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Pt oxide and oxygen reduction at Pt(111) studied by surface X-ray diffraction

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Abstract

The influence of the oxygen reduction reaction on the oxidation of Pt(111) is studied by surface X-ray diffraction. The oxygen reduction reaction does not significantly influence the place-exchange process during the initial stages of oxidation and there is no change in the onset potential and kinetics.

Keywords: oxygen reduction reaction, Pt(111), Pt oxide, place-exchange, surface X-ray diffraction

1. Introduction

The slow oxygen reduction reaction (ORR) kinetics at Pt affect the performance of proton exchange membrane (PEM) fuel cells. That Pt oxide inhibits the kinetics has been known for a long time and has been incorporated into ORR models on polycrystalline and fuel cell electrodes [1–4] because oxide is present on the fuel cell catalyst surface under some operating conditions [4–6]. Despite this, many mechanistic studies of the ORR consider only adsorbed species on unreconstructed surfaces [7–14]. One conclusion of these studies is that adsorbed OH plays a key role in limiting the kinetics of the ORR, either as

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a blocking species or as an intermediate that is removed in a rate determining step. However, experimental studies of the ORR on Pt(111) typically avoid higher potentials where oxide formation causes irreversible restructuring of the surface through a place-exchange (PE) process, and therefore the role of the surface oxide is unclear.

The term oxide is not used consistently in the literature and can include strongly-adsorbed species, PE Pt, and 2D or 3D phase oxides. Here our interest is on Pt(111) and the PE process, in which a Pt atom relocates to a position above its original lattice site, which is filled with an oxygen atom. The PE has been directly observed *in-situ* by surface X-ray diffraction (SXRD)[15–20], and we here use this technique to investigate the effect of the PE on the ORR.

The reverse effect, that the ORR may affect the oxide formation, is also of interest since the formation and removal of the oxide promotes dissolution [21–27] and the presence of oxygen is known to enhance the dissolution upon potential cycling [28]. Given the above, the presence of O_2 may affect the initial stages of the oxide formation and lead to faster dissolution and reduced lifetime of Pt catalysts. Recent *in-situ* experiments [29] have provided some evidence for this on polycrystalline Pt and Pt nanoparticles and the conclusions have been supported by density functional theory (DFT) calculations [30]. In contrast, measured dissolution rates on both single crystals [21] and polycrystalline electrodes [24] suggest that the ORR itself does not shift the onset potential for surface oxidation or the PE. For fuel cell electrodes, some studies find that oxygen affects the oxide coverage but others do not [4–6].

Here, the PE process on Pt(111) is directly observed in the presence and absence of oxygen. We are able to show that the PE process in this case is not significantly influenced by oxygen, and that the ORR current decreases at potentials before the PE occurs, confirming that the PE is not a limiting factor in the ORR kinetics.

2. Material and Methods

The SXRD experiments were performed at the European Synchrotron Radiation Facility (ESRF) in Grenoble, ID03 beamline. The 22.5 keV X-ray beam was focused to a size of $300\mu m \times 50\mu m$ (h×v relative to the plane of the sample surface) at the sample position. The incidence angle of the beam was set to 0.3° relative to the surface plane. The Pt(111) single crystal (7 mm dia., Surface Preparation Laboratory) was annealed in an induction oven under Ar atmosphere before each experiment. Potentials were measured against a Ag|AgCl|3.5 M KCl (eDaq company) reference electrode (0.274 V vs RHE), but are reported vs the reversible hydrogen electrode (RHE). The solutions were prepared from ultrapure $HClO_4$ (Normatom, VWR) and ultrapure water (18 MΩ cm). The experimental setup and data analysis techniques are further discussed in [20].

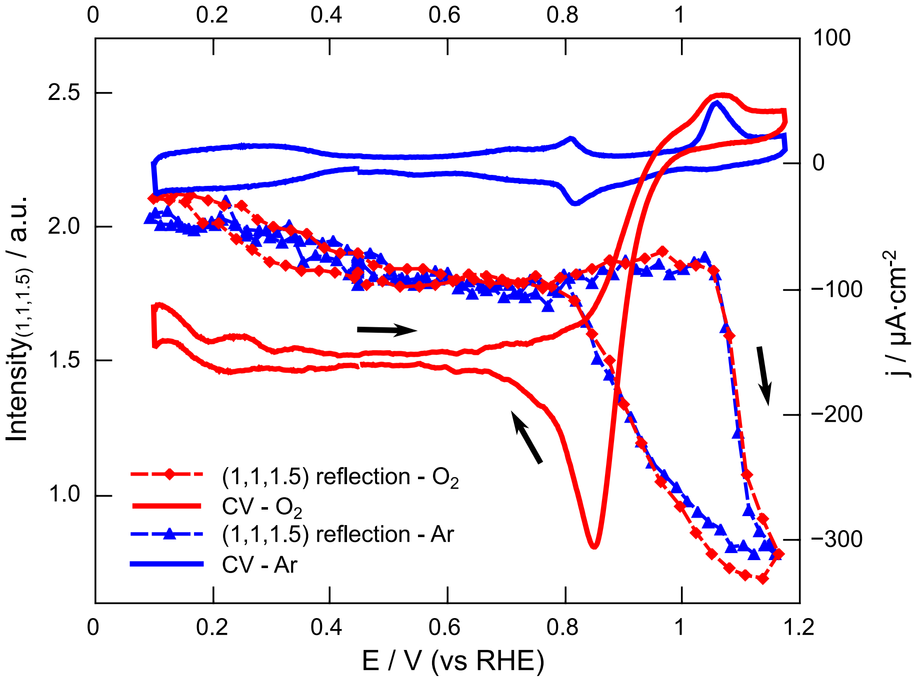

Figure 1: Cyclic voltammogram (solid) and intensity of (1,1,1.5) reflection (dashed) during cycling in Ar-saturated (blue), and O_2-saturated (red) 0.1 M $HClO_4$. Sweep rate 20 mV s^{-1}. The curves were obtained in the same experiment, those for Ar-saturated electrolyte have been previously reported (Ref. [20]).

3. Results and Discussion

The same methods were used as in our previous work [20], where we showed that monitoring the (1,1,1.5) reflection measures the PE process independently of other interfacial processes. During a cyclic voltammogram (CV) in Ar-saturated 0.1 M $HClO_4$ (Fig. 1), the PE initiates (decreasing X-ray reflection intensity) at the oxide peak at 1.06 V vs. RHE and recovers on the reverse sweep, but shows significant hysteresis. The reflection recovers to the same intensity, consistent with the fact that the voltammogram can be cycled to this upper potential (1.17 V) for many cycles without irreversible degradation of the surface.

The association of the PE with the oxide peak is clear, and the hysteresis is consistent with the irreversible current profile in the CV. By differentiating their SXRD data, Liu et al. [19] proposed that the PE solely determines the shape of the oxide peak, though Gómez-Marín et al. [31] have shown that this peak contains two kinetically-distinguishable processes.

We verified that the (1,1,1.5) reflection was unchanged by *in-situ* exchange of the Ar-saturated 0.1 M $HClO_4$ electrolyte with O_2-saturated electrolyte at 0.45 V. A voltammogram in the presence of oxygen (Fig. 1) shows that the

PE is not significantly different when oxygen is absent. During the cycling the O_2-saturated electrolyte was flowed through the hanging meniscus cell at a rate of 20 μL s^{-1}. Beam effects on both voltammograms were small, as shown earlier [20], and take the form of a small anodic contribution to the current.

On the positive-going sweep, the oxygen reduction current drops between 0.80 V and 0.95 V. This is near the end of the OH adsorption (butterfly) peak and before the oxide peak, which is still seen at 1.06 V. The lack of change of the (1,1,1.5) intensity as the ORR current decreases shows that the ORR does not affect the onset of the PE and vice versa. The absence of any noticeable structural change in this potential range suggests that the decreasing current and high ORR overpotential is solely due to the slow ORR mechanism on an unreconstructed surface. The presence of adsorbed OH in this region is in agreement with the critical role suggested for this intermediate.

Upon sweep reversal, there is a large reduction peak and then the current levels off to the diffusion-limited ORR current. The reverse PE process, resulting in recovery of the smooth Pt surface is not different than that in the absence of oxygen. Part of it overlaps with the onset of the ORR, so there is the possibility that the PE species influences the ORR. However, the ORR onset potential corresponds closely to its decay potential on the forward sweep, suggesting that the same phenomemon is controlling its kinetics and the PE species are a spectator. It is possible, however, that the PE species are associated with the large reduction peak. Gómez-Marín et al. [31, 32] suggested that this peak is due to an unknown soluble species.

Even though we do not observe any difference in the intensity profiles during the potential cycling, it is possible that the kinetics of the PE differ when O_2 is present. However, potential steps to successively higher potentials showed the same dependence of the PE coverage on ln(time) (predicted by the Conway model [33] in the presence and absence of oxygen (example shown in Figure 2). The slight difference in intercept is most likely caused by a small variation in the initial states of the surface (as judged by the different intensities), and should not be interpreted as a real reactivity difference.

In total, our results show that the PE proceeds on the surface independently of the ORR, suggesting that the ORR does not affect the PE. Gómez-Marín et al. [34] interpret the small decrease in the oxide peak current at 1.06V as an O_2 effect on the oxide. Although we also see this difference in the current, it is very small, and any difference in the X-ray intensity curves is not significant given the reproducibility from run to run and the counting statistics.

There are a few other studies of the effect of the oxide on Pt(111) at potentials more negative than 1.15 V. Tanaka et al. [35] found that holding the potential at 1.0 V reduced the limiting current and attributed this to oxide formation. Kuzume et al. [36] found that holding at potentials as low at 0.78 V had a blocking effect and attributed this to oxide growth on defects or adsorbed OH. It is possible that PE can occur at lower potentials after longer times, but we did not investigate this possibility here.

Although we definitely rule out a significant influence of O_2 on the PE for Pt(111) in $HClO_4$, the situation may be different on other surfaces and for other

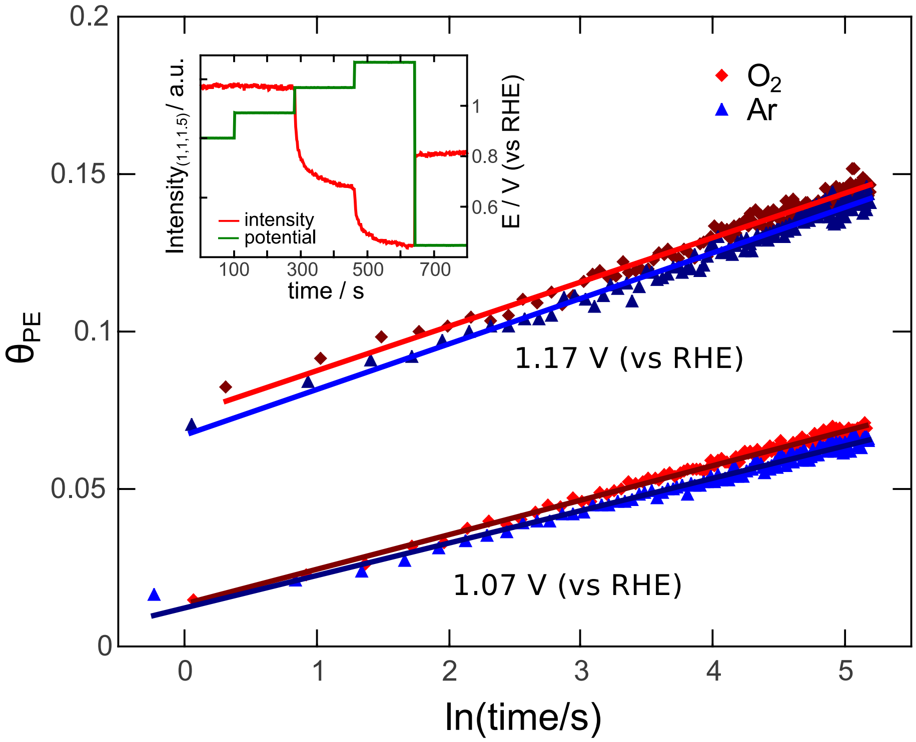

Figure 2: Potential step experiment in O_2-saturated 0.1 M $HClO_4$ plotted as a coverage of PE sites vs. ln(time). The intensity response of (1,1,1.5) reflection upon stepping to 1.07 V and subsequently to 1.17 V is shown in the inset. The coverage of exchanged sites were obtained from the model described in [20]. The curves for Ar-saturated electrolyte were taken from [20].

electrolytes, where the oxidation kinetics can be different. For example Matsumoto et al. [28] came to the opposite conclusion. They observed by STM at 0.6 V in O_2-containing H_2SO_4 solution a significant increase in surface roughness, although after much longer time periods than reported here. This surface roughening was attributed to PE at low potentials. Kongkanand and Ziegelbauer [29] found no difference between the formation rates or the coverage of the surface oxides in N_2- or O_2-saturated $HClO_4$ electrolytes, based on coulometric measurements on polycrystalline Pt. However, their X-ray absorption near edge structure (XANES) measurements on Pt nanoparticles suggested that the PE mechanism commences as soon as 0.75 V. These XANES observations could be due to a different oxidation reactivity associated with the finite size as well as the presence of other crystal facets and step sites on the nanoparticles. Indeed, GISAXS measurements of nanoscale roughened Pt(111) surfaces also provided evidence of the surface oxidation shift to lower potentials, which was attributed to the step edge oxidation[37].

4. Conclusions

For Pt(111) in $HClO_4$ at potentials more negative then 1.15 V, where the PE process is reversible, the PE occurs but does not influence the ORR in the positive-going sweep. The kinetics appear to be limited by the nature of the adsorbed species on the surface. Reciprocally, the presence of oxygen also has no significant influence on the PE for both positive- and negative-going sweeps. However, a possible influence of the reverse PE process on the ORR during negative sweeps cannot be ruled out. While these results need to be extended to other electrolytes and other surfaces, including those restructured by cycling, the present results suggest that the PE atoms are spectator species rather than dramatic influencers with respect to the ORR.

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