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### A laboratory-based multifunctional near ambient pressure Xray photoelectron spectroscopy system for electrochemical, catalytic, and cryogenic studies

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## A laboratory-based multifunctional near ambient pressure X-ray photoelectron spectroscopy system for electrochemical, catalytic, and cryogenic studies



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### ABSTRACT

A versatile multifunctional laboratory-based near ambient pressure x-ray photoelectron spectroscopy (XPS) instrument is presented. The entire device is highly customized regarding geometry, exchangeable manipulators and sample stages for liquid- and solid-state electrochemistry, cryochemistry, and heterogeneous catalysis. It therefore delivers novel and unique access to a variety of experimental approaches toward a broad choice of functional materials and their specific surface processes. The high-temperature (electro)catalysis manipulator is designed for probing solid state/gas phase interactions for heterogeneous catalysts including solid electrolyzer/fuel cell electrocatalysts at pressures up to 15 mbar and temperatures from room temperature to  $1000 \,^\circ$ C. The liquid electrolytes and the third one for experiments for ice and ice-like materials at cryogenic temperatures to approximately  $-190\,^\circ$ C. The flexible and modular combination of these setups provides the opportunity to address a broad spectrum of *in situ* and *operando* XPS experiments on a laboratory-based system, circumventing the limited accessibility of experiments at synchrotron facilities.

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### I. INTRODUCTION

In times with drastically increasing need to explore new routes toward reduction of anthropogenic green-house gases and to utilize these to generate sustainable fuels and energy vectors, it is necessary to foster existing techniques to large scale and industrially relevant application. In fact, numerous different approaches for so called  $CO_2$  capture and utilization (CCU) exist and appear to be promising candidates for reducing radiative forcing on our atmosphere.<sup>1,2</sup> However, despite immense research efforts to promote CCU, nearly all these concepts still only prevail in laboratory-scaled dimensions or at most in pilot plants and are still far away from having a significant impact on global warming. The main reasons for the slow progress of upscaling CCU are high investment and production costs for renewable electric energy, and, once the electricity is generated, the low efficiency of energy conversion and storage processes. Suitable (electro)catalysts allow to tackle the latter aspect, thus allowing for more price-competitive renewable energy carriers. Some materials on which the (electro)catalysts are based, consist of rare and expensive noble metals, such as Rh, Pt, or Pd.<sup>3–7</sup> To identify and develop more abundant and less costly materials for efficient, heterogeneous, (electro)catalysts, it is of outstanding importance to gain better understanding of the fundamental processes occurring especially at the surface/interface of such alternative materials.<sup>8–14</sup>

In the last few decades, x-ray photoelectron spectroscopy (XPS) evolved as a powerful technique in catalyst development, as it probes a material's surface with respect to chemical composition, element distribution, and oxidation states.<sup>8,15-21</sup> The great advantage of this technique is its inherent surface sensitivity, which is a consequence of the mean free path of (photo)electrons inside a material of only a few (<10) nanometers.<sup>22,23</sup> However, a huge drawback of conventional XPS is the requirement of ultra-high vacuum (UHV) to investigate a sample's surface. Such pressures are far away from realistic reaction conditions, as most catalytic processes occur at elevated temperatures and pressures. Therefore, Siegbahn et al. came up with near-ambient-pressure-XPS (NAP-XPS) in the 1970s, allowing for in situ experiments under "close-to-real" conditions, while simultaneously detecting photoelectrons.<sup>24-26</sup> Continuous development has improved NAP-XPS to modern instruments, allowing for spectroscopy at pressures of several mbar by utilizing high-intensity focused x-ray sources in combination with efficient, differentially pumped electrostatic lens systems. Utilizing small apertures of several hundred micrometers while keeping up high pumping speeds allows achieving a pressure difference of several orders of magnitude between the analyzing chamber and the first differential pumping stage.<sup>16,26</sup> Consequently, the sample can be exposed to gas atmospheres in the mbar range while simultaneously collecting XP-spectra, which offers the opportunity to observe chemical changes at a working (electro)catalysts surface online ("in situ") under reaction conditions. However, most of the available systems are located at synchrotron facilities,<sup>16,26-28</sup> where availability of beamtime on the instrument is competitive and very limited. Furthermore, the highly specialized instruments at the synchrotron facilities often cannot be easily adapted to a broader range of sample environments. This makes it challenging to individually adapt and optimize experimental parameters, such as sample type and sample stage design. Therefore, an increasing choice of commercially available laboratory-based NAP-XPS systems became available in recent years, which provide new opportunities for research facilities to tune the experimental setups with respect to their individual requirements.<sup>10</sup> <sup>(8,29</sup> Despite commercial availability, the systems strongly differ from each other in terms of experimental setup and attached instruments depending on the specific research topic.

Here, we present a highly customized NAP-XPS instrument that can provide a vast range of experimental conditions. The entire system has been designed, constructed, and built in close cooperation between the *Institute of Physical Chemistry* at the University of Innsbruck and the XPS analysis system manufacturer *SPECS nano-surface analysis GmbH* headquartered in Berlin, Germany. The result of this co-development is a unique laboratory-based ultra-flexible NAP-XPS system providing the choice of performing catalytic, solid-state, and liquid-electrochemical as well as cryo-chemical investigations in the pressure range from  $10^{-9}$  to 25 mbar and in the temperature range from -196 to +1000 °C. Mass spectrometry, electrochemical current-voltage characterization, and electrical impedance spectroscopy are coupled to the

instrument, which enables *operando* electro-, photo-, and thermochemical experiments with synchrotron XPS data quality. A combination of three different custom-made and easily interchangeable manipulators and their respective sample stages allows for the investigation of a broad range of specimens in a single multifunctional *in situ* XPS instrument: (1) (inter)metallic and metaloxide composite model catalysts and supported catalysts; (2) solid oxide-gas electrodes; (3) solid–liquid and battery electrodes; (4) photochemically functionalized surfaces; and 5) cryogenic ice-based samples.

### **II. INSTRUMENT OVERVIEW**

The instrument features a unique modular design and represents a custom-extended version of a state-of-the art NAP-XPS setup (i.e., focused x-ray source, monochromator, and hemispherical analyzer), including a three-stage electric refocusing lens system with differential pumping. Figure 1 depicts a general overview of the setup with its specific vertically oriented analyzer geometry and two simultaneously attached manipulators at the main chamber in a 180° horizontal orientation to each other. All parts of the setup can be baked out separately by means of custom-made baking tents and custom-compartments, and are fully UHV-compatible. Additional features comprise an independent sample preparation chamber, a flow-controlled gas manifold and dosing unit, a diode infrared laser sample heating system, a flood gun, various customized tools, such as quadrupole-mass-spectrometers (QMS), a sputter gun, a heated gas dosing unit, and a UV-light source for in situ sample irradiation. All mentioned features are depicted and indexed in Fig. 1 and will be subsequently described, while an index-citing logic is provided to the reader for a better overview.

The x-ray source (1) is a micro-focus system (SPECS XR 50 MF) generating Al K<sub>a</sub> radiation (E = 1486.7 eV) using an aluminumcoated silver anode with a maximum voltage +15 kV at powers ranging from 10 to 150 W (maximum power 200 W). It features an additional x, y, z manipulator that allows, in combination with the adjustable ellipsoidal crystal monochromator (SPECS  $\mu$ -FOCUS 600 NAP; quartz single crystal mirror) (2), to position and vary the x-ray spot on the sample in the range between 200  $\mu$ m and 1 mm diameter.

The analyzer is a SPECS PHOIBOS 150, consisting of a differential pumped column in vertical orientation (3) with built-in electron optics and a hemispherical electron energy analyzer (4) equipped with a 1D delay line detector (DLD) (Surface Concept GmbH, 55124, Mainz, Germany). The analyzer allows experiments in the kinetic energy range from 0 to 3500 eV, which provides the possibility to use x-ray sources with higher radiation energies than Al  $K_{\alpha}$  radiation (e.g., Zr or Ag based anodes). A maximum energy resolution of <10 meV (KE < 200 eV) is achieved by the possible combination of eight interchangeable entrance slits (straight  $0.1-7 \times 25$  mm and 1-3 mm curved) and three exit slits. The radius of the central trajectory through the outer and inner hemisphere is 150 mm, allowing pass energies up to 550 eV. A 1D DLD detector, consisting of a readout unit with meander-structured onedimensional delay line and a Chevron microchannel plate stack for pulse amplification, captures the electrons and determines their position of impact in two dimensions. This gives the opportunity to



FIG. 1. Overview of the modular NAP-XPS instrument with the vertically aligned analyzer and two simultaneously attached manipulators (left side: gas-solid manipulator, right side: electrochemistry manipulator) in 180° orientation to each other.

measure a limited energy range very quickly in the "snapshot" mode beyond conventional scanning.

The PHOIBOS NAP analysis unit consists of a three-stage differentially pumped electrostatic lens system separated by apertures and the differentially pumped analyzer itself. When ejected from the sample, the electrons travel through the first nozzle with a diameter of 0.3 mm and an acceptance angle of  $60^{\circ}$  into the pre-lens, which constitutes the first stage of the differential pumping system and focuses the electrons onto the working point of the second stage of the analyzer. A 2 mm aperture as well as a pneumatic gate valve separates the pre-lens stage from the second stage and allows us to isolate the rest of the analyzer and the pre-lens unit from each other. Stages two and three contain further electrostatic lenses and pumps to successively lower the pressure and to guide as many electrons as possible toward the entrance slit of the hemispherical energy filter. The nozzle with a typical diameter of 0.3 mm allows for pressures of 15 mbar inside the main chamber while the pressure inside the pre-lens does not exceed 10<sup>-6</sup> mbar, which optimizes the number of electrons guided toward the further stages where ultra-high-vacuum conditions  $(10^{-10} \text{ mbar})$  are successively approached.

To measure the gas phase composition and products formed during the *in situ* XPS experiments, two QMS (5) (i: MKS Instruments Inc., MA, Andover, USA; Model: e-vision2; detector: multichannel plate dual; mass range: 1–100 amu; ii: Hiden Analytical Limited, WA5 7UN, Warrington, U.K.; Model: HAL 100; detector: Faraday cup; mass range: 1–100 amu) are placed in the first and second differential pumping stage, respectively, and can be used depending on the sensitivity requirements with regard to the pressure. Gases evolving at the sample surface inside the recipient are pumped through the nozzle and can be detected online without delay, giving live information on product formation at the sample surface.

For experimental extension of the standard in situ NAP-XPS setup, three different manipulators (6, 7a, 7b) were specifically designed and customized for this system to cover a maximum range of research topics, including functional materials for sustainable energy conversion, energy storage, greenhouse gas recycling, and atmospheric chemistry processes, each requiring strikingly different experimental approaches.<sup>30–32</sup> Therefore, each manipulator setup is designed to fulfill highly specific tasks and will be described in three separate sections in the following. Basically, the main requirements can be divided into three categories, namely, investigations in heterogeneous (electro)catalysis for solid state/gas phase reactions and electrode processes (in the following denoted as "gas-solid manipulator"), energy-relevant solid/liquid interface electrochemistry ("EC manipulator"), and atmospheric/ice chemistry at cryogenic temperatures ("cryo manipulator"). More details regarding the manipulators can be found in the supplementary material under Sec. A and in Fig. S1. Details of XPS analysis and fitting parameters of the further presented XP-spectra illustrated in each of the three manipulator sections [Secs. III A–III C] are summarized in the supplementary material under Sec. B, Tables S1 and S2. The data evaluation and fitting of all XP-spectra was performed using the CasaXPS software program, version 2.3.24 PR1.0 (Casa Software Ltd.).

Here, it should be noted that the "EC manipulator" in Fig. 1 is currently mounted on the right-hand side on a rail platform (8) that allows for fast exchange with the "cryo-manipulator." For experiments using the "gas-solid manipulator" mounted on the left-hand side the samples are transferred into the recipient via an additional transfer rod through a load lock/preparation chamber (9). This load lock is designed to facilitate the exchange of pre-cleaned/prepared samples without the need for intermediate venting. When introduced to the load lock, the samples can be temporarily stored in an extra sample holder with five slots and transferred to the manipulator sample stage by means of a 500 mm magnetically coupled linear transfer rod. Furthermore, the preparation chamber is equipped with a monoatomic  $Ar^+$  sputter gun (Thermo VG Scientific, RH19 1UB, East Grinstead, U.K.; model: EX03; beam energies: 500–3000 eV) for cleaning the samples and an additional leak valve for a possible gas exposure or CVD coating procedure.

The spherical  $\mu$ -metal (to shield from external fields) main chamber (10) functions as a central part of the analysis instrument connecting the x-ray source and monochromator compartment, the differential pumped analysis compartment and the manipulators. The main chamber is equipped with a flood gun (SPECS, FG 22) to prevent charging of isolating samples under UHV



FIG. 2. (a): Schematic setup of the gas mixing system; the gas lines behind the main chamber represent the small bypass (SB), large bypass (LB), and the main gate valve outlet (AO: all open), [(b) and (c)] Zr3d XPS spectra and integrated intensities obtained at the indicated CO<sub>2</sub> pressures in the main chamber.

measurement conditions. A near-infrared diode laser (11) (IPG Laser GmbH, 57299, Burbach, Germany; model: DLR-100-AC; max. power: 100 W) is connected to the bottom of the main chamber to heat samples up to 1000 °C. An in-house manufactured heated gas dosing unit enables to supply gas with a controlled temperature (up to 700 °C) to the sample surface, to overcome delayed reactivity of weakly sticking gas molecules under ambient temperature. A UV/Vis/NIR-light source (B & W Tek Inc., NJ 08536, Plainsboro, USA; model: BDS130A D<sub>2</sub>/W; wavelength range: 190–2500 nm) is utilized to irradiate samples and investigate UV-induced functionalization (e.g., polymerization reactions) *in situ* via an optical fiber directed to the sample surface.

An automated gas mixing system (12) is located beneath the main chamber, allowing for backfilling of the recipient with variable gas compositions and pressures. Figure 2(a) schematically depicts the gas mixing system, which is basically comprised of six mass flow controllers (MFCs) [BRONKHORST HIGH-TECH B.V., 7261, AK Ruurlo, Netherlands; model: EL-FLOW Prestige (for gases) and LOW-ΔP-FLOW (for liquid vapors; volume flow: 1-50 ml/min)] attached to a gas manifold, an automated pressure control valve (VAT Vakuumventile AG, 9469, Haag, Switzerland; model: 59.0 UHV all-metal variable leak valve) for gas supply into the main chamber, and the respective roughing pump for evacuation of the manifold. Two of the MFCs are specifically dedicated to the dosing of evaporated liquids from attached round-bottom flasks, which makes it possible to introduce, e.g., H<sub>2</sub>O, ethanol, or vapor mixtures, to the main chamber. We note that the gases/vapor flasks attached to the MFCs shown in Fig. 2(a) can be individually exchanged anytime by other gases and liquids and represent the preferred setup at the time of writing of this review. As can be deduced from Fig. 2(a), the main chamber can be pumped via three downstream outlets/bypasses differing in diameter and therefore resulting in different pumping rates. In combination with the choice of the remotely proportional integral differential (PID)controlled VAT pressure control valve vs conventional UHV leak valves upstream to the main chamber, the small (SB), and large bypass (LB) as well as the main gate valve (AO: all open) allow to precisely control the gas flow through the chamber and the pressure at the sample. This system, therefore, provides the opportunity to bridge the entire "pressure gap" continuously between ultra-high vacuum  $(10^{-9} \text{ mbar})$  and near-ambient pressure (up to 25 mbar) conditions. The signal intensity trends of the XPS data in Figs. 2(b) and 2(c) reveal that spectroscopic experiments can be performed under gas pressures ranging from  $10^{-9}$  mbar up to several millibars. The total signal integrals of a Zr 3d spectrum under the chosen CO<sub>2</sub> atmosphere show a rather minor signal intensity loss up to pressures around 1 mbar, whereas at higher pressure the signal decreases quickly. However, as will be shown in Sec. III, we are able to record highly resolved XP spectra with satisfactory signal-tonoise ratio even at pressures above 15 mbar. To monitor pressures different gauges have been installed: Pirani gauges (PG) (PFEIF-FER VACUUM, 35614, Asslar, Germany; Model: TPR), capacitive gauges (CG) [INFICON AG, 9496, Balzers, Lichtenstein; model: CDG (1 mbar range) and Leybold GmbH, 50968, Köln, Germany; Model: CERAVAC CTR (100 mbar range)] and ion gauges (IG) (JEVATEC GmbH, 07743 Jena, Germany; Model: ATMION). As a roughing pump a scroll pump (SP) (Leybold GmbH; model: SCROL-LVAC) is attached to the system. UHV conditions are ensured via

various turbo molecular pumps (TMP) (all PFEIFFER VACUUM; model: HiPace with different pumping capacities).

#### III. REPRESENTATIVE EXPERIMENTAL RESULTS OBTAINED WITH THE SPECIFIC MANIPULATOR SETUPS

# A. Gas-solid manipulator setup and *in situ* electrocatalytic experiments on a Ni/8-YSZ SOFC/SOEC sample

The thermally assisted co-electrolysis of CO<sub>2</sub> and water to form renewable fuels using solid oxide electrolysis cells is likely to become a key technology in the 21st century.<sup>33</sup> For instance, recent studies have successfully extended synchrotron-based NAP-XPS to *operando* studies of solid-oxide-electrolyzer-cell (SOEC) and solidoxide-fuel-cell (SOFC)-relevant doped perovskite materials.<sup>17–20,34</sup> However, most studies and experiments of this type are limited to granted beamtime at synchrotron facilities. Here, we demonstrate that our "laboratory-based" setup allows for simultaneous *operando* NAP-XPS analysis and electrochemical impedance spectroscopic (EIS) analysis and mass spectroscopic (MS) analysis of SOFC/SOEC exchange currents/activities/products at pressures up to 15 mbar. This allows us to unambiguously link the electrocatalytic performance of the electrodes to their active electronic structure and redox state.

The sample mounting stage of the gas-solid manipulator can be equipped with different sample holders based on the standard SPECS plate design. Simple plates are used for metal-based model catalysts or pressed powders, but for solid-state electrochemistry purposes, six-contact SOFC/SOEC cell sample holders as depicted in Fig. 3 have been developed for our instrument. This design allows the samples to be electrically connected to a potentiostat (BioLogic Science Instruments, 37081, Göttingen, Germany; model: Biologic SP-200) and, therefore, to perform state-of-the-art operando electrochemical investigations from simple polarization experiments to cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS) measurements during XPS operation. For contactfree heating of the samples from the backside at elevated pressures, an 8 mm hole in the bottom of the sample holder [Fig. 4(a)] allows us to directly irradiate the backside of the specimen with the attached IR-laser to temperatures between room temperature and 1000 °C,



FIG. 3. Stainless steel six-contact SOFC/SOEC cell sample holder with 8 mm hole for laser heating from the backside. Two contacts are dedicated for the K-type thermocouple, the others for electrical connections of the sample cell and the sample holder.



FIG. 4. SOFC/SOEC model cell setup for *in situ* XPS experiments using the "gas–solid manipulator." (a) Schematic cross section of the sample cell stack and the experimental setup. (b) Six-contact sample holder with mounted Ni/8-YSZ solid oxide cell. The indicated numbers are explained in the legend of (a). (c) Sample in measuring position in front of the analyzer nozzle under operating conditions. The marked area represents an optical micrograph of the catalytically active zone under investigation for CO<sub>2</sub> splitting.

using a diode infrared laser with a maximum output power of 100 W. The control of pulse amplitude and width modulation with a PID heating controller (Eurotherm, BN13 3PL, Worthing, U.K.; model: 2604) allows for a precise sample temperature adjustment between room temperature and 1000 °C, with the option of implementing user-defined temperature programs. The actual temperatures are monitored with a K-type thermocouple attached or spot welded directly to the sample (Fig. 4).

Figure 4 shows the six-contact sample holder together with a SOFC/SOEC button-cell sample mounted and electrically connected. In Fig. 4(a), a simplified scheme of the cell stack together with the sample holder discloses the detailed experimental SOFC/SOEC setup used for the operando electrochemical XPS experiments. The respective sample stage placed directly beneath the nozzle, with the IR-laser beam irradiating the Pt-back plate during the *in situ* XPS experiment is visible in Fig. 4(c) [i.e., a glowing ring shining through the quartz isolation ring (6)]. The inset in (c) presents a micrograph of the marked area of the cell surface showing the electrochemically active zone (i.e., the mechanically uncovered interface of the Ni/YSZ cermet working electrode and the YSZ solid oxide electrolyte) imaged by optical microscopy. In the vicinity of the bright area (the uncovered YSZ solid oxide electrolyte), sufficiently thin cermet layers for observation of active triple-phaseboundary (TPB) regions, which are accessible both for ionic and electronic transport, are provided.

In a proof-of-principle experiment, a spin-coated, thermally sintered, and pre-reduced Ni/8-YSZ cermet layer (1:1 volume ratio) was investigated regarding its activity toward carbon dioxide splitting. A platinum–gadolinium doped ceria (Pt-GDC) cermet with high surface area served as counter electrode on a commercial 8-TSZ button cell (Kerafol GmbH & Co. KG), featuring minimized overpotential contributions.<sup>35</sup> To investigate the catalytically active solid electrolyte interface (SEI), a small notch was milled into the as-synthesized sample [Fig. 4(c)].

The corresponding XP-spectra of the Ni  $2p_{3/2}$  and the Zr 3d region at open circuit voltage (OCV) and upon cathodic polarization at -1 V vs the counter electrode (denoted as  $V_{CE}$ ) at 550 °C

under 0.5 mbar CO<sub>2</sub> are shown in Fig. 5(a). At OCV, the typical peak shape of metallic Ni with a peak maximum at 852.6 eV, as well as the zirconium-containing oxide solid electrolyte with its Zr 3d spin orbit couple at 182.8 and 185.2 eV, respectively, can be observed.<sup>36,37</sup> Upon polarization no binding energy shift should occur on the grounded cermet working electrode (WE), as it is fully metallic-conducting. Consequently, the energies remain fixed to the analyzer potential, whereas a -1 eV/V shift of the electrolyte species should provide proof of a successful electrochemical polarization experiment. This -1 eV/V shift is exactly what we find for the Zr 3d signals, which demonstrates that the electrochemical setup provides proper ionic conductivity. This allows the investigation of processes going on at the SEI in the operando mode, as the potential-dependent electrolysis current can be directly correlated with the spectroscopically characterized chemical state of the electrode surface. The much smaller shift in binding energy of the Ni 2p signal, along with some peak broadening, is attributed to electrochemically not fully percolated Ni domains within the bulk Ni/8-YSZ layer, i.e., to intensity contributions from single, electronically decoupled particles dispersed on top of the electrolyte [visible in the optical micrograph given in the inset of Fig. 4(c)]. A related argumentation involving incompletely percolated YSZ is proposed for the decreased resolution and peak broadening of Zr 3d under polarization (-1 V).

The XP spectra in Fig. 5(a) were recorded at the indicated potentials during the electrochemical experiment shown in panel B. The cyclic voltammogram together with the simultaneously recorded QMS signal (m/z = 28) correlates the sample potential with the CO<sub>2</sub> electrolysis current, i.e., the evolution of CO at the SOFC/SOEC surface. In Fig. 5(c), subsequently measured electrochemical impedance data are shown. Depending on the applied frequency, the experiment reveals distinct electro-chemical processes in the electrochemical cell. The experimental data are fitted via the electrical equivalent circuit derived from Ref. 38, as shown in the inset of panel (c). The capacitance is calculated using  $C_i = ((R^{1-\alpha} \cdot Q_i)^{1/\alpha})/A$  with  $A = r^2 \cdot \pi$  being the button cell area (r = 5 mm).  $Q_i$  and  $\alpha$  are fit parameters of the constant phase



FIG. 5. In situ XPS and simultaneous electrochemical polarization experiments on the Ni/8-YSZ SOFC/SOEC sample at 550 °C under 0.5 mbar CO<sub>2</sub>. (a) Ni  $2p_{3/2}$  and Zr 3d XP spectra at open circuit potential and polarization to -1 V (upper and lower panels, respectively); (b) cyclic voltammograms (10 mV/s) of the Ni/8-YSZ sample at 550 °C. The lower panel shows the correlation of CO evolution (m/z = 28) vs time during periodic cycling; (c): Electrochemical impedance spectroscopy data (amplitude voltage: 15 mV; frequency range: 1 MHz–10 mHz) of the Ni/8-YSZ sample with equivalent circuit fitting. (R<sub>1</sub> = 8.1  $\Omega$ ; R<sub>2</sub> = 1.8  $\Omega$  and C<sub>2</sub> = 1.02 × 10<sup>-2</sup> F cm<sup>-2</sup>; R<sub>3</sub> = 11.4  $\Omega$ ; and C<sub>3</sub> = 1.00 × 10<sup>-2</sup> F cm<sup>-2</sup>).

element. The intercept on the x-axis represents the electrolyte ohmic resistivity (R1). The left semi-arc is related to the first RC-element [non-ideal capacitor represented with a constant phase element (CPE) and a resistor in parallel]. It can be associated with the mass transport via linear surface diffusion toward the three-phase boundary of the Ni/8-YSZ interface,<sup>39</sup> typically occurring at frequencies in the range of 10-100 Hz. The right semi-arc is fitted by a second electrical RC element in series (again resistor and non-ideal capacitor) and is related to dissociative adsorption of CO2 at the solid-gas interface (herein most likely  $CO_2 \rightarrow CO + O_{ads}$ ).<sup>39</sup> The frequency for this reaction is ~1.5 Hz. The data shown in Fig. 5 highlight the instrument to be capable of performing close-to-real electrocatalytic characterization by EIS at elevated temperatures and pressures (up to 1000 °C and 15 mbar) while simultaneously recording operando XP spectra and detecting gaseous reaction (by-) products by means of the online mass spectrometer in the first pumping stage. This synchronous instrumental interplay provides the exclusive possibility to not only identify catalytically active species at the samples surface but to clarify entire surface processes and reaction mechanisms for novel functional materials.

### B. Electrochemistry manipulator–Cell setup and experimental *in situ* XPS results on a polarized Pt sample in aqueous Na<sub>2</sub>SO<sub>4</sub> electrolyte

Besides electrochemistry performed at the SEI, we can also track processes at the solid/liquid interface with the electrochemistry manipulator. In principle, two different approaches can be utilized to perform electrochemical *in situ* XPS measurements: either the solid/liquid interface is probed from the backside of the electrode<sup>40</sup> or from the electrolyte side.<sup>41,42</sup> Herein, we focus on the latter case, as this allows us to probe any sample independent of its morphology. The main requirements that have to be fulfilled to successfully investigate the electrified solid/liquid interface *in situ* are as follows:<sup>43</sup>

 (i) The electrolyte layer must be thick enough to exhibit ionic conductivity but simultaneously thin enough that photoelectrons (PEs) ejected from the core levels of the respective working electrode (WE) can be detected.

The equilibrium vapor pressure, e.g., of water, in the analyzing chamber must be set as low as possible to minimize gas phase absorption and thus to maximize the quantity of electrons reaching the detector. The equilibrium gas atmosphere additionally helps to avoid undesired boiling retardations.

#### (ii) The electrolyte film has to be stable for several hours

Regarding the first point (i), the inelastic mean free path (IMFP) of an electron in liquid water is strongly dependent on its kinetic energy (e.g., 0.986 nm at 54.6 eV; 4.8 nm at 1334.4 eV; 10.78 nm at 3640.9 eV),<sup>44</sup> and hence, on the material investigated, more specifically on the energy of the respective core level and the x-ray source utilized. Hence, most electrochemical in situ measurements in aqueous electrolyte were performed at synchrotron facilities hitherto,<sup>26,27,45-48</sup> as flexible adjustment of the beam energies (usually in the "tender" x-ray regime ~1.5-5.0 keV) allow for electrolyte films of about 30 nm thickness. In case of laboratorybased systems, however, the beam energy is fixed to the energy of the x-ray source (in most cases, an Al  $K_{\alpha}$  source with an energy of 1486.6 eV). Considering an IMFP of about 6 nm in water for the photoelectrons, the electrolyte film thickness must not exceed 18 nm if both the electrode and electrolyte shall be probed simultaneously. Furthermore, the lower brilliance compared to synchrotron radiation results in additional attenuation of the signal. This can be compensated for by reduction of the background pressure in the analyzing chamber from 25 mbar (standard settings at synchrotron facilities) down to <10 mbar, which leads to reduced gas-phase absorption and a significant increase of XPS signal intensity. Yet, at these low pressures, the electrolyte would evaporate if kept at

room temperature (water vapor pressure is around 25 mbar at RT). Therefore, the manipulator, the sample stage as well as the homebuilt EC-cell were specifically designed to allow the liquid electrolyte to be cooled down to  $\sim 2 \,^{\circ}$ C – a temperature at which a stable (aqueous) electrolyte film at reduced pressures can be maintained. This is achieved via stainless steel capillaries (1 mm inner diameter) connected to a thermostat, led through the manipulator and fixed to the sample stage. Figure 6 depicts the self-designed and homebuilt EC cell and the respective sample stage for electrochemical *in situ* XPS experiments.

The sample stage is comprised of copper and possesses cooling lines fed through the Cu block using ethanol as cooling agent. To optimize the contact area of cell and stage for increased thermal conductivity, the EC cell is covered with an additional Al shell that precisely fits inside the cutout of the Cu block. The EC cell itself is composed of polychloro-trifluoro-ethylene (KEL-F) for high chemical inertness and moderate hydrophilicity when using aqueous electrolytes. For facilitated sample/setup preparation inside the manipulator, two graphite rods serve as reference (RE) and counter electrode (CE) and can easily be connected with the quick-connect adapter. This component allows us to remove and load the EC cell from the sample stage for preparation (e.g., exchange of working electrode and electrolyte) without the need for opening the manipulator flange. To fulfill the above-mentioned conditions for in situ EC XPS experiments, a modified, tilted angle approach is applied. That is, the cell exhibits a geometry in which the WE can be immersed partly at an inclination angle of  $20^{\circ}$  so that an ultrathin electrolyte film is formed above the electrolyte level due to capillary forces, as schematically shown in Fig. 6(a). This design allows for the compromise of an electrically conductive electrolyte layer on top of the WE, which is at the same time thin enough for photoelectrons to penetrate and reach the detector.

To prove the capability of this lab-based setup, we exemplarily show here the potential-dependent redox behavior of polycrystalline platinum (Pt) in 0.1 M Na<sub>2</sub>SO<sub>4</sub>. For this experiment, a flameannealed Pt foil is used as working electrode (WE). We note that the WE is connected with the spectrometer ground in the experiment, and the potential difference is applied via the counter electrode (CE). Two graphite rods serve as CE and reference electrode (RE), respectively. Prior to the measurement, the electrolyte was cooled down to 2 °C, followed by a degassing step in the preparation chamber by pumping down to 7 mbar and waiting for 20 min until equilibration was reached. Then, the sample was introduced into the analyzing chamber (background water pressure ~7-10 mbar) and approached toward the analyzer nozzle. During the spectroscopy step, the sample was irradiated with x rays and the electron counts were measured as a function of distance. The ideal working distance is found when counts are maximized so that the best signal to noise ratio during the in situ experiment is guaranteed.

Then, O 1s and Pt 4f spectra were acquired at 0 V vs the reversible hydrogen electrode ( $V_{RHE}$ ) to prove that the measured spot allows us to probe the electrolyte-covered substrate and the thin



FIG. 6. Electrochemical setup for *in situ* XPS experiments in aqueous/liquid electrolytes. (a) Scheme of the electrochemical cell, utilizing a modified tilted angle approach. Slightly above the electrolyte level, an ultrathin electrolyte film is formed on top of the working electrode. (b) 3D sketch of the sample stage and cell. [(c) and (d)] Setup in measurement position and inside the preparation chamber, respectively. WE: working electrode; CE: counter electrode; and RE: reference electrode.

electrolyte film simultaneously (Fig. 7). The O 1s region exhibits two distinct peaks attributed to gas phase water (GPW; dark blue) and liquid phase water (LPW; light blue), which originate from the back-ground H<sub>2</sub>O pressure and the electrolyte, respectively. Additionally, two peaks can be observed in the Pt 4f region, which are related to the Pt  $4f_{7/2}$  and Pt  $4f_{5/2}$  spin orbit couple of metallic Pt (Pt<sup>0</sup>). This suggests that the electrolyte film is sufficiently thin to allow for the photoelectrons to escape from the metal, penetrate the ultrathin film, and get detected.

To verify that the electrode is homogeneously covered by electrolyte under potential control (in contrast to a situation where the used x-ray spot with an area of  $100 \times 300 \ \mu\text{m}^2$  partly irradiates non-wetted Pt and partly electrolyte regions being already too thick for photoelectrons ejected from the metal to penetrate), an anodic potential of +1.2 V was applied and XP-spectra were recorded simultaneously [Figs. 7(a) and 7(b), bottom panels]. A distinct shift in the binding energy can be observed for the GPW and LPW related signals, while the binding energy of the Pt 4f peaks does not change. This is expected upon measuring the actual solid liquid interface of

a metallic electrode connected to the spectrometer ground and is in good agreement with literature results.<sup>42</sup> The electrochemical shift of the binding energy in the O 1s spectra is due to changes in the electric field when the polarization is altered, while the substrate is grounded alongside with the analyzer and hence is not affected by the applied potential.

Interestingly, additional features occur in the Pt 4f region, which can be clearly attributed to oxidized Pt species [green component in Fig. 7(b), bottom panel] and which are in excellent agreement with the CV depicted in Fig. 7(c), as an anodic current related to the oxidation of platinum can be observed in the CV at these potentials. These preliminary results represent one of the first successful *in situ* NAP-XPS measurements of a bulk electrode in aqueous electrolyte solution using a laboratory-based XPS instrument. They furthermore prove that it is clearly possible to probe the electrified solid/liquid interface using soft X-rays from a standard laboratory source. This demonstrates the enormous potential of the novel instrumental setup as well as of our homebuilt customized electrochemical cell.





### C. Cryo manipulator–*In situ* XPS experiments on ice under CO<sub>2</sub> atmosphere

The focus of our cryo-research is on the anomalies of supercooled liquid water,49 glassy water,50,51 and the polymorphism of In addition to pure water, we also study aqueous solutions at ice. cryogenic conditions, in which ice-like materials, such as clathrate hydrates, are of interest.<sup>54</sup> This includes studies on homogeneous and heterogeneous ice nucleation in liquid water upon cooling the stable liquid as well as upon heating the amorphous solids. Also, chemical reactions at cryogenic temperatures in ice matrices are of great interest. For instance, the protonation of carbonates with strong acids to produce carbonic acid (H<sub>2</sub>CO<sub>3</sub>) takes place on the time scale of minutes above 120 K, but is kinetically hindered below 100 K.<sup>55</sup> This process might even produce carbonic acid in Earth's troposphere from calcite.<sup>56</sup> That is, using cryotechniques instable species, such as H<sub>2</sub>CO<sub>3</sub>, that immediately decompose at room temperature can be isolated and studied. In Earth's stratosphere, ice clouds act as a catalyst, converting chlorine reservoir species (such as HCl and ClONO<sub>2</sub>) to active chlorine species (such as Cl<sub>2</sub> and HOCl), which cause the ozone hole above Antarctica upon sunrise in polar spring.<sup>57</sup> In space, the chemistry going on in amorphous ices in interstellar clouds upon high-energy irradiation is at the heart of the evolution of molecules.<sup>58</sup> While, in the past, we have studied these processes in the bulk thoroughly, a clear understanding of the chemical changes taking place at the ice surface is largely lacking. For instance, the formation of a quasi-liquid layer upon HCl adsorption of ice or surface-induced crystallization have been inferred, but not directly observed. Using NAP-XPS, we will now be able to tackle such questions.

Although XPS studies on hexagonal ice (ice  $I_h$ ) using only Peltier elements for cooling exist, no XP-spectra of any of the other 20 crystalline ice phases known today were recorded up until now. A sample holder that allows the samples to be kept at liquid nitrogen temperature inside the XPS chamber has so far not been available, to the best of our knowledge.

Therefore, the EC manipulator can easily be exchanged with the cryochemistry manipulator using the rail platform. This manipulator is equipped with stainless steel pipes connected to a copper cooling finger, with drilled notches of different diameters and depths serving as a sample stage, as depicted in Fig. 8. The circular wells

to hold the samples are designed for a snug fit of the ice specimens produced in our high-pressure cells so that ideal thermal conductivity between the cooling finger and the ice samples is guaranteed. By feeding liquid nitrogen through those cooling pipes, a temperature of 85 K can be achieved and maintained, and temperature stability and control can be tracked via a K-type thermocouple spotwelded on the sample stage [Fig. 8(a)]. Furthermore, the system is equipped with wires dedicated to resistive heating, which are connected to a cryogenic temperature controller and allow to precisely adjust any temperature between 85 K and room temperature. Therefore, the cryo-manipulator along with its cooled sample stage allows us to investigate the properties of ice, adsorption processes thereon, and cryo-chemical reactions at and near the ice surface in situ over the entire temperature range from liquid nitrogen temperature to room temperature for the first time in a laboratory-based NAP-XPS system.

To illustrate the working principle of the cryo-setup, the adsorption properties of CO<sub>2</sub> on ice were investigated. To this end, the sample stage was cooled to 85 K, followed by the transfer of an ice specimen immersed in liquid nitrogen to the sample stage. For this experiment, ice XII was utilized and further investigated by XPS. Ice XII-specific results are not shown here (details regarding the preparation of the specimens are described elsewhere<sup>59</sup>). Ice XII represents a high-pressure phase of ice, undergoing a phase transition to stacking-disordered ice I<sub>sd</sub> when heated above 140 K with a 40% volume expansion.<sup>60</sup> As this volume expansion was not observed, we conclude that the temperature of the sample never exceeded 140 K during the transfer, which was followed by differential pumping of the manipulator to about  $10^{-7}$  mbar.

After transferring the sample to the measurement position, an optically visible layer of ice was present on top of the copper cooling finger. This can be explained by the sublimation of water from ice XII and recondensation at around  $10^{-7}$  mbar. The recondensed ice on top of the copper cooling finger is ice I<sub>h</sub>, i.e., the common form of ice on Earth, and hence the primary model ice phase to evaluate the capabilities of the setup. Therefore, we recorded O 1s and C 1s spectra of the recrystallized ice I film. Measuring XPS of ice causes some difficulties, as ice has isolating properties, which cause charging of the sample surface during the experiments. This issue could be partially compensated by employing the attached flood gun



FIG. 8. Setup for cryochemistry applications. Panel (a) shows the sample stage that allows for temperatures down to 85 K. Panel (b) depicts the sample in the analysis chamber in front of the nozzle. A crystalline ice film on top of the copper cooling finger due to sublimation/recrystallization from the adjacent ice XII specimen can be observed.



**FIG. 9.** XP spectra of adsorbed  $CO_2$  on an ice I<sub>h</sub> film and respective binding energy calibration at a background pressure of  $5 \times 10^{-7}$  mbar in the main chamber. In panel A, the O 1s spectra and, in (b), the C 1s spectra are depicted. The top panels represent the measurement before controlled exposure to  $CO_2$ , but already show minor amounts of  $CO_2$  from background gas adsorption, and the bottom panels represent the state after the controlled 60 L  $CO_2$  exposure. The transparent datasets show the peak positions before binding energy calibration.

(energy: 5 eV, emission: 30  $\mu$ A) that provides a sufficient electron flux to the sample to reduce this effect. However, an additional BE calibration had to be performed, as sample-charging shifts the BEscale by several eV. For this purpose, and to demonstrate the general possibility of investigating gas adsorption and absorption processes on ice samples, a small amount of CO<sub>2</sub> was dosed into the main analysis chamber (1 min at 10<sup>-6</sup> mbar, 60 L).

Figure 9 depicts the O 1s and C 1s spectra of the hexagonal ice layer before and after controlled CO2-exposure. The as-measured O 1s spectrum prior to CO<sub>2</sub> exposure (top panel, transparent signals) shows a Gaussian like shape and already exhibits a small shoulder at the high binding energy edge of the spectrum. Via peak fitting, two O 1s components can be distinguished, i.e., one related to the ice lattice (blue) at 536.9 eV and a minor component related to a small amount of adsorbed or absorbed CO2 (red) at 538 eV originating from residual CO<sub>2</sub> in the background gas of the recipient. The presence of some CO2 at or near the surface can also be observed in the C1s spectrum at 295 eV (top panel, transparent signal) and can already be utilized to perform a proper calibration of the BE. By adjusting the BE of the C 1s peak-maxima (transparent signal) to the literature-reported value of condensed CO<sub>2</sub> of 292. 8 eV<sup>61</sup> and shifting the O 1s-spectra accordingly, a corrected BE scale can be obtained. This is verified by comparison of the BE of the hexagonal ice-related peak in the O 1s spectrum, which then accurately fits to the reported literature values between 533.8 and 534 eV.62

In the O 1s spectrum of the deliberately CO<sub>2</sub>-exposed state, again two components can be observed, but now the CO<sub>2</sub>-related component (red) is more pronounced compared to the hexagonal ice-related component (blue). Furthermore, the C 1s signal is significantly increased after CO<sub>2</sub> exposure. The increased O 1s and C 1s peak areas are confirming the adsorption and surface-condensation of CO<sub>2</sub> on top of the ice layer. For a better comparison the recorded spectra (transparent) have been calibrated with respect to the CO2related C 1s component. Thereafter, the O 1s and C 1s peak maxima before and after CO<sub>2</sub> exposure coincide perfectly, and hence prove the general validity of the BE-calibration procedure, which works even with minor amounts of CO2. Generally speaking, such a BEcalibration (i.e., via the C 1s of CO<sub>2</sub> impurities) derived from a single experiment is beneficial for the calibration of the O 1s spectra of any form of ice. Additionally, we note that the condensation of ice I<sub>h</sub> from the background gas on top of the ice samples (e.g., ice XII) can also serve as a possible route for BE-calibration of the O 1s region, via the utilization of literature-reported standards for the O 1s BE of ice I<sub>h</sub>.<sup>62</sup>

### **IV. CONCLUSION**

This report describes a high-end, user-customized *in situ* NAP-XPS instrument for non-synchrotron laboratory use in the low mbar range together with three application-specific, newly developed manipulators and their respective highly specialized sample stages. Each manipulator/sample stage is dedicated to cover a certain field of functional materials research, demanding significantly differing experimental setups. The manipulator designed for investigation of solid state/gas phase interactions (denoted as "gas-solid manipulator") enables in situ/operando NAP-XPS experiments on different types of heterogeneous catalysts (model type, realistic powder type) requiring temperatures from room temperature to 1000 °C. For this setup, infrared laser irradiation at the back side of the samples/sample holder is used for contact-free heating. Besides model catalysts (foils, intermetallic discs, etc.) also technologically relevant pelletized powder catalysts can be probed. Beyond conventional thermal catalysis, the gas-solid manipulator and its sample stage are specifically designed to accept a six-contact sample holder allowing to perform in situ and operando investigations on solid oxide fuel/electrolyzer model cells. These samples can be electronically connected to an electrochemical impedance workstation with potentiostatic/galvanostatic control to apply the full range of electrocatalytic characterization methods at realistic pressures and temperatures during operando XPS operation.

The second manipulator (denoted as "EC-manipulator") is designed for probing electrochemistry at solid electrode/liquid electrolyte interfaces using focused laboratory x-ray sources in the soft x-ray regime. A home-built electrochemical cell has been shown to fulfill highly demanding experimental requirements, as the use of liquid electrolytes for XPS experiments requires cooled electrolyte films with a thickness as low as a few nanometers. The cell design follows a tilted geometry approach for the sample, which is immersed with an angle of  $20^{\circ}$  with respect to the electrolyte surface. The cell body is covered with an Al metal shell fitted inside a cooled Cu sample stage, allowing to cool the electrolyte to 2 °C to attain the lowest possible equilibrium water vapor pressure inside the XPS chamber before the onset of freezing. The principle of operation for this setup could be successfully shown by in situ observation of an anodically polarized and partially oxidized Pt sample in an aqueous Na<sub>2</sub>SO<sub>4</sub> electrolyte.

The third manipulator ("cryo-manipulator") is designed for cryogenic experiments especially on crystalline and amorphous ices or other ice-based materials, such as clathrates. The dedicated Cu sample stage is efficiently supplied with liquid nitrogen via cooling lines to maintain the samples at temperatures around 85 K. Furthermore, the resistive heating option of the sample stage allows us to precisely adjust any temperature from 85 K to room temperature. The challenge of binding energy calibration for an insulating material such as ice has been mastered in our first experiments by adsorbing CO2 or H2O from the background gas deliberately. This setup will allow for investigations of surface-specific processes such as the formation of a quasi-liquid layer enhancing the chemical reactivity of ice on polar stratospheric clouds at -80 °C. In conjunction with an UV-irradiation setup, this manipulator will also allow us to study the UV-induced formation of new molecules, mimicking the processes taking place on interstellar clouds.

In synopsis, the described multi-purpose NAP-XPS instrument provides a hitherto unavailable, extremely broad spectrum of realizable experimental conditions, regarding the pressure range from  $10^{-9}$  to 15 mbar and with respect to the temperature range from -196 to +1000 °C. It therefore covers vastly extended materials research options on a laboratory based *in situ* NAP-XPS system, beyond the time-related and experimental limitations at typically highly specialized synchrotron end-stations.

### SUPPLEMENTARY MATERIAL

See the supplementary material for detailed manipulator description, details of XPS analysis, and fitting parameters.

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### AUTHOR DECLARATIONS

### **Conflict of Interest**

The authors have no conflicts to disclose.

### Author Contributions

L.H., C.G., C.W.T., D.W., and T.M. contributed equally and share first authorship.

Leander Haug: Conceptualization (equal); Data curation (equal); Formal analysis (equal); Investigation (equal); Methodology (equal); Writing - original draft (equal). David Schumacher: Conceptualization (equal); Methodology (equal); Resources (equal); Software (equal). Karsten Dierschke: Conceptualization (equal); Methodology (equal); Resources (equal); Software (equal). Norbert Köpfle: Conceptualization (equal); Methodology (equal). Simon Penner: Supervision (equal); Writing - review & editing (equal). Martin K. Bever: Conceptualization (supporting); Funding acquisition (equal); Methodology (supporting); Project administration (supporting); Resources (supporting); Supervision (supporting). Thomas Loerting: Conceptualization (equal); Funding acquisition (equal); Investigation (equal); Methodology (equal); Project administration (equal); Resources (equal); Supervision (equal); Writing review & editing (equal). Julia Kunze-Liebhäuser: Conceptualization (equal); Funding acquisition (equal); Investigation (equal); Methodology (equal); Project administration (equal); Supervision (equal); Writing - review & editing (equal). Bernhard Klötzer: Conceptualization (equal); Funding acquisition (equal); Investigation (equal); Methodology (equal); Project administration (equal); Resources (equal); Supervision (equal); Validation (equal); Writing - review & editing (equal). Christoph Griesser: Conceptualization (equal); Data curation (equal); Formal analysis (equal); Investigation (equal); Methodology (equal); Writing – review & editing (equal). **Christoph Walter Thurner**: Conceptualization (equal); Data curation (equal); Formal analysis (equal); Investigation (equal); Methodology (equal); Writing – review & editing (equal). **Daniel Winkler**: Conceptualization (equal); Data curation (equal); Formal analysis (equal); Investigation (equal); Methodology (equal); Writing – review & editing (equal); Toni Moser: Conceptualization (equal); Data curation (equal); Formal analysis (equal); Investigation (equal); Data curation (equal); Formal analysis (equal); Investigation (equal); Methodology (equal); Writing – review & editing (equal). **Marco Thaler**: Visualization (equal); Writing – review & editing (equal). **Pit Bartl**: Investigation (equal). **Manuel Rainer**: Formal analysis (supporting); Investigation (equal); Methodology (supporting). **Engelbert Portenkirchner**: Resources (equal); Writing – review & editing (equal).

### DATA AVAILABILITY

The original data are available from the corresponding author upon reasonable request.

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