

# Probing of operating electrochemical interfaces by photons and neutrons

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**Abstract:** The operation of all electrochemical energy-related systems, such as supercapacitors, batteries, fuel cells, *etc.* depends largely on the processes occurring at electrochemical interfaces at which charge separation and chemical reactions occur. Evolution of structure and composition at the interface between electrodes and electrolytes affects all the device functional parameters including power and long-term performance stability. The analytical techniques capable of exploring the interfaces are still very limited, and more often only *ex situ* studies are performed. This sometimes leads to loss of important pieces of the puzzle hindering the development of novel technologies, as in many cases intermediates and electrochemical reaction products cannot be “quenched” for post process analyses. Techniques capable of *operando* probing of electrochemical interfaces by photons and neutrons have become an extensively growing field of research. This review aims at highlighting approaches and developing ideas on the adaptation of photoelectron, x-ray absorption, vibrational spectroscopy, nuclear magnetic resonance, x-ray and neutron reflectometry in electrochemical studies.

## Abbreviations

CP	cross polarization
EDL	electric double layer
EXAFS	extended X-ray absorption fine structure
FEL	free electron laser
FY	fluorescence yield
IL	ionic liquid
IMFP	inelastic mean free path
IR	infrared
MAS	magic angle spinning
NAP	near ambient pressure XPS (sometimes denoted as AP)
NEXAFS	near edge X-ray absorption fine structure
NMR	nuclear magnetic resonance
NR	neutron reflectometry
OER	oxygen evolution reaction
ORR	oxygen reduction reaction
PEMFC	polymer electrolyte membrane fuel cell
PZC	potential of zero charge
SANS	small angle neutron scattering
SEI	solid-electrolyte interphase
SERS	surface enhance Raman scattering
SFG	sum frequency generation
SLD	scattering length density
SOFC	solid oxide fuel cell
STXM	scanning transmission X-ray microscopy
SXRD	surface X-ray diffraction
TEY	total electron yield
UHV	ultra-high vacuum
XAS	X-ray absorption spectroscopy
XPS	X-ray photoelectron spectroscopy (in case of using synchrotron radiation often called photoemission spectroscopy)
XRR	X-ray reflectometry

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## 1. Introduction

Electrochemical energy conversion and storage systems often play a crucial role in overall performance of a wide variety of devices that occur in everyday life – ranging from portable phones, laptops and power tools – to large facilities including power/heat cogeneration fuel cell systems, railway locomotives and power grid leveling facilities.

Electrochemical energy storage systems (supercapacitors<sup>[1]</sup>, rechargeable batteries<sup>[2]</sup>), electrochemical water splitters<sup>[3]</sup> and fuel cells<sup>[4]</sup> all deal with the electrochemical interfaces at which charge separation and chemical reactions occur. The evolution of the structure, composition and chemistry at the interfaces between electrodes and electrolytes affects all the functional parameters of the device including power and long-term performance stability. This has motivated the research into the chemical processes at the interface itself and transport phenomena in the boundary layers.

The desired parameters include the (1) chemical composition at the interface, (2) chemical state of the atoms and its variations

as a results of chemical/electrochemical reactions and (3) structural evolution in the interface region. *Ex situ* studies provide only part of the information needed since the chemical reactions taking place during operation of the electrochemical devices result in intermediates and products that sometimes cannot be “quenched” for post-process studies. An in-depth understanding of the atomistic mechanisms underlying different electrochemical processes (electric double layer formation or Faradic processes involving heterogeneous electron or ion transfer) often requires recording large sets of data under *operando* conditions with temporal and, sometimes, spatial resolution. Thus electrochemical studies nowadays face a double challenge in obtaining both the necessary information selectively from the electrochemical interfaces and in recording the data from operating systems.

The analytical techniques capable of exploring the interfaces are still very limited. In most cases, electrochemists work blindly, having a difficulty in accomplishing of electrochemical data with direct experimental characterization of the chemical transformations and the structural evolution of the interface.

There are few surface sensitive and bulk sensitive tools, which might potentially address the problem. However, real electrochemical interfaces are buried, so that they are inaccessible directly to the common surface science tools. At the same time the bulk sensitive techniques suffer from a minor contribution of the interface to the signal.

Nowadays, intense research in the *operando* studies of electrochemical interfaces is observed, providing rapid progress even at its onset.

In this paper we attempt to review a range of tools that can be helpful in solving the above-mentioned problems. To help the reader navigate the analytical tools [have been divided](#) into three main groups and the basic methodology ideas for their implementation are supplied:

1. Attempts to implement the traditional surface sensitive tools with increased probing depth and/or minimized electrode or electrolyte layer thickness.
2. Application of the techniques with intrinsic interface sensitivity (surface X-ray scattering, neutron reflectometry, vibrational sum frequency generation spectroscopy, surface enhanced Raman spectroscopy).
3. Efforts at enhancing surface sensitivity for the traditionally “bulk-sensitive” techniques, such as NMR and X-ray absorption spectroscopy.

Next, to illustrate the progress in the *operando* analytical tools, we briefly summarize some achievements in electrochemical research, which became possible due to the recent development of the new tools and approaches based on x-ray and neutron probes. The techniques considered in this review are summarized in table 1.

## 2. Progress in analytical techniques observed in electrochemical interface studies

### 2.1. Surface science tools

Analyzing the materials surface from monolayer range to depths of tens of nanometers, the modern analytical tools yield different pieces of the puzzle. Although some of the methods based on ion sputtering can to some extent be informative, they will not however be considered here as the scope of this review is limited to non-destructive approaches essential for the *operando* studies of electrochemical interfaces. The electron microscopy and scanning probe tools (scanning tunneling and atomic force microscopy) are also beyond our consideration as they don't employ X-rays or neutrons as a probe.

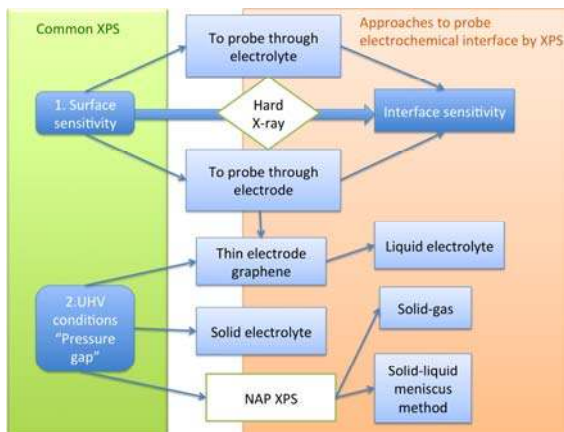
Non-destructive surface chemical analysis is mainly associated with photoelectron spectroscopy, since it is the most powerful and direct technique with which the information on chemical transformations and electron transfer can be extracted, thus to enabling tracing the reaction pathways as was brilliantly demonstrated in catalysis.<sup>[6]</sup> XPS uses the simplest one-electron process of the electron emission from the occupied ground states revealing quantitative element abundance and the chemical state extracted from the chemical shifts of core levels and valence band features.<sup>[6]</sup> Nowadays, efforts in XPS methodology and metrology are focused both on improving of a lateral and temporal resolution with the revolutionizing pump-probe approach and also on optimizing an in-depth resolution for non-destructive compositional and chemical state profiling, achieved by the variation of a photon energy or a detection angle, both of which influence the electron attenuation depth.

Today, lots of examples of the *ex situ* photoelectron spectroscopy studies in electrochemistry-related materials science can be found. In good practices the electrodes are transferred to the analysis chamber without exposure to air. The information obtained, nevertheless, is in many cases irrelevant for true interface characterization. The number of *operando* studies is however very limited, although tremendous development is currently observed in this field.

Two challenges hinder an embodiment of the *operando* XPS for electrochemical interfaces. Firstly, a low inelastic mean free path of electrons in condensed matter, from a few Angstroms to nanometers, otherwise beneficial for electron spectroscopy surface-sensitive analysis becomes seriously limited in the electrochemical interface studies, as the electrode/electrolyte interfaces are always buried. Added to that, a rather short IMFP of electrons is observed not only in condensed matter, but also in gases, giving rise to the second problem, the “pressure gap”. Experiments in surface science are normally performed under UHV implying an extremely clean environments. The analytical chambers used in surface science are thus incompatible with liquids, while the major part of the electrochemical processes in the hand-on devices occur at the interfaces with the liquid electrolytes having significant vapor pressure *e.g.* about 15 mbar for water, or about 75 mbar for acetonitrile at room temperature. The base pressure in the analytical XPS chamber on the other hand varies from  $10^{-8}$  to  $10^{-10}$  mbar.

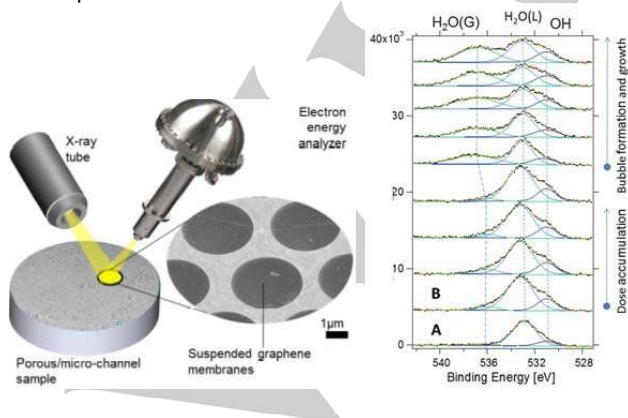
Current concepts to solving these difficulties are summarized in figure 1. Generally, two possibilities means of acquiring a signal from the interface exist, i.e. “looking” through either an electrode or electrolyte layer. Using excitation photon energies common for surface science and thus limited in probing depths, we can

investigate only the electrodes of a very small thickness (near to a single atomic layer). Scaling down the liquid electrolyte layer thickness is practically impossible. Higher photon energy can be used to probe deeper, although an essential contribution of the surface layers will still be observed due to the Beer-Lambert law.



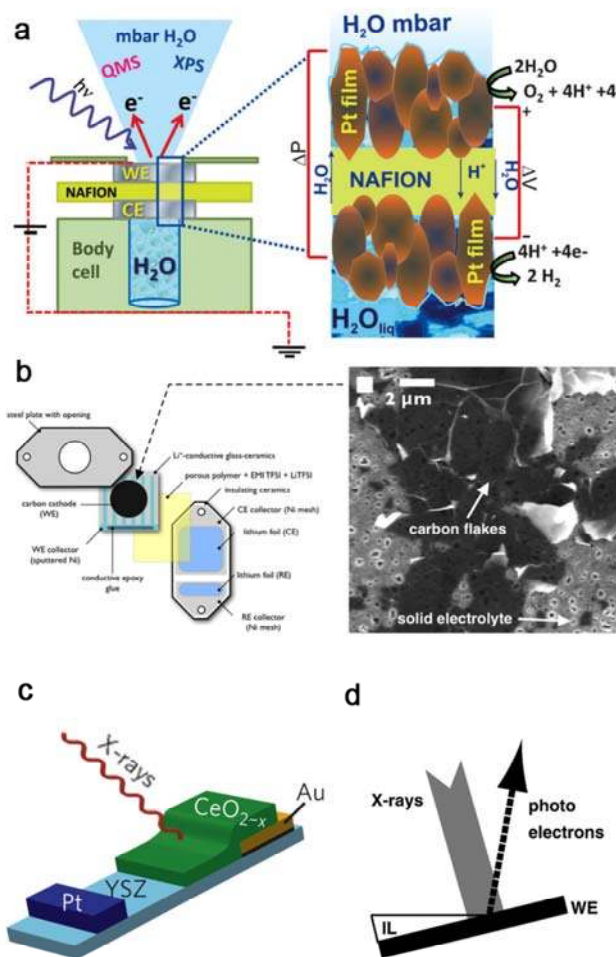
**Figure 1.** Schematic diagram of the routes used to adapt the XPS for electrochemical interface studies.

The thinnest imaginable electrode, graphene of course, which possesses high electronic conductivity, good mechanical properties, and indeed, reasonable transparency to photoelectrons excited by soft X-rays.<sup>[7]</sup> A fair degree of success has been achieved in fabricating of the cells with single or few-atomic layer graphene membranes that act as a “window” for photoelectrons. However, such a cell, which is sketched in figure 2, was only used to acquire the photoemission spectra from a liquid beneath the membrane.<sup>[8]</sup> No observations of electrochemical phenomena using such kind of membranes have been reported yet. Utilizing graphene as both window for XPS in UHV with soft X-rays and working electrode remains an attractive idea, though the problems of radiolysis of the electrolyte, bubble formation under the graphene among others, make it a challenge. Fortunately, significant progress in the preparation and transfer of the large-scale high quality graphene sheets leaves room for hope that this approach will be further developed.



**Figure 2.** An illustration of XPS observation through graphene. (a) The main concept of micro-porous substrates consisting of the high-density individual micro-volumes separated from vacuum by electron transparent membrane. The sample can be filled (impregnated) with the electrolyte. (b) Successive O1s spectra showing the temporal evolution of liquid (L) and vapor (G) components of water band; for comparison the spectrum A recorded on the graphene covered support outside the membrane is displayed. Reproduced from ref.<sup>[8]</sup> by permission of The Royal Society of Chemistry.

Utilizing harder X-rays as an excitation source for XPS makes it possible to also work with thicker membranes for the reliable separation of the liquid electrolyte from UHV. Recently the researchers were able to observe silicon anodic oxidation in aqueous electrolyte through silicon nitride 50 nm thick membrane under *operando* conditions.<sup>[9]</sup> Today such ideas partially drive a construction of new facilities, able to deliver several keV X-ray probe to the XPS end stations (e.g. EMIL facility at BESSY II).<sup>[10]</sup>



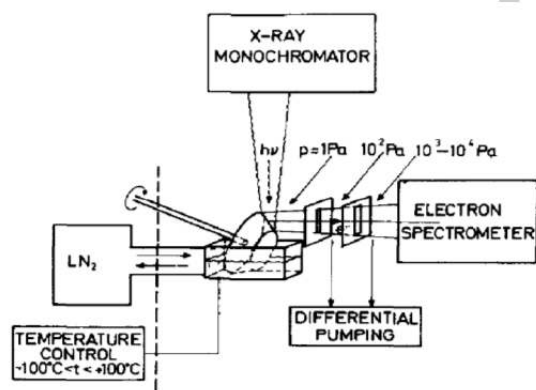
**Figure 3.** Layouts of the cells for *in situ* and *operando* electrochemical XPS using solid electrolytes: Nafion membrane (a, reproduced from ref.<sup>[11]</sup> by permission of John Wiley & Sons Ltd), NASICON-type lithium ion conductor (b, reprinted with the permission from ref.<sup>[12]</sup> Copyright 2013 American Chemical Society), oxygen conductive yttria-stabilized zirconia (c, reprinted by permission from Macmillan Publishers Ltd: ref.<sup>[13]</sup>, Copyright 2010)) or low



vapor pressure ionic liquids (d, reprinted from ref.<sup>[14]</sup>, Copyright 2012, with permission from Elsevier).

In some cases, the application of solid electrolytes enabled the investigations avoiding any liquids. These studies still used soft X-rays, and the signal was collected from the three-phase boundaries between the solid electrolyte, the electrode material that non-uniformly covers the solid electrolyte surface, and the gas phase/UHV, where photoelectron flux is registered. The idea of using solid electrolyte for the *in situ* XPS observations of electrochemical systems was for the first time proposed rather long ago<sup>[15]</sup> for the investigation of non-Faradaic electrochemical processes. Today, the Faradic processes are also monitored using the cells with solid inorganic superionic conductors as electrolytes (figure 3). The examples include the XPS investigation of oxygen reduction in solid oxide fuel cells<sup>[13]</sup> and lithium-air batteries.<sup>[12,16]</sup> Polymer proton exchange membranes (Nafion) were used for the observation of the oxygen reduction<sup>[17]</sup> and evolution<sup>[11]</sup> reactions over Pt. Molecular oxygen and water were supplied at reasonable pressures in the analytical chambers for those studies using XPS systems with differential pumping discussed below.

There are also few cases when electrochemical reactions were studied at three-phase boundaries between the electrode, UHV and a liquid electrolyte possessing an extremely low vapor pressure, namely ionic liquid.<sup>[14]</sup> Although such studies give important clues for model systems, it should be noted that they can hardly provide direct interface-related information in many cases where conventional liquid electrolytes are involved.



**Figure 4.** The schematic of the first XPS study of liquid using differential pumping approach. Setup allows studying of thin liquid layer covering rotating cone. Designed by the Siegbahn group. Reprinted from ref.<sup>[18]</sup>, Copyright 1981, with permission from Elsevier.

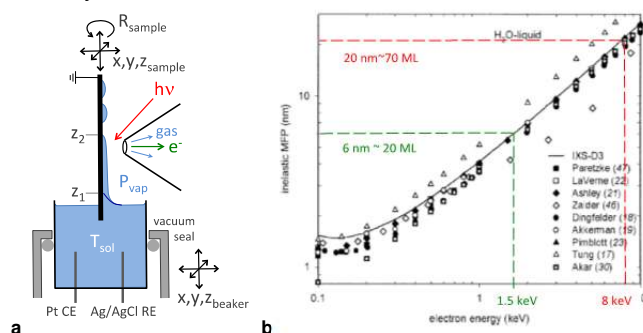
For this reason the development of a photoelectron spectrometer able to operate under liquid environments and “see” though liquids has become the “Holy Grail”. XPS applied to liquids has been in development since 1973.<sup>[19]</sup> Siegbahn et al. pioneered the use of differential pumping stage to gradually reduce the pressure and get the analyzer in a safe pressure range thus reducing the effective photon-electron path in gas

(see figure 4). However, this setup was not much developed further and was not operated at a synchrotron radiation facility. For that reasons low counts rates were detected.

Nowadays, much effort is devoted to experiments in which a liquid is introduced by micro jets injection directly into the main analysis chamber (mbar pressure)<sup>[20,21]</sup> or using droplet train.<sup>[22]</sup> These approaches are nonetheless unwieldy due to the lack of a thermodynamic equilibrium (i.e. the measured spectra always characterize a mixture of signals from gas and liquid) and impossibility of applying bias between electrodes under such conditions withal.

Another significant advance achieved in this field has been through incorporation of an electrostatic pre-lens system which increases the photoelectron transmission by up to an order of magnitude. Thus, NAP XPS<sup>[23]</sup> has become a technique that enables the study of the surface interactions under more realistic conditions compared to previous studies at UHV. Currently, the use of high brightness light sources as well as highly focused beams has substantially enhanced the capabilities of NAP-XPS.<sup>[24]</sup> In particular, the use of smaller apertures has allowed significant increases in the operation pressures up to about 100 mbar. Many researchers are trying to reach 1 atmosphere or even higher pressures in the operational photoelectron spectrometer to date, but it is still challenging technically.

While the mentioned approaches used to overcome the “pressure gap” are based on differential pumping of the electron energy analyzer system, there is another approach called “dynamic high pressure XPS”. In such setups, e.g. the one developed at ELETTRA,<sup>[25]</sup> a capillary nozzle is introduced into the analysis chamber and its tip is positioned near the sample surface. The gases are injected in a series of short pulses (few milliseconds duration), the pressure near the sample can reach up to 100 – 200 mbar. It has already been reported that such dosing allows the sample exposure in the dynamic regime equivalent to a static pressure of  $10^{-3}$  –  $10^{-2}$  mbar. Such setup have been used for the observation of platinum/phosphoric acid electrolyte electrochemical interface.<sup>[26]</sup>



**Figure 5.** An illustration of the XPS study of the interface through the electrolyte layer using “tender” x-ray (hanging meniscus method). a) Schematic of the meniscus produced by the preparation of thin liquid film. Over the presence of water vapor pressure close to the saturation the thin film liquid can be stabilized. The tail of the meniscus is in contact with the bulk solution and in front of the aperture of the differential pumped and lens system of the NAP XPS system. This approach additionally allows potentiostatic control. b) Dependence of the electron inelastic mean free path in liquid water on the electron kinetic energy. Reproduced from Ref.<sup>[27]</sup> by permission of The Royal Society of Chemistry.

Being able of working at relatively high pressures, researchers today also try to examine the electrochemical interfaces involving liquids without any membranes that separate electrolyte from the analysis chamber. Recently, a combination of relatively hard X-rays with keV photon energy (sometimes referred to as “tender” X-rays) providing photoelectron IMFP of some tens of nanometers with meniscus technique for minimization of the electrolyte layer thickness was used to observe the electrified interface with aqueous electrolyte (figure 5).<sup>[27]</sup> In contrast to previously discussed approaches, this one is more versatile in terms of electrode selection. At the same time, the minimal electrolyte layer thickness is determined by the surface tension and can be rather high. In cases where the electrolyte layer is enough thin for spectroscopy however, high Ohmic losses due to high electrolyte resistance arise.

Although the mentioned techniques significantly advance the electrochemical interface probing by NAP XPS, spectromicroscopy through membranes, *etc.*, they require X-ray of high brightness nonetheless. An increase of the source brightness, in turn, makes the analysis more destructive causing radiation damage, especially significant in the case of soft matter. To avoid misinterpretations, this fact should always be kept in mind during every experiment.

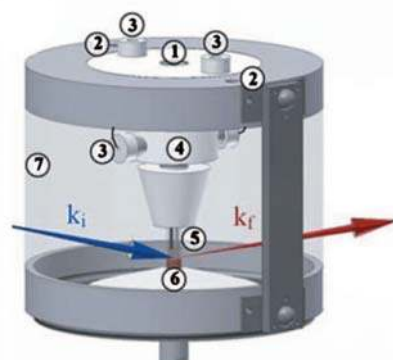
## 2.2. Traditional interfacial techniques

**X-ray scattering.** In these experiments the structural information on the distribution of scattering centers (atoms) within the materials is derived from the analysis of the intensity of the scattered photons as a function of the momentum transfer – the difference between the wave vectors of the incident and scattered waves in the Fraunhofer diffraction mode. The diffraction studies employing the characteristic X-ray wavelengths (about 0.1 nm) make this type of experiments informative for the investigations in a 0.1 – 100 nm scale range. Since the beginning of the 1990s<sup>[28-30]</sup> surface X-ray diffraction (SXR) at the high-brilliance synchrotron radiation sources has been intensively used for *in situ* analysis of the electrochemical interface structure under the potential control. The electrochemical cells comprised single crystalline electrodes covered by a liquid electrolyte. The crystalline structure of the electrode surface layers, its evolution in the electrochemical processes and the formation of SEI phases were analyzed using in-plane (in-plane surface structure)<sup>[28,31-36]</sup> and out-of-plane diffraction, or specular reflectivity (surface-normal structure)<sup>[28,30-44]</sup> from specially oriented samples. In the first case, the grazing angle of the incident X-ray beam to the electrode surface is below a critical angle of the total optical X-rays reflection, so that the totally externally reflected waves penetrate only up to a few nanometers into the material yielding extremely high surface sensitivity. As a result, the in-plane Bragg diffraction is observed for the crystalline planes, which are perpendicular to the electrode surface. In the second case, the grazing angle is higher than the critical angle, so the waves penetrate deeper into the electrode material but meet the Bragg diffraction conditions for the crystalline planes, which are parallel to the electrode surface. Both diffraction types make of the atomic

coordinates in the crystal unit cell possible, i.e. the characteristic scale level of these methods lies within 0.1 – 1 nm. Another experimental mode, X-ray reflectometry, appears when the grazing angle lies between the critical angle and the Bragg diffraction region. Here, a decrease in the specular reflectivity is sensitive to the formation of nanostructures (1 – 100 nm) at the interface and can be analyzed in terms of the distribution of the scattering length density mostly along the interface depth with the signal averaging all over the electrode surface.<sup>[30,40-44]</sup> Liquid metal electrochemical interfaces can also be studied by XRR in the same way.<sup>[45]</sup>

In X-ray scattering techniques the incident beam passes through a liquid electrolyte before it meets the electrode. Two alternative cell geometries for reflection and transmission modes have been suggested.<sup>[40]</sup> In the first case, the liquid electrolyte gap should be constricted to a layer with a thickness of few microns that can lead to the loss of meaningful potential control because of a large uncompensated iR-drop. In the alternative (transmission) geometry, which mainly avoids these problems, the beam goes in and out of the cell through the windows, which are perpendicular to the interface. Although the beam intensity is largely attenuated in this case, the beam path length in the liquid electrolyte can be optimized to a reasonable level.<sup>[40]</sup>

The cells with hanging drop shown in figure 6 were developed and used by Keller et al.<sup>[46]</sup> for studies of EDL by SXR technique. The profile order of the solvated cations and interfacial water within the outer Helmholtz layer were studied using Cu (100) single crystal working electrode in 5mM H<sub>2</sub>SO<sub>4</sub> electrolyte.

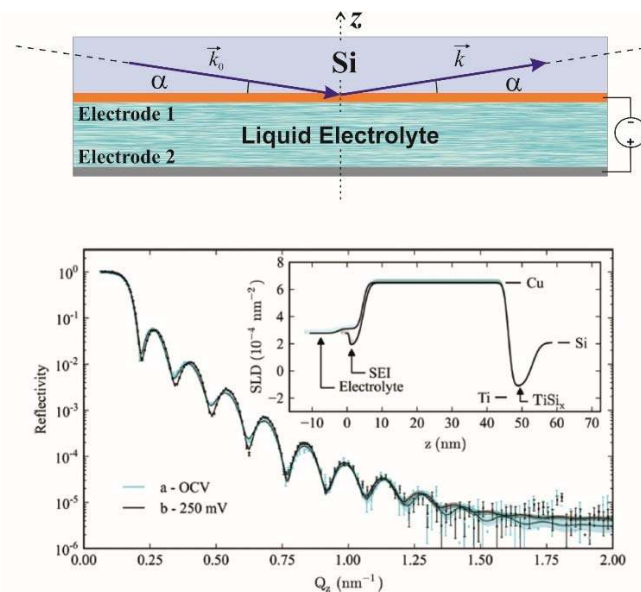


**Figure 6.** Schematic of the electrochemical SXR cell.  $k_i$  and  $k_f$  are the wave vectors of the incoming and diffracted x-rays, respectively. 1 – electrolyte input, 2 – gas inlet, 3 – electrical feed throughs, 4 – electrolyte reservoir, 5 – capillary with electrodes (CE and RE), 6 – working electrode, 7 – Kapton window. Reprinted with permission from ref.<sup>[46]</sup> Copyright 2010 by the American Physical Society.

**Neutron reflectometry.** Neutron based methods are widely used in electrochemistry-related materials science primarily thanks to diffraction techniques that are indeed more useful for bulk studies.<sup>[47]</sup> Less spread neutron reflectometry, in contrast, provides an intrinsic interface sensitivity enabling *in situ* studies of electrochemical interfaces. The same principles apply as in XRR experiments and, in general, specific modulations of the

specular reflectivity above the critical momentum transfer is exploited, revealing an SLD profile over the interface depth. The main difference however lies in extremely high neutron penetration ability making it possible to send a neutron beam through rather massive substrates (often monocrystalline silicon) without significant attenuation and scattering. As a result, interfaces of a working electrodes (e.g. film deposited onto the thick silicon single crystal) with liquid electrolyte can be explored without limitations to the electrolyte layer thickness. Compared to X-rays, use of thermal neutrons (energy of  $\sim 10$  meV or wavelength within 0.1 – 1 nm) is of additional advantage for electrochemical interfaces, considering the following aspects. Firstly, neutron scattering is a weak interaction and samples under study are not destroyed or even influenced by the neutrons. Secondly, the isotopic  $^1\text{H}/^2\text{H}$  substitution in the interface components provides a wide range of possibilities for varying the scattering contrast in the system. Hence, as opposed to XRR, the neutron reflectivity is sensitive to the distribution of light elements, especially hydrogen. Restrictions in the neutron scattering experiments are mainly ascribed to the fact that the present-day high-flux neutron sources (reactors and spallation sources) still cannot compete with the synchrotrons in the relation to the incidence beam intensity. To get sufficient statistics for one neutron reflectivity curve over a wide momentum transfer range, samples with rather large surface areas (order of  $10\text{ cm}^2$ ) have to be exposed during a characteristic acquisition time of at least 1 h, determining the minimal time step for *in situ* NR experiments.

The first *in situ* NR electrochemical studies were devoted to systems with aqueous electrolytes and entailed determination of the thickness and density of oxide layers on Ti formed during electrochemical passivation in different regimes,<sup>[48,49]</sup> and to analysis of nickel hydroxide redox.<sup>[50]</sup> The typical cell arrangement for such experiments is shown in figure 7. Today, in addition to the evolution of the metallic surfaces<sup>[51-53]</sup> in the electrochemical processes, a range of other electrode materials are being examined by *in situ* NR, including polymer-modified electrodes,<sup>[54-56]</sup> anode<sup>[57-59]</sup> and cathode<sup>[44,60]</sup> materials for lithium storage. In the recent years the NR experiments focused on the analysis of the structuring in a liquid phase were also performed in order to determine the EDL structure in ionic liquids near the electrified gold interfaces.<sup>[61,62]</sup>



**Figure 7.** General layout of the NR experiment with an electrochemical cell. The plane neutron beam bypasses a single-crystal Si and falls on the interface between a thin electrode film (Electrode 1) on the silicon substrate and liquid electrolyte. The ratio of the specular reflected (wave vector  $k$ ) and the incident (wave vector  $k_0$ ) neutron beams is known as the reflectivity, which is plotted as a function of the Z-projection of the momentum transfer  $Q = k - k_0$ ,  $Qz = (4\pi/\lambda)\sin\alpha \approx 4\pi\alpha/\lambda$ , where  $\lambda$  is the wavelength and  $\alpha$  is the grazing angle. The reflectivity analysis gives the SLD profile along Z-axis of the interface, where SEI can be observed after application of potential to the cell electrodes. Reprinted with permission from ref.<sup>[62]</sup> Copyright 2012 American Chemical Society.

As already mentioned, NR measurements generally involve rather long data acquisition times, often precluding access to kinetics. To overcome that, a special methodology has been proposed for the electrochemical NR experiment.<sup>[50,55,56]</sup> This is based on the synchronization of potential (or current) steps in voltametric studies with the pulsed neutron source. For reversible (or quasireversible) systems this enables gathering of a reasonable statistics across a wide potential range.

In some cases, small-angle neutron scattering (SANS) – another technique sensitive on a nano-scale but employed mainly to bulk systems investigation – was also successfully employed for the electrochemical interface studies. Thus, the effect of ion sorption on SANS curves in electrodes was recently revealed in *in situ* experiments.<sup>[63,64]</sup> The absolute volume of the electrochemical interface is often rather small (for low specific surface electrode materials) restricting detailed structure analysis by SANS. Nevertheless, mesoporous electrodes, of a practical interest in some cases, can be studied more effectively as for instance, in the formation and evolution of SEI and lithium intercalation into the mesoporous hard carbons where SANS curves are significantly affected.<sup>[65]</sup>

**Vibrational sum frequency generation.** Nonlinear second order optical processes, such as sum and difference frequency generation, are forbidden in a bulk centrosymmetric media, as is the case for many solids and all liquids. Inversion symmetry, broken at the interface between two different media however,



makes SFG spectroscopy<sup>[66]</sup> an intrinsically interface sensitive tool. Focusing visible laser light with a fixed wavelength and an IR source with a tunable energy at the same point in the sample leads to generation of SFG signal originating from the interface buried under the electrolyte. IR light emitted by free electron lasers enables effective acquisition of spectra in the far infrared region probing vibrations of heavy atom bonds, electrode skeleton vibrations, etc The laboratory tunable IR sources can be useful for monitoring vibrational fingerprints of various functional groups (CN, CO, OH and others).<sup>[67]</sup> FELs provide more intense IR irradiation that is indeed crucial as electrolytes and electrodes are strong IR absorbers. Surface plasmon resonance on the electrode surface can help in enhancing the recorded signals,<sup>[68]</sup> though it unfortunately limits the electrode selection.

Investigations of the electrochemical interfaces with the tunable IR sources, both laboratory ones and FELs, began in the '90s. The first works were focused on the monitoring of the adsorbed species (e.g. cyanide ions,<sup>[69-71]</sup> carbon monoxide,<sup>[69,71]</sup> hydrogen<sup>[71-73]</sup>) at electrified metal interfaces. Later few groups started to use SFG to support theoretical knowledge on EDL structure in some ionic liquids near metal electrodes under controlled potential.<sup>[74-77]</sup> In electrocatalysis SFG spectroscopy can be used in combination with isotope labeling giving more insights into the electrochemical reaction pathways as it was demonstrated for ethanol electrooxidation.<sup>[78]</sup>

In the majority of cases, the light is sent to the interface via the electrolyte layer while the arrangement with the lasers reaching the electrode / electrolyte boundary through graphene electrode was recently used for the investigation of ionic liquid.<sup>[79]</sup>

Replacing the fixed wavelength visible radiation source by a tunable one has extended SFG spectroscopy to so-called two-color SFG (2C-SFG) making both vibrational and electronic fingerprints of the interface accessible.<sup>[67]</sup> However, no *operando* research on electrified interfaces has been reported yet.

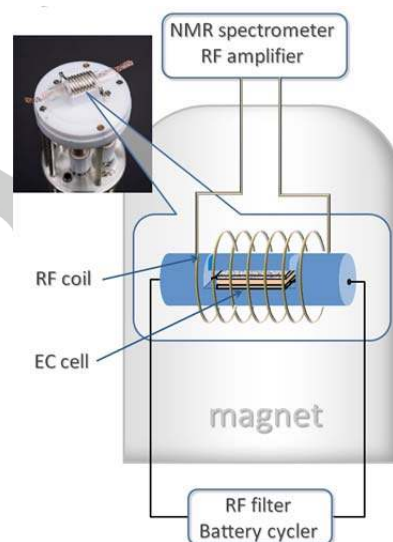
The vibrational modes of the interfacial species can also be detected by the surface enhanced Raman spectroscopy. However, in contrast to SFG, Raman scattering is observed for only bulk condensed phases and liquids that makes it challenging to collect enough signal from the interface. SERS is however sometimes employed in the studies of interfacial phenomena in lithium-ion batteries by adding of the metal nanoparticles with a special morphology to the electrode materials. These attempts are reviewed in detail elsewhere.<sup>[80]</sup> In cases, when the model metallic electrodes exhibiting surface plasmonic resonance are acceptable for studies, SERS can be applied for revealing of some electrochemical intermediates, as it has been done in oxygen redox studies for instance.<sup>[81,82]</sup>

### 2.3. Adaptation of “bulk-sensitive” techniques

**Nuclear magnetic resonance.** Among the experimental approaches which enable direct observation of the structural moieties over the whole sample volume, nuclear magnetic resonance (NMR) is advantageous with respect to the broad range of information available. Solid-state NMR offers unique possibilities for studying both the structure and mobility in

crystalline and amorphous solids. Exploiting appropriate NMR tools, e.g. measurement of NMR relaxation times (relaxometry) and self-diffusion (diffusometry),<sup>[83-85]</sup> two-dimensional exchange spectroscopy<sup>[86]</sup> or lineshape analysis,<sup>[87]</sup> motional processes on quite different timescales can be investigated. It has been recently demonstrated that <sup>7</sup>Li NMR relaxometry is an efficient tool in studying Li<sup>+</sup> dynamics in lithium ion conductors.<sup>[84,85]</sup> When the structural information is required, solid state NMR offers a good choice because of its unprecedented selectivity and sensitivity to the structural features.

In adopting solid-state NMR in order to characterize the electrochemical processes *in situ*, it needs to be borne in mind that a high-resolution advantage afforded by magic angle spinning of the sample is limited to *ex situ* analysis. However, the spectral information on electrochemical processes can also be obtained from static NMR (without MAS) since the chemical transformations during the electrochemical system operation are associated with changes in the electronic environment around the nucleus. These changes result in strong shifts in the NMR spectra and hence in diverse NMR chemical shifts parameters.



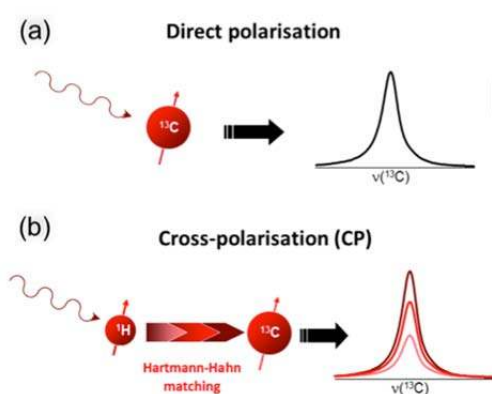
**Figure 8.** A set-up for *in situ* NMR experiments. Electrochemical cell connected to an external potentiostat/galvanostat is placed in an rf-coil of the NMR probehead within the magnet. Inset shows a custom-built *in situ* NMR probe with a plastic bag cell. Adapted with friendly permission of Dr. O. Pecher and Prof. C. P. Grey (University of Cambridge, Cambridge, UK) and NMR Service GmbH (Erfurt, DE).

A typical *in situ* NMR experimental setup is shown in figure 8.<sup>[88]</sup> Given a whole cell is assembled and placed in an NMR probehead rf-coil, the *operando* NMR spectra can be recorded enabling the identification of the intermediates and short-lived metastable states as well as the reaction products once their spectral signatures appear at different states of charge. Tuning the NMR probehead to an appropriate resonant frequency (Larmor frequency), depending on the gyromagnetic ratio of a particular isotope and the external field strength, a specific

nucleus present in either phase (e.g.  $^1\text{H}$  in electrolyte or  $^{13}\text{C}$  in carbon-based electrode) or in all phases (e.g.  $^7\text{Li}$ ) can be probed. During the last decade, a number of *in situ* NMR studies of electrochemical processes have been reported,<sup>[88-93]</sup> although mainly bulk substances have been analysed. As the present survey focuses on the studies of electrochemical interfaces, the advantages of NMR technique in respect to the studies of interfaces will be highlighted.

Modifying a pulse sequence in NMR can enable suppression or assist specific nuclear spin interactions in the certain regions of the sample. Thus, both selective excitation and detection as well as spectral editing in established NMR experiments can be immensely useful for studies of electrochemical interfaces for energy storage and conversion.

The heteronuclear correlation approach, based on the transfer of magnetization from one nuclear species (present in an electrolyte phase for instance) to another (in an electrode phase) via the dipolar or scalar coupling between these nuclei, is most suitable for investigating the interfacial phenomena at molecular level.<sup>[94]</sup> In cross-polarization (CP) NMR, illustrated in figure 9, the transfer of magnetization is facilitated by the so-called Hartmann-Hahn matching condition<sup>[95,96]</sup> and is applied generally for signal enhancement or for correlation spectroscopy and spectral editing, i.e. filtering out the signals from the nuclei located in the interface region. This approach has been extensively employed in studying interfacial phenomena in the different composite materials of technological and biomedical relevance, where the interactions in the interfacial layer between the inorganic and organic components play a crucial role.<sup>[97-101]</sup> With the participation of quadrupole nuclei in CP, the situation becomes more complex due to the difficulty in spin-locking the magnetization. Some quadrupolar nuclei (e.g.  $^{23}\text{Na}$ ,  $^{27}\text{Al}$ ) do produce strong signals however, so that CP experiments can be conducted.<sup>[102]</sup> In principle, double CP can also be employed – initial CP is used for signal enhancement and the second magnetization transfer to enable filtering out signals from the interface.



**Figure 9.** Direct excitation of  $^1\text{H}$  spin polarization (direct polarisation, (a)) and heteronuclear cross-polarisation with magnetisation transferred from  $^1\text{H}$  to  $^{13}\text{C}$  nuclei spins (b).

Lastly, cross-polarization kinetics is sensitive to the inter-nuclear distances and molecular mobility. This enables probing the nuclei at selected distances from the interface in CP experiments by selecting contact times, hence observing structural variation as a function of a depth.

Unfortunately, CP NMR efficiency suffers from the lack of coherency due to the high mobility of spin-bearing species. On the other hand, this can be utilized in some cases to separate contributions from the cell components, where restricted mobility is expected; for example, in distinguishing the signals from SEI and that of the electrolyte bulk, with the species more mobile at room temperature and thus only contributing weakly to the CP process.

Additionally, several other approaches can be utilized when interface-sensitive NMR experiments are required.

Isotope labeling with NMR-active isotopes is often used to enhance sensitivity of the NMR experiments. When one of the cell components is isotopic labeled, the contributions from the different electrochemical cell components can be separated. Enrichment of the common electrode materials with the stable isotopes e.g.  $^{13}\text{C}$ ,  $^{17}\text{O}$ ,  $^{29}\text{Si}$ , allows the reaction products to be determined on the specifically labeled component, while deuterating the electrolyte solvents enables spectral editing. Moreover, the electrode surface can be isotope-enriched to selectively enhance the surface related signals.

Another approach is the chemical modification of electrode surfaces with the NMR-active nuclei, which can serve as sondes for probing the structural changes during the battery cycling.

In contrast to the aforementioned approaches, an echo-editing method offers an easier and cheaper means of determining the, for example, SEI-related immobile surface species, by suppressing signals via mobility filter.

Finally, the skin-effect, which limits the penetration of the alternating magnetic field in metals, enables suppressing contributions from the metal bulk while emphasizing those occurring on the electrode surface in the NMR spectra. Given that the skin-effect becomes more pronounced in the higher external magnetic fields, magnetic field strength variation can be used to separate and quantify contributions from the metal bulk and surface microstructures, as in lithium dendrite growth investigation for instance.

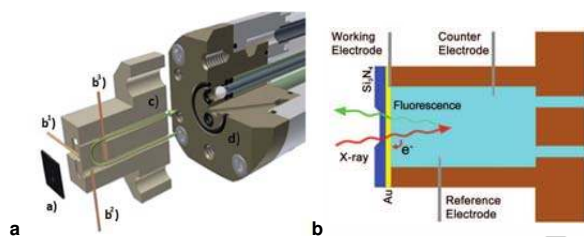
**X-ray absorption spectroscopy.** XAS is a powerful tool in material science. The absorption edge is given here by the first permitted core transition energy. The XAS spectra provide direct information on the electronic transitions from core levels to unoccupied final states in the target element, making possible the identification of the atomic composition, chemical state, coordination number and inter-atomic distances.

Absorption spectroscopy generally includes two different techniques: near edge X-ray absorption spectroscopy and extended X-ray absorption fine structure.<sup>[103]</sup> Few eV near edge structure is sensitive to atomic chemical state. When the energy is extended to a range of several tens of eV above the absorption edge, EXAFS oscillations appear. It happens due to the scattering by the neighbouring atoms determining the wavefunction of the scattered photoelectrons. The amplitude is proportional to the number of neighbouring atoms at a given



distance. Due to the fact that the XAS spectrum is determined by the local geometry irrespective of the crystalline order, it is used to extract information on the bond length and coordination number of atoms in complex systems including amorphous phases.

XAS data collected in transmission mode (by recording the intensity ratio of incident and transmitted beams with the use of ion chambers) can hardly be used for monitoring the interfaces since it provides information only on the sample bulk. There are other possibilities to acquire absorption spectra however, – fluorescence yield or total electron yield, which deliver intensities proportional to number of core holes created, and thus giving an estimation of the unoccupied electronic states' density. FY is a bulk sensitive technique given by the X-ray penetration depth, typically ranging from hundreds of nanometers to few microns, while the short IMFP of electrons makes TEY a really surface sensitive tool. For instance, the effective attenuation length of secondary electrons with energies of about 530 eV (from the O K-edge excitation) is estimated to lie between 5 – 10 Å in liquid water,<sup>[104]</sup> so for aqueous electrolytes the TEY signal originates from the first 3–4 water layers. It makes XAS a really powerful technique capable of distinguishing between the surface and bulk electronic states.

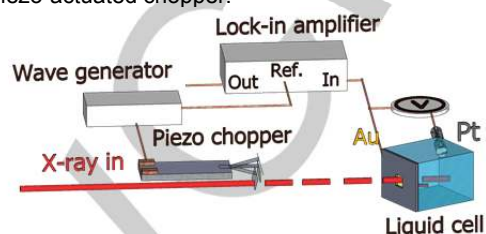


**Figure 10.** (a) Drawing of the electrochemical cell used in the XAS electrochemical experiments. Reprinted from ref.<sup>[105]</sup>, Copyright 2012, with permission from Elsevier. (b) Schematic of such cell, adapted for EDL studies at water/gold interface.<sup>[106]</sup> Reprinted with permission from AAAS.

As the electrochemical interfaces contain a liquid phase, the depth sensitivity of photon-in-photon-out XAS techniques (hundreds of nanometers<sup>[107]</sup>) is beneficial for making the electrochemical cells, in which the electrolyte is separated from the UHV by ultra-thin liquid-tight membranes (e.g. Si<sub>3</sub>N<sub>4</sub> membranes). A liquid flow cell based on this concept made investigation of material behaviour in aqueous media under potential control possible (see figure 10). This setup was first employed in studies of electrochemical oxidation of copper<sup>[105]</sup> (in FY mode) and more recently, in the investigation of the electrochemical stability of a graphene electrode<sup>[108]</sup> in TEY mode. Ideally, secondary electron yield should provide the essential information of the interface region due to the short electron IMPF. However, similar to photoelectron spectroscopies, extremely thin electrodes, e.g. graphene membranes set a limitation here. The cell was also adapted for the investigation of the interaction between water and graphene depending on the incidence x-ray angle under static conditions.<sup>[109]</sup> Such flow-cell designs are being further optimized at ALS.<sup>[110]</sup> Besides to Si<sub>3</sub>N<sub>4</sub>,

polyimide films with deposited electrodes also served as membranes for such kind of cells.<sup>[111]</sup>

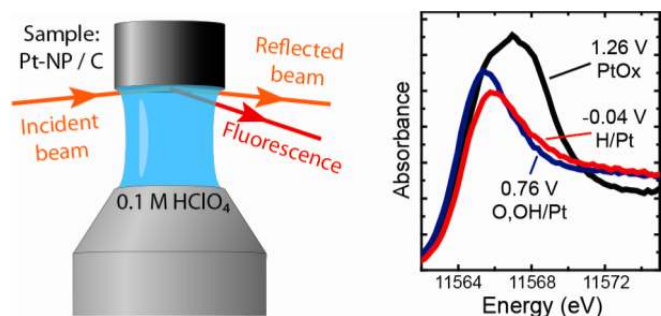
It is worthy to note that the surface sensitive TEY mode requires recording of the sample photocurrent, which is much smaller in comparison with EDL charging and Faradic currents flowing through the electrode. To separate the photocurrent and the electrochemical signals, a special detection scheme, figure 11, was used.<sup>[106]</sup> The incoming X-ray beam in this case is pulsed with a piezo-actuated chopper.



**Figure 11.** Detection scheme used to decouple photocurrent flowing through the electrode under investigation and electrochemical currents.<sup>[106]</sup> Reprinted with permission from AAAS.

Naturally, soft X-rays are used to probe light element like C, O, N, etc. However, the relatively small energy separation between core levels makes the analysis of EXAFS rather tricky. For heavier elements with deeper core levels EXAFS in combination with X-ray diffraction enables tracing the variation of the local and crystal structure of active electrode materials in bulk under electrochemical conditions. In the last decades, this well-established approach has been applied for *operando* investigation of Li-based rechargeable batteries. For such systems, which require isolation from environmental air, a number of cells employing X-ray transparent membranes were designed and used for investigation of the electrochemical reactions under working conditions.<sup>[111]</sup> However, these studies mostly relate to the bulk structure of electrode materials evolution during the battery cycling process.

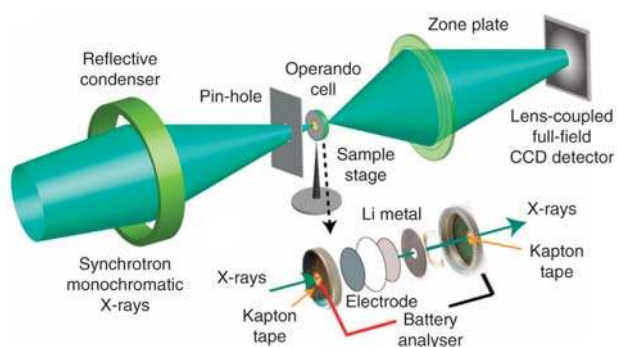
Although hard x-rays are capable of penetrating even a millimeter-thick electrolyte layer, bulk or surface sensitive (in TEY mode) hard x-ray absorption and EXAFS analyses are generally not directly relevant to electrochemical interfaces except where the fraction of surface atoms becomes significant comparative to those for bulk. This is met in nanomaterials such as electrocatalysts in fuel cells – Pt nanoparticles in PEMFC are a vivid example. In such systems, EXAFS yields the information on interfacial phenomena – including chemical transformations during ORR – extracted from bond length analysis (Pt – O and Pt – H bonds are much shorter than Pt – Pt) and variation of the near edge absorption structure.<sup>[112–114]</sup> The hanging meniscus electrochemical cell used in these studies is shown in figure 12. Hard X-ray absorption is also useful for the interface studies of metal plating where metal-metal bonds form. Examples include probing of interface region by NEXAFS of a single monolayer of absorbing Cu atoms on a Au working electrode.<sup>[115]</sup>



**Figure 12.** Electrochemical *in situ* cell and NEXAFS Pt K-edge evolution during electro-oxidation. The working electrode is the top one, counter and reference electrodes are integrated into the tube in the bottom. Pt K-edge spectra are shown at different potentials noted vs. Ag/AgCl reference electrode. Reprinted with the permission from ref.<sup>[114]</sup>. Copyright 2012 American Chemical Society.

Hard X-ray XAS in FY mode was also employed to probe electrochemical interfaces in total reflection condition.<sup>[116]</sup> The reported approach enabled the analysis of changes in the surface of lithium-ion battery electrode, prepared in the form of thin polycrystalline film and to compare the results with bulk.

**X-ray microscopy.** The ability to focus X-rays using zone plates or other optics (capillary optics, Schwarzschild objectives) enables spatial resolutions in submicrometer range often needed in monitoring the various electrochemical processes. Scanning transmission x-ray techniques (STXM) through a thin film of both aqueous and non-aqueous electrolytes with lateral resolutions in the range of tens of nanometers have been performed. The photon energy dependent contrast is generated by the X-ray absorption spectrum features originating from different chemical species. This approach was implemented by the confinement of the electrolyte between two ultra-thin  $\text{Si}_3\text{N}_4$  membranes or Kapton tape and collecting the intensity decay of the transmitted X-rays through it (figure 13). Although this tool can only indirectly provide interface-specific information, such approach is being successfully used at ALS<sup>[117]</sup> and ELETTRA<sup>[118]</sup> to monitor electrochemically driven polymerization *in situ* with the lateral resolutions of several tens of nanometers. Conversion reactions with lithium were also monitored.<sup>[119]</sup>



**Figure 13.** Schematic illustration of the transmission X-ray microscope (TXM) experimental setup. Figure from ref.<sup>[119]</sup> used under the terms of the Creative Commons Attribution license.

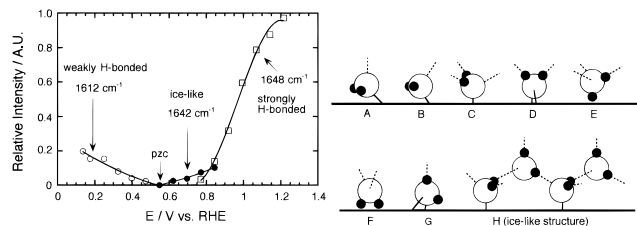
A new setup with high temporal and spatial resolution is shown in figure 13. Hard X-ray spectroimaging can visualize electrochemically driven phase transformations, but demands considerably large samples with strong absorption signal so far. Using a new data analysis method it was possible to visualize electrochemically driven solid-state phases transformation at the nanoscale range with high spatial resolution. Taking the advantage of the strong hard X-ray penetration ability and the possibility of chemical analysis, it was possible to explore the progression of an electrochemical reaction in a realistic electrode. Further, the temporal and spatial resolution of the chemical phase mapping will be improved with the development of brighter synchrotron light sources, together with the improvement of lensless imaging methods achieving better data processing algorithms.<sup>[120]</sup>

### 3. Selected highlights of *operando* electrochemical interface observations

#### 3.1. Electric double layer studies

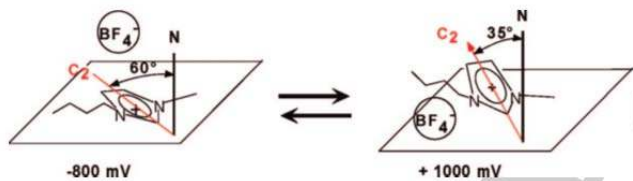
The EDL structure is relevant for all electrochemical energy storage systems, being a key factor in supercapacitors, for example. The first model of the EDL structure was suggested as early as mid 19th century by Helmholtz. Theoretical knowledge on the EDL structure was much developed in 20<sup>th</sup> century through the works of Gouy, Chapmann, Grahame, Bockris, Devanathan, Müller, Trasatti and others. Experimental approval of the classic theories mainly included the electrochemical data. Nowadays, developments in analytical tools drive spectroscopy and reflectometry studies of the EDL structure at electrified interfaces (EDL on colloidal particles is also being actively studied, and is out of the scope of this review, however).

Surface enhanced infrared spectroscopy was used to investigate the interfacial structure of water in aqueous electrolyte (0.5 M perchloric acid).<sup>[121]</sup> Authors demonstrated, that the interfacial water molecules are weakly hydrogen-bonded at potentials below the PZC and form a strongly hydrogen-bonded ice-like structure at potentials slightly above the PZC. The ice-like structure is broken at more positive potentials due to the specific adsorption of perchlorate ions. These changes are accompanied by the re-orientation of water molecules as it is sketched in figure 12. Being element-specific, XAS recently approved these observations.<sup>[106]</sup> Using electron yield researchers were able to collect the signal from the gold/water interface and demonstrated that at cathodic polarization there is a large population of water molecules arranged on the electrode surface, as the electric field favors an orientation of the water molecules with their H atoms toward the gold surface, which increases the number of dangling hydrogen bonds. At open circuit and anodic polarizations the interfacial water forms a highly structured network of saturated hydrogen bonds.



**Figure 12.** The orientation of [BMIM]<sup>+</sup> cation on the surface of the Pt electrode at different polarizations. Reprinted with the permission from ref.<sup>[121]</sup>. Copyright 1996 American Chemical Society.

The classic theories on the EDL structure hinge on dilute-solution approximation. A lot of practical electrolytes are however rather concentrated solutions. Even stronger ion-ion interactions are observed for the ionic liquid-based electrolytes containing no solvent at all. Being melts, ionic liquids represent both an interesting system with an unclear EDL structures and a convenient object for *operando* research, as they possess extremely low vapor pressure that is beneficial for some research methods. *In situ* SFG results, obtained for imidazolium-based ionic liquids, demonstrate the existence of compact ion layer and the diffuse layer species.<sup>[75,77]</sup> Polarization of the electrode leads to the reorganization of the compact layer accompanied by the rotation of organic cations near both metallic<sup>[74,76]</sup> or carbon interfaces<sup>[79]</sup> as shown in figure 13.



**Figure 13.** The orientation of [BMIM]<sup>+</sup> cation on the surface of the Pt electrode at different polarization deduced from SFG studies. Reprinted with the permission from ref.<sup>[76]</sup>. Copyright 2008 American Chemical Society.

The existence of the compact layer was also recently confirmed by *in situ* NR.<sup>[61]</sup> Pyrrolidinium-based IL interface with gold was probed and a little excess of pyrrolidinium cations was found even at anodic polarizations.

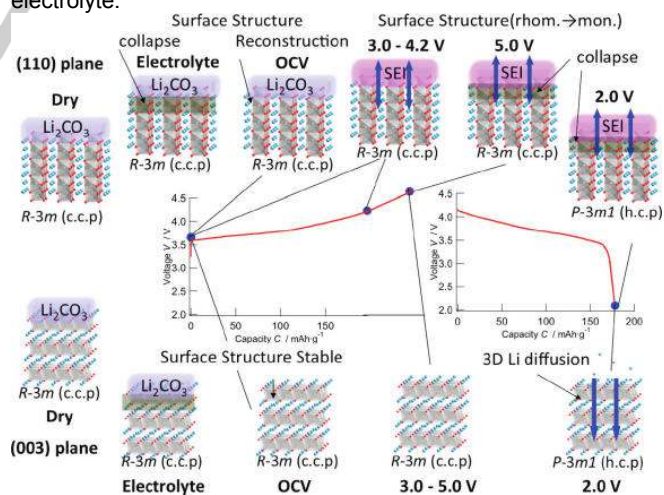
**3.2. Metal plating/stripping**

Metal plating/stripping lies at the core of many industrial processes. In electrochemical energy research much interest is paid to lithium plating/stripping as occurs in lithium-metal-polymer, lithium-sulfur and lithium-air cells. Nonetheless, lithium dendrite growth sufficiently hinders practical applications of the rechargeable lithium-metal batteries. Thus the factors, which control the dendrite growth and lithium encapsulation are becoming a focus for researchers. The effects of different molecular and IL electrolytes on dendrite formation and growth have been investigated using <sup>7</sup>Li *in situ* NMR.<sup>[91]</sup> Using a symmetric lithium metal bag cell, utilizing a quantitative

character of an NMR approach, and assuming a constant mass of lithium metal, a growth of Li microstructures can be monitored by analysis of the peak intensity in <sup>7</sup>Li *in situ* spectra. It has been demonstrated that the dendrites can be seen in the NMR spectra before becoming apparent in analysis of the electrochemical data. The key to using this method for the dendrite characterization is the fact that Li spins only in a “skin depth” of lithium metal can be probed, that is those within 15 μm from the anode surface in the magnetic field of 4.7 T as well as the dendrites, which are an order of magnitude thinner. This approach is thus considered surface-sensitive, particularly when the higher magnetic fields are used, as penetration depth decreases with increasing field strength.

**3.3. Interface evolution during ion insertion/extraction and SEI formation**

Although the first factor determining performance for insertion lithium-ion battery electrode materials is the bulk structure and its evolution, lots of evidence nowadays point to interfaces of active material particles with electrolyte also being involved to a large extent, significantly affecting power parameters and the long-term cycling stability. Formation of SEI and the surface structure evolution of lithium-ion battery insertion electrode materials are being studied by means of *in situ* SXRD and NR scattering using epitaxial-film electrodes (including LiNi<sub>0.8</sub>Co<sub>0.2</sub>O<sub>2</sub>, LiMn<sub>2</sub>O<sub>4</sub>, LiFePO<sub>4</sub>).<sup>[34,36,41-44]</sup> Thus, the observed orientation dependence in the surface diffraction of the LiNi<sub>0.8</sub>Co<sub>0.2</sub>O<sub>2</sub> film electrode and its changes during charge-discharge processes indicated the different Li insertion/extraction mechanisms for the different crystalline planes of the electrode material (figure 14), involving in one of the cases ((110) plane) surface reconstruction. Different planes were also found to possess different reactivities towards electrolyte.



**Figure 14.** Evolution of LiNi<sub>0.8</sub>Co<sub>0.2</sub>O<sub>2</sub> epitaxial film surface structure during lithium extraction and insertion. Reprinted with the permission from ref.<sup>[34]</sup>. Copyright 2009 American Chemical Society.



The NR of the SEI layer as a function of a potential in a working lithium half-cell<sup>[52]</sup> enabled following the effective SEI thickness that was found to reach 4.0 and 4.5 nm after 10 and 20 cyclic voltammetry cycles, respectively. It grew twice up to about 9 nm after a series of potentiostatic holds which simulated a charge/discharge cycles. Authors also revealed that there is a uniform mixing of SEI components in the layer. The SEI formation was also studied by *in situ* NR during delithiation of lithium-ion battery anodes, *e.g.* amorphous silicon with Li rich SEI also having several nanometer thickness.<sup>[58]</sup>

### 3.4. Oxygen redox

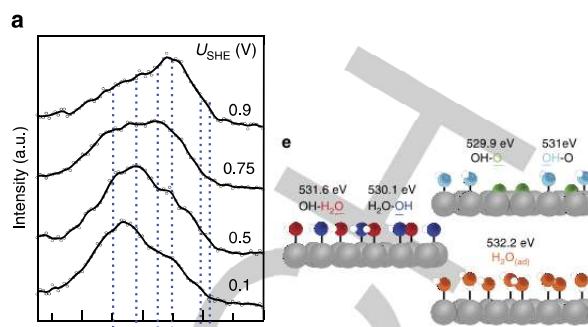
Insights into oxygen redox pathways are crucial for various important applications. ORR efficiency is a central issue in high and intermediate temperature SOFC and low temperature PEMFC. Along with OER, these reactions determine the possible development of rechargeable high-energy metal-air batteries, Zn-air and Li-air.

Perovskite oxides are being actively studied as the ORR catalysts for both high temperature SOFCs and alkaline FCs. *Operando* X-ray absorption spectroscopy was used to investigate oxygen redox on thin-film iron and cobalt perovskite oxides.<sup>[122]</sup> Authors repudiated the conventional view that the transition metal cations are the dominant redox-active centres, finding that the surface oxygen anions are a significant redox partners to molecular oxygen due to the strong hybridization between oxygen 2p and transition metal 3d electronic states. They suggest that a narrow electronic state of oxygen 2p character near the Fermi level exchanges electrons with the oxygen adsorbates.

Recent *operando* NAP XPS studies of ceria – gas interface revealed that the electron transfer between cerium cations and hydroxyl ions is the rate-determining step in OER.<sup>[123]</sup> At the same time oxygen vacancies were found to be easily reactive with water molecules, while additional vacancies and polarons are rapidly exchanged with the bulk.

Oxygen evolution<sup>[11]</sup> in aqueous media was studied in the model cells with Nafion membrane. *Operando* NAP XPS combined with mass spectral gas-phase analysis during OER<sup>[11]</sup> allowed authors to separate the transient active state on Pt from a more stable oxidic deactivated state. It was also confirmed that manipulating of the electrode Fermi level enhances the OER kinetics as stronger Pt-O bonds in a stable oxidic phase induce overpotential.

The ORR over Pt was also recently studied using a similar electrochemical cell and approach.<sup>[17]</sup> As it can be seen from figure 15, near the open-circuit potential, non-hydrated hydroxyl is the dominant surface species. As the removal of the hydroxyl hydration affects the ORR activity, its tuning near the triple phase boundary can be crucial to designing active fuel cell cathodes.



**Figure 15.** O 1s XPS spectra of a fuel cell Pt cathode at different potentials (a) and the schematic models and binding energies for oxygenated species (b).<sup>[17]</sup>

Employing high energy resolution XAS to investigate the Pt monolayer electrode in a hanging meniscus cell enabled unambiguous differentiation of the signatures of chemisorbed oxygen-containing species and several platinum oxides.<sup>[112]</sup> The results indicated low oxygen coverage at potentials up to 1.0 V vs. Ag/AgCl, and Pt oxide formation at potentials above this. A surface oxide at Pt nanoparticles can form already at lower potentials,<sup>[114]</sup> therefore, destabilization of platinum oxide could be an important ORR catalyst design criterion.

The reactions at Pt catalyst in high-temperature PEMFC with phosphoric acid were also recently monitored in the operating conditions.<sup>[26]</sup> Although these studies were focused on the redox of hydrogen rather than oxygen, an important observations on Pt-catalysed reactions leading towards reduced phosphorous species were done.

Oxygen redox in aprotic media is attracting a special attention today due to numerous attempts to demonstrate rechargeable Li-O<sub>2</sub> cells, which still suffer from a lot of side reactions with ORR products and intermediates. *Operando* NAP XPS analysis of ORR in the presence of Li ions was firstly used for the cells comprising solid electrolytes and V<sub>2</sub>O<sub>5</sub><sup>[16]</sup> or carbon<sup>[12]</sup> electrodes. These studies demonstrated that although lithium peroxide can be reversibly oxidized at the electrode surface, practically viable electrode, such as carbons, are vulnerable to superoxide-promoted oxidation leading to carbonates. Relatively stable superoxide species formed after the first electron transfer were also found at the interfaces with liquid aprotic electrolytes by the means of SERS<sup>[81,82]</sup>.

Identification of the structure of the intermediates remains an unresolved issue, however, a significant progress is achieved by using NMR. Although no reports related to the *operando* NMR studies in Li-air batteries are yet available, the significant efforts made in the group of Clare P. Grey to employ a multi-nuclear solid-state NMR approach<sup>[124,125]</sup> give a hope that the reported <sup>17</sup>O NMR spectral library can be potentially utilized for the future *in situ* NMR studies of aprotic ORR. It is worth to mention that, although expensive due to requirements for higher magnetic fields and <sup>17</sup>O isotope labelling, solid-state <sup>17</sup>O NMR is considered to be sufficiently sensitive to detect minor parasitic impurities in contrast to <sup>1</sup>H and <sup>6,7</sup>Li NMR, those chemical shifts are expected to be less sensitive in the static NMR experiments.

## 4. Summary and outlook

For a rather long time, the electrochemists' desire to acquire the electrochemical data and simultaneously probe the electrified interphase boundary structure and chemistry remains unsatisfied. The interfacial species formed in the electrochemical processes are always hidden from the surface analysis tools or give rather weak contribution in signal of bulk sensitive methods. Meanwhile the lack of the direct chemical and structural information often hinders the development of new exciting technologies and propagating the research via trial-and-error routes.

Fortunately, the tools for *operando* probing of the interfaces buried under the electrolyte layers have been in active development starting from 1980s – 1990s, when the techniques with true intrinsic interface sensitivity were firstly employed. Today a lot of effort is focused on adapting either typically surface tools or traditionally bulk sensitive techniques for interface probing. These techniques are briefly summarized in this review.

NMR, which was traditionally used to probe the materials bulk by radiofrequency photons, today seems a powerful technique to study the local atomic environment and transport interfacial phenomena in the energy storage and conversion systems. NMR offers a range of approaches for gathering the signal selectively from the interfacial region and includes isotope labeling, heteronuclear polarization transfer and echo editing. Withal, for many energy related electrochemical systems a wide dispersion of the corresponding NMR chemical shifts yields a satisfactory spectral resolution even without use of a fast spinning of the sample (MAS). Thus, these have all become the important prerequisites for the NMR experiments on electrochemical interfaces to be performed under specific conditions in order to follow up the evolution of the electrochemical interfaces during its operation. Up to now however, at least to the best of our knowledge, there have been no published works reporting direct *in situ* observations of interfaces using NMR techniques, though recent progress in this allows us to believe that a rapid progress can be expected.

Probing by photons in infrared range gives valuable information on the interfacial species bond structure and orientation. Phenomenon of sum frequency generation at the interface and surface enhanced Raman scattering provide a true interfacial sensitivity and make the corresponding techniques really helpful in electrochemical research. Light, used as a probe in that case is normally routed to the interface through the electrolyte and indeed is scattered much. However, laser or synchrotron light intensity is enough to provide a reasonable signal. SFG and SERS are already actively used for interfacial studies, and a number of works employed these vibrational spectroscopies to grasp an insight into EDL formation, oxygen redox intermediates and others.

X-ray based surface science spectroscopic tools, which provide valuable information on the chemical composition, oxidation states and local potentials, are being adapted for interfacial studies by adjusting the probing depth. Two arrangements, *i.e.* probing through electrodes and through electrolytes, are being

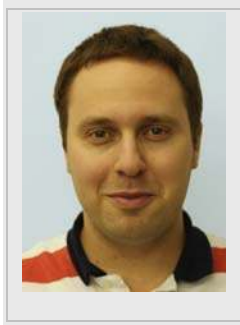
both developed today using primarily model electrochemical systems. The photoelectron kinetic energy varied proportional to X-ray photon energy determines the maximal thicknesses of the electrodes or electrolyte layers, which can be used. Today employment of the photon with appropriate energy and bright beams of synchrotron facilities enables XPS and XAS investigations through a number of electrodes, ranging from a single layer graphene to few tens of nanometer membranes coated with the desired electrically conductive films. The photons with the energies up to few keV make it possible also to monitor the interface through a liquid layers of the thicknesses reasonable for adequate working electrode potential control. Although, in our opinion, there are no breakthroughs in electrochemical energy conversion and storage, manifested only thanks to *operando* X-ray interface probing, we, nevertheless, expect that the tools already developed can significantly help in solving of a number of electrochemical problems in the near future. We also hope that some of these tools would be even available soon in the laboratories instead of large synchrotron facilities that will change a routine electrochemical research practice.

At the moment however, synchrotron light sources play crucial role in this turbulently developing field. Several facilities dedicated for energy-related research, including electrochemical interface studies, are under construction at different synchrotrons around the world. This list includes the Advanced Materials Beamline for Energy Research (AMBER) at the ALS, the Energy Materials In-situ Laboratory (EMIL) at BESSY II, the Versatile Soft X-ray beamline (VERSOX) at DIAMOND and the Material for Energy and Environment beamline (ME2) at Shanghai Synchrotron Radiation Facility. It is worth noting here, that high brilliance helps to get reasonable signal-to-noise ratio maintaining temporal resolution. Nonetheless, this can be a source of artifacts caused by the radiation damage of the electrodes/electrolytes under investigation. Thus a thorough control of the beam brightness is needed to keep investigating the desired system instead of measuring the radiolysis products. X-ray probing is not being limited to spectroscopy, but also provides a structure sensitive probe. SXRD is for a long time used for electrochemical interface analysis. However, it is useful for analysis of the single crystalline electrode surface structure evolution. Formation of nanostructures can be detected by other experimental mode X-ray reflectivity.

A high penetration ability makes neutron a convenient probe for the interfacial studies, which are not limited much by the electrode or electrolyte layer thickness. It makes neutron reflectometry a versatile tool, already being involved in the *operando* electrochemical studies. The density profiles in the direction perpendicular to the electrode surface, which are yielded from NR experiments, can provide necessary information on EDL structure, SEI and electrochemical reaction product distribution. Unfortunately, the current neutron sources cannot compete with synchrotrons in terms of the beam intensity, thus causing rather long acquisition times, which are the challenge for *operando* research. However, a recent advances in methodology help to improve the temporal resolution of such neutron-based techniques.

The development of the novel advanced technologies for the *operando* assessment of the electrochemical interfaces, although challenging, proceeds expeditiously nevertheless. We anticipate that in near future the progress in that field will be much more involved in everyday electrochemical practice providing useful atomistic insights in various electrochemical phenomena.

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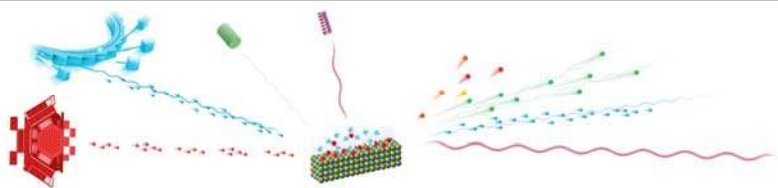
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Table 1. Comparison of the photon- and neutron-probe based tools, which can be used for electrochemical interface studies.

Technique	Probe	Information provided <sup>[a]</sup>	Type <sup>[b]</sup>	Observation geometry	Lateral resolution (if available)	Temporal resolution <sup>[c]</sup>
XPS*	0.1 – 1.5 keV photons	C, CS, SC	<b>S</b> (0.5 – 10 nm)	through thin electrode	50 nm – 100 $\mu$ m	~ 10 s – 10 min (down to 100 fs for FELs)
Tender XPS*	3 – 10 keV photons	C, CS, SC	<b>S</b> (10 – 20 nm)	through electrolyte/ through electrode	50 nm – 100 $\mu$ m	~ 10 s – 10 min
Soft XAS	0.1 – 1.5 keV photons	CS	<b>S</b> (~ 1 nm, TEY, PEY, AEY modes) <b>B</b> (FY mode) <b>I</b> (total reflection XAS)	through thin film membrane	~ 1 $\mu$ m	5 – 30 min
Hard XAS, EXAFS	5 – 30 keV photons	CS, LS	<b>S</b> (~ 1 nm, TEY, PEY, AEY modes) <b>B</b> (FY mode)	through electrolyte	$\mu$ m-range	5 – 30 min
SXRD	5 – 30 keV photons (grazing angle)	PC/S	<b>S</b> (~ 0.1 nm)	through electrolyte	sub- $\mu$ m	1 s – 10 min
XRR	5 – 30 keV photon (grazing angle)	M	<b>I</b>	through electrolyte	sub- $\mu$ m	~ 1 min
SFG	IR + visible photons	V	<b>I</b>	through electrolyte	$\mu$ m-range	sub-s – ~ 1 min (fs-range in pump-probe SFG)
SERS	IR photons	V	<b>S</b> (~ 0.1 – 1 nm)	through electrolyte	$\mu$ m-range	~ 1 min and more
NR	10 meV thermal neutrons	M	<b>I</b>	through electrode	not available	1 h
NMR	radio frequency photons	CS, LS, D	<b>B</b> <b>I</b> (with CP)	whole cell inside the NMR probe	not available	10 min hours (for relaxometry)
SAXS	photons	M	<b>B</b>	through electrode	not available	down to 1 ms

[a] C – composition, CS – chemical state, SC – static charge, PC/S – phase composition/structure, LS – local structure, D – species dynamics, M – microstructure non-uniformity, V – vibration modes/functional groups. [b] Technique sensitivity to surface (S), interface (I) or bulk (B). For surface sensitive tools probing depth is presented in brackets. [c] Typical times needed for spectrum/pattern acquisition are given.





The operation of all electrochemical energy-related systems depends largely on the processes at the electrode/electrolyte interfaces, which should be explored. *Ex situ* studies solely often lead to the loss of some pieces of the puzzle as the reaction products and intermediates can't be "quenched" for post process analysis. In this review we discuss the approaches for the interface probing *in operando* in electrochemical studies.

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