I08-SXM WORKSHOP – PROGRAMME

Wednesday 5th October 2011

Diamond Light Source

9:00–9:45 Registration with tea and coffee

9:45–10:00 Welcome

10:00–10:30 Conceptual design outline of the Diamond SXM BL I08
***Burkhard Kaulich**, Diamond Light Source, UK*

Beamline I08 will provide a state of the art scanning x-ray microscope (SXM), in which a focused x-ray microprobe is raster-scanned over the specimen. The central theme of the beamline is the ability to obtain morphological and chemically-specific information on a full range of materials (inorganic/organic) under conditions close to the natural environment, providing a facility that will be new to the UK. The I08 SXM combines spatial 2D resolution down to 20 nm with the capability to produce high quality spectroscopic (XANES) data for chemically-sensitive analysis, and x-ray fluorescence (XRF) mapping for trace-elemental analysis in the 250 – 4200 eV photon energy range. The potential of the I08-SXM beamline is outlined and the current status of the conceptual design of the instrument described.

10:30–10:50 Phase-sensitive imaging techniques and the role of soft x-ray ptychography for I08
***Graeme. R. Morrison**, King's College London, UK*

The extended operating energy range for the I08 beamline means that it is essential to include the capability for phase contrast as well as absorption contrast imaging with the transmitted x-ray signal. At energies above 1 keV, for many elements of interest, the phase change associated with the real part of the complex refractive index of the sample will produce a higher contrast image than one relying on absorption alone, so that phase contrast images can be obtained with a lower dose to the sample. In a scanning x-ray microscope phase contrast imaging can conveniently be achieved with a segmented detector. The sum signal from all detector elements provides an incoherent brightfield signal with absorption contrast, while image signals generated from antisymmetric detector combinations produce differential phase contrast images. Both forms of image contrast are available simultaneously from the same scan of the sample, with perfect registration between the image signals.

An extension of this idea is to record a full x-ray diffraction pattern from every position in a raster scan of the sample. If there is significant overlap in the areas illuminated by adjacent pixels in this scan, then ptychographic reconstruction algorithms can be applied to yield quantitative amplitude and phase information at spatial resolutions that can be significantly higher than size of the illuminating probe on the sample. Some of the benefits of this
approach to imaging will be considered.

10:50 – 11:10 Tea and coffee break

11:10–11:30 Cryo scanning microscopy: opportunities, approaches, and challenges
***Chris Jacobsen**, Dept of Physics & Astronomy, Northwestern University/ X-ray Science Division, Advanced Photon Source, USA*

Cryo methods offer a way to minimize but not eliminate the effects of radiation damage in studies of hydrated organic materials, as well as a way to image particular time points in chemical reactions. A brief outline of approaches to cryo scanning microscopy will be presented, and the Bio Nanoprobe cryo scanning instrument now being installed at Argonne Lab will be described.

11:30–11:50 *In-situ* nanoscale chemical imaging of catalytic solids and nanomaterials
***Frank de Groot**, Inorganic Chemistry and Catalysis, Utrecht University, Netherlands*

We discuss the present status of *in-situ* Transmission X-ray Microscopy (TXM)[1]. Nanoscale chemical imaging of catalysts under working conditions is outlined using cobalt and iron Fischer-Tropsch catalysts as example[2]. We show that soft x-rays STXM-XAS can image a catalytic system under relevant reaction conditions and provides detailed information on the morphology and composition of the catalyst material. The nanometer resolution combined with powerful chemical speciation by XAS and the ability to image materials under realistic conditions opens up new opportunities to study many chemical processes. I indicate some future directions of in-situ nanoscale imaging of catalytic solids and related nanomaterials, including the application of STXM to photonic crystals[3].

[1] F. de Groot, E. de Smit, M. van Schooneveld, L. Aramburo, Bert Weckhuysen, ***ChemPhysChem*** 11, 951 (2010)
[2] E. de Smit, I. Swart, J. F. Creemer, G. H. Hoveling, M. K. Gilles, T. Tyliszczak, P. J. Kooyman, H. W. Zandbergen, C. Morin, B. M. Weckhuysen, F.M.F. de Groot ***Nature***. 456, 222 (2008).
[3] M.M. van Schooneveld, J. Hilhorst, A.V. Petukhov, T. Tyliszczak, J.A. Wang, B.M. Weckhuysen, F.M.F. de Groot, E. de Smit, ***Small*** 7, 804 (2011)

11:50–12:10 *In-situ* electrochemial soft X-ray spectromicroscopy
***Benedetto Bozzini**, University of Salento/ Lecce, Italy*

This talk will review the *in situ* electrochemical soft X-ray microspectroscopy activities performed by the Electrochemistry Group of the University of Salento (Italy) in collaboration with the TwinMic beamline of the ELETTRA Synchrotron, aimed at developing, implementing and engineering a novel *in situ* spectroelectrochemical method for studies at the solid-liquid interface under potential control. Initially, we have tested a wet-cell with lithographed electrodes for in situ electrochemical experiments and performed morphological dynamic mapping of corroding Ag electrodes and Ag electrodeposits[1,2]. Subsequently, we developed this capability, by combining STXM, XRF and XAS, for studies of corrosion processes of metallic PEMFC bipolar plates (BP); a selection of results will be presented, encompassing the following systems: (i) Fe electrodissolution[3,4]; (ii) corrosion and re-deposition of Ni[5]; (iii) corrosion of Fe in the presence of Nafion[6]; (iv) corrosion of Ni in a room-temperature ionic liquid[7]; (v) electrochemically controlled corrosion of Fe in an ionic liquid[8]. Eventually, we have carried out tests of STXM and position-dependent XAS spectroscopy on the electrodeposition processes of Mn and Au-Mn from an eutectic ionic liquid[9], examining the anode, cathode and electrolyte region of a thin-layer of a specially designed electrochemical cell.

Our work at TwinMic has proved the unicity of soft X-ray spectromicroscopy for electrochemical materials-science investigations. This unicity lies in the possibility of acquiring dynamically *in situ* compositional, structural and morphological information at the mesoscopic scale, with time constants broadly suitable for electrochemical problems.

The potential of the Diamond SXM with improved spatial resolution and time structure will be outlined.

[1] B. Bozzini, L. D'Urzo, A. Gianoncelli, B. Kaulich, M. Kiskinova, M. Prasciolu, A. Tadjeddine, J. of Phys.: Conf. Series. 186 (2009) 012103.
[2] B. Bozzini, L. D'Urzo, A. Gianoncelli, B. Kaulich, M. Kiskinova, M. Prasciolu, A. Tadjeddine, Electrochem. Commun. 10 (2008) 1680.
[3] B. Bozzini, C. Mele, A. Gianoncelli, B. Kaulich, M. Kiskinova, M. Prasciolu, Microelectronic Engineering, 88 (2011) 2456.
[4] A. Gianoncelli, B. Kaulich, M. Kiskinova, M. Prasciolu, L. D'Urzo, B. Bozzini, Micron 42 (2011) 342.
[5] B. Bozzini, L. D'Urzo, A. Gianoncelli, B. Kaulich, M. Prasciolu, I. Sgura, E. Tondo M. Kiskinova, J. Phys. Chem. C. 113 (2009) 9783.
[6] B. Bozzini, A. Gianoncelli, B. Kaulich, M. Kiskinova, M. Prasciolu, I. Sgura, Chem. Sus. Chem. 3 (2010) 846.
[7] B. Bozzini, A. Gianoncelli, B. Kaulich, M. Kiskinova, C. Mele, M. Prasciolu, Phys. Chem. Chem. Phys., 13 (2011) 7968.
[8] B. Bozzini, A. Gianoncelli, B. Kaulich, C. Mele, M. Prasciolu, M. Kiskinova, "Corrosion of Fe interconnects in ionic liquid-based nano-PEMFC half cells studied in situ by soft X-ray microscopy", submitted.
[9] B. Bozzini, A. Gianoncelli, B. Kaulich, C. Mele, M. Prasciolu, M. Kiskinova "Fabrication of manganese oxide nanowires by electrodeposition from eutectic urea/choline chloride ionic liquid: an in situ study based on soft X-ray spectromicroscopy and VIS reflectivity", paper in preparation.

12:10–12:30 Applications of SXM in earth and environmental sciences
Sam Shaw, *University of Leeds, UK*

12:30–12:50 Examination of catalytic bionanoparticles on bacterial surfaces
Lynne Macaskie, *University of Birmingham, UK*

Bacteria can be used to reduce soluble forms of precious metals to nanoparticles of less than 5 nm diameter which are scaffolded and supported on the cell surface. These NPs have high catalytic activity and potential applications in energy, green chemistry and environment. The catalytic efficacy and specificity depends on the precise cellular localisation and local environment as well as the synergy of enzymatic manufacture and biochemical support, with the organic and inorganic 'partners' both playing crucial roles. It is also possible to biomanufacture structured core-shell bimetallics, moving towards 'designer' bionanocatalysts. As well as being able to image and analyse the catalyst surface (atomic arrangements, kinks terraces etc), which influences reaction specificity, we also need to relate structure to function, with the role of the light elements (C, S, N, P, O) within their biochemical arrangements (carbohydrate, lipid, protein) at the living/nonliving interface that are also responsible for the novel properties that we observe.

12:50–13:10 X-ray analysis of trace metals in biological samples
Joanna Collingwood, *University of Warwick, UK*

Synchrotron X-rays provide the necessary sensitivity and specificity to detect trace metals in biological tissues. Based on recent imaging and spectroscopy work at the Diamond I18 and APS ID10 beamlines, we will look at examples of how metal ion changes in neurodegenerative disorders are being investigated by microfocus X-ray fluorescence and XANES. We will also briefly consider some current challenges and potential developments in this field.

13:10–14:00 Lunch break (Diamond House Atrium)

14:00–15:00 Open discussion round on the conceptual design outline of BL I08 and experimenters' requirements

15:00 Tea and coffee (Diamond House Atrium)

15:00–16:00 Round table of the I08 User Working Group