Soft X-ray Spectroscopy Meets Electrochemistry

A new in-situ Cell for X-ray Absorption and Emission

Core and valence based X-ray spectroscopies host many well-established element specific methods to study the electronic structure of materials and to reveal information, such as oxidation state, ligand field strength, and charge transfer effects. However, when it comes to investigations with soft X-rays, which are required to study, e.g., the L-edges of transition metals like cobalt and iron or the K-edges of light elements like oxygen and nitrogen, the experimental requirements are often more challenging compared to hard X-ray based spectroscopies.

Since soft X-rays are strongly absorbed by air, experiments have to be carried out under vacuum conditions. Whereas for solid samples this requirement is straightforward, more sophisticated experimental setups are required for investigating solution or interface processes between solid and liquid. Indeed, liquids often play a significant role for studying functional materials in a realistic environment as, e.g., the catalysts for solar water splitting under in-situ conditions. For such purpose a specific in-situ cell was recently developed that allows investigating such catalysts in direct contact with liquids as an electrolyte solution and under applied voltage with soft X-ray absorption as well as emission spectroscopy.

Design of the Electrochemical Flowcell

The design of the in-situ cell is schematically shown in Figure 1. A 100 nm thick Si$_3$N$_4$ membrane separates the liquid from the vacuum surrounding and serves at the same time as substrate for the working electrode and the solid sample of interest. As a working electrode a 20 nm gold layer is deposited on the membrane. A tight sealing is achieved with a Viton O-ring. The main body of the cell consists of PEEK in order to ensure a high chemical resistivity. Via the liquid in- and outlet the liquid chamber of the cell can be filled and liquids can be circulated or replaced during operation using a peristaltic pump. A minimum liquid sample volume of 0.8 ml is required for a complete filling of the tubes and the liquid chamber.
A reference and a counter electrode are implemented into the liquid chamber. A leak-free microminiature Ag/AgCl electrode (Harvard Apparatus) serves as reference electrode, as counter electrode a platinum wire is used. For potentiostatic measurements and capacitance-voltage profiling an Emstat3+ (Palmsens) is applied, which allows a maximum current of ±100 mA in a voltage range of ±4 V.

**Soft X-ray Absorption and Emission Spectroscopy**

X-ray absorption spectroscopy (XAS schematically shown in Figure 2 left) allows obtaining information about the unoccupied electronic states. The XA spectra are recorded upon scanning the monochromatic synchrotron radiation energetically over the absorption edge of interest. When the incoming photon energy is sufficient to transfer an electron of the probed atom in the sample from a core level to an unoccupied state, the photon can be absorbed. This transferred electron leaves an empty hole, which is very quickly refilled (within the core-hole life time which is in order of a few femtoseconds) with an electron from the higher levels eventually leading to emission of a photon. The total number of emitted photons is often considered to be proportional to the absorption cross section. For the total fluorescence yield mode (TFY) the emitted photons are detected with a diode in dependence of the incoming photon energy. Sometimes this proportionality can be distorted, however, e.g., due to background effects. Alternatively, absorption spectra can be recorded in the partial or inverse partial fluorescence yield, PFY or iPFY mode, respectively. For PFY, not all emitted photons are detected, but only those with a dedicated energy, which can be correlated to a specific element as well as a specific transition in the sample. Accordingly, the photons released by the element of interest can be selected and the photons from the background which can distort the XA spectrum are omitted. For the iPFY the absorption process is monitored via an energetically lower transition. The reduction in emission originating from the lower lying transition upon scanning through the absorption
edge of interest is then used for recording inverse absorption spectra, which are less affected by background effects or other measuring artefacts. In a simple picture, the iPFY is based on watching the shadow of the probed element on a photon background. Once this shadow is inversed, it gives the XA spectrum of the probed element. For measurements in the PFY and iPFY modes an energy dispersive detector is required.

A second complementary X-ray based method is X-ray emission spectroscopy (XES schematically shown in Figure 2 right). It allows obtaining information about the occupied valence states. Upon exciting the core-electron of a specific atom in the sample with the required photon energy, a valence electron relaxes into the created core-hole which can lead to the emission of a fluorescence photon. Whereas in TFY XAS the total photon yield is collected with a single diode, in XES the emitted photons are sent to a grating that disperses them and each photon energy (corresponding to different valence state) is detected separately. In conclusion, XAS methods map partially the unoccupied states while XES maps partially the occupied states. Note that the word "partial" is used as only the states fulfilling the symmetry selection rules are to be seen. For example, if electrons from s-type orbitals are excited, p-type orbitals will be probed. Its element selectivity (e.g. oxygen, nitrogen...) and symmetry selectivity (s-type, p-type ...) make X-ray based spectroscopies powerful tools to map the local electronic states of the probed element in detail.

**The Experimental Setup**

For the above described modes of soft X-ray spectroscopy the electrochemical *in-situ* cell is implemented into the LiXEdrom setup at the BESSYII synchrotron facility. The setup is schematically shown in Figure 3. In the vacuum environment the soft X-rays from the synchrotron enter the experimental chamber and penetrate the transparent membrane of the *in-situ* cell (the membrane is transparent to the incoming photon-energy, assuming that the elements of interest are not contained in the membrane material). Inside the cell the sample interest is irradiated. A part of the emitted fluorescence photons from the sample are detected with a GaAs diode for the TFY XA measurements. For PFY and iPFY measurements as well as X-ray emission measurements a grating is used to discriminate between different photon energies, as mentioned above. In the LiXEdrom setup at BESSYII four different gratings are available that cover an energy range from 20-1000 eV. The photons are detected with a multi-channel plate (MCP) detector, which consists of a fluorescence screen and a CCD camera. Photons with higher energies result in a line on the CCD camera that lies lower than the line from lower energy photons.
For first proof of principle measurements with the in-situ cell the iterative deposition of cobalt on the gold-coated membrane surface was monitored with soft XAS and XES. For this purpose, cyclic voltammetric curves were recorded from a 10 mM solution of cobalt chloride (CoCl2) hexahydrate in water within the electrochemical in-situ cell. With a scan potential rate of 100 mV s\(^{-1}\) a sharp increase of cathodic current is observed upon scanning towards negative potentials. This increase is in literature correlated to the inset of cobalt nucleation. Accordingly, a static potential of \(-1\) V was applied to the in-situ cell for various time periods to initiate an iterative deposition process. The thickness of the resulting metal layers on the membrane was calculated with the following formula:

\[
d = \frac{M}{n \cdot F \cdot A \cdot \rho_{\text{metal}}} \int I \, dt
\]

where \(M\) is the atomic weight of the deposited metal, \(I\) is the current recorded during the deposition time \(dt\), \(n\) is the number of electrons taking part in the reduction, \(F\) is the Faraday constant, \(A\) is the area of deposition, and \(\rho_{\text{metal}}\) is the density of the deposited metal. Using this equation, layer thicknesses of \(\sim 0.05 \, \mu m\), \(\sim 0.18 \, \mu m\), and \(\sim 0.42 \, \mu m\) were estimated for 45 s, 145 s, and 345 s deposition time. After each time an X-ray absorption spectrum was recorded. Upon increasing deposition time an increase of signal intensity from the Co L-edge was observed in the spectra. The overall spectral shape could be correlated to the characteristics of a Co metal film. This effect was also observed in the X-ray emission spectra, where the emission signal of the Co L\(_{\alpha}\) and L\(_{\beta}\) was monitored.

After this successful proof of principle the cell is now available for indoor research activities as well as collaborators and users of the BESSYII synchrotron facility. With the three electrode system, electric potentials can be applied and cyclic voltammetry measurements can be carried out before X-ray experiments or in parallel. With these options it now possible to study e.g. the in-cell deposition of catalytic metal oxides directly followed by the investigation of the function of these materials in contact with a realistic electrolyte solution.

**Authors**

Dr. Kathrin M. Aziz-Lange, Helmholtz-Zentrum Berlin für Materialien und Energie Berlin, Germany
Contact

Helmholtz Zentrum Berlin
Albert-Einstein-Str. 15
12489 Berlin
Phone: 030/8062-15059