X-ray absorption spectroscopy probing hydrogen in metals

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ABSTRACT

X-ray absorption spectroscopy (XAS) is a widely used technique for determining the electronic structure of matter. In contrast to X-ray photoelectron spectroscopy (XPS), XAS makes use of photons only, and therefore suffers less from absorption of the probe beam, i.e., electrons or photons, respectively. This is true for hard X-rays probing, e.g., the K-edges of d-metals in metal hydrides (albeit with limited chemical information). Soft X-rays, which are suited to analyze the electronic structure of hydrogen in solids, have a limited absorption length in gases. Photons with energies of less than 50 eV ("hydrogen K-edge" <20 eV) are absorbed in less than 1 mm at ambient pressure, which is needed for technical hydrides. Recently, we developed a membrane-based approach to study materials exposed to high hydrogen "pressures" while keeping analysis chamber under high vacuum - thus effectively achieving high pressure XPS analysis. In this paper, we demonstrate that the membrane approach originally designed for XPS can be equally well used for XAS. We show first results on the electronic structure of hydrogen in Pd-Ag alloy as measured by *in situ* XAS using a laboratory extreme ultraviolet (EUV) source.

Keywords: XAS, XPS, Pd-Ag membrane, electronic structure.

1. INTRODUCTION

X-ray absorption spectroscopy (XAS) is a well-established non-destructive characterization technique that is used for determining local electronic and geometric structure of matter. At its core lies obtaining a characteristic element specific fingerprint of surface via detection of absorption edges, i.e. X-ray beam photon energy (0.1-100 keV) that leads to excitation of core electrons [1]. The obtainable information can be divided into two regions: X-ray absorption near-edge structure (XANES) and extended X-ray absorption fine structure (EXAFS). Compared to the former, the latter occurs at higher kinetic energy range and contains information about the neighboring, rather than primary atoms [1].

XAS has found application in various fields ranging from surface science to chemical characterization of applied materials, due to the offered advantages, such as non-destructive analysis suitable for detection of solids, liquids, gasses and amorphous material [2]. XAS can be adapted to offer the possibility to investigate most elements of the periodic table in a time-resolved manner under extreme conditions of high magnetic field or temperature [3]. However, the limitations are reached when measuring the lower energy edges, such as K edges of first row elements or L edges of transition metals [4]. Due to the absorption cross-section these require the vacuum conditions and are, therefore, incompatible with the *operando* analysis. Also, XAS is generally synchrotron-based, due to the superior intensity and tunability of produced X-ray beams [4]. Unfortunately, this limits the accessibility and applicability of the technique. The recent progress in development of table-top plasma-based extreme ultraviolet (XUV) or soft x-ray sources for the XAS application helps to overcome the challenges of synchrotron-based X-ray sources by providing a cheap and accessible alternative [5]. However, the difficulty of acquiring *in situ* 'real-life' relevant data remains.

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XAS can be measured in either transmission or reflection mode. In transmission, light absorbance of the sample is simply defined as the ratio between the incident and transmitted light intensity [4]. For reflection, similar relations hold; however, working in reflection is practically challenging due to higher sensitivity to polarization and alignment [6]. The lack of reference samples is an additional complication of reflection mode: while transmission spectroscopy can be used without a reference, the reflectivity can only be derived from measurements of difference spectra. On the other hand, it enables measurement of technical samples relevant for applications, because X-rays in transmission mode will be heavily absorbed by the sample. Also, the mechanical replacement of sample and reference in reflection mode is error prone. In this paper, we want to introduce a method, which prevents a mechanical movement of the sample by probing chemical changes induced without touching the sample and thus with constant X-ray beam direction.

In this paper, we make use of the changes of the electronic structure of a hydrogen absorbing material upon hydrogen sorption. Palladium and Pd alloy membranes are used for hydrogen separation and purification [7] and are crucial starting materials and intermediates in various fields of research, such as in water reduction [8] or CO_2 hydrogenation [9] catalysis, hydrogen embrittlement [10] and hydrogen detection. Moreover, hydrogen is a promising medium for alleviating current energy-storage related problems. Recently, we developed a membrane holder for analysis under *operando* conditions using X-ray photoelectron spectroscopy [11]. Briefly, the approach includes a hydrogen permeable, robust membrane that is exposed to near ambient or ambient pressures of hydrogen gas on one side and ultra-high vacuum (UHV; around 10^{-9} mbar) on the other side. As the kinetics of hydrogen permeation through the membrane are desorption, rather than diffusion limited, the analysed surface of the membrane is exposed to the similar pressure of hydrogen (~1 bar) as in the hydrogen chamber (Figure 1). Overall, membrane mediated high pressure XPS analysis could be achieved without compromising resolution or requiring costly facilities [11].
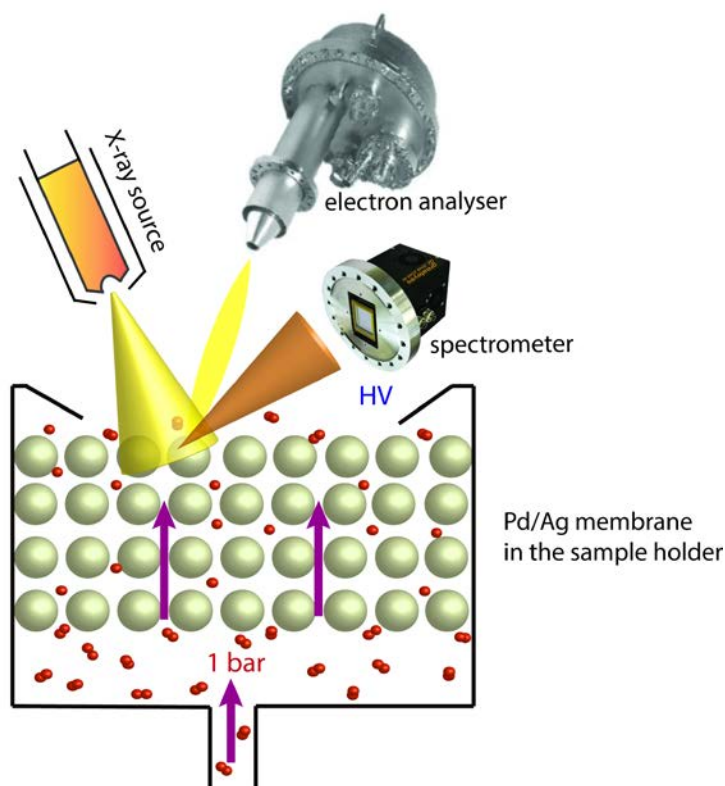

Figure 1. Schematic representation of the principle behind membrane-based ambient pressure XPS and XAS set-up with hemispherical electron analyser and X-ray spectrometer respectively. The hydrogen gas diffuses from the ambient pressure (1 bar) side into the high vacuum (HV) analysis chamber.

For this study, the crucial factor is the ability to follow hydrogen-induced changes in the electronic structure of the material while studying with *in situ* XPS (as published [11]) or XAS without moving or even changing the sample by

simply adjusting the feed pressure on the feed side of the membrane. XAS is a 'photons in-photons out' technique, as opposed to 'photons in-electrons out' XPS (Figure 1). Both techniques are relatively surface-sensitive, though XPS is only sensitive to the topmost layer (1 nm), whereas XAS will also contain information about the bulk (~10 nm) [2]. However, due to the differences in the excitation energy, electron beam is capable of providing the information of the higher energy electronic states of matter, whether XAS is used to gather higher resolution data on the lower energy orbitals, e.g. hydrogen K edge. Last but not least, due to the short mean free path of electrons (1 m at 10^{-6} mbar), XPS requires UHV conditions in the analysis chamber (10^{-9} mbar) [12]. This disadvantage is less prominent in XAS, where the pressures required for unimpeded high-resolution analysis is magnitudes higher (1m at 10^{-2} mbar).

In this paper we focus on the photoelectric X-ray absorption at relatively low energies (<100 eV). In this case one photon is annihilated and creates one photoelectron. For an interaction with an isolated atom, one derives [13]

$$\sigma_{ph} \propto |M_{if}|^2 \delta(E_{kin} - (\hbar\omega - E_B)) \tag{1}$$

where σ_{ph} is the cross section (probability) of the event, $|M_{if}|$ is the matrix element, and $E_{kin}, \hbar\omega, E_B$ are the kinetic energy of the photoelectron, the photon energy, and the binding energy of the core electron respectively. This results in the following relations for XAS and XPS respectively:

XAS: $\sigma_{ph}(\hbar\omega) \propto |M_{if}|^2 \delta((\hbar\omega - E_B))$, because we integrate over all kinetic energies of the photoelectron   (2)

XPS: $N_e(E_{kin}) \propto |M_{if}|^2 \delta(E_{kin} - (\hbar\omega_0 - E_B))$ (3)

Although XAS is measured by the variation of the photon energy, while XPS measures the kinetic energy of the electrons at fixed photon energy, both distributions are related to the corresponding binding energies of the core levels. This means that in first order the XPS spectrum is the derivative of the XAS spectrum. This simple relation is of importance for XAS-XPS comparison, as the obtained XAS spectra are not absolute, but rather the change of the reflectivity upon hydrogenation, i.e., upon the applied hydrogen pressure:

$$\Delta R(p) \propto \frac{I(p) - I(P=0)}{I(p=0)} = \frac{\Delta I}{\Delta p} \to \frac{\partial \sigma_{ph}}{\partial x_H} \tag{4}$$

Here, we make use of the fact that hydrogen content in the sample x_H is related to the applied pressure p. This relation is usually not linear (e.g., Sieverts' law in the solid solution: $x_H \propto \sqrt{p}$), which is neglected for this estimation for the purpose of simplicity.

Therefore, the reflectivity can be related to XPS via

$$\Delta R(p) \propto \frac{\partial \sigma_{ph}}{\partial E} \frac{\partial E}{\partial x_H} \to \Delta R \propto \frac{\partial XAS}{\partial E} \propto XPS \tag{5}$$

In the last step, we assumed that $\frac{\partial E}{\partial x_H}$ is constant, as the hydrogen absorption "edge" is at much lower energies than those analysed in this paper. The relation between XPS and XAS is based on a very simplified picture of the photoelectric X-ray absorption and is not applicable to high energy X-rays, where additional effects occur (e.g., EXAFS interference due to wave nature of the electrons [14]). However, XAS in the soft-X-ray regime probes the core levels accessible by XPS, which is usually restricted to energies below 1500eV, with the similar information depth [15]. The possibility of a direct comparison is thus of high value.

The aim of this paper is to demonstrate a XAS study on the PdAgH system using a lab-based soft X-ray source [9] with the adapted XPS membrane approach [11] described above. The model system was chosen, because the amount of hydrogen in the alloy can be adjusted between 0 and 0.7 [H]/[M] within the applicable hydrogen pressure range (0 to 2.4 bar) [16]. Furthermore, the Pd-Ag alloy membranes are very robust, with fast rates of hydrogen uptake and desorption [16]. The results are then compared to XPS-measurements of the same sample confirming empirically the above derived interdependencies.

2. METHODOLOGY

The experimental set-up was the adaptation and merging of two previously reported techniques: the sample holder from membrane-based XPS [11] and Lab-based X-ray plasma source for XAS [5].

The plasma required for the X-ray beam generation was based on argon as working gas, which was filling a chamber between two Mo electrodes powered by a capacitor bank (C = 960 nF). Once the capacitor was charged to the breakdown voltage (2.5 kV for 0.2 mbar Ar in a chamber diameter of 6 mm), a high-current (10-20 kA) pulse was generated in the plasma chamber. The magnetic field created by the current compressed the generated plasma in the radial direction, leading to emission of XUV radiation. After passing through the pinhole in the plasma chamber, the XUV beam was reflected by the sample and passed through the slits and variable line space grating (Hitachi). Finally, the signal was detected by a back-illuminated X-ray CCD camera (Greateyes GE2048 512 BI UV1) (Figure 2). Stability and calibration of the XUV source are described elsewhere [5].
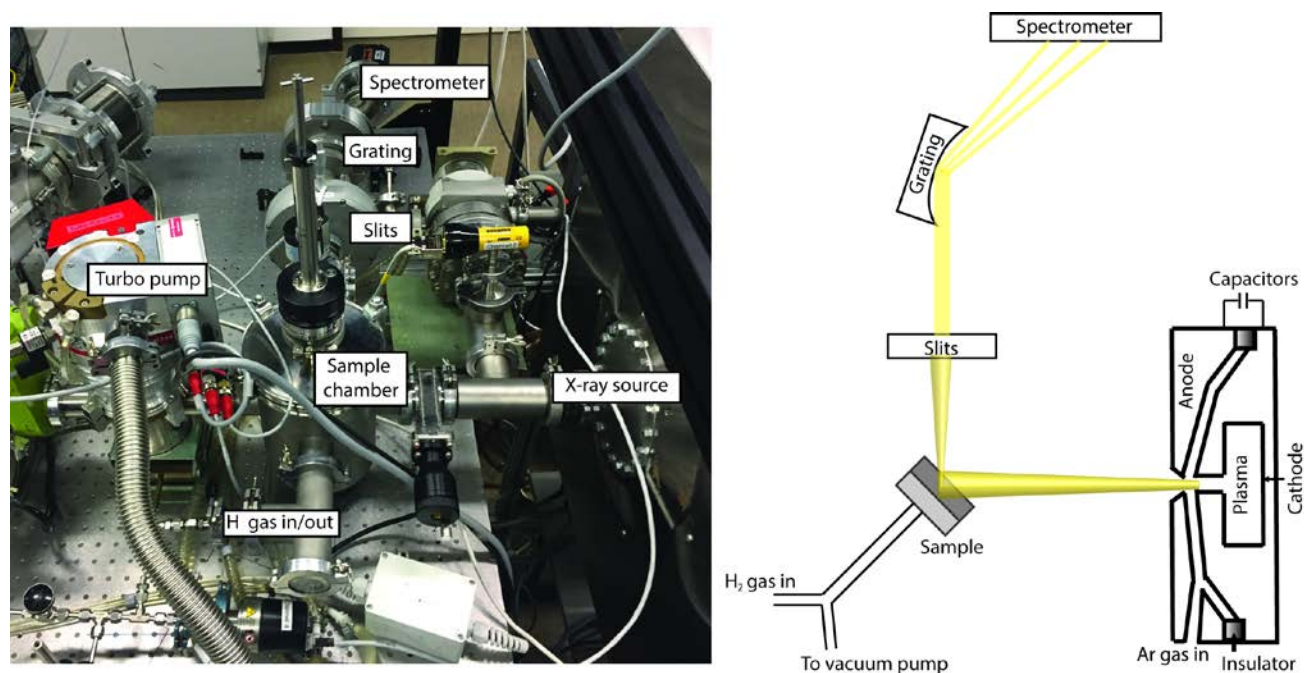

Figure 2. Assigned picture (left) and scheme (right) of the XAS experimental set-up.

Specialised sample holder was positioned in the middle of the sample chamber and exposed to the hydrogen gas flow and a vacuum pump (for venting) via a metal tube (d = 1 mm). The sample (d = 1 cm) consisted of (75-25) Pd-Ag alloy membrane (150 μm; GoodFellow) clamped between the two parts of the sample holder, one side of which was exposed to vacuum in the sample chamber (10^{-4} mbar) and the other – to the flow of hydrogen gas (~1 bar). For details see Ref. [11].

XPS-measurements were conducted using a PHOIBOS 100 electron analyser and an Al-X-ray tube (Specs). The detector assembly consisted of a five-channel electron multiplier (MCD-5) arranged as a single compact block, providing high count rates and good durability. XPS measurements were carried out in fixed analyser transmission (FAT) mode with a pass energy of 50 eV [11].

3. RESULTS AND DISCUSSION

A major difference between synchrotron and plasma-based sources is the spectral uniformity of the light intensity [5]. While synchrotrons deliver light with a very uniform energy distribution, light generated from plasma has a discontinuous line spectrum. In the latter case, already small misalignments will cause large errors in reflection mode, because misalignment will also change the beam direction entering the spectrometer.

The energy scale conversion from the spectrometer domain into eV was performed as described in prior literature [5]. Figure 3 illustrates the camera signals from PdAg membrane upon addition of H_2 gas (700 mbar) to the feed-through side of the membrane taken at 0, 0.5 and 10 minutes. The clear trend emerges, as the signal intensity drops with addition of hydrogen, signifying structural and electronic changes of the PdAg membrane. The "spiky" spectrum is one of the reasons why XAS in reflection is extremely sensitive to alignment errors: a small shift of the optical axis results in a shift of the optical projection into the spectrometer and thus a shift of the energy scale. As the absolute XAS-intensity is derived from a difference measurement between reference and sample, such an energy shift is detrimental.
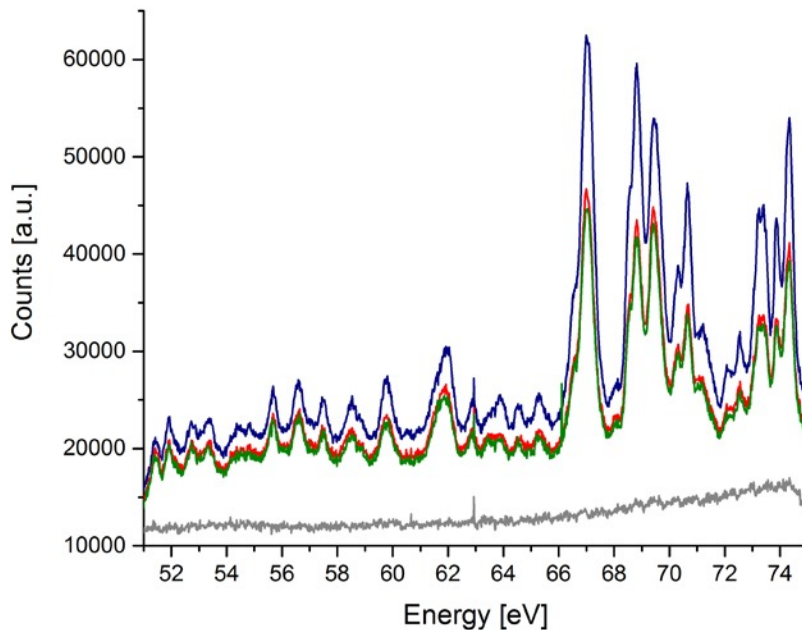

Figure 3. Camera signals of sample with source switched off (gray, I_{dark}), spectrum of PdAg before addition of hydrogen (blue, I_0) and after 0.5 and 10 minutes of hydrogen gas flow at 700 mbar (red and green respectively, $I(p)$).

The corresponding differential XAS reflectivity is calculated as follows:

$$\Delta R(p) \propto \frac{I(p) - I_0}{I_0 - I_{dark}} \qquad (6)$$

where $I(p)$ is the signal intensity upon hydrogenation, I_0 is measured intensity of the alloy without hydrogen applied and I_{dark} is the intensity without X-ray source (CCD-background, see also Figure 3). The resulting graphs were smoothed to suppress the influence of the line spectrum of the source. This reduces the spectral resolution to around 1 eV. The intensity of the differential XAS signal was found to decrease with increasing hydrogen gas feedthrough pressures, tested for the range from 0 to 2400 mbar (Figure 4).
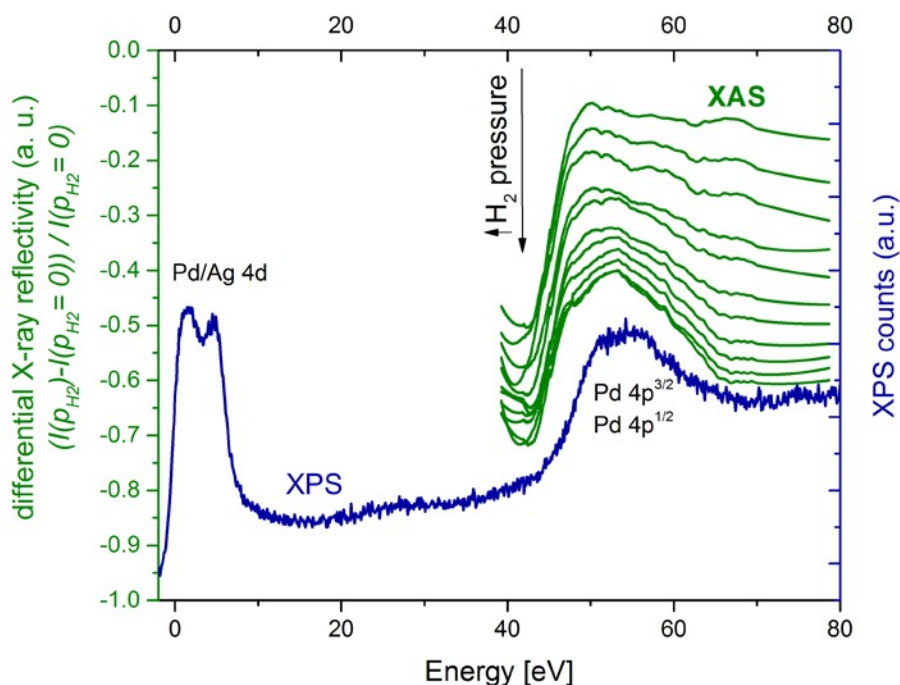
Figure 4. Differential X-ray reflectivity of a PdAg membrane collected with constant time-periods of 10 min at different hydrogen pressures of 350, 450, 550, 700, 850, 1300, 1600, 1850, 2000 and 2400 mbar going from the top to the bottom of the graph respectively (green) and corresponding XPS spectrum of the same system (blue).

As outlined in the introduction, the measured differential reflectivity is proportional to the derivative of the absolute XAS-spectrum. In its turn, the derivative of XAS is proportional to its XPS analogue. This link is confirmed by the measurements at hand (Figure 4). With increasing hydrogen pressure and thus content, an XAS spectral feature forms at ~53 eV which overlaps perfectly with the XPS-signal from the $Pd4p^{3/2}$ and $Pd4p^{1/2}$ states [11]. We can thus interpret the observations as a two-fold effect of hydrogen in the Pd-Ag membrane: (a) it lowers the overall reflectivity, due to the increasing number of hydrogen electrons with an absorption "edge" around 13 eV, which enhances the absorption of photons; (b) furthermore, hydrogen may cause a roughening of the surface, which also contributes to a constant decrease in reflectivity. The second effect is not directly linked to the absorption of photons by hydrogen, but by changes of the Pd chemical state induced by hydrogen intercalation. The hydrogen-metal interaction leads to a chemical shift of around 0.1 eV for the Pd 3d states, as measured by XPS [11]. This shift cannot be resolved in absolute XAS spectrum. However, as we measure a differential signal these relatively small changes are strongly amplified, making the method an ideal tool for the study of hydrogen-metal interactions.

Figure 5 demonstrates the relationship observed between hydrogen pressure and XAS signal. This pressure composition isotherm derived from reflectivity measurements was found to not correlate fully with the prior literature [16]. One reason for it could be the finite hydrogen concentration gradient in the membrane (Figure 5), meaning that the actual pressure at the analysed membrane surface is close to, but not exact to the feedthrough hydrogen pressure [11]. Furthermore, we observed time dependent changes of the spectra despite choosing one of the fastest hydrogen-metal systems [16]. Thus, the finite kinetics of hydrogen sorption and permeation may influence the measured hydrogen content. We will study these phenomena with the method at hand in the future [11].

Finally, various approximations were needed to establish the link between hydrogen content and measured X-ray reflectivity. These approximations will add a degree of error to the derived values of hydrogen content. Various more precise methods to measure the hydrogen content in solids exist [17]; however, the quantitative determination of hydrogen at the surface remains a challenge. This method provides information of the first 5-

10 nm, with the possibility of depth profiling using angular dependent measurements. EUV photons are absorbed by hydrogen, but with a much longer attenuation length than electrons (mean free path of 1 m for electrons and photons is reached at 10^{-6} mbar and at 10^{-2} mbar respectively). The soft-X-ray absorption spectroscopy as utilised here still requires special devices, such as the described above membrane holder, or differential pumping devices, but at much lower technical effort than needed for so-called near ambient pressure X-ray photoelectron spectroscopy [18]. Furthermore, the greater information depth of soft XAS compared to XPS means that the former may allow *in situ* surface spectroscopy of less defined, i.e. technically relevant samples, which are often covered with a contamination layer.
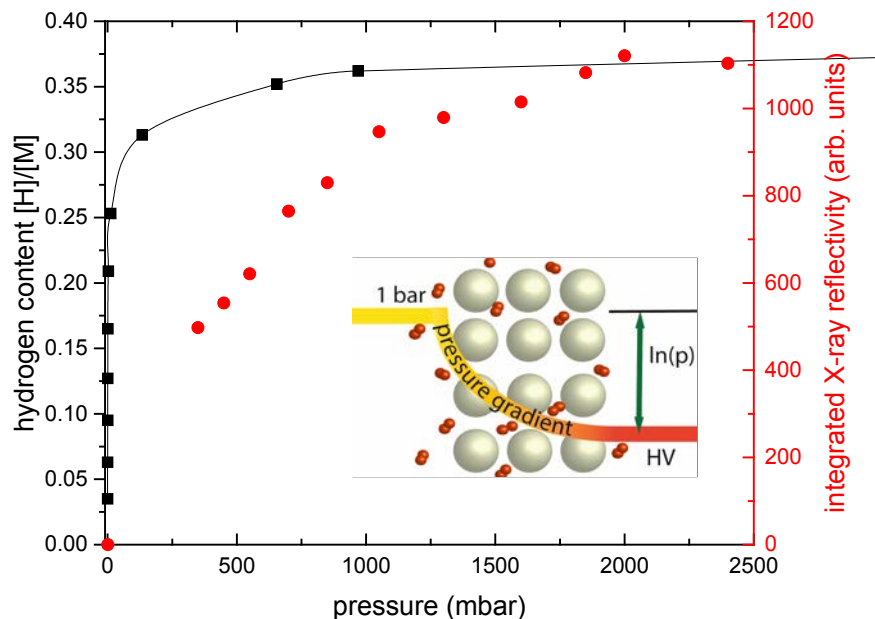

Figure 5. Pressure composition isotherm of the PdAg-H system: bulk data from Ref. [16] (black) and integrated X-ray reflectivity as a measure of the hydrogen pressure applied to the feedthrough side of the PdAg-membrane (red).

4. CONCLUSIONS

High-pressure membrane-based XAS measurement in reflection without using a reference sample was achieved for PdAg/H system, in combination with XPS, demonstrating the versatility and applicability of the membrane approach in the context of two different spectroscopic techniques.

We show that the permeation of hydrogen gas through the metallic membrane from the ambient pressure to the vacuum side of the membrane can be observed and followed by XAS in reflection. The differential X-ray reflectivity spectra show clear time- and hydrogen pressure-dependent decrease in the intensity of the overall spectra, which signify structural and electronic changes of PdAg membrane.

Moreover, a clear link between XPS and XAS was observed, shown for Pd 4p states (spectral feature at ~53 eV), experimentally supporting the theoretical XAS-XPS relation: $\Delta R \propto \frac{\partial XAS}{\partial E} \propto XPS$.

However, the hydrogen pressures at the analysed surface were determined to be lower than at the feedthrough side of the membrane, indicating a finite hydrogen concentration gradient in the membrane.

As the next step we aim to expand on the obtained results by including the source X-ray energy ranges beyond 40-80 eV accessible with the available set-up. Observing changes in Pd 4d states upon hydrogen intercalation is of particular interest. In addition, the presented membrane-based XAS set-up can be adapted

to study other phenomena, e.g. the electrochemistry of Li$^+$ in lithium ion batteries, at *operando* conditions. In this case, the perturbation is not induced by changing the hydrogen pressure, but by the electric potential applied between the two sides of the membrane.

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