



Review

Membrane concept for environmental surface science

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ABSTRACT

The electronic structure of hydrogen chemisorbed to surfaces can be measured using standard surface science techniques, because the required hydrogen pressure is compatible with the UHV-technology. However, processes relevant for energy conversion and storage take place at several atmospheres hydrogen pressure; and thus valuable information on these systems is not accessible by commonly used surface science methods due to their incompatibility with high pressures. In this paper, we review the membrane approach for high pressure XPS for Lab-based systems. The method is based on a specimen holder, which is a metallic, hydrogen permeable membrane fed on one side with a high hydrogen pressure and exposed on the other side to the X-ray beam at UHV-pressures. We discuss a quantitative model for the permeation of hydrogen through a Pd-membrane and the future prospects and limitations of the method for hydrogen related surface reactions.

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1. Introduction

The understanding of gas–solid interactions is a central scientific challenge in various fields of research, such as catalysis and electro-catalysis, corrosion, hydrogen embrittlement and the development of various types of hydrides (i.e. metallic, complex, and organic) for hydrogen detection, permeation and storage. The static thermodynamic properties, such as chemisorption and adsorption enthalpies, are relatively easily accessible by state-of-the-

art methods such as the measurements of pressure-composition isotherms (pcT), calorimetry, etc. [1–3]. Methods to follow dynamical phenomena such as hydrogen permeation [4] and the measurements and modelling of sorption kinetics [5–7] exist as well.

The limits of the state-of-the-art methods are reached when it comes to the rational design and optimisation of the materials suitable for the above-mentioned applications. One reason is that the investigation of the surface as gateway for gases between (bulk) solid and gas requires sophisticated technology. In particular, *in situ* information about chemical bonds and/or the electronic configuration of valence states is of utmost importance. This includes the active solid material itself, adsorbates and reaction intermediates on the surface. X-ray photoelectron spectroscopy (XPS)

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is a powerful surface characterisation technique, providing insightful information about the elements present on a given surface, including their respective chemical states and concentrations across as many as a few tens of atomic layers. However, the mean-free path of electrons with energies below 1500 eV in a gaseous environment is typically below a micrometer at ambient pressure, rendering XPS technique unsuitable for investigation under realistic experimental conditions [8,9]; furthermore, Ultra-High-Vacuum (UHV)- conditions are required for the safe operation of X-ray anodes and channeltrons [8,9].

These problems can be partly overcome by performing so-called “environmental”, “near ambient pressure” or “high pressure” XPS [9]. These techniques are based on the use of differential pumping stages, which lower the high pressure at the sample stepwise down to the required vacuum level. The most important step (“key component”, see Fig. 1) consists of a small orifice at a distance z to the sample similar to its diameter d . The distance must be below the mean free path length of electrons at the desired gas pressure [9]. In state-of-the-art systems, the pressure at the sample may reach a few tens of mbar, with acceptable photoelectron intensity losses [9]. Despite their success, these techniques suffer from drawbacks, such as reduced energy resolution and specimen freedom of movement, high cost and impeded accessibility to the facilities, as most of them are limited to operation at synchrotron light sources. The latter is a consequence of the small orifice diameter requirement (d and z are typically less than 1 mm): electrons, which are able to enter the aperture of the analyzer, can only come from an area similar to the opening of the orifice. The maximum distance corresponds to the mean free path of electrons λ_e , which scales with the pressure: for electrons of 400 eV kinetic energy is about 4 mm in 1 mbar oxygen, and reduces to 4 μm in 1000 mbar. The X-rays exciting those electrons have to be focused onto the accordingly small area on the sample [9]. This is finitely possible with special laboratory-sources, but is perfect for synchrotron radiation. However, the so-called “pressure gap” in XPS can still only be partially overcome with a limited maximum pressure, and high cost.

An alternative principle of accessing high pressure phenomena by XPS is as follows. The window separates near ambient pressure (sample) mini-cell from the UHV (analysis) side, while X-rays and the thus generated photoelectrons penetrate through the window and allow for analysis of the window-sample interface. A number of

developments have been achieved in applying robust ultrathin XPS window for AP XPS [10–13]. The general approach has been recognized by the community to be a valuable tool and various windows have been investigated for this purpose, among others silicon [10], graphene [11,12] and graphene oxide [13]. However, one of the major drawbacks of this technique is the limited variety of materials that can be used as the window. The materials have to be able to withstand the pressure difference while still being permeable not only to X-rays, but more importantly to the generated photoelectrons. Thus, even in case of ultrathin membranes (10–100 nm), the applicability of the technique is limited to synchrotron-based or other high photon energy sources while only the interfaces can be studied [10–13], which may be different to a free surface.

Recently, we developed a different membrane-based approach to study materials exposed to high hydrogen pressure of 1 bar while keeping analysis chamber under high vacuum - thus effectively achieving high pressure XPS analysis. The core idea of the approach is similar to this used in the window approach, as described above: the membrane device, which is exposed to UHV in the analysis chamber on one side and ambient pressure hydrogen on the other. However, the substrate permeates through the membrane and is analysed close to the UHV, rather than ambient pressure side. The hydrogen flux from the surface into the vacuum is desorption, rather than diffusion, limited, leading to ambient pressure conditions at the surface of the membrane on the side exposed to UHV [14]. The validity of the approach for hydrogen related surface reactions has been demonstrated [14].

In this paper, we review the concept in view of possible applications, extending the idea to reactants other than hydrogen, i.e. water. This includes the quantitative description of the process parameters, such as temperature, pressure, and membrane properties. From this, the setup is then adapted to the sought applications.

2. Membrane approach for hydrogen related surface reaction

The underlying physics of the membrane approach for surface reaction is the continuity of the chemical potential from the feed side to the vacuum side of the membrane (Fig. 2). The slope of the chemical potential inside the membrane depends on the hydrogen diffusion in it; if diffusion is not rate limiting, the slope, and thus the

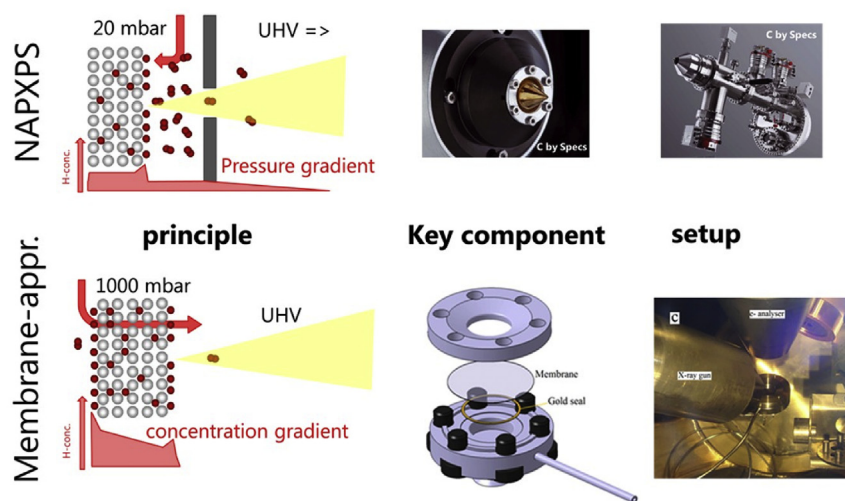


Fig. 1. Top: Principle, key component and commercial realisation of near ambient X-ray photo-electron spectroscopy (NAPXPS). Photographs from Specs [29] Bottom: Corresponding counterparts of “high-pressure” XPS based on the membrane approach [14].

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