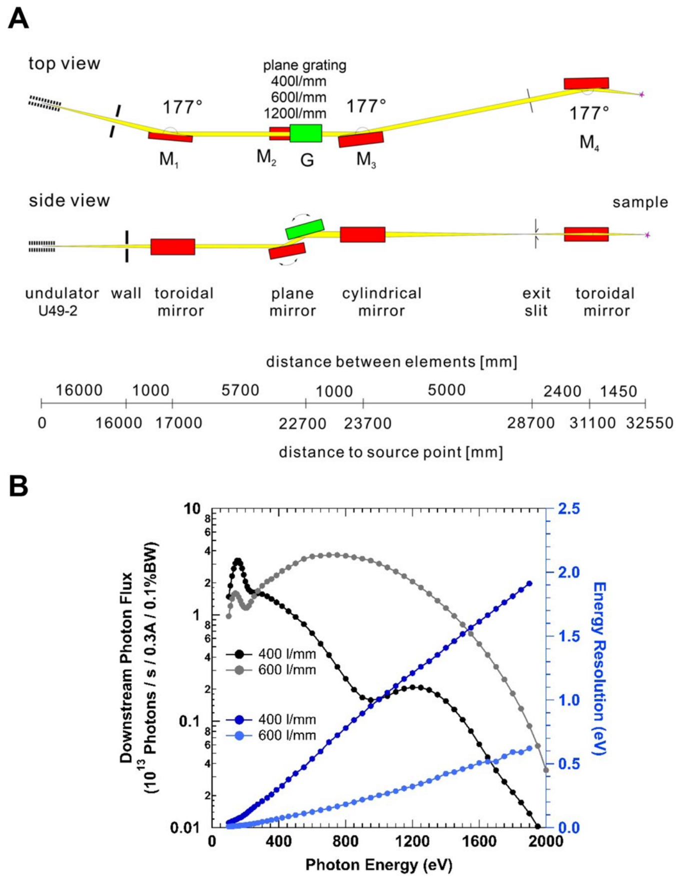

Figure 2: (A) Optical layout (top and side views) of the future BElChem plane grating monochromator (PGM) beamline. The concept of the beamline is based on a SX700-type monochromator working in collimated light served by a planar undulator U49-2 providing photons within the soft X-ray range. (B) Results of ray tracing simulations showing the PGM beamline performance. The photon flux at sample position (left) and the beamline resolution (right) is displayed for two of the three available gratings (400 l/mm and 600 l/mm, respectively).

the operation of small aperture reaction cells, but still avoids high density spots that enhance beam damage for sensitive samples, such as polymeric membranes often used in electrochemical systems. It also perfectly matches the 300 µm entrance aperture of the NAP-XPS spectrometer of the BElChem-PGM endstation.

Some special features of the BElChem-PGM beamline are of particular note. First, when using a low line density grating at high photon energies, the photon energy stability and accuracy might be compromised, since small deviations in the angle of the grating G and the mirror M2 might translate into a significant energy offset. Within the BElChem-PGM beamline project, a study is underway to develop an innovative technical solution, which allows fine-tuning of the grating and mirror positions with the help of piezo drives in the mechanics of the monochromator to maintain photon energy accuracy and stability. Another benefit of integrating these piezo drives into the monochromator motion control is the possibility to toggle quickly between photon energies within a narrow range around a central energy. This could be used, for example, to switch between two resonance positions in NEXAFS studies or resonant photoemission. A second special feature of the BElChem-PGM beamline is the integration of a fast mechanical chopper with a continuous rotation speed of up to 1 kHz. This chopper is built in cooperation with the ALBA synchrotron [6]. Using the chopper to modulate the intensity of the incoming X-rays allows lock-in techniques to be used. This is particularly beneficial in electrochemical studies that make use of total electron yield X-ray absorption spectra measured via the sample drain current. In this way, the continuous, electrochemically driven currents can be separated from the spectroscopic measurements since the drain current is modulated by the chopper [7]. In addition, the BElChem-PGM endstation will be connected to the beamline via a unit containing multiple differentially pumped stages; this is currently in the final stages of development. This differentially pumped interface will allow windowless operation of in-situ experiments when requested by the user. At the BElChem-PGM, we aim to allow a pressure differential of up to 1 bar between the XPS measurement chamber and the UHV conditions in the refocusing mirror chamber M4 of the beamline.

Modularity

A specific feature of in-situ and operando measurements is that not only a broad variety of sample types are studied, ranging from single crystals and model systems to applied materials, but also a wide range of experimental conditions are applied during the measurements. These experimental conditions can potentially range from the general use of gases or liquids, a wide range of sample temperatures, and include ultra-clean environments to highly corrosive or toxic environments. This requires a large amount of flexibility in the endstation configuration to accommodate such wide-ranging experimental conditions. At BElChem this is achieved through a modular approach. This approach allows the easy adaptation of the experiments to the needs of the specific measurement while keeping the spectrometer aligned and optimized with the beamline. At BElChem, modularity is implemented on different levels (see Figure 3).

The top level of modularity is a complete experimental module including the analysis chamber, and all ancillary equipment required for an experiment, such as gas dosing equipment, product analysis instrumentation, and/or complementary analytical techniques. These standalone modules are mounted on their own detachable frame and can be a fully operational setup for experiments that do not require synchrotron radiation. This has the advantage that reaction conditions can be optimized, preliminary experiments conducted, and users trained on the actual piece of equipment to be used, thereby increasing the efficiency and productivity of beamtime. An added advantage of using independent experimental modules is the reduction of cross-contamination between various experiments. Such experimental modules must have standardized interfaces to the spectrometer, spectrometer frame, and beamline. These interfaces have been defined so that experimental modules can be mounted on both BElChem-PGM and BElChem-DCM endstations, as

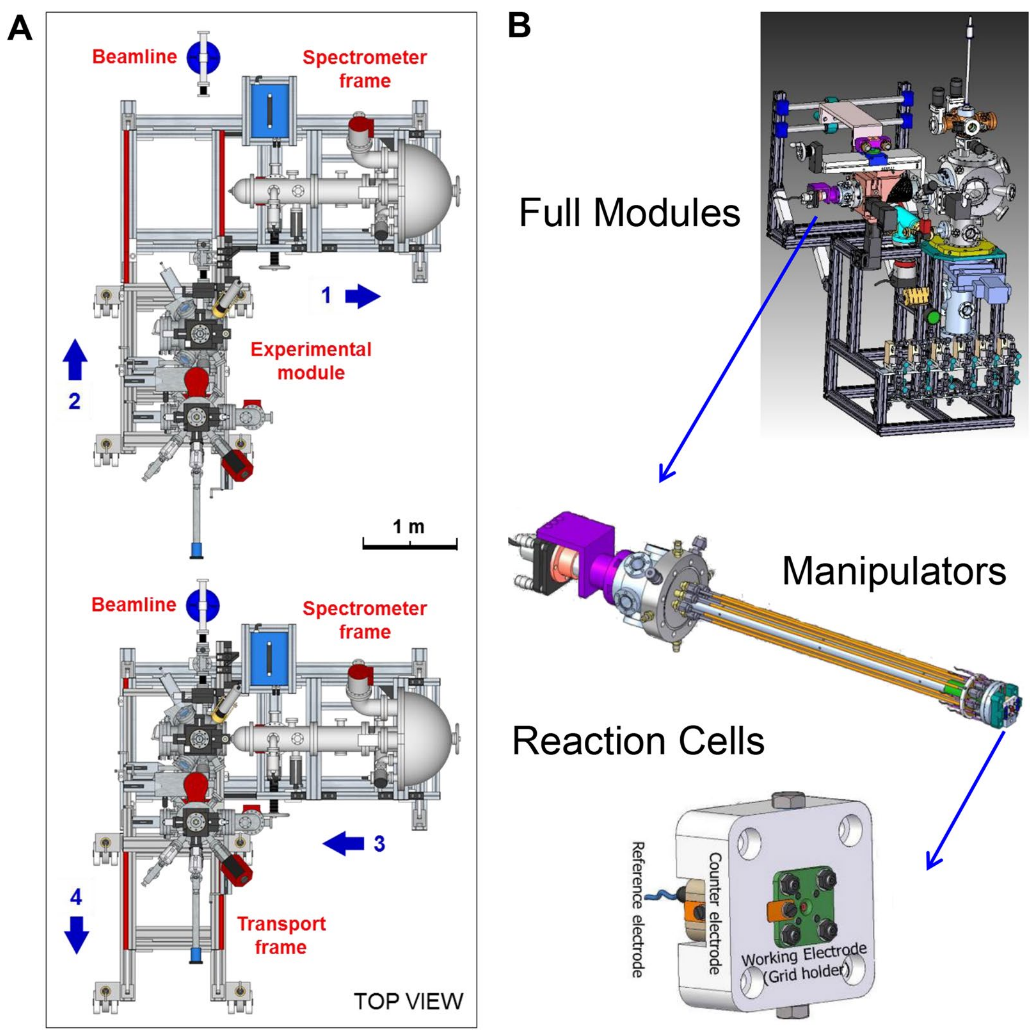

Figure 3: Schematic presentation of the modularity offered at the BElChem facility: (A) Experimental modules are exchangeable onto and off of the spectrometer frame. (B) Different levels of modularity at BElChem: Full modules, manipulators or manipulator rods, and reaction cells or inlays.

well as other facilities operated by the Max-Planck Society at BESSY II, including the ISISS and CAT@EMIL facilities. External user groups are welcome to develop their own modules specifically tailored for their experiments of interest.

At BElChem, two additional levels of modularity are available (Figure 3). First, manipulators on existing analysis chambers can be easily replaced by user manipulators. This allows users to develop their own liquid supply, sample heating and cooling capabilities, and construct specific sample exchange systems, while still being able to use the existing endstation equipment, such as gas dosing, product analysis, and additional analytical techniques. Currently, manipulator exchange between the BElChem-PGM and BElChem-DCM modules is not possible, due to restrictions of the existing experimental modules. The manipulator on the BElChem-DCM modules is a top-mounted DN100-CF flange, whereas on the BElChem-PGM the interface is through a standard DN63-CF gate valve. At the BElChem-PGM endstation, another option is to simply bring a rod with a sample stage that can be mounted directly on the installed manipulator. This approach has recently been successfully used, for example by Kooser et al., at the ISISS station. A description of the dual chamber reaction cell of this group is given in [8].

The smallest unit of modularity that can be easily exchanged is to replace the sample stage by individually designed devices or "inlays." This option is frequently used to implement reaction cells in a "cell in cell" approach where a smaller reaction cell is operated inside the surrounding analysis chamber that mainly serves as an interface to the beamline, spectrometer, and analytics. An example of this cell-in-cell approach is given by Falling et al. [9] for a solid-liquid interface reaction cell used for electrochemical studies. This shows the versatility of such an approach in that the cell can even be used in different instruments, such as NAP-XPS and environmental scanning electron microscopy, ESEM. A similar approach is available at the BElChem-DCM endstation, with a newly developed 3-electrode H-cell ("cell in cell" approach) that can be used in both static and flow conditions [3]. The manipulators implemented at the BElChem-PGM facility offer a standardized interface disk with up to four tubing connections that, for instance, can be used to directly dose gases or liquids to the inlay. Also, four insulated electric contacts are available and up to two thermocouple type-K connectors. This "inlay" option offers the easiest and most cost-effective way to create individual reaction environments and can be used to adapt the NAP-XPS spectrometer to user sample carrier systems that are not standard in the BElChem-PGM facility. Again, all inlays are interchangeable with the other NAP-XPS stations operated by the MPG at BESSY II ("ISISS" and "CAT@EMIL").

Spectrometers and endstations

The BElChem-DCM beamline serves the SpAnTeX (Spectroscopic Analysis with Tender X-rays) endstation. Currently, two experimental modules are operated at the SpAnTeX endstation: (1) the "Dip-and-Pull" module, which is used to study electrified solid/liquid interfaces relevant for (photo)electrocatalysis; and (2) the "Droplet Train" module where nanoparticles in solution, in particular semiconducting nanoparticles used to drive photocatalytic reactions, gas uptake by liquid solutions, and bulk liquid reactions, are investigated. The key component of the SpAnTeX endstation is a SPECS PHOIBOS 150 HV NAP (Near Ambient Pressure) spectrometer [10]. The spectrometer consists of a differentially pumped electrostatic pre-lens and lens system and a 180° hemispherical analyzer with 150 mm mean radius, and is capable of detecting photoelectrons with kinetic energies up to 10 kV. A 3 D delay-line detector (DLD) enables time-resolved NAP-HAXPES studies using a continuous tender X-ray source, with sub-ns time resolution. In addition, using a new plug-in lateral resolution entrance nozzle and lateral resolution lens mode, we recently showed that the SpAnTeX endstation enables laterally resolved measurements under realistic working conditions ($p \geq 20$ mbar) at a resolution of 30 μm or better [10].

The endstation of the BElChem-PGM beamline currently serves four experimental modules: the "electrochemical module" and three standard modules, which are used for the investigation of electrochemical reactions and heterogeneous catalytic reactions, respectively. The endstation is equipped with a homemade differentially pumped NAP spectrometer based on a modified SPECS PHOIBOS 150 electron spectrometer using a 2 D delay-line detector [11].

Hutch

The BElChem-PGM and BElChem-DCM facilities are enclosed in individual hutches that share a common wall (see Figure 4). The ISISS station (Innovative Station for In-Situ Spectroscopy) is located next to the BElChem hutch, which allows an easy exchange between the BElChem and ISISS endstations. The BElChem-DCM hutch provides facilities for the operation of the SpAnTeX endstation and the storage and testing of one additional module. Ample workbench space is available for the preparation of the experiments. In-situ NAP-XPS spectroscopy demands the flexible supply of reactive gases to the NAP-XPS experiment. This must include flammable (e.g., hydrocarbons), toxic (e.g., carbon monoxide), and corrosive gases (e.g., ammonia). The gas supply at BElChem will include permanent gases (Ar, He, N_2, O_2, CO, CO_2, H_2) in safety cabinets outside the hutch and the option to install up to four extra gases in a separate safety cabinet for the BElChem-PGM laboratory. This combination provides permanent high-quality availability of standard gases with the flexibility to add gases specifically needed for individual experiments. The sophisticated gas management and gas safety system implemented in the BElChem hutches, in combination with the separation of the BElChem ventilation system from the surrounding BESSY experiment hall, is optimized for automatic and non-supervised operation of the BElChem-PGM endstation and beamline. This special feature of the BElChem-PGM facility provides options for a wide range of in-situ remote operation modes that are unique for synchrotron facilities. The control room for the BElChem-PGM endstation is separated from the experimental room to allow for safe control of the beamline and endstation. Another rather unique feature is the availability of a preparation lab within the BElChem hutch and directly connected to the BElChem-PGM lab. This preparation

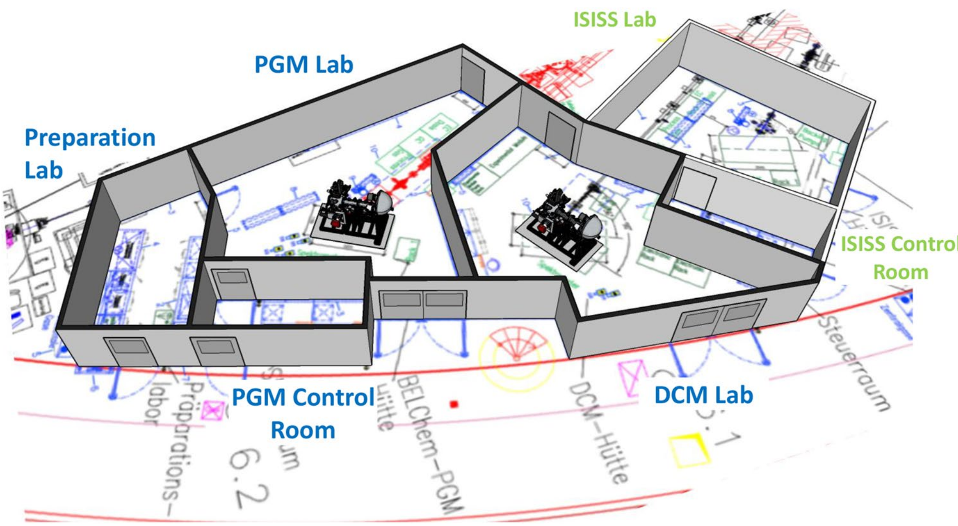

Figure 4: Planned layout of the BElChem hutches at the BESSY II synchrotron in Berlin, Germany. BElChem consists of the PGM and DCM Labs, PGM Control Room, and the Preparation Lab. BElChem will be located next to the ISISS facility, which is operated by the Max-Planck Society. Background floor plan used with permission from Dr. Heinekamp, GmbH.

lab contains, among other equipment, a fume hood, safety cabinets for chemicals, and workbench space to prepare electrolyte solutions. Balances and pellet presses are available as well.

User support

The BElChem facility staff from both the Max-Planck Society and the Helmholtz-Zentrum Berlin is available for providing help and advice. User support will be provided for preparation of the experiment, performance of the measurements, and advice on data analysis. The users are invited to come to the lab to perform test experiments in the modules, which can be operated as standalone units. They can optimize the conditions of the heterogeneous catalytic- or (photo)electrochemical reaction, conduct preliminary measurements, and get trained in using the modules prior to beamtime to make their beamtime most efficient. In the future, a lab focused exclusively on providing offline testing and optimization of modules will be constructed. This future facility will have five stations equipped for testing five individual modules simultaneously.

Summary

The Berlin Joint Lab for Electrochemical Interfaces (BElChem) at the BESSY II synchrotron provides state-of-the-art facilities for the investigation of (photo)electrochemical interfaces using NAP-XPS and NAP-HAXPES. A central concept of the BElChem facility is modularity. Modularity is built-in on multiple levels, from stand-alone experimental modules to small reaction cells, allowing users of BElChem great flexibility in tailoring experiments for their research needs. Combining this modularity with the wide photon energy range covered by the beamlines, BElChem enables a wide range of experimental possibilities. Infrastructure allowing the use of different gas types further broadens the experimental scope of BElChem. Offline testing facilities will allow users to optimize their experiments and experimental conditions prior to beamtime, leading to increased efficiency and productivity of the X-ray-based experiments. We look forward to many exciting years of research on electrochemical interfaces at BElChem and encourage external users to join us on this fascinating journey!

Acknowledgments

The authors would like to gratefully acknowledge the staff at the BESSY II synchrotron in Berlin, Germany. They would also like to acknowledge members of the sample environment group, in particular Dr. Bastian Klemke, Dr. René Grüneberger, Dr. Matthias Neeb, and Dr. Klaus Kiefer.

Funding

Funding for part of the BElChem Joint Lab was provided by the Helmholtz Association through the Helmholtz Energy Materials Foundry (HEMF, GZ 714-48172-21/1) and from the BMBF through the CatLab project (Förderkennzeichen 03EW0015A). This support is gratefully acknowledged. ■

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