The Next-Generation Pair-Distribution-Function Beamline (NG-11IDB)

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Beamline mission: *The NG-11IDB beamline will continue as the world leading instrument for Pair-Distribution-Function (PDF) measurements, with extended capabilities for simultaneous SAXS, and powder diffraction measurements. The NG-11IDB Beamline will allow complex structures to be probed covering the angstrom to the submicron length scales to explore functional materials properties, particularly on materials under in-situ, operando, and extreme conditions.*

Primary Technique: PDF
Combined Techniques: SAXS, & Powder Diffraction

We propose upgrading the infrastructure and enhancing the capabilities of the 11-ID-B beamline (currently the only dedicated X-ray PDF beamline in the world) to a next generation world-class instrument for the simultaneous study of structure both on the local length-scale (with PDF, Q_{max} ~40Å^{-1}), nanometer length-scale (with SAXS, Q_{min} ~0.01Å^{-1}), and long-range length-scale (with powder/Rietveld ($\Delta Q/Q$ ~ 8 x 10^{-4}). This upgrade represents a direct response to emerging needs in the characterization of functional materials identified by the Department of Energy, amongst which are the areas of hydrogen storage and production, and materials development for catalysis, battery technology, and energy storage. This upgrade proposal seeks to balance both the *emergent science drivers* with *technical advances* in instrumentation, to ultimately yield what will remain a world class resource for materials research over next decade. In doing so, we significantly enhance the current scientific program, respond to current developing needs for investigation of structure, and simultaneously extend into entirely new scientific areas.

Emerging Scientific Drivers

The need to address emergent technological needs has driven researchers to explore increasingly complex functional materials. The pool of new materials with potential technological applications has risen far faster than our ability to fully characterize each material. Thus, the largest remaining obstacle in the push for truly *rational* materials design and development is rapid multi-lengthscale characterization. Once a researcher discovers an interesting material that they would like to characterize and identify a suite of methods (for example, PDF, SAXS, and powder diffraction) they would likely need to submit multiple beamtime proposals, and make several trips over a period of up to a year. By rationally combining measurement needs, this proposal seeks to offer an instrument that is transformative in the science it will enable. While it is expected all materials research would benefit from such an instrument, we highlight four areas of major impact:

Catalysis: The reactivity of heterogeneous catalysts relies both on the control of short range and structure on the nano-meter length scale.

Battery Technology: The push to develop batteries that charge/discharge rapidly has driven materials design to focus on nano-sized materials for application both in anodes and cathodes.

CO_2 Sequestration: The need to sequester CO_2 has lead to the investigation of geological formations as reservoirs. For example unminable coal seams have been identified as a candidate. Here interest is in both how CO_2 binds to coal (short range interactions) and how the microstructure is perturbed (i.e. does the coal swell and fracture?).

Extreme Conditions: Non-ambient studies provide fertile ground for the formation of new materials. Extreme conditions, including pressure, can induce disorder in crystalline and nano-crystalline materials.

Time-Resolved Structural Changes in Heterogeneous Catalysis:
The President's call for a hydrogen economy has resulted in an increased drive to develop an economically and technologically viable supply of hydrogen, and the fuel cells and hydrogen storage materials necessary to make it a functional energy source. Pivotal to this goal is the fundamental understanding of catalytic hydrogen production from petroleum and of fuel cell catalysis. The understanding of the associated structure-activity relationships, at the molecular level, will enable the rational development of catalytic materials with improved capabilities. A vital question in heterogeneous catalysis remains the structure of nano-scale particles, the understanding of their formation, and how their structure is perturbed under reaction conditions. This has lead to the drive to develop and apply time-resolved PDF measurements. However fitting of the time resolved PDF data for particle size/shape does not yield a unique answer, and has lead us to propose incorporation of simultaneous SAXS for the irreversible time resolved reactions of interest in catalysis. By incorporating a secondary probe that interrogates size and shape of nano-particles we will be able to fully answer the questions, *How do catalytic nano partcles grow? How is there structure perturbed during catalysis?*

Energy Security-CO_2 sequestration and Alternative Fossil Resources:
Global warming is an issue that stands at the forefront of world interest and will likely become a driving economic and political force in the 21st century. The realization that CO_2 emissions must be curtailed while maintaining energy production has lead to a drive to develop economically viable routes to sequester CO_2 in geological formations. Amongst potential candidates are unminable coal seams, depleted oil fields, and saline formations. However crucial questions remain that will ultimately mitigate the potential for long term sequestration of CO_2. *How is CO_2 bound in geological formations? Does the sequestration of CO_2 alter the structure of the formations? Does chemistry convert CO_2 to solid carbonates?* These questions require detailed *in-situ* structural studies, probing both how CO_2 binds and how it perturbs the structure of the host material. These studies need the synergistic information provided by the PDF/SAXS/powder approach, to probe the binding interactions of CO_2, the structure of the host, and the composition and structural of crystalline mineral components.

Local Structural Drivers in Energy Storage - Advances in Battery Technology:
New applications such as hybrid electric vehicles, power backup and power tools require rechargeable batteries that combine high energy density with high charge and discharge rate capability. The current generation of lithium-ion batteries (LIBs), while meeting many of the criteria required for lap-tops and other portable electronics, are too slow to charge and discharge, and are associated with safety issues. Materials particularly suited to the approach include intermetallic anode materials (eg. InSb and Cu_6Sn_5), which are often nanoparticulate in size, either initially or following electrochemical cycling, and transition metal oxide cathode materials (eg. $LiFePO_4$, $LiMO_2$). Structural changes not only occur on the short range scale during charging/discharging but also on the nano-meter length scale as internal particle stresses build and can cause fracturing of large particles.

Pressure Dependent Structural Response of Functional Framework Materials:
When either pressure or stress are applied to matter, atoms are brought closer together, ultimately altering a material's structural, electronic and mechanical properties in radical and often unexpected ways: pressure causes proteins to unfold, s-metals to become d-metals, materials to reach their yield strength, and phase transitions, including amorphization, to occur. Non-ambient

studies provide fertile ground for the formation of new materials, the measurement of mechanical properties in crystalline and nano-crystalline materials. This is evidenced by myriad new transitions in the most basic materials, such as H_2, H_2O, nano-materials and glasses, and classes of new materials (eg. metal-organic frameworks) have yet to be explored at high pressure. *Entirely new classes of substances and phenomena are appearing under compression, and understanding their functionality requires precise in situ studies of their atomic structure in their crystalline and amorphous states.*

Added Value of the Midterm Upgrade

Multi-lengthscale characterization: Dedicated detectors and flexibility in their positioning will allow higher values of momentum transfer *Q* (40 Å-1) to be investigated, to distinguish bonds of similar length (<0.1 Å) using PDF analysis. Simultaneous SAXS patterns will be collected, and will retrieve information on the sub-micron length scales, while high resolution powder diffraction will allow phase identification and transformation to be investigated.
Time resolved studies: The fast readout of the detector (as fast as 30 Hz) allows irreversible chemical reactions to be probed, from the angstrom to nanometer length-scale.
High-sensitivity experiments: the fast readout of the detector effectively increases the dynamic range by allowing measurements to be averaged over large periods of time to probe weakly scattering or highly dilute features such as those encountered in solutions or hydrogen storage systems.
Simultaneous crystal structure analysis: The ability to offer a high resolution position-sensitive-detector (PSD) for high resolution powder diffraction will allow extension into other scientific areas, eg. ceramics, strongly correlated electron systems, high-T_c, etc. These have need for both local structural information and a mechanism to probe subtle phase transitions with powder diffraction.
Discriminating sample scattering: The incorporation of a radial collimator system will allow samples scattering to discriminated from strongly scattering environments. This will enable samples in gas pressure cell/PE cells to be discriminated form the strong scattering of the sample environment.

Expected User Communities

Materials chemistry: solid state chemistry, nano-scale materials characterization, high throughput screening, ceramics.
Condensed Matter Physics: strongly correlated electron systems, semiconductors, glasses.
Energy Materials: Batteries, capacitors, fuel cells, CO_2 sequestration.
Catalysis: high throughput characterization, *operando* studies.
Extreme Conditions: The structure of materials at the extreme conditions of high pressure and high temperature.

The user community has already shown significant interest in PDF measurements and in upgrading the 11-ID-B beamline. Two proposals were submitted to DOE within the last year (with ~30 letters of support from the user community) requesting capital investment at the beamline; "*Acquisition of an Optimized Detector for High Resolution and Time Resolved Pair Distribution Function (PDF) Measurements at the Dedicated PDF Beamline (11-ID-B) at the Advanced Photon Source*," (C.P. Grey, P.I.), and "*High Energy X-ray and Neutron Scattering (HEXANS) for Studies at Extreme Conditions*," (J.B. Parise P.I.). These proposals highlight the significant interest of the user community in the beamline, and the need for continuing development through targeted upgrades.

Enabling Technology/Upgrade Infrastructure

Beamline:

Undulator: An undulator optimized for brightness at 60 keV (in vacuum and suyperconducting device options will be explored).

Decoupled Operation*:* The upgrade will allow decoupled operation from other stations through independent insertion device. This may be accomplished through canting the undulators and increasing the length of the straight section to accommodate a third undualtor, or alternatively relocating the program to an open sector.

Primary Optics Upgrade: The primary monochrometer will be a cryogenically cooled and ideally allow different resolutions (from $\Delta E/E=1x10^{-3}$ to $1x10^{-2}$) to be readily selected.

Focusing "On Demand": Compound refractive lenses will be used to obtain a user selected focus down to 100 microns. The design will enable the lenses to be dropped in and removed as necessary during the experiment.

Experimental Station:

Detectors: Two large area (40 cm x 40 cm) detectors capable of fast readout (30-60 Hz) will be used for PDF while a smaller (20 cm x 20 cm) detector will be used for SAXS data collection. The PDF detectors will be located at a variable distance from 0.1 to 2 meters from the sample, while the SAXS detector will be located at 4-5 meters. A microstrip detector will be mounted to simultaneously collect high resolution powder diffraction data, this detector will be placed 1 meter from the sample

Radial Collimator: A radial collimator for high energy structural studies will be designed and built as part of the upgrade. This will enable strong scattering from complex sample environments to be experimentally discriminated. The largest benefit will be in the use of pressure cells, specifically gas pressure cells and Paris-Edinburgh cells.

Gas Pressure Cell: A gas pressure cell will be designed to access pressures up to 10 kbar. This will be based on a cell in use at the IPNS, and will be unique at synchrotron sources. The aluminum cell will produce significant scattering which will be discriminated with the radial collimators described above. The precise pressure and temperature control afforded by such a cell will allow novel investigations of framework properties identified for use in energy applications.

Budget

A two phase upgrade is proposed that will both maximize scientific impact and minimize potential reduction of user operations. Phase I will focus on the experimental station and will take approximately 8 months to complete. This will be followed immediately by Phase II, upgrades to optics, and "things behind the wall," with estimated time to completion of 4 months. Phase II requires significantly more engineering support and lead time for acquisition of components. These costs do not include engineering or software support.

Phase I: Detectors (*600k*), Computing Support and data storage (*200k*), stages/hardware (*200k*), ancillary equipment (*500k*)

Phase II: Monochrometer (*300k*), focusing optics (*200k*), "things behind the wall", i.e. undulator/front end (???k)