

APS Renewal Chemical Sciences and Engineering

Team Members

Jeff Miller (ANL)

Simon Bare (UOP)

Pete Chupas (ANL)

Jim Penner-Hahn (UMich)

Debbie Myers (ANL)

Lynda Soderholm (ANL)

Nenad Markovic (ANL)

1. Executive Summary

Science context

The characterization of solutions, interfaces and nano-particle samples will play a central role in both fundamental and applied Chemical Science and Engineering in the near future. Among others, new challenges will be to provide new, abundant, and environmentally safe energy for the nation. Solution and nano-material sciences offer great potential to create novel materials with tailored properties that strongly depend on the specific hierarchy of chemical or physical components, organized at different length scales. The function and behavior of these new materials can, therefore, only be understood if their microscopic structure and dynamics are known over all length scales down to the molecular and atomic levels are known. Synchrotron X-ray techniques provide unprecedented level of structural detail, even on materials lacking long range order, typical of those in Chemical Science and Engineering. The primary techniques will be diffraction, scattering, and absorption spectroscopies, in both static and time-resolved modes. For systems and materials of importance to Chemical Sciences and Engineering materials it is include measurements under *in situ* conditions such as elevated temperatures, pressures, and applied potentials, as well as in reactive and corrosive solutions.

Key questions

X-ray based synchrotron techniques can provide the unrivaled, multilevel information necessary to explore structural correlations over a broad range of length scales to answer high impact scientific questions such as:

1. What determines the structural details of complex catalytic nano-particles and how these change under differing reaction conditions?
2. How do structure, morphology, size, support and promoters, etc., affect performance including catalysts capable to new chemistry and with selectivities approaching that of biological systems?
3. What is the atomic level spatiotemporal structure of a working catalyst in a catalytic reactor?
4. How does the structure of a solution-electrode interface impact the chemistry, efficiency and stable delivery of reactions including those important to electrical power in fuel cells?
5. What novel, non-noble metal nano-particle compositions and synthesis methods to produce high efficiency fuel cells?

6. How does solution chemistry of metal-ion speciation, including coordination, ligation and oligomerization, affect chemical reactivity, electrode and electronic response, and solubility?

New capabilities are necessary that will help scientists to understand and find answers to questions such as those listed above by providing unique information on the quantification and chemical state of complex structures of nano-particles, solution complexes, the interfacial boundary of solid-solid, solid-gas, solid-liquid and liquid-liquid, as well as trace elements at unprecedented sensitivity and spatial resolution, and, ultimately with time dependence. Hard X-rays include the added benefit of enabling specific sample environments so that real systems in their near native environments can be studied.

Expected user communities

Chemical Sciences and Engineering addresses scientific questions over a broad range of disciplines. Research groups in industry, academia and national laboratories have extensive research programs in these areas. The unique information provided by the techniques at the APS provides the greatest level of detail and understanding for many problems. While most scientists perform their analysis with laboratory methods, it is not always possible to analyze samples under *in situ* conditions. While improved capabilities will attract new users, wider availability of beamlines with gas handling and other equipment needed to make *in situ* measurements will greatly increase the number of users in the Chemical Sciences and Engineering field.

2. Introduction

Catalysis

Catalytic technology is essential for economic prosperity, energy security and environmental preservation in the 21st century. Catalytic science and technology has an extraordinary impact on the U.S. economy and the quality of life with applications to the fields of agriculture, transportation, petroleum refining, chemicals, batteries, fuel cells, electronics, health care and environmental stewardship. The Department of Commerce estimates that about 90% of chemical manufacturing processes, and nearly 30% of all manufactured goods, in the U.S. are dependent upon a catalytic process to achieve the desired combination of economics and functional performance.

The importance of catalysis research to meet the energy needs of the nation and the central role of DOE facilities in advancing catalytic sciences has been specifically identified in the Energy Policy Act of 2005. The world demand for energy is expected to double by the year 2050. Compounding this challenge is the growing need to protect our environment by increasing energy efficiency and developing clean, safe renewable energy sources. The solution to these challenges is vital to our future energy security, to address global climate change, and for continued economic prosperity. Recent reports on *Basic Research Needs to Assure a Secure Energy Future* and *Basic Research Needs for the Hydrogen Economy* (DOE, Office of Basic Energy Sciences (BES)) have recognized that solutions will require scientific breakthroughs and revolutionary developments. Within this context, nano-science and nano-technology present exciting and requisite approaches to addressing these challenges. Moreover, from the BES DOE's recent reports entitled *Basic Research Needs: Catalysis for Energy, Solar Energy Utilization,*

Clean and Efficient Combustion of 21st Century Fuels, and Research Needs for the Hydrogen Economy, it is clear that catalysis will play a major role in advancing the research and technology needs for the nation. As part of the reports on specific research needs, DOE also identified five Grand Challenges for Science and the Imagination. Mastery of catalysis and catalytic systems will require advancement in all five of these challenges. The development of future technology will result from the synthesis of new catalytic materials, with the properties of unprecedented activity, selectivity and stability.

Fuel Cells

Within the overall context of the critical role catalysis plays in energy-related technologies is the electro-catalytic conversion of chemical energy to electrical energy within a fuel cell. Due to its ability to efficiently convert fuels to electrical energy at low temperatures, its high efficiency and power density, the polymer electrolyte fuel cell has the greatest potential to replace the internal combustion engine in vehicles, eliminate or greatly reduce greenhouse gas emissions, and decrease world dependence on petroleum-based fuels.

The successful deployment of advanced fuel cells depends critically on the development of new materials that can meet the demanding performance requirements under extreme conditions of high voltage, temperatures and corrosive electrochemical environments. The two most significant challenges to the widespread implementation of this promising technology are the high cost and limited durability of the platinum and platinum alloy nano-particle cathode electro-catalyst. Though Pt loadings have been drastically reduced in the past decade by reducing particle size, alloying, and nano-scale structuring of the catalyst particles (e.g., base metal core-Pt shell), further advances are necessary to achieve practical costs and sufficient catalyst durability. These advances are only obtainable through rational design based on composition-structure-activity-durability relationships. Significant improvements are needed in the *rational-design* of the structures of advanced materials that can efficiently transform chemical energy of hydrogen, hydrocarbons and oxygen into electrical energy. Materials development for energy conversion systems operation has been treated primarily as an empirical, trial-and-error endeavor with limited understanding of the underlying physical and chemical phenomena, limited *predictive* capability to tailor the active sites, and inadequate understanding of stability of these sites under the reaction conditions. There is also limited understanding of the fundamental, molecular-level, processes associated with O-O, H-H, O-H, and C-H bond making and bond breaking events at inherently multi-component electrochemical interfaces. To date, experimental tools and theory have not adequately addressed the complexity of multi-electron reactions and the formation of short-lived reaction intermediates. There is an urgent need to extend the limited capability of connecting chemical and physical properties of interfaces to the nano-scale structure and understanding the unique properties of *metal-electrolyte interfaces* on the basis of the atomic-level structural features. The strategic goal is to acquire fundamental understanding of atomic/molecular level interactions that occur at electrified solid-liquid interfaces. This fundamental knowledge will eventually lead to the design and synthesis of selective, robust, impurity-tolerant, low-cost, and highly-efficient tailored nano-scale electro-catalysts for fuel cell electrodes, thereby assisting in achieving one

of DOE's mission goals for "*Revolutionary advancement in electro-catalysts and dramatically enhanced energy transfer in fuel cell systems.*"

Solution Chemistry

Aqueous solutions containing dissolved metal ions have historically been viewed as homogeneous systems in which a solute (a metal ion for example) is evenly distributed in a solvent (water). There is mounting evidence that this description is often inadequate and that significant solute organization can occur¹ with a measurable impact on a wide range of behaviors ranging from metal solubilities and reactivities to chemical separations. Dissolved metal-ion speciation, including coordination, ligation and oligomerization, plays a central role in chemical reactivity, electronic response and solubility. Solute organization, including ion pairing, can dominate solute energetics and reactivity and therefore must be included in attempts to understand and predict solution chemistry, particularly in the areas of metal reactivity, precipitation reactions, and interfacial partitioning between solution/solid and solution/solution phases. This chemistry plays a critical role in a wide variety of energy-related technologies, including catalysis, the environmental fate and transport of heavy metal ions, and the separation of metal ions for purification and use. A necessary first step to a predictive understanding of metal-ion solution chemistry is a comprehensive picture of metal ion speciation. This picture is currently in its infancy and needs to be developed to adequately assist theorists and modelers in a wide variety of technology areas.

3. Key Science Drivers

Catalysis by Nano-scale Materials

Catalysis controls the rates at which chemical bonds are formed and broken, thereby controlling the yields of desired products over undesired ones in chemical reactions. Catalysis is, therefore, central to energy conversion and environmental protection, as well as contributing to a healthy economy. Achieving a high degree of selectivity in catalysis is recognized as a crucial challenge for the coming decades. While nature attains near 100% selectivity with enzyme catalysts, such selectivity in synthetic systems is rarely obtained. Nano-particles and nano-structured (single-site) materials offer new avenues of controlling catalytic function. The geometrical structure and electronic properties of nano-scale catalyst particles play a major role in selectivity; therefore, highly controlled particle-size distribution, composition and morphology is essential. Furthermore, at the nano-scale, the catalytic rate and selectivity of metallic, alloy and oxide nano-particles cannot presently be predicted from the properties of the bulk materials.

It has long been known that the oxide surface and promoters also has a strong influence on the performance of the nano-particle, but how these alter the performance of the nano-particles is largely not understood. The most significant research challenge needed to address these issues is to create (and characterize) interfaces and nano-structures that are tailored to optimize catalyst performance. The possibilities include fabricating interfaces using a wide variety of materials and chemical combinations, along with interface shapes patterned at the nanometer length scale. To accomplish this, a diverse array of synthesis methods ranging from top-down lithography through self-assembling materials growth,

wet-chemical processing, and biological assembly must be combined to create novel structures. In parallel, experimental techniques for nano-scale characterization must be developed and used to relate structure and function. Finally, during reaction, the operating environment, e.g., gas composition, temperature, pressure, etc., alter the surface composition. Few methods provide the structural and electronic details that allow for a fundamental understanding of how these properties affect the performance.

The research challenge for catalysis is learning to tune the nano-particle properties to control the chemical reactivity. Future catalysts will not only enable new reaction pathways, but will control the product selectivity with unprecedented selectivity. For example, catalysts with very high selectivity would eliminate the need for additional catalytic process steps or separations, thus significantly improving energy efficiency and reducing cost. Drawing from the lessons of biology, nano-structured materials must be designed to match both the structure and conformation of the reactants to control the reaction pathway to the desired product. To accomplish this, new and efficient methods of *in situ* characterization combined with rapid high throughput testing of catalytic properties will be required. The choice of materials, structural parameters, and the experimental design must be guided by a continually improving fundamental understanding of the structure-function relationships of the nano-structured catalysts.

Electro-chemical Fuel Cells

The major challenges for the development of a new generation of materials required for the efficient energy conversion in fuel cells is to develop fundamental understanding of metal-electrolyte interfaces. The activity depends on their atomic-level properties.² These properties include oxidation state, particle size, local atomic environment of the reactive site, electronic structure, inter-atomic bond lengths, and short-range order.³ Characterization of these properties, especially while the catalyst is in the reactive environment, allows a correlation of these properties with activity, identification of the active catalyst site, an understanding of degradation mechanisms, and ultimately improvement of the catalytic activity and durability. For example, identification of the active site allows synthetic methods to be tailored to maximizing the density of these sites, leading to higher catalyst specific and volumetric activities. Characterization of oxidation state and particle size in the reactive environment also provides critical knowledge regarding degradation mechanisms and the link between operating conditions and degradation which allows tuning of catalyst composition and operating conditions to extend lifetimes. In addition, determination of the catalyst atomic structure during synthesis, such as during the heat-treatment step for converting the precursors to metals and alloys, provides critical knowledge on the temperature necessary to form the desired phase but limit nano-particle growth. It is also of paramount importance to determine the mechanisms that control the microstructure, activity, and stability of nano-structured materials that are certain to find application in the next generation of fuel cell systems. To reach this goal, we need to resolve relationships between the *structure*, *chemical nature*, and *composition* of the electrochemical interface and its *activity* and *stability*. To address these challenges, we have to learn how to: (i) *create* novel states of catalytic materials by manipulating their surface electronic and crystal structure; (ii) *characterize*, at the nano-scale, atomic and electronic properties of nano-structured interfaces by developing and using ex-

situ and in-situ surface characterization techniques and state-of-the-art theoretical methods to explore structure/function relationships; (iii) *understand*, at atomic/molecular level, fundamental principles that govern efficient bond-making and bond-breaking at electrochemical interfaces; and (iv) *optimize* the active sites by an iterative process, guided by the fundamental understanding of structure-function relationships at multi-metallic electrochemical interfaces.

Solution Chemistry

One of the Chemistry Grand Challenges is to understand, predict, and control the behavior of dissolved metal ions in solution. The basic first step in realizing this challenge is a comprehensive picture of speciation, specifically the structure of ligands surrounding the ion of interest. Unfortunately some of the most powerful analytical tools for structure determination, X-ray and neutron diffraction require long-range correlations for their application and thus are not useful for solution work. Recently single-ion probes such as NMR and EXAFS have broadened our knowledge of solute environments, even in dilute solutions. EXAFS has emerged as the tool of choice for probing metal-ion speciation in solution because this tunable, single-ion spectroscopy can be used to directly determine oxidation state, coordination number, and, in selected cases, coordination symmetry.⁴ An emerging frontier for EXAFS is the routine application of time-resolved EXAFS to characterize solution reactivity. Over the last decade, the development of relatively inexpensive, easy to use stopped-flow UV-visible spectrometers has revolutionized the study of inorganic chemistry, allowing inorganic chemists to ask much more sophisticated question about the kinetic (and ultimately, the mechanistic) properties of their materials. It is now becoming possible to extend these techniques to EXAFS, and this promises a similar advance in the detailed understanding of chemical kinetics (particularly if UV-visible and EXAFS stopped flow can be combined on the same system).

Although EXAFS is broadly applied to many solution-based problems, it is not able, except in unusual situations, to give statistically reliable coordination information beyond the first coordination sphere, so that any ion-ion correlations at distances longer than about 0.4 – 0.5 nm are not consistently revealed by EXAFS studies as demonstrated in Figure 1 (left). This information is critical for characterizing solute-solvent interactions, and consequently the characterization of solute-solute and solute-solvent correlations has largely been limited to indirect techniques including colligative properties measurements, such as vapor pressure osmometry, and spectroscopic techniques such as UV/visible, Raman and infrared spectroscopies.

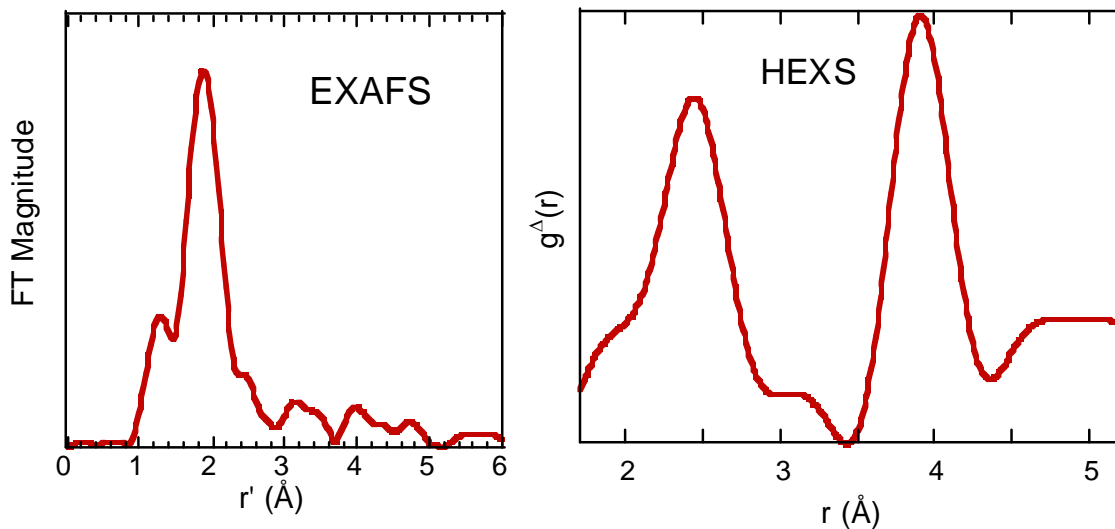


Figure 1: A comparison of Fourier transformed EXAFS (left) and HEXS (right) data taken on the same Th solution. The peak at 4 Å in the HEXS data is attributable to Th-Th interactions, which are not observable in the EXAFS data. Not explicitly shown is the higher resolution available in the EXAFS data, which allows the observation of splitting within the first coordination sphere.⁵

Understanding these correlations is particularly important when studying oligomerization, aggregation and precipitation reactions, which require information at distances longer than those of the first coordination sphere. Secondly, coordination numbers are usually significant only to about $\pm 10\%$, an error too large for many applications. For example, information about the coordination number of a lanthanide ion in solution often requires discerning whether the ion is 8 or 9 coordinate, a question that is not unequivocally resolved with EXAFS spectroscopy.

The research challenge for solution chemistry is to extend our understanding of self-assembly and correlations that occur in amorphous systems and at their interfaces with either a solid or another solution. This understanding needs to include an accurate means of assessing first coordination sphere ligation of a solute ion, oligomeric interactions, ion pairing, second and more distant coordination spheres. The data needs to include distances, and the nature and number of ligating ions. Within solutions themselves, self-assembly and ordering of ions or molecules at interfaces is important in many biotic and abiotic processes. Phase transfer catalysis, pharmaceutical drug delivery, many electrochemical processes, nano-particle synthesis and numerous chemical reactions take place at the interface between two immiscible liquids. Important environmental processes that rely upon interactions at interfaces include tertiary oil recovery, solvent extraction of radionuclides from nuclear waste, and permeation liquid membranes used for the cleanup of ions in the environment. For example, biological membranes at aqueous-aqueous boundaries provide are fundamental to cell chemistry and processes. In the area of separations science, a cornerstone to the chemical industry, solvent extraction and other metals separations technologies rely heavily on the transfer of metal ions across an interface.

4. Significance of the APS

Understanding solution and materials chemistry requires knowledge of structure at the atomic level. Most of the standard structural characterization tools provide high-quality information on bulk, periodic, or crystalline materials. Equally high-quality characterization is needed for amorphous materials, solutions, and complex nano-structures. Synchrotron-based techniques can now be used to characterize samples irrespective of their state of crystallinity via different scattering and spectroscopic methods. X-rays are providing structural details at length scales that encompass local structure about an ion to the long range ordering present in well formed crystalline materials and have found applications in solutions, glasses, liquids, poor-quality crystals, powders (which can be multiphase), assemblies of micro-crystals, adsorbed surface layers, etc. Moreover, the evolution of structure under reaction conditions is also an important feature of a catalytic system that needs to be investigated and understood. Techniques most often used for analysis of catalytic materials include X-ray diffraction and scattering, pair distribution function (PDF), small angle scattering (SAXS) and X-ray absorption spectroscopy (EXAFS and XANES).

Current APS Techniques and Potential Upgrades in Capabilities

Synchrotron X-ray powder diffraction (SXRPD) is a core-competency for structural analysis of catalytic nano-particles. The major application of SXRPD is structural analysis of new catalytic materials using Rietveld refinement (e.g. zeolites and mixed oxides). In recent years, there has also been much interest in *in-situ* catalyst research. Having a beamline with capabilities for *in-situ* measurements would be highly advantageous to the catalysis community since many metallic nano-particles are highly oxidized in ambient air. There is also an urgent need for X-ray diffraction analysis on nano-particles smaller than about 5 nm. For example, precise identification of the alloy phase in nano-particles is often not possible. In addition, bimetallic catalysts may contain several structurally distinct phases and determination of the fraction of each is also currently not possible. Therefore, the determination of the fraction and structure of each phase in multi-component, nano-particle catalysts is crucial for identification of the catalytically active phase. Also, often nano-particles in bimetallic catalysts form alloy phases, which are not known in bulk compositions. Similarly, new structures may occur in bimetallic catalysts, e.g., core-shell nano-particles, which do not occur in bulk phase. Development of *in situ* SXRPD for determination of the structure and composition of 1-5 nm oxide and metallic nano-particles would provide unprecedented level of detail and lead to a new level of understanding about the structure and function of catalytic surface.

The atomic Pair Distribution Function (PDF) is the real space representation of the scattered intensity. The PDF directly recovers structural parameters in the form of a distribution of atom-atom correlations (i.e., inter-atomic distances) with a spatial resolution considerably finer than the length scale of a chemical bond ($\sim 0.1 \text{ \AA}$) and extending out to distances as far as several nanometers.^{6,7} Measurements up to high values of Q are needed to obtain high resolution PDF's, which necessitates the high flux of high energy, X-rays ($>60 \text{ keV}$) available at the APS. Recent work performed at the APS using area detectors has demonstrated PDF measurements as fast as 30 milliseconds,

i.e. orders of magnitude shorter than conventional experiments.⁸ With this time resolution and by measuring PDF differences between loaded and unloaded supports, meaningful *in-situ* PDF studies on nano-particles are now possible, which allow both the local and intermediate-range (1-4 nm) structure of supported clusters to be probed directly and simultaneously. A specialized application of PDF, the differential PDF (D-PDF) approach, is ideally suited to directly probing support nano-scale catalysts, as it allows the selective recovery of only the atom-atom correlations arising exclusively from the catalyst particle (i.e. only those involving the atoms of the catalytic clusters deposited on the support). It can be obtained by direct subtraction of a reference PDF for the bare support from that of the cluster/support complex. Differential PDF measurements can be used to monitor the structural changes of supported particles that occur under realistic reaction conditions. *In-situ* measurements are possible under realistic catalytic conditions using specially designed flow cells that enable gas flow across samples with heating up to temperatures of 1,000 °C.⁹ PDF is complimentary to other scattering techniques and can be combined with simultaneous SAXS measurements to yield information not just regarding local structural changes but also particle shape.

When applied to high surface area and flat catalytic materials, SAXS and GISAXS, respectively, can provide both *ex-situ* and *in-situ* information on cluster size, shape and inter-particle distance. The ability to compare the two classes of materials will validate the formation of identical structures on the two support morphologies. GISAXS can also give depth profile information, and the aspect ratio (height/diameter) of a cluster can be calculated from the GISAXS data to obtain the interfacial energy using the Wulff-Kaishew construction.¹⁰ The GISAXS experiments are performed in a reaction chamber equipped with a heated sample holder and gas introduction system mounted on a goniometer. Products can be monitored by mass spectrometry and gas chromatography. During heat treatment, scattering data can be collected as a function of time and temperature.

Anomalous SAXS, or ASAXS, offers an extension to standard SAXS experiments in which the energy of the probing X-rays is tuned near the absorption edge of an element in the sample. By performing SAXS experiments near the characteristic absorption edge of any given atom, it is possible to vary the contrast for scattering by that particular element. This method overcomes the problem of separating the scattering of clusters from that of the support, or a second metal center. For the first time anomalous GISAXS have been obtained on Au metal clusters on surfaces¹¹. This approach has also been used also for Pt (L-edge) and is possible for both Pd and Cu (K-edges).¹²⁻¹⁴

X-ray absorption fine structure (XAFS) and X-ray absorption near-edge fine structure (XANES) have become the workhorse techniques for catalyst characterization over the last 30 years. The popularity of these techniques is primarily the result of their power to provide *in situ* element-specific atomic-level chemical and geometric information on the structure of real working catalysts (both heterogeneous and homogeneous). While, in general, the structure of homogeneous and supported single-site catalysts is too complex to determine by EXAFS, by analysis of the difference spectra (between the starting structure and that under reaction conditions, for example) one can follow the changes in structure during pre-treatment or under reaction. The difference spectrum indicates

which ligands were lost and by comparison with the initial structure allows for determination of the active species. Likewise the difference spectrum can allow for determination of small changes in the structure of nano-particles occur under reaction conditions. Structural details in the difference spectrum, however, require significantly improved signal to noise up to high k values. For determination of subtle structural features, significantly improved signal quality is required. Finally, accurate determination of the catalyst structure simultaneously with measurement of the reaction kinetics will allow for identification of the active nano-phase when several structures are present. Thus, it is not only necessary to obtain the analysis under reaction conditions, but also be able to simultaneously make high quality kinetics measurements.

From the XANES spectra, the oxidation state and geometry of the metal atoms may be determined. During pre-treatment, for example, from the time-dependent XANES spectra, the kinetics of reduction (or oxidation) can be determined. The kinetics of changes in structure under different reaction conditions can similarly be determined. Changes in the occupancy and energy of the d-orbitals affect the chemical reactivity and small changes are important. Changes in XANES intensity of the L_{III} and L_{II} edges are proportional to the number of d electrons. A significant improvement in the resolution of the XANES spectra can be obtained by high-energy-resolution fluorescence (HERF) XANES measurements and represents an important new capability in catalysis research. Figure 2 shows significantly enhanced intensity and energy resolution of the HERF spectra compared to the transmission XANES for Au foil.¹⁵ This method is especially important for determination of the small differences, which occur during reaction conditions.

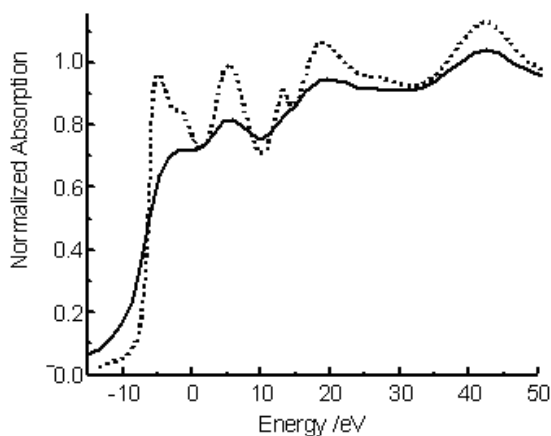


Figure 2: Comparison of the high-energy-resolution fluorescence XANES (dotted) to the transmission XANES (solid) for Au foil.¹⁵

In many catalysts the catalytically active element of interest is present in a mixture of forms. In synchrotron-based investigations as they are currently performed, the signal (spectroscopic or otherwise) is an average characterizing the various species that contain that particular element. For a fundamental understanding active catalytic species, it is necessary to be able to separate the signal characterizing the element in each of the structures and configurations. Emerging techniques such as high resolution x-ray fluorescence spectroscopy (HRXFS), X-ray emission spectroscopy (XES)¹⁶ and resonant

X-ray scattering (RIXS)^{17,18} are showing the potential for determining the local electronic and geometric arrangement of an element in such complex, non-uniform samples as typical solid catalysts. The grand challenge is to conduct such investigations of catalysts as they function in a time-resolved manner.

When a reactant adsorbs or interacts with the catalyst surface, it changes the electronic structure of the catalyst, primarily in the valence band. With a probe that can interrogate these electronic changes, the fundamentals for surface bonding can be determined. Changes to the electronic structure have been demonstrated to be measurable by careful analysis of the X-ray fluorescence spectrum (HRXFS) emitted from the sample. In particular, the K β lines exhibit a wealth of fine structure and therefore, information about the sample's valence states. For example, the energy of one of the K β satellite peaks has been shown to be directly related to whether a transition metal is coordinated to N, O, or F.¹⁶

The power of the HRXFS technique is that it then may be combined with X-ray absorption spectroscopy (XAS) to become RIXS. By measuring the X-ray fluorescence intensity as a function of both incident energy and emitted energy (or energy loss) around a particular fluorescence line, additional electronic structure can be resolved compared to the standard XAS measurement where the fluorescence is not energy analyzed. This additional structure can be related to the electron density of states.

This combination has the potential to isolate the X-ray absorption spectrum due only to the atoms interacting with the reactants, i.e., surface sensitive, and then provide data on the oxidation state and near-neighbor environment (neighboring elements and distances) of only the active atoms in the catalyst particle. The specificity of this technique already has been demonstrated for spin state, site occupation, and valence states

The integral nature in the way that EXAFS data has traditionally been collected also means that no spatial information is obtained. In many cases in catalysis there is spatial variation in the catalyst structure. What is required is spatially-resolved molecular structure information, preferably under reaction conditions. Two different approaches have recently been applied to bring spatial information to EXAFS: full field transmission micro-tomography, and scanning X-ray micro-tomography. Each of these methods has specific advantages and disadvantages, but has been demonstrated to reveal spatial information under reaction conditions for several different catalytic reactions. There is an urgent need to implement these techniques at the APS. A natural extension of this work is in the temporal domain in order to obtain spatiotemporal structural detail of the working catalyst.

Electrochemical interfaces play a crucial role in many aspects of analytical, synthetic and materials chemistry, as well as in chemical and photochemical energy conversion. In the past, these interfaces have been treated empirically with limited understanding of the fundamental, molecular-level processes associated with bond making and bond breaking events at an inherently complex multi-component environment. This has motivated the development of *in-situ* surface sensitive probes, most notably synchrotron-based surface x-ray scattering

(SXS) and scanning tunneling microscopy (STM), and since the early 1990s these techniques enabled the transformation of electrochemistry from a largely phenomenological subject into a discipline that addresses atomic/molecular-level issues in a level of detail that is to what has been accomplished in UHV-based surface science.

The SXS method takes advantage of the ability of x-rays to penetrate thin solution layer, along with simple theory of backscattering, allowing very detailed spatial information. Of particular interest has been to explore *potential-driven* phenomena at ambient temperatures, ranging from ordering, phase transitions and mobility in metal surface atoms and adsorbed layers,^{19,20} to the surface compositions and segregation profiles of bimetallic systems.^{21,22} Although such potential-dependent interfacial transformations are important, the successful deployment of advanced electrochemical systems depends critically on the development of *in-situ* methods capable of providing information on *temperature-dependent* surface structures at a level of sophistication that is equivalent to that obtained in potential-dependent studies. To overcome the existing “temperature-gap”, electrochemical SXS cells now operate over the range 275-325 K. With new temperature controlled SXS cell it will be possible to study *in situ* temperature-induced reconstruction and relaxation of surface atoms, stability of active sites and the nature of active sites, structure and nature of adsorbates and reactive intermediates.

In addition to surface x-ray diffraction, in-situ x-ray fluorescence spectroscopy (EXAFS and XANES) and wide-angle diffraction techniques are used to characterize the electronic and structural properties of multi-metallic nano-particle catalysts during (half)-cell operation. One of the main advantages of x-ray techniques is its versatility to various forms of nano-particle catalysts.

Until the recent application of high-energy (>30 keV) X-ray photons to the problem of metal-ion speciation in solution,^{23,24} X-ray scattering was essentially limited to crystalline and amorphous solids. Some early work using in-house X-ray sources, and Mo K radiation, showed the potential of the technique but the lack of both flux and Q range significantly limited the systems for study and the information obtainable.²⁵ The availability of a high flux of high-energy photons at selected third-generation synchrotrons, including the APS, brings an opportunity to enhance and further develop high-energy X-ray scattering (HEXS) as a tool for studying correlations in solution.

There are three specific advantages to the use of high-energy photons. The first advantage involves the minimal absorption by aqueous solutions, which permits data acquisition in the transmission mode, thereby limiting the need for geometric corrections. As a result, absorption effects, which can be a significant source of error in scattering or diffraction experiments conducted at more conventional energies (8 – 20 keV), are typically small enough to be neglected for higher-energy data. The second advantage, also related to the low absorption cross section is the increased stability of redox-active metal ions in the beam. Lower energy photons have a propensity to influence the oxidation state of ions in solution and thus vitiate the data. The third significant advantage gained from using high-energy X-rays comes from the extended Q -range generally available, since $Q = 4 \pi$

$(\sin\theta) / \lambda$, where θ is the scattering angle and λ is the x-ray wavelength. Thus higher energies, or shorter wavelengths, result in higher Q s for the same scattering angle. Higher Q -range data are necessary for accurate background subtraction and resolution in the Fourier transformed data. Background correlations arising from solvent-solvent interactions are the main limiting factor to the use of X-ray scattering for probing solute correlations and can be accurately removed only with the information on self-scattering that is available at higher Q . These advantages are demonstrated in Figure 1 (left).

There are two different X-ray scattering experiments of particular use in studying solutions and their interfaces. The first experiment involves the Fourier transform of background-subtracted HEXS data to provide a direct picture of solute correlations in solution. This technique has been recently used to study the solution environment of a dissolved metal ion^{5,23, 26-29} and provides evidence of remarkable organization about the solute ions. Of particular interest is the detailed information about nano-cluster formation, structure, and surface ligation, as exemplified in Figure 3. The second use is for probing liquid-liquid interfaces.³⁰ Recent X-ray surface scattering studies have determined the distribution of ions at these interfaces. These experiments are sensitive to the different chemical environments of an ion in the bulk and at the interface. High-energy scattering from interfacial ions, analogous to those just described in the bulk solution, may provide information on the local ionic structure near the interface. Such experiments can also probe the interaction of ions with molecular assemblies at the interface. This provides an opportunity to observe the effects of different solvation structures on ionic interactions.

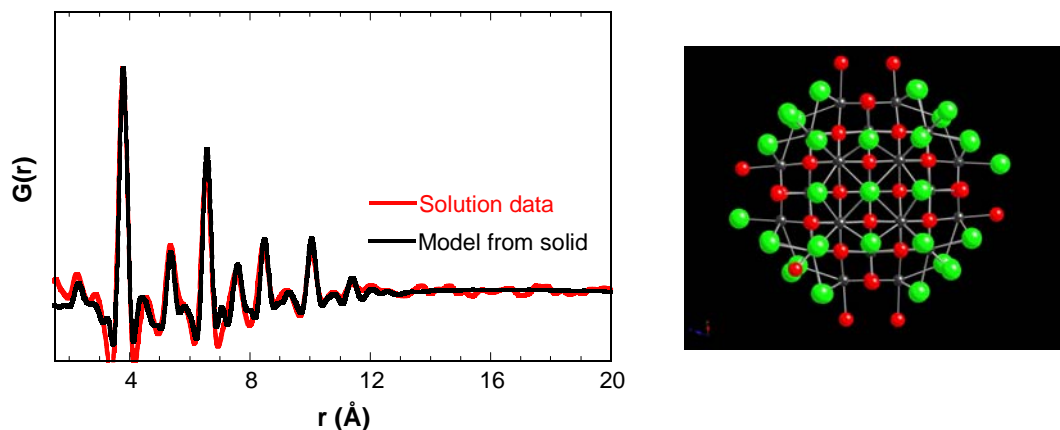


Figure 3. The FT of HEXS data obtained from a $[\text{Pu}_{38}\text{O}_{56}\text{Cl}_{54}]^{14-}$ cluster in solution is compared with a model obtained using atomic positions obtained from a single-crystal structure of the same cluster. The data were obtained on the mother liquor from which crystals were harvested, indicating that the clusters were pre-organized in solution.²⁹

Initial X-ray studies also demonstrated that surfactants at liquid/liquid interfaces behave very differently than at the liquid/vapor interface, though in a manner that is different than expected. The presence of an aqueous and an organic phase leads to strong interactions with both the polar and non-polar parts of surfactants. Depending upon the surfactant, this may lead to solvent mixing into surfactant monolayers and a re-ordering of the monolayer. X-ray studies have demonstrated the role of surfactant tail-group

flexibility, surfactant head-group interactions, and solvent chain length on interfacial ordering at both the liquid/liquid and liquid/vapor interfaces. Control of the interfacial electric field at a liquid/liquid interface allows for the investigation of electrostatic effects on surfactant organization. Additionally, chemical reactions occur between molecules solvated in the two phases that meet only at the interface.

The development of x-ray scattering from liquid interfaces has been closely tied to advances in synchrotron sources and instrumentation. These experiments usually require a very brilliant x-ray beam. Buried interfaces, such as liquid/liquid interfaces can benefit from higher X-ray energies. Focusing techniques that are optimized for the study of liquid interfaces are needed to study heterogeneous interfaces, small biological interfaces, and highly curved interfaces. Also, new time-resolved instruments are required to meet the need for studying kinetic and dynamic interfacial processes at interfaces.

5. Scientific Community

An enhanced, catalyst research beamline with capabilities for situ XAFS, powder diffraction and kinetics measurements would benefit the entire catalysis community, i.e., ANL, academia and industry. The beamline and its staff would also serve as a focal point for expanding catalyst research to other APS beamlines using advanced techniques not routinely applied to catalyst systems, e.g., SAXS, XES, XIRS and HRXFS. Development of these latter methods would position the APS as a leader in this area and attract leading scientists from all over the world. It is expected that new users would initially characterize their materials and identify appropriate systems for specialized techniques.

Throughout the U.S. and the world, there are countless research groups working to develop the enabling material in fuel cell catalysis: an oxygen reduction electro-catalyst that is less expensive and more durable than platinum.^{31,32} A few of these research groups utilize synchrotron-based X-ray techniques to characterize their electro-catalysts, however these studies are almost exclusively in environments mimicking the reactive environment or are *ex situ*. A notable exception is the catalyst development effort being led by Los Alamos National Laboratory, which encompasses many catalyst development approaches and involves many university and national laboratories. As part of this project, ANL researchers have recently developed the capability to characterize catalysts containing low atomic number elements in an operating fuel cell using XAFS at the APS. Utilizing this cell, Figure 4, ANL has recently determined the active site in a cobalt-containing catalyst. This capability would be extremely useful to other catalyst development teams around the country and around the world and it is envisioned that a dedicated APS electro-catalysis beam line could be designed and made available to these teams. The neutron source at NIST has a beam line dedicated to studies of water transport in fuel cells which has provided invaluable information for fuel cell materials design. This APS beam line would be the catalyst counterpart to this NIST beam line.



Figure 4: Cell for *in situ* X-ray absorption studies of fuel cell catalysts. Standard Fuel Cell Technologies cell hardware was machined to allow X-ray fluorescence studies of cathode electro-catalysts in an operating membrane-electrode assembly (fuel cell).

A molecular level understanding of the interactions and correlations that occur in solution and between solution phases is essential to building a predictive capability of a metal ion's solubility, reactivity, kinetics, and energetics. Until the recent availability of tunable, high-energy X-rays, this understanding has been significantly limited by the absence of structural probes. APS, with its high flux of high-energy X-rays is the ideal synchrotron source to provide this new information, which is critical to the advancement of solution chemistry. The utility of high-energy X-rays is currently being demonstrated as part of a Partner User Program (PUP-52) and has received high visibility, including an Inorganic Chemistry feature cover.²⁸ This effort is interesting a cadre of solution chemists that to date have not been part of the user base at synchrotron facilities. The extension of high-energy capabilities from simple PDF experiments to more complex liquid-liquid interfaces is expected to significantly broaden this new interest group into areas including soft matter studies.

References:

1. Antonio, M. R.; Soderholm, L., X-ray absorption spectroscopy of the actinides. In *Chemistry of the Actinide and Transactinide Elements*, Third ed.; Morss, L. R.; Fuger, J.; Edelstein, N., Eds. Springer: Dordrecht, 2006; pp 3086-3198
2. "Catalysis and Electrocatalysis at Nanoparticle Surfaces", A. Wieckowski, E.R. Savinova, and C.G. Vayenas (Eds), Marcel Dekker, Inc., New York, NY, 2003.
3. S. Mukerjee, "In-Situ X-ray Absorption Spectroscopy of Carbon-Supported Pt and Pt-Alloy Electrocatalysts: Correlation of Electrocatalytic Activity with Particle Size and Alloying", in *Catalysis and Electrocatalysis at Nanoparticle Surfaces*, A. Wieckowski, E.R. Savinova, and C.G. Vayenas (Eds), Marcel Dekker, Inc., New York, NY, 2003, 501-530
4. Teo, B. K., *EXAFS: Basic Principles and Data Analysis*. Springer-Verlag: Berlin, 1986; p 349
5. Chupas, P. J.; Qiu, X.; Hanson, J. C.; Lee, P. L.; Grey, C. P.; Billinge, S. J. L. *Journal of Applied Crystallography* **2003**, 36, 1342-1347
6. Egami, T.; Billinge, S. J. L.; Editors *Underneath the Bragg Peaks: Structural Analysis of Complex Materials*, **2003**

7. Nield, V. M.; Keen, D. A. *Diffuse Neutron Scattering From Crystalline Materials*, **2001**
8. Chupas, P. J.; Chapman, K. W.; Lee, P. L. *Journal of Applied Crystallography* **2007**, *40*, 463-470
9. Chupas, P. J.; Ciruolo, M. F.; Hanson, J. C.; Grey, C. P. *Journal of the American Chemical Society* **2001**, *123*, 1694-1702
10. Revenant, C.; Leroy, F.; Lazzari, R.; Renaud, G.; Henry, C. R. *Physical Review B: Condensed Matter and Materials Physics* **2004**, *69*, 035411/1-035411/7
11. Lee, B.; Seifert, S.; Riley, S. J.; Tikhonov, G.; Tomczyk, N. A.; Vajda, S.; Winans, R. E. *Journal of Chemical Physics* **2005**, *123*, 074701/1-074701/7
12. Vajda, S.; Wiederrecht, G. P.; Bouhelier, A.; Tikhonov, G. Y.; Tomczyk, N.; Lee, B.; Seifert, S.; Winans, R. E. *Collection of Czechoslovak Chemical Communications* **2007**, *72*, 121-128
13. Vajda, S.; Winans, R. E.; Elam, J. W.; Lee, B.; Pellin, M. J.; Seifert, S.; Tikhonov, G. Y.; Tomczyk, N. A. *Topics in Catalysis* **2006**, *39*, 161-166
14. Winans, R. E.; Vajda, S.; Ballentine, G. E.; Elam, J. W.; Lee, B.; Pellin, M. J.; Seifert, S.; Tikhonov, G. Y.; Tomczyk, N. A. *Topics in Catalysis* **2006**, *39*, 145-149
15. van Bokhoven, J. A., Louis, C., Miller, J. T., Tromp, M., Safonova, O. V., and Glatzel, P., *Angw. Chem. Int. Ed.*, **45**, 4651-4654 (2006)
16. Luo, G.; Malkova, S.; Yoon, J.; Schultz, D. G.; Lin, B.; Meron, M.; Benjamin, I.; Vanysek, P.; Schlossman, M., *Science* **2006**, *311*, 216-218
17. U Bergmann, CR Horne, TJ Collins, JM Workman and SP Cramer, *Chem. Phys. Lett.* **302** (1999) 119-124
18. P Glatzel, L Jacquamet, U Bergmann, FMF de Groot and SP Cramer, *Inorg. Chem.* **41** (2002) 3121-3127
19. Markovic, N.M. & Ross, P.N., *Surf. Sci. Reports* **45**, 117-230 (2002)
20. Markovic, N.M. & Ross Jr., P.N., *Cat. Tech.* **4**, 110-126 (2000)
21. V.R. Stamenkovic, B. Fowler, B.S. Mun, G. Wang, P.N. Ross, C.A. Lucas, N.M. Markovic, *Science*, **315**(2007)493-497
22. Stamenkovic, V. *et al.*, *Nature Materials* **6**, 241-247 (2007)
23. Soderholm, L.; Skanthakumar, S.; Neuefeind, J., *Anal. Bioanal. Chem.* **2005**, *383*, (1), 48-55
24. Skanthakumar, S.; Soderholm, L., *Mater. Res. Soc. Symp. Proc.* **2006**, *893*, (Actinides 2005--Basic Science, Applications and Technology), 411-416
25. Magini, M.; Licheri, G.; Paschina, G.; Piccaluga, G.; Pinna, G., *X-ray diffraction of ions in aqueous solutions: hydration and complex formation*. CRC Press Inc.: Boca Raton, 1988; p 267
26. Skanthakumar, S.; Antonio, M. R.; Wilson, R. E.; Soderholm, L., *Inorg. Chem.* **2007**, *46*, 3485-3491
27. Neuefeind, J.; Soderholm, L.; Skanthakumar, S., *J. Phys. Chem. A* **2004**, *108*, 2733-2739
28. Wilson, R. E.; Skanthakumar, S.; Burns, P. C.; Soderholm, L., *Angew. Chem. Int. Ed.* **2007**, *46*, 8043-8045
29. Wilson, R. E.; Skanthakumar, S.; Sigmon, G.; Burns, P. C.; Soderholm, L., *Inorg. Chem.* **2007**, *46*, 2368-2372

30. Soderholm, L.; Almond, P. M.; Skanthakumar, S.; Wilson, R. E.; Burns, P. C., *Angew. Chem. Int. Ed.* **2008**, 47, 493-498.
31. P Glatzel and U Bergmann, *Coord.Chem. Rev.* **249** (2005) 65–95
32. R. Borup, J. Meyers, B. Pivovar, Y. S. Kim, R. Mukundan, N. Garland, D. Myers, M. Wilson, F. Garzon, D. Wood, P. Zelenay, K. More, K. Stroh, T. Zawodzinski, J. Boncella, J. E. McGrath, M. Inaba, K. Miyatake, M. Hori, K. Ota, Z. Ogumi, S. Miyata, A. Nishikata, Z. Siroma, Y. Uchimoto, K. Yasuda, K. I. Kimijima, N. Iwashita, *Chemical Reviews* 107 (2007) 3904-51
33. H. A. Gasteiger, S. S. Kocha, B. Sompalli, F. T. Wagner, *Applied Catalysis B-Environmental* 56 (2005) 9-35