

In-situ study of gas phase water electrolysis on Pt by NAP-XPS

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Water electrolysis is critical for integrating renewable primary electricity into existing energy systems. However, for practical grid-scale application, the electrolyzers need improvements in performance and stability. Material science tries improving the efficiency of the process by finding an electrode with low intrinsic over-potential as well as exhibiting stability against corrosion upon OER (1-4) during cyclic operation. Knowledge of the structural transformation of the electrocatalyst surface upon OER is essential to design a better electrode material. Pt is one of the most used materials for PEM fuel cells (5) and has been considered as model system to study the structural transformation upon polarization (4-11). In aqueous medium, high anodic polarization results in oxygen dissolution into the metallic electrode and under extreme conditions oxygen evolution. That is, the OER occurs only after achieving the relevant condition of oxygen population into Pt(8). Pioneering work by Bockris (6) by means of in-situ ellipsometry identified the formation of a PtO₂ phase before OER takes place and transition to instable PtO₃, as the mechanism of OER(11). In contrast, ¹⁸O experiments aimed to clarify the involvement of the oxide layer for the OER are contradictory (10,11).

XPS was early applied to reveal the nature of the anodic oxide at the Pt surface (7-13). Most of these studies have been carried out by coupling electrochemical methods with XPS in an *ex situ* fashion. For instance, the Pt4f XP spectra obtained *ex situ* of Pt surface after anodic polarization (12,14) show components at the same BE shift as the thermally oxidized Pt under high O₂ pressure or by O₃ treatment (15) and are attributed to a mixture of Pt²⁺ and Pt⁴⁺. More recently, in-situ X-ray absorption Spectroscopy (XANES) study of the electrochemical oxidation of Pt nanoparticles in HClO₄ has shown that the oxide component in the Pt L₃-XANES spectra,

continuously growing within 30 min, is mainly composed by Pt²⁺ (16). Interestingly, the onset potential for oxide formation was lower and the oxide component growth more rapid on Pt/C than on Pt/Rh indicating that the energy barrier for oxygen dissolution into the Pt subsurface plays an important role in the oxide formation.

The objective of this work is to study the chemical reactivity of the electrode surface under OER for low temperature gas-phase electrolysis by means of the NAP-XPS end-station at the ISSS beamline (HZB/BESSY II) (17-18). Low pressure gas phase electrolysis limits the chemical potential of oxygen and offers the possibility that the oxide phase growth is thermodynamically and/or kinetically hindered. In this way the early stages of chemical transformation can be seen and its direct involvement can be evidenced in the electrocatalytic oxygen formation. Chronoamperometry (CA) is applied to the electrode system in combination with *in situ* XPS investigation. The gas composition is continuously monitored by online mass spectrometry (MS). The system under investigation is a Pt/Nafion-based electrode. The Nafion[®] membrane electrolyte is sputter-coated on both sides by the electro-active element (Pt), functioning as cathode on one side and anode on the other.

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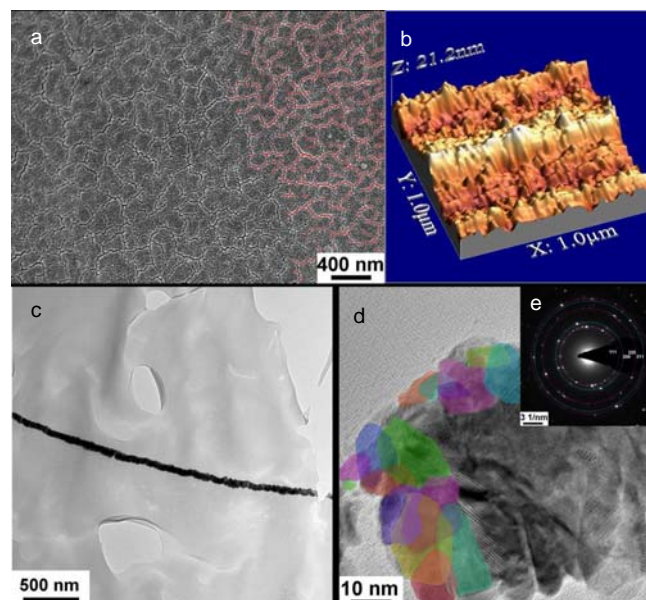


Figure 1. The SEM image (A) is a top view of the Pt film showing a peculiar morphology of the film randomly interrupted by cracks. The cracks are highlighted in red on the right side to evidence that each domain is interconnected. The AFM image (B) enables to access a three-dimensional representation of the film and evidences the high surface roughness of the 70nm thick Pt film (C). The film is composed by agglomerates of nanoparticles (HRTEM image in D). The colored areas indicate the extension of crystallographic planes belonging to individual particles and aim to better visualize that the nanoparticles are in contact with each other. This is also shown by the typical

Moeré fringes for overlapping lattice. The film accommodates on the Nafion® (upper side in D) according to its morphology and this gives rise to thickness variation as well as roughness. The very thin region in D (10nm) corresponds to the cracks observed in the SEM image (A). Selected area diffraction image (E) shows that the film is polycrystalline metallic Pt.

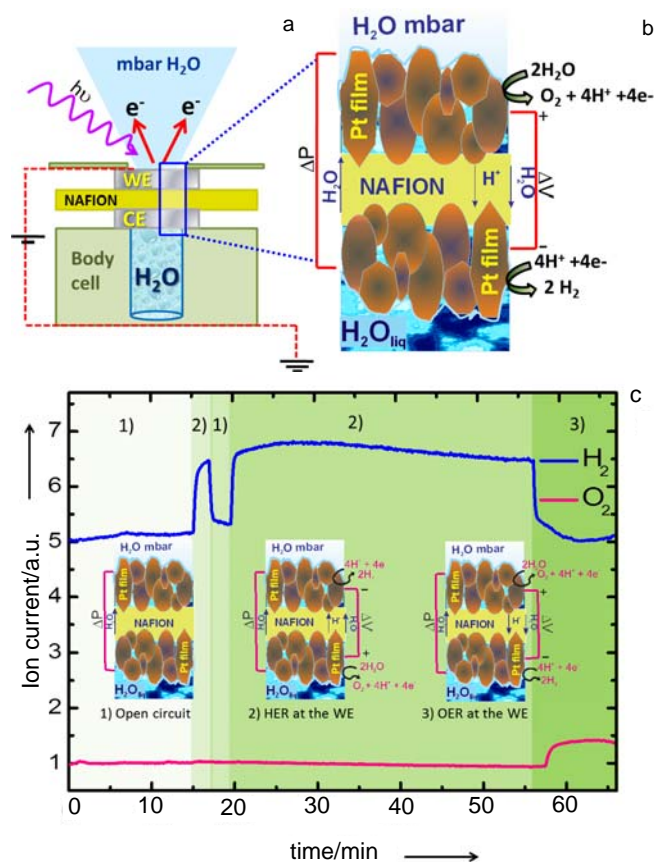


Figure 2. A cell for in-situ investigation with a liquid reservoir is represented in (A). Due to the pressure difference the water in the liquid reservoir diffuses through the membrane and generates a water pressure in the XPS chamber in the range of mbar (B). The porosity of the Pt film allows the water transport. The electrode exposed to X-rays is the WE. Depending on the potential applied at the WE, OER (+2V), or HER (-2V) occurs and the m/z 2 for H₂ or m/z 32 for O₂ are detected by QMS (C).

The morphological and nano-structural characterization before in-situ investigation is presented in Fig.1. The sputter-coated Pt film is not a bulk Pt film but a nanostructured Pt film. Electron micrographs (EM) reported in order of increased magnification in spatial dimension enable to reveal information about the Pt film from macroscopic level down to the atomistic level allowing picturing the film in three dimensions. The polycrystalline Pt film is approximately 70nm thick and is composed of interconnected nanoparticles forming a network with multiple percolation pathways. The typical survey spectrum for the Pt film electrode shows beside peaks due O and Pt core-levels also the presence of C and F (fig. S1) verifying the intended holey nature of the Pt required for mass transport. The on-purpose designed cell is sketched in Fig. 2A. The cell has a reservoir for liquid, which is leak-tight and sealed through the coated Nafion® membrane, that is in direct contact at one side to the liquid water. Liquid water in the reservoir serves two purposes: on one hand it supplies the reactant molecules to both the electrodes

due to the permeability of the Nafion® membrane and the porosity of the Pt film; on the other hand it guarantees a good hydration of the membrane which is fundamental for achieving good ion conductivity. The electrode directly in contact with the liquid water functions as counter electrode (CE), while the electrode exposed to photons is the working electrode (WE). During measurements the CE Fermi edge (FE) is aligned with the FE of the spectrometer and therefore any potential difference between the two electrodes is observed as a shift in the binding energy (BE) scale of the XPS peak. More information is in supporting information (fig.S2). The sketch in Fig. 2B depicts the porous Pt film composed by agglomerated nanoparticles electrically interconnected. The water transport through the Nafion® membrane and the porous film results in a pressure up to 10⁻² mbar in the XPS chamber. The MS traces of H₂ and O₂ in Fig. 2C show the response of the system to the applied potentials. Switching from open circuit potential (configuration 1 in Figure 2C) to the configuration such that the WE functions as cathode (configuration 2 in Figure 2C) and back produces an appreciable change in the H₂ trace. When the WE functions as anode (configuration 3 in Figure 2C), the O₂ trace increase. These results indicate that the in-situ cell/electrode assembly works as functional water splitting device.

The transformation of the Pt4f and O1s spectra during OER at different anodic potential are reported in Fig. 3. The corresponding QMS signal for O₂ increases with increasing the potential from 2V to 2.5V indicating an increase in the OER rate (fig.3A): the current is representative of the "mass balance" of the product. The Pt4f spectra are reported in Fig. 3B. Differences in the spectra are described as changes of the three components, Pt1, Pt2 and Pt3. Pt1 corresponds to metallic Pt (71eV) (9,15) and Pt2 and Pt3 are shifted 0.6eV and 1.3eV to higher BE, respectively. The Pt2 component is found on Pt foil under oxygen at 250°C and partly persists after exposure to H₂O (fig. S3): such a species is attributed to O on Pt to form 2D surface oxide clusters (9). The Pt3 component at 72.5eV is observed also on electrochemically oxidized Pt foil in acidic media together with a component Pt4 at 74.5eV (Figure S5C) (6, 9,15). Those two components are attributed to Pt species with a formal valence of 2+ and 4+, respectively. The Pt2 and Pt3 components increase as response to the increased potential (fig. 3B). The abundance of Pt2 and Pt3 is higher in the most surface sensitive XPS measurements and decrease towards the bulk (fig. S4) establishing the interfacial character of these species. The intensity of Pt2 increases with higher OER activity suggesting that it is connected with the function of the electrode either as active site or as immediate reaction product. The increase of the O population leads to the evolution of the Pt3 species representing a divalent state of a hydrated Pt²⁺ oxide as evidenced below.

To better evaluate the involvement of the Pt²⁺ species in the OER, the WE was subjected to an O₃ treatment with the purpose to increase its oxidation state. The measured current upon anodic polarization and the corresponding Pt4f are reported in Fig. 4A. The higher abundance of the Pt(3) as well as the additional components at higher BE (pink peak at 73.7 eV) in the Pt4f spectrum of the O₃ treated Pt film correspond to a reduction of the current at 2V with respect to the case of the Pt film before the O₃ pretreatment. Interestingly, increasing the potential to 4V favors the Pt reduction and correspondingly the current is significantly increased. The current represent the OER rate: note that the Pt(1)/Pt(2) is lower when the OER rate is higher. Such results rule out any positive effect on the presence of the Pt(3) species.

The BE chemical shift of the oxygen component of Figure 3C can be correlated to the degree of surface hydration: a shift to higher BE indicates oxygen bound to an increasing number of hydrogen.

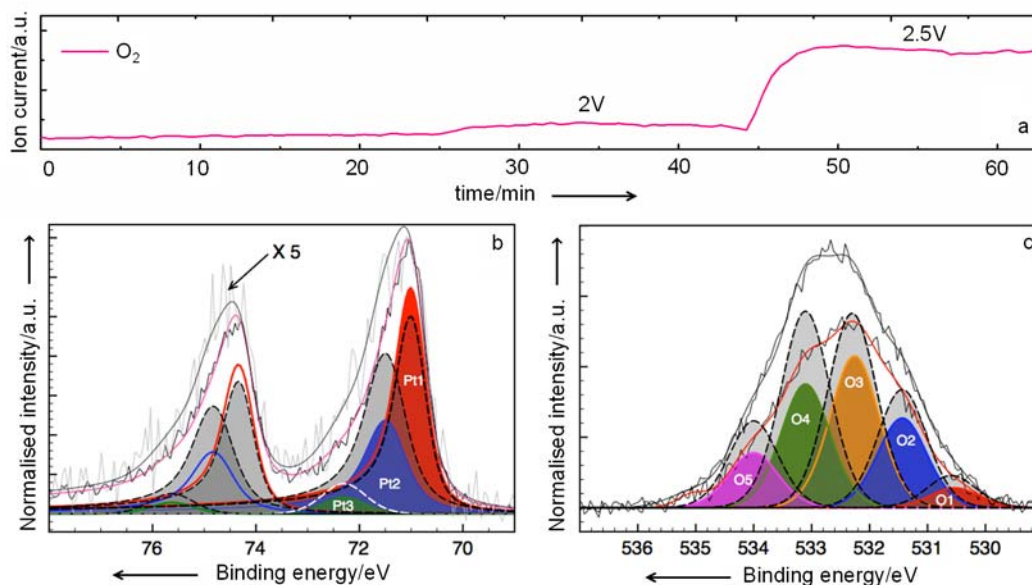


Figure 3. Pt/ Nafion® /Pt system: **A)** QMS O₂ traces during the anodic polarization of the WE; XPS spectra with KE=150eV corresponding to an information depth approximately 0.5nm: **B)** deconvoluted Pt4f XP spectra: red (Pt1), blue (Pt2) and green (Pt3) components for the spectrum during OER at 2V and corresponding components at 2.5V in dashed line and grey filling. **C)** deconvoluted O1s XP spectra: components in color at 2V and components at 2.5V in dashed line and grey filling.

In agreement with literature (8,15,19) the components are assigned to Pt-O (O1 at 530.4 eV), strongly bound hydroxyl (O2 at 531.4 eV), hydrated O:H₂O complexes (O3 at 532.2 eV) and chemisorbed H₂O (O4 at 533 eV). An additional component (O5 at 534 eV) present on the rough from water penetrated in-situ electrode is attributed to a multilayer film of water (19,20). As the Pt film contains C impurities, C-O species may contribute to the components O2 and O3 (21).

With increasing the anodic potential from 2V to 2.5V, each O component increases (fig.3C) but the relative abundance of the O components is differently affected by the potential as shown in (tab.S1). The O4 and O5 components for molecular water increases most while the component for the Pt-O surface (O1) increases least. Although the exact comparison for the surface O:H₂O (O3) and OH (O2) species is hampered by the possible carbon impurity contributing to the components (Fig. S6), it can be seen that indeed their relative abundance decrease as the OER is boosted (differently the absolute abundance of the C-O species increases with increasing potential in Fig. S6). One can assume that their surface population is lowered due to the higher positive potential which lowers the binding energy and favors the OER.

The relative abundance of oxygen species vs current upon potentiostatic anodic polarization for the Pt film before and after O₃ pretreatment are reported in Figure 4B. Note that the data are reported in order of increasing current but do not represent the real order of the experiments which is indeed reported in Fig. 4A. The O₃ treated Pt film is characterized mainly by Pt-O species at 529.6

eV (O0) and at 530.4 eV (O1), Pt-OH species at 531.4 eV (O2), while H₂O:O complexes at 532.2 eV (O3) on Pt and the molecularly chemisorbed water (O4 at 533 eV and O5 at 534 eV) are less abundant. The increase of the OER upon anodic polarization is accompanied by a decrease of the Pt-O components (O0, O1 and O2) while relatively the abundance of O species involved in H-bonding, O3 (O:H₂O) and molecularly chemisorbed O4 and O5 species increases. A higher potential is required on oxidized Pt²⁺ such to decrease the binding energy of the oxygen species on Pt (O0, O1 and O2) and to induce Pt reduction: on such a surface the OER is favored. The extended and stable carpet of O chemisorbed layer may prevent the chemisorption of molecular H₂O on metallic Pt and hinders the formation of Pt-O:H₂O-Pt complexes (O3) as intermediates for OER.

The results presented here give a consistent picture about the chemical dynamics of Pt in the OER reaction that brings together fragmented literature findings. The key result in the present study is a dual structure of the Pt over layer under potential of proven oxygen evolution. A metallic state with oxygen often termed as “surface oxide” adsorbs and dissociates water. Oxygen modification of clean Pt is a prerequisite for dissociative adsorption of water (23). Together with this state a divalent hydrated Pt species also occurs with the OER activity. Tetravalent or higher oxidized species are not necessary for OER. Tetravalent hydrated Pt oxide is formed, however as secondary product upon extensive OER activity in acid electrolyte.

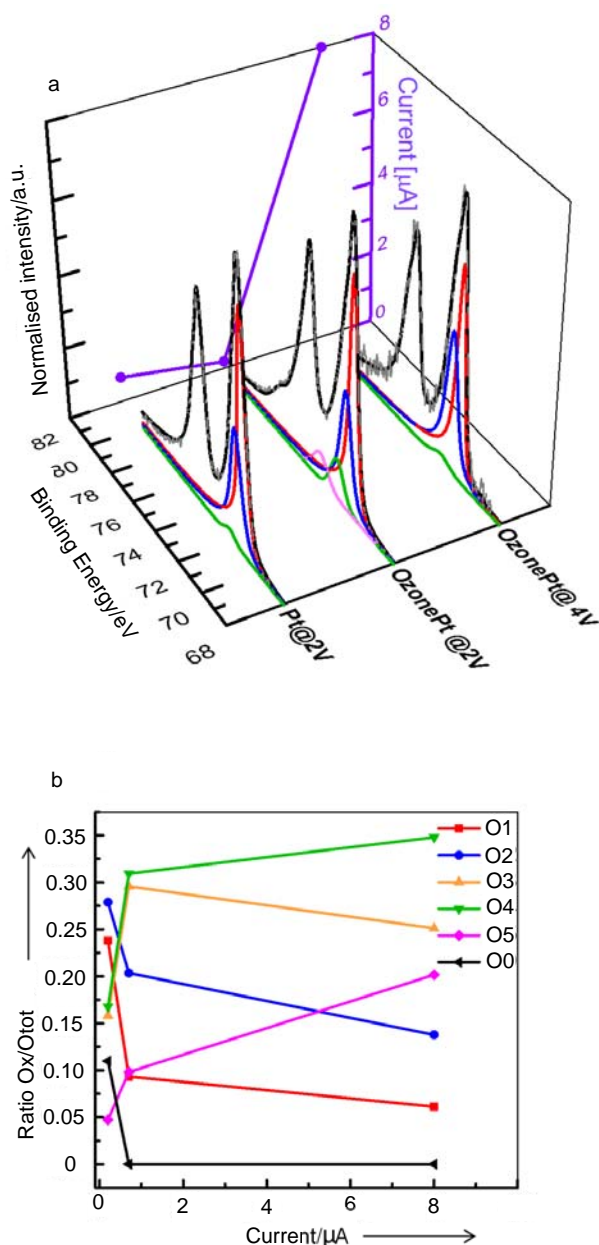
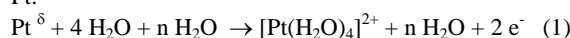


Figure 4. Pt/ Nafion®/Pt vs. Ag wire reference electrode: **A)** Pt4f spectra with KE=150eV during constant anodic polarization and the corresponding measured current for the sputtered Pt film WE at 2V, and at 2V and 4V after a pretreatment in 1 bar O₃; the order indicates chronological sequence of the experiments; **B)** Relative Abundance of oxygen species versus current relative to the experiments in (A).

A double layer structure of the Pt oxide formed in OER was clearly identified from electrochemical data. (24, 25) It was noted that a thin highly active layer is covered by a thicker gel-like structure and speculated that the highly active layer should be composed of high-valent Pt oxides. This is inconsistent with the present spectroscopic data of an unprecedented surface sensitivity at high resolution of chemical states. The fact that the reacting surface is still metallic may well account for the effective discharge of the dissociated oxygen species in accordance with the electrokinetic findings. The metallic nature of highly active Pt was also recently speculated to occur in Mn-oxide modified Pt systems. (26). The finding that the active layer of OER is metallic rather than oxidic has implications

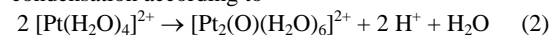
on the theoretical analysis of resistances. (30) It is not necessary to assume non-conventional electron transport through an oxide interface as characteristic feature of OER. The resistivity may well arise from transport processes associated with the formation of the thick oxide layer. This is of relevance as then modifications of the Pt surface are possible that kinetically inhibit the formation of a thick layer of oxide without interfering with the function of an OER electrode. Kinetic control of the oxide stripping process (31) has indeed been observed.

The present work explains the enigmatic (24, 27, 30, 32, 33) initial reaction of Pt oxidation at ambient temperature under electrochemical control. The formation of a surface oxide electronically partly decouples the surface of the Pt metal from the electronic structure of the bulk leading to reduction in the density of states in the valence band as seen in the shift of the Pt 4f spectrum by 0.6 eV (Figure 3B). This is pre-requisite for dissociative adsorption of water (see O1s spectra in Figure 3C and reference experiments on Pt foil in Figure S3) but also for the mobilization of Pt:



Reaction (1) becomes energetically feasible through the energy gain by solvation. If this is reduced by working at low pressure or in gas phase electrolysis it can be expected that the near surface oxide stays more stable and disintegration is reduced.

In the presence of the electrolyte the Pt aquo complex undergoes condensation according to



The dimer (2) can either continue to condense to hydrous PtO or oxidize further to $[\text{Pt}_2(\text{O})_2(\text{H}_2\text{O})_4]^{4+}$ from which hydrous PtO₂ (24) and mixed valent oxides are formed by continuing condensation. These reactions giving rise to the chemically in-equivalent OH and H₂O species detected in the O1s spectra of OER electrodes (34) (see Figure 3C) creating the gel structure (25, 27) seen in Figure S5. Adjusting the pH of the electrolyte and kinetically disturbing the precipitation of the hydrous oxides may extend the integrity of working electrodes.

In conclusion, in this work by in-situ spectroscopy, we observe the reacting interface under gas-phase water electrolysis and verify its electro-catalytic function by on line product analysis. This study allowed separating the transient electrode active state, from a more stable oxidic state that represents a deactivated state. The impact of the voltage on the OER indicates that the reaction kinetic is enhanced by the manipulation of the electrode Fermi level: stronger Pt-O bonds in stable oxidic phase induce overpotential. The present results offer the possibility that structural modifications on bare Pt may be possible that extend the integrity of the dynamical working surface by preventing the formation of unnecessary oxide over layers during OER.

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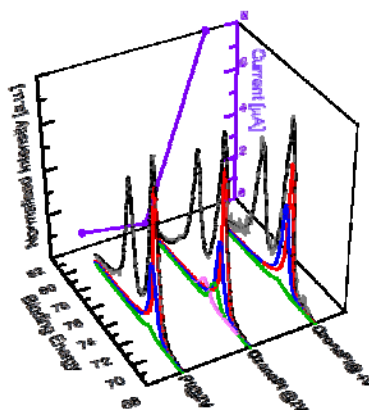
Layout 1:

A Hydrated Pt metal phase with dissolved oxygen in the subsurface is active for the OER during in-situ NAP-XPS study

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Page – Page

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PtO₂ is believed to be the chemical state of a Pt electrode during the anodic oxygen evolution reaction (OER). We have used near ambient pressure X-ray photoelectron spectroscopy (NAP-XPS) to study in-situ the surface of a Pt electrode during OER. We have found that during gas phase water electrolysis a hydrated Pt metal phase with dissolved oxygen in the near-surface region is active for the OER. This phase is seen as precursor to the analytically detected PtO₂ being in fact the deactivation product of the electrode.