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Electrooxidation of Pt(111) in acid solution

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Abstract

The electrochemical oxidation of Pt has regained new interest in recent years, motivated by its importance for Pt electrocatalyst stability. New experimental data obtained by *in situ* methods, detailed electrochemical studies, and complementary results from *ab initio* theory and gas phase studies have led to significant advances in the understanding of this process on the atomic scale. Here, an overview of recent work on the electrooxidation of Pt(111) single crystals in acidic electrolytes, primarily perchloric acid solution, will be given. The complex potential- and time-dependent changes in the adsorbate layer on the electrode surface, the place exchange of oxygen species with Pt surface atoms, the formation of an ultrathin Pt oxide layer, and the structural changes of the electrode surface structure upon oxidation/reduction cycles will be described.

Keywords: Platinum, oxidation, atomic processes, OH adsorption, restructuring, place exchange

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Introduction

Platinum (Pt) is a key material for electrochemistry, being the most active element for many central electrocatalytic reactions. In particular in electrochemical energy conversion and storage, e.g., in polymer electrolyte membrane fuel cells (PEMFCs), it still is the most important catalyst for applications and remains the benchmark for electrocatalyst materials. The activity and stability of Pt under electrochemical reactions such as hydrogen evolution, hydrogen oxidation, methanol oxidation, ethanol oxidation, oxygen reduction, and oxygen evolution has been extensively researched in the last decades.[1, 2, 3, 4, 5, 6] In this context, also the oxidation of Pt surface in aqueous environment has received considerable attention, because it is responsible for the diminishing activity towards most surface reactions and for the degradation of Pt based catalysts. The latter point is especially important for the oxygen reduction reaction in fuel cells and is currently one of the last issues to be solved to make PEMFCs commercially competitive.

Although Pt oxidation and Pt oxide reduction have been studied for a long time,[7, 8] renewed interest in this topic and advances in *in situ* surface structural characterization and *ab initio* computational methods have led to new insights and provided a detailed atomistic picture of this important process. This can serve as a basis for theoretical research, can help to explain many experimental observations, and can guide research into Pt degradation. Here we give a brief overview on the current state of research on Pt oxidation in acid solutions. We will focus on Pt(111) in the weakly absorbing electrolyte $HClO_4$, but also will provide a brief comparison to the specifically adsorbing case of H_2SO_4. We will also emphasize the locations of the Pt atoms in the various structures, which have been relatively neglected in earlier literature.

The potential-dependent oxidation processes are summarized in Fig. 1, together with the corresponding cyclic voltammograms (CVs). The detailed behavior in the different potential regions (all given with respect to the reversible hydrogen electrode) will be discussed in the following sections.

H UPD and butterfly regions

The surface at 0.05 V has 2/3 ML of underpotentially adsorbed H atoms and a lattice expansion of about 1-2% between the first and second Pt layers [9, 10, 11, 12], similar to the expansion on a clean surface in vacuum.[13] Desorption of H over the range 0.05-0.4 V reduces the interlayer expansion to about 1% or less.[12, 14, 9, 10] This range is followed by the double region 0.40-0.60 V, over which the interlayer spacing is constant. No adsorption occurs in this region.[15]

The "butterfly" region, 0.60-0.95 V in $HClO_4$, consists of two parts, the sharp peaks at 0.8 V and the broader region leading up to them. These are due to adsorption and desorption of adsorbed OH. The assignment to OH is from the lack of shift vs RHE as the pH is changed, consistent with one-electron oxidation of water to H^+ and adsorbed OH, and a thermodynamic analysis that shows transfer of one electron per adsorbed OH.[16] However, the perchlorate concentration dependence implies involvement of perchlorate, and it has recently been suggested that perchlorate anions specifically adsorb in competition with OH,[17] or that perchlorate in the double layer strongly interacts with adsorbed OH.[18], though chloride contamination can confound the interpretation in perchloric acid.[19, 20]

In the case of sulfuric acid electrolyte, the adlayer structure in the butterfly region is well established by concentration dependence studies,[21, 22] radiochemistry,[23] STM[24, 25] and infrared spectroscopy[26] to be due to specific adsorption of 0.2 ML of sulfate or bisulfate, with uncertainty about the exact species. The thermodynamic analysis yields an approximate charge number of 2, suggesting sulfate, but this number has to be carefully interpreted in the light of possible coadsorption.[27] Infrared spectroscopy suggested that bisulfate predominates for $pH < 3.3$,[26] while later revision by careful thermodynamic analysis showed that sulfate is preferentially adsorbed in the whole butterfly region for $0.8 < pH < 3.8$.[22]

The sharp peaks are associated with a fast phase transition, where the coverage of a disordered phase increases in the broad region and transitions to an ordered adlayer structure in the sharp peak.[28, 29] In the case of H_2SO_4, the phase transition is from disordered bidentate (bi)sulfate to an ordered $(\sqrt{3}\times\sqrt{7})$ overlayer of tridentate (bi)sulfate with coadsorbed water, and the phase transition has been directly observed by STM[30], SFG[31] and SXRD[12].

There is less direct evidence for the phase transition for $HClO_4$. Recent *in situ* SXRD studies show a continuous increase in the coverage of oxygen species (OH_{ads}, H_2O, H_3O^+) and a concomittant relaxation of the spacing of the topmost Pt layer in the entire double layer regime.[12] In accordance with results for Pt(111) oxidation in the gas phase and DFT calculations, Kondo et al. reported a $p(2 \times 2)$ phase in their *in situ* SXRD studies and assigned it to a mixed layer of OH_{ads} and H_2O. Furthermore, they observed in potential-dependent measurements of the non-specular crystal truncation rod a distinct two-step process. This behavior was attributed to random adsorption in the broad region, followed by the formation of a transient $p(2 \times 2)$ adsorbate phase and a subsequent phase transition to a $p(1\times1)$ adlayer at the sharp peak. SXRD studies by Liu et al. found in addition the formation of a buckled top Pt layer in the butterfly region,[32] in a good agreement with DFT predictions.[33] Both authors modeled their data with the oxygen atoms in fcc or hcp hollow sites, as suggested by DFT[34] and gas-phase studies[35, 13], though with different coverages.

Although the theory for the order-disorder phase transition explains both the broad and sharp component components of the peak with one type of adsorbate, it has also been suggested that the two components could result from OH interacting with two types of water species.[19] More detailed kinetic studies suggest there may be additional complexity.[36, 37]

At the end of the butterfly peak at 0.90 V, electrochemical measurements suggest an OH coverage of 0.5 ML.[36, 37, 16] In contrast, DFT calculations suggested that OH coverages cannot exceed 0.33 ML until much higher potentials.[38] This has led to suggestions that some of the butterfly coverage may be O rather than OH, which is supported by photoelectron spectroscopy (XPS).[39] However, Farkas et al. have pointed out the neglected role of Pt surface buckling for coverages above 0.4 ML that may reduce repulsion between oxygen species and enable higher coverages at lower potentials than otherwise.[40] Alltogether, the exact composition of the layer in this regime is still unknown. As described above, all current studies propose an adlayer containing different oxygen species, but with different surface stoichiometries.

Pt oxide peak

The anodic peak at ≈1.05 V is traditionally assigned to the further oxidation of OH_{ads} to O_{ads}. [36] However, first *in situ* SXRD measurements on the structure of the oxidized Pt surface by You et al. showed that place exchange (PE), in which a Pt surface atom exchanges with an oxygen species, occurs in the potential region of this peak.[41] This process is structurally reversible, in the sense that cycling returns the Pt atoms to their original state, and thus the voltammogram is stable for many cycles at typical sweep rates. Later, the same group presented cycling experiments,[42] which showed hysteresis in the SXRD intensity that paralleled the asymmetric voltammetry peaks. Unfortunately, these data have been largely ignored in the literature. Most discussions of this peak considered only adlayer structures and neglected the role of Pt surface restructuring, which was assumed only to be important at higher potentials.

With advances in synchrotron-based techniques parallel voltammetric and SXRD studies are nowadays possible, enabling direct correlation between the structural and the electrochemical data (Fig. 2).[14, 32] These clearly confirm the earlier SXRD results, demonstrating unambiguously that the onset of X-ray intensity changes due to PE occurs precisely at the Pt oxide peak.[14] Furthermore, they revealed a common log time dependence of the PE coverage determined from electrochemical measurements and from the intensity changes. The correlation of PE with an electrochemical current is not obvious, since in principle, the translocation of the Pt atom need not necessarily be concerted with electron transfer or motion of an oxygen-containing species. It suggests that the PE may occur in the composite process OH(ads) + Pt → PtO(exchanged) +

$H^+ + e^-$, probably with motion of the Pt as the rate-determining step. Much of the literature referring to the simpler OH(ads) → O(ads) + $H^+ + e^-$ may be reinterpreted as the net reaction above, though there may be conditions under which the Pt, O, and electron motions are not as tightly coupled.

Interestingly, the anodic Pt oxide peak has no cathodic counterpart and the current corresponding to the reduction is distributed over a broad potential range between 1.00 V and 0.80 V. This is corroborated by the *in situ* SXRD measurements, which show a slow recovery of the intensity over this potential range (Fig. 2b). Based on electrochemical measurements, it has been concluded that multiple Pt oxide species, OH_{ads}, O_{ads}, and subsurface oxygen (O_{sub}), inter-convert in this potential region and that the relative coverages strongly depend on the total surface coverages rather than the potential.[36, 37] The hysteresis between oxidation and reduction is apparently an effect of the stability of the oxide, which depends on the overall coverages of the oxygenated species. Specifically, it was suggested higher coverage results in a greater stability and subsequently in a less positive reduction potential.[36, 37]

Electrochemical studies also revealed an influence of both pH and $ClO_4{}^-$ concentration on the position of the anodic peak. This has been partially explained by the competition of the ClO_4 adsorption and H_2O oxidation pathways.[17] This view is supported by recent Raman spectroscopy experiments, where the ClO_4 presence in the vicinity of the surface and in the potential window of the anodic oxide peak has been confirmed.[18]

For low coverages of place exchanged Pt atoms (Pt_{exch}) the Pt(111) surface structure fully recovers after oxide reduction. In this case, the Pt_{exch} do not interact laterally and apparently can directly move back into their original lattice site upon reduction. According to detailed SXRD measurements (Fig. 2a), [14] the Pt_{exch} are exactly located above the vacancy sites, created in the Pt lattice during PE. This position most likely is stabilized by oxygen species in the vacancy as well as on the surrounding Pt surface and may explain the high reversibility of the place exchange process. As a consequence of the slow PE kinetics, fast cycling up to 1.20 V still does not result in a Pt_{exch} coverage above the critical value and the CV thus is reproducible during subsequent cycles. Also the apparent non-reversibility of the anodic peak can be attributed to this slow PE kinetics.

From the above results it can be concluded that the "more stable oxide" responsible for the anodic peak asymmetry and hysteresis[36] and the platinum-peroxo-like and platinum-superoxo-like 2D surface oxides reported in Raman spectroscopy measurements,[18] refer to a Pt surface partly covered by (isolated) Pt_{exch}. Although this geometry was not considered in the study by Huang et al., such spectroscopic data should shed light on the local Pt-O bonding of the place exchanged atoms.

Further insight into the PE process comes from recently DFT studies of Pt(111) oxidation.[43, 44] According to these calculations the Pt extraction, i.e., the first step of the PE, depends on i) the local O_{ads} coverage where 3 adjacent fcc adsorption sites need to be occupied and ii) the presence of surface H_2O, which stabilizes the Pt_{exch}. Therefore, Pt extraction is favored for (local) O_{ads} coverages $> 0.5\,\mathrm{ML}$ while the subsequent O substitution in the resulting hole is favored at coverages $> 0.75\,\mathrm{ML}$.

3D oxide film and surface restructuring

Increasing the potential for extended times above 1.15 V leads to irreversible changes in the CVs for all Pt surfaces. In both $HClO_4$ and H_2SO_4 this results in the growth of sharp peaks in the H_{UPD} region assigned to H adsorption on {100}- and {110}-like defects.[45] The specific adsorption of anions has two seemingly contradictory effects: high sulfate concentrations decrease the speed of the surface reordering, while low concentrations increase this speed. This has been assigned to the role of water dissociation during oxidation.[45]

Recent *in situ* SXRD studies provided detailed data on the potential-dependent structure of the (steady-state) oxide film on Pt(111) in $HClO_4$, formed by keeping the potential for several minutes in this range.[46] Between 1.17 and 1.62 V a continuous transition from a surface covered by a high Pt_{exch} coverage (≤ 0.2

ML) to a rather uniform, ≈ 5 Åthick oxide layer was observed. Simultaneously, the Pt surface atoms in the two layers of the Pt oxide became gradually more disordered, indicating a largely amorphous structure at the upper potential limit. These observations are in qualitative agreement with the Raman spectroscopy data at these potentials, which report a 3D α-PtO_2.[18]

The interaction between neighboring Pt_{exch} and the decreasing lattice order are most likely responsible for the irreversibility in the oxidation/reduction process in this range. As shown previously, the latter leads to the formation of a roughened surface, covered by nanoscale Pt islands.[47] The structural reordering induced by oxidation/reduction cycles, was recently studied in detail by *in-situ* grazing incidence small angle scattering (GISAXS). [48] This technique allowed quantitative characterization of the nanoscale surface morphology as a function of upper potential limit and the number of cycles (Fig. 3a). The results indicate a continuous increase in the height of the nanoscale islands and a more and more homogeneous island distribution with increasing number of cycles, whereas the characteristic distances between the islands predominantly dependent on the potential limit. This growth dynamics resembles the one observed in Pt deposition and surface erosion experiments under UHV conditions. It can be rationalized by the nucleation and growth of Pt adatoms and vacancies, formed on the surface after oxide reduction.

Finally, the oxidation behavior near steps and defect sites may be distinctly differ from that of atomically smooth low-index Pt surfaces. *In operando* GISAXS studies, obtained during the cycling of Pt(111) electrodes already roughened by previous potential cycles, indicated an onset of Pt restructuring at 0.80 V, which was attributed to step edge oxidation, followed by more pronounced restructuring above 1.05 V, i.e., the potential of PE on Pt(111) terraces (Fig. 3b).[46]

Conclusion

In recent years, Pt electrochemical oxidation has received renewed interest, triggered by the relevance of this process for the stability of Pt oxygen reduction catalysts. Detailed studies by state-of-the-art *in situ* techniques and *ab initio* theory provided an atomistic picture of the surface during oxidation and new insight into the elementary mechanisms of oxidation and oxide reduction. A complex sequence of potential-dependent changes in the chemical composition of the adsorbate layer and the structural arrangement of the Pt surface atoms has emerged from this work. Specifically, gradual changes in the Pt-Pt bonding at the surface have been revealed, starting with the relaxation and buckling of the surface layer and progressing with the slow formation of place-exchanged atoms up to a saturation coverage, which approaches 0.5 ML at potentials of $\approx$ 1.6 V, corresponding to a well-defined $\approx$ 5 Åthick Pt oxide. Apart from its basic importance for Pt electrochemistry, these results are also instrumental in order to improve the Pt catalyst stability in PEMFCs.

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Annotated References

[12]**: *In situ* surface X-ray scattering studies of the initial stages of oxidation in perchloric and sulfuric acid solution. A complex potential-dependent sequence of changes in the adlayer structure and Pt surface relaxation was found.

[11]*: *In situ* surface X-ray scattering measurements in perchloric acid solution, which indicate Pt surface buckling in the potential range positive of the butterfly peak.

[14]*: Studies of the place exchange kinetics by *in situ* surface X-ray scattering in perchloric acid electrolyte. The data show that place exchange is fully reversible below a critical coverage and exhibits a logarithmic time dependence.

[48]**: First quantitative *in situ* grazing incidence small angle X-ray scattering studies of the Pt surface roughening induced by oxidation/reduction cycles in perchloric acid solution. The observed dependence of the characteristic lateral dimensions of the formed nanoscale islands on potential and cycle number are rationalized by a microscopic model based on the known surface dynamics under vacuum conditions.

[18]*: *In situ* surface-enhanced Raman studies of Pt oxidation. The interaction of perchlorate anions with adsorbed OH and the formation of peroxo- and superoxo-like surface oxides is reported.

[43]**: Based on density functional theory calculations, a novel mechanism for the place exchange of a Pt surface atom with oxygen is suggested. It involves interactions with neighboring chemisorbed oxygen as well as with surface water.

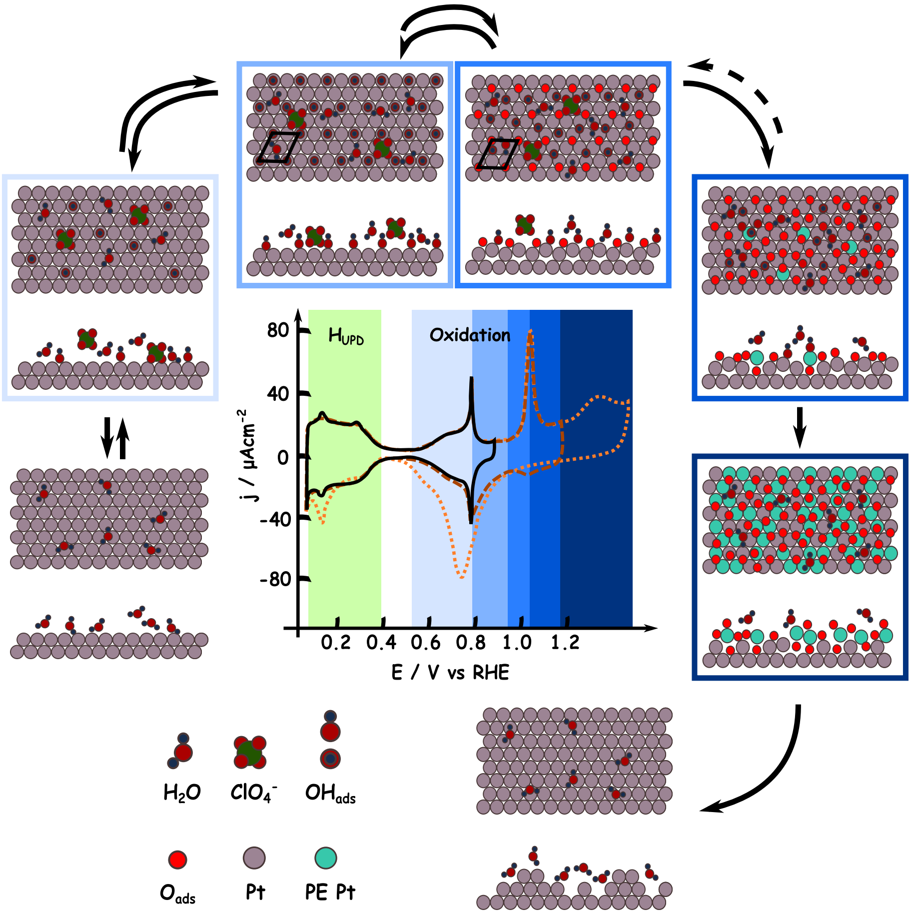
[46]*: Studies of Pt oxidation in perchloric acid solution by a combination of *in situ* X-ray scattering techniques. Detailed structural data on the oxide film at different potentials up to 1.6 V are reported. Step edge oxidation on cycled surfaces occurs at potentials as low as 0.8 V.

Figure captions

Figure 1: Typical cyclic voltammograms of Pt(111) in 0.1 M $HClO_4$. The atomic-scale surface structures in the different potential regions are schematically illustrated.

Figure 2: In situ X-ray surface diffraction studies of Pt(111) oxidation in 0.1 M $HClO_4$. (a) Characteristic crystal truncation rods of the surface before (blue) and after (red) oxidation at 1.17 V, indicating strong surface restructuring due to place exchange. (b) CV and parallel X-ray intensity transient, showing place exchange at potentials > 1.05 V and full subsequent recovery of the surface structure after oxide reduction. (c) Kinetics of place exchange derived from SXRD studies, revealing an increase in the coverage of place exchange atoms by an ln(t) law (after Ref.[14]).

Figure 3: Results of *in situ* GISAXS studies on Pt(111) surface restructuring by oxidation/reduction cycles in 0.1 M $HClO_4$. (a) Increase of characteristic distance between neighboring nanoscale Pt islands as a function of upper potential limit and number of cycles. In the upper panel, background-subtracted GISAXS data are shown, which illustrate the intensity increase of the diffuse side wings after 5, 10, and 15 cycles to 1.62 V, respectively, indicating vertical island growth (after Ref. [48]). (b) *In operando* GISAXS measurements of the time-dependent intensity profiles (top) and the integrated intensity of the diffuse side wings (bottom) during the 20th cycle to 1.37 V. In the sweep in positive direction, two stages of the oxidation process are visible, i.e., a shallow decrease above 0.8 V, which is attributed to step edge oxidation, followed by a steep intensity drop at > 1.05 V due to place exchange on Pt(111) terraces (after Ref. [46]).



80
40
0
-40
-80
j / µAcm^{-2}
H_{UPD}
Oxidation
0.2
0.4
0.6
0.8
1.0
1.2
E / V vs RHE
H_2O
ClO_4^-
OH_{ads}
O_{ads}
Pt
PE Pt

Figure 1:

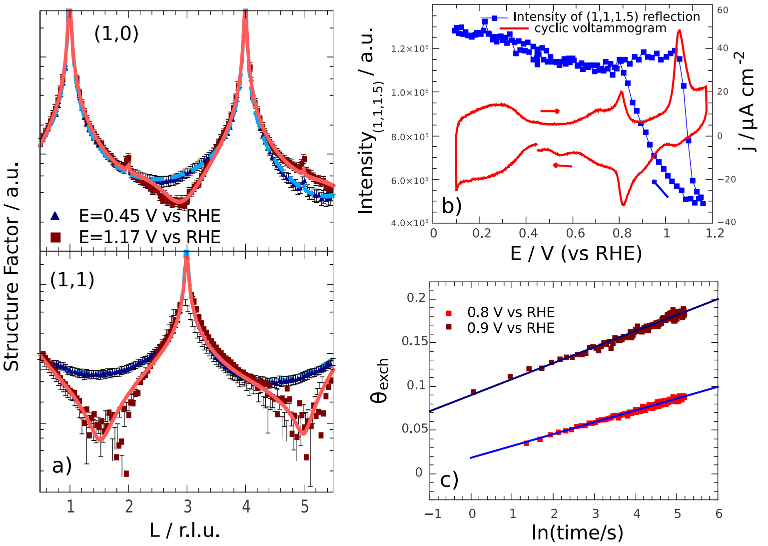


Figure 2:

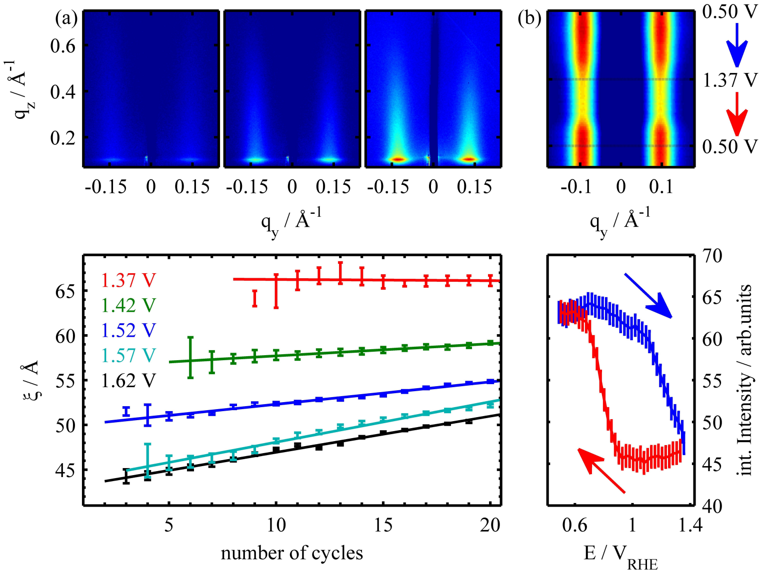


Figure 3: