Electrochemistry / Geochemistry Group Report for XIS Workshop, Jan. 10-11, APS, ANL.

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Interfacial chemistry is a wide area of science covering electrochemistry, geochemistry, catalysis, polymer science, and tribology, most of which have impacts directly related to energy and environmental sciences and industrial technologies. This working group is comprised of scientists from US and Europe who are mostly interested in such buried interfaces. Excitement existed among the participants for the prospect of the availability of new x-ray capabilities, substantially improved compared to capabilities that previously existed at other synchrotron sources or the currently operating beamlines at the APS. We anticipate that the new capabilities will meet the needs of the ever-expanding interface science community.

This report summarizes the new x-ray capabilities for this community and the associated technical specifications for the APS upgrade plan, specifically the upgrade plan for surface/interface sciences. The new capabilities include surface-interface resonance x-ray scattering (RSXS), x-ray reflection interface microscopy (XRIM), and surface-interface coherent x-ray scattering (CSXS). We summarize the necessary beamline characteristics, diffractometers, detectors, software, ancillary equipment, laboratories, associated staff support, and relationship and opportunities with internal and external programs and initiatives.

Beamline Optics Including Additional Performance

- **Energy range and bandwidth**

Surface-interface resonance x-ray scattering[1,2,3] applied to chemical processes at interfaces requires a variable-energy, fixed-exit, high-energy-resolution monochromator, scannable from 4 keV to 40 keV with 10^{-4} or narrower bandwidth. This monochromator setup must be capable of delivering a fully spectroscopic-quality x-ray beam, with an added requirement of beam-position stability of ~10 microns over 1 keV energy scan range. This requirement is compatible with the specifications of the variable-energy undulator beamline in the current upgrade plan document (CD-1). The energy extremes, from 4 to 6 keV and between 30 and 40 keV, are currently poorly served as beams produced at those energies either have low flux or are unstable for reliable energy scanning. There are many elements in this energy range (e.g., Ca, Ti, Cs, Ba) that are important for this community and the monochromator must perform reliably to access those elements.

There are several additional capabilities, which are not specifically mentioned in the CD-1 document. These additional capabilities that this group recommends range from a minor addition to a significant development project. This group recommends considering these additional capabilities as much as the resources are available. Some of these capabilities may overlap with other interest groups. The options may be considered widely over all the available sectors and interest groups.

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[2] Y. S. Chu, H. You, J. A. Tanzer, T. E. Lister, and Z. Nagy, Phys. Rev. Lett., 83, 552 (1999)
[3] C. Park, P. A. Fenter, K. L. Nagy, N. C. Sturchio, Phys. Rev. Lett. 97, 016101 (2006)

Polarization tunability: This capability can be added by inserting a diamond phase plate. This addition is a minor addition to the existing CD-1 plan. The phase plate option was already well developed for XMCD or magnetic scattering. This capability enables the control of the linear polarization with respect to the surface normal. Resonance surface x-ray scattering depends on polarizations,[4,5] even for non-magnetic scattering. The p-polarization is generally more sensitive to the chemical state of the surfaces and the s/p difference signal is particularly useful for measuring the presence of low-Z species chemically bound to the surfaces. The ability to measure both polarizations nearly simultaneously by a rapid polarization switching will be a simple yet powerful addition to RSXS technique. In addition, the phase plate can be used for magnetic x-ray reflectivity measurements, under water or under gaseous conditions, or even under (user-provided) magnetic fields.

Polychromator and multilayer monochromator: Substantial reductions in RSXS data collection times (by at least a factor of 30) can be achieved if a polychromator[6] is used instead of the scanning monochromator. Using a multilayer monochromator (or pink beam optics), a ~1% broad-band beam can be fed to the set of polychromator crystals, either in reflection at low energy or in transmission at high energy, to produce an energy-dispersive fan of radiation focused on the sample. Using a six-circle diffractometer in a vertical scattering geometry, the in-plane fan of x-rays can be effectively detected without loss of the energy information by an array detector. A simple polychromator was previously tested at Sector 11/12 (formerly BESSRC) for fast spectroscopic measurements. With recent development of x-ray optics, the technique can be further improved and optimized for the RSXS technique. This enhancement would make possible RSXS measurements of interfacial processes in real-time. It will also makes the data more reliable to compare them under different chemical conditions since the energy scans can be performed with no moving parts.

X-ray reflection interface microscopy[7] needs energy selectability even though the measurements are performed at a single fixed energy. This will allow optimization for each measurement. For example, liquid-solid interfaces are best studied using photon energies of ~17 keV, while vacuum-solid or air-solid measurements might be optimized at ~10 keV. With the energy selectability, differential resonant dispersion can also be employed to image elemental (and potentially) chemical heterogeneities at interfaces by imaging at two energies, i.e., near and far-from an absorption edge of a specific element. Additional capability of the medium-band monochromator below will significantly improve the image quality of XRIM.

Medium-band monochromator will substantially increase the image quality. XRIM is normally done with a high resolution monochromator. Our preliminary calculations indicate that a band-width of 10^{-3} would maximize the useful flux delivered to the sample while minimizing chromatic aberrations and enable real-time XRIM measurements. Schemes for producing this bandwidth are available. This medium-band monochromatic beam can be obtained by careful design of multilayer optics as demonstrated at CHESS and elsewhere. A suitable and convenient set of optics scheme must be developed and implemented.

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[5] A. Menzel, et al., Europhys. Lett. 74, 1032 (2006)
[6] Pascarelli, et al., J. Synch. Rad. 13, 351 (2006)
[7] P. A. Fenter, C. Park, Z. Zhang, and S. Wang, Nature Physics 2, 700 (2006)

Coherent surface x-ray scattering is an excellent choice for one of the fixed energy hutches as CSXS does not require scanning energy. Generally, the horizontal single-bound monochromator provides the most coherence-preserving optics for coherence scattering. Compound or Kinoform[8] lenses will significantly improve the intensity with little added complexity to the beamline design. These lenses can be used with or without the standard KB mirrors. More importantly, this setup imposes no limit in using the hutch as a normal surface scattering line with KB mirrors only. However, coherence drops rapidly at the 3rd and 5th harmonics and the primary undulator harmonics of ~10 keV or less will be desirable. The option of CSXS leads to 10/30/30 (or 8/24/24, if we decided to go a lower energy) options in terms of energy selections for the fixed-energy hutches. Use of the off-axis 2nd harmonics can also be considered to offer the 10/20/30 option, even though the focusing may be compromised.

X-ray emission spectroscopy from interfaces is an additional capability for chemically sensitive interface measurements. Surface-sensitive high-resolution x-ray emission spectroscopy[9] can yield chemical state of the interface or interfacial region, more sensitively than any other x-ray-in/x-ray-out techniques. However, high-resolution analyzer that can collect a sufficient solid angle for improved signals can be challenging, and data collection can be time consuming. Nevertheless, this technique can provide chemical information that no other technique can provide for buried interfaces. This is an *option* to consider.

Hard x-ray photoelectron spectroscopy[10] is gaining popularity in Europe and in Japan. There are various workshops focused on this electron-based interface-sensitive technique. This technique is brought up by J. Zegenhagen for our community to consider. We are aware that this technique is in part covered by other communities, but XIS community's involvement on the development of this technique was strongly recommended. Development and availability of this technique, either in our community or jointly with other community, will significantly enhance our ability to examine the chemical nature of the interfaces.

- **Beam size, divergence, and focusing requirements**

The key word here is *flexibility*. Our group will benefit broadly from a flexible beam size, divergence and focusing. The needs described below are required elements of the variable-energy line, with some aspects desired components of the fixed energy stations as well. Beam size/divergence needs to be controlled and tuned for the specific experiment. For non-resonant and resonant scattering, focus size is chosen based on issues of sample size and beam sensitivity. For a polychromator system in RAXR, the use of transverse focusing will be needed to disperse the beam so that resonant modulation can be seen on an area detector. The shape and divergence of the incoming beam can be a critical issue for polarization-dependent measurements. Our group neither needs nor intends to use a nanofocused beam. Our requirement for the focusing is typically down to ~10 microns. However, it is important to maintain flexibility in focusing, i.e., by using the secondary source. In particular, for XRIM, details of the

[8] K. Evans-Lutterodt et al., Phys. Rev. Lett., 99, 134801 (2007)
[9] Bergmann et al., J. Synchrotron Rad. 8, 199 (2001)
[10] S. Thiessa, C. Kunzb, B. Cowiea, T.-L. Leea, M. Reniera, J. Zegenhagen, Solid Stat. Comm. 132, 589 (2004)

focusing and divergence are critical to the imaging process, and need to be optimized carefully. Therefore, the flexibility in focusing optics is critical for XRIM.

- **Detectors**

This group recognizes that detector developments are critical to enable robust measurements, especially usingn energy-dispersive detectors and 2D pixel detectors.

Energy-dispersive detector: Currently, Vortex detectors of various form factors are widely used and significantly better than previous energy-dispersive detectors in relatively small form factors. They are particularly effective and efficient at lower energies (below ~15 kV). However, the efficiency of the Vortex detector decreases rapidly for high x-ray energy where Ge detector is desirable. Ge detectors, however, were designed and developed for stationary applications such as spectroscopic fluorescence measurements. They are usually too heavy and cumbersome to be mounted on a detector arm of ordinary diffractometer. Therefore, it is desirable to develop a small form factor detector with higher energy stensitivity, and/or to include more robust detector arm on the diffractometer that will accommodate the Ge detectors.

2D detectors: the directly detecting CCD detectors currently used for coherent scattering has a significant limitations in terms of quantum efficiency and saturation levels. Also, they have no energy discriminating capability, which results in high background. The CCD detectors in general suffer from the lack of photon counting capability (leading to an intrinsic dark background), and are easily damaged. More recent Pilatus detectors address some of the limitations of CDD detectors, but their pixel size is still too large for many applications. It is our understanding that a new generation of array detectors is currently developed by European collaborations, known as MAXIPIX. This pixel detector represents a significant improvement with a smaller pixel size, higher saturation level, and low- and high-pass filters. Our group is extremely interested in this new development and recommending APS to explore a way to acquire the MAXIPIX[11] including collaborations with ESRF as needed. Additional detector development of area detectors that are efficient at higher energies (e.g., 20-40 keV) are also needed.

- **Hutches and experimental stations**

Need a flexible hutch that is fully "vented" (i.e., like a hood). It would be ideal if the hutch is designed to incorporate needs for chemical research. This could be enabled by having a chemical lab space (including hood, sink, ultra-pure water) adjacent to (and perhaps in) the hutch, along with the capability of portable glove boxes for radiological and atmospheric sensitive samples.

Toxic or Flammable Gas Handling: Hutches intended for use by the electrochemical and geochemical communities require air handling systems to ventilate inert gasses used in sample cells and chambers to prevent unwanted exposure of samples to O_2, CO_2, or other reactive gases. A capability to allow for use of H_2, CO, and other gases with flammability or toxicity concerns should be built into the relevant hutches as well.

[11] http://www.esrf.eu/UsersAndScience/Experiments/TBS/ISG/maxipix

Vibration and Temperature Stability: As for all scattering experiments minimization of sample vibrations and drift from thermal expansion and contraction is important. Diffractometers should be stable and not warp or rock when motors are moved over their designed angular range. This is critical when using small samples (e.g., 1 mm or less) in a flow-through cell with a vertically-focused beam needed for preventing spill-off. Temperature stability warrants careful consideration as hutches often have many heat sources that can raise their temperature above ambient conditions. As kinetic behavior will be explored in many future experiments, relevant hutches should be well ventilated or climate controlled to maintain a stable temperature. Diffractometer motors, especially those associated with the sample mounting stage, should not generate substantial heat or must be actively cooled to prevent heat conduction, especially to small samples in environmental cells. The hutch also needs a capability to handle heat produced during deliberate sample heating such as in hydrothermal cell.

Chemical Handling: This community requires one or more hutches at the new sector designed with chemical handling in mind. The hutch should be designed similar to a wet chemistry laboratory. A bench near the diffractometer should be available for mounting of peristaltic pumps, recirculators, pH meters, and similar equipment need for in situ electrochemical and geochemical studies. The diffractometer should be configured so that minor chemical spills, such as from a leaking sample cell, do not contaminate the instrument. Systems should be established to monitor chemical instrumentation from outside the hutch and also to remotely control fluid handling equipment (e.g., remote control of syringe pumps for fluid injection into sample cells). A system should also be developed to mount samples in a controlled gas environment on the diffractometer.

- **Laboratory requirement**

Substantial laboratory space is a critical need for this community. Two specific needs have been identified:

Wet Chemistry Laboratory: A laboratory equipped for wet chemistry is needed with multiple fume hoods, substantial bench space, and a stable temperature. An ultrapure water system (Type 1+) that can produce deionized water with a resistivity of 18.2 MΩ·cm and a TOC of <5 ppb should be available in the wet chemistry lab. The lab should also provide at least two glove boxes for sample preparation at the sector. One should be configured for low O_2, CO_2, and water content for electrode preparation. The other should ideally be a flexible design that maintains anaerobic conditions for geochemical studies when needed but is also capabale of working with other gas head spaces, such as 1 bar of CO_2. Space should be provided for chemical storage for users and basic chemicals common to users, such as common solvent, simple salts, and standard acids and bases, should be kept in stock. The ideal lab will also have equipment for crystal surface preparation for users. Desired equipment includes a basic polishing wheel, muffle furnace, tube furnace with alumina or ceramic tube, and a UV-ozone cleaner.

Capability for Handling Samples with Trace Radiological Components: The geochemical community would benefit from a capability to handle samples with trace radiological components at the APS. The ideal configuration would be a glove box stored in the hutch that would allow for manipulation of samples, such as immersion in a dilute uranium solution. The samples could then be sealed in sample

cells in the glovebox and returned to the diffractometer (following appropriate swipe tests). Alternately, this need could be served by a laboratory at the APS where samples containing trace levels of radionuclides can be manipulated. At present, the handling of radioactive samples can only be done at the Actinide Facility (in CSE), but this capability cannot be accessed readily in the evenings and weekends when the special materials staff is unavailable. For most experiments, this comprises most of the beamtime an XIS user receives at the APS, and this places substantial limits on productivity. The XIS community should coordinate with other user communities to explore possible training and laboratory options.

- **Off-line characterization facility and instruments**

Our group also needs access to basic offline characterization tools. These include AFM/STM, XPS, XRD, etc. Access to such characterization methods in a larger facility, such as a new materials institute or at the CNM would be perfectly acceptable and in fact preferred. These facilities do not need to be specific to the XIS sector; XIS users just need access to such instrumentation. The APS is encouraged to coordinate with other facilities at Argonne to establish a facility that users may access to perform offline sample characterization.

Equipment pool: Similar to the detector pool, an equipment pool will be useful. Equipment needed includes various in-situ cells, potentiostats, and other generic temperature controlling devices such as heaters and cryostats.

- **Software support**

Software support by the APS for the users at the beamline to perform preliminary assessment of the on-going data will significantly improve the productivity of this group. We are aware that the APS already assembled an APS-wide software-support team. Therefore, it will be important to assemble and maintain programs and software that are commonly used among various user groups. For example, program modules or macros specific for 2D Pixel detectors include on-line data treatment/reduction : ROIs of various geometry, operation as 0D (point) or 1D detector; on line data reduction, e.g. peak integration, half-width, position; necessary correction algorithms; Q-space mapping of data; visualization programs. Also, similar programs or macros must be available for spectroscopic detectors include: On-line peak extraction, peak fitting, handling of ROIs, batch handling of data, visualization software. For on-line data evaluation: COBRA and/or direct method software should be available from different groups (Marks, Lyman, Moritz, Torrelles, etc) but the interfaces to those programs can be further improved. Also, programs of phase retrieval methods via oversampling are of interest in our group. In addition, various higher level software for the web-based data browsing and monitoring will be very much desirable.

- **Anticipated staffing requirements**

This group is mostly associated with the variable energy line, which makes up ¼ of the users of the sector. The minimum requirements for this portion of a new sector includes ~ ½ support engineer for the off-line support lab(s) such as chemistry lab and surface preparation and characterization laboratory

and the beamline instrumentation, ½ technician for day to day maintenance of the lab and equipment, 1 staff scientist dedicate scientific support of the users, and 1.5 postdocs or 1 postdoc plus 1 student who can work with the staff scientist and/or users for collaboration and facility improvement. Additional staffing will be needed for support of the fixed energy line for coherent scattering measurements.

- **Potential partners**

Under the topics energy research, environment, corrosion, and similar industrial partners can be found. Because of economic and social relevance strong outreach programs can be developed, possibly for acquisition of funds. Strong link with theory groups is desired e.g. for ab-initio structure calculations (DFT or similar), resonant scattering theory for our group. Below, we listed the ANL initiatives relevant for our group's interests.

- Alternative Energy and Efficiency : Solar energy
- Energy Storage : Battery research and energy conversion (e.g. hydrolysis)
- Materials for Energy : Oxides for solar hydrolysis