

Supporting Information

For

Electrochemical Stripping of Atomic Oxygen on Single Crystalline Platinum: Bridging Gas-Phase and Electrochemical Oxidation

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Temperature of Pt crystal in contacting with O₂

Investigations of thermal dissociation of O₂ on Pt(111) by UHV shows that the coverage of O generated at 420 K and 620 K are different.¹ Therefore, the temperature of Pt crystal should be monitored prior to contact with O₂. Figure S1a shows the temperature of a flame-annealed semi-

bead Pt(111) crystal as a function of time in the round bottom flask under an Ar flow. It can be seen that the temperature of the crystal is 1026 ± 6 K (higher than the temperature of O_2 desorption of ~ 800 K²) when the crystal enters the flask ($t=0$), which implies the surface is not oxidized in air during the transfer. The deviation of less than 6 K also indicates the high reproducibility of the temperature in separate measurements. Figure S1b shows the voltammograms of Pt(111)- O_{GAS} for different cooling times and corresponding temperatures (the temperature at the moment of contacting O_2 can be estimated from Figure S1a; estimated temperatures are given in Figure caption). Compared with the standard voltammogram of Pt(111) (dashed line), the voltammograms of Pt(111)- O_{GAS} show the characteristic peak at 0.12 V with a higher peak current density compared to the situation in which the crystal is cooled down to the room temperature prior to contact with O_2 , which indicates that {111}-type defects have been introduced. With the cooling time decreasing from 10 min to 0 s (and temperature increasing from 0 to 1026 K), more defects are introduced and the stripping potential of atomic oxygen shifts negatively. Thus, the Pt- O_{GAS} generated with a 10 min cooling time is used for further discussion in the main manuscript in order to correlate the Pt(hkl)- O_{GAS} with Pt(hkl) electrochemistry.

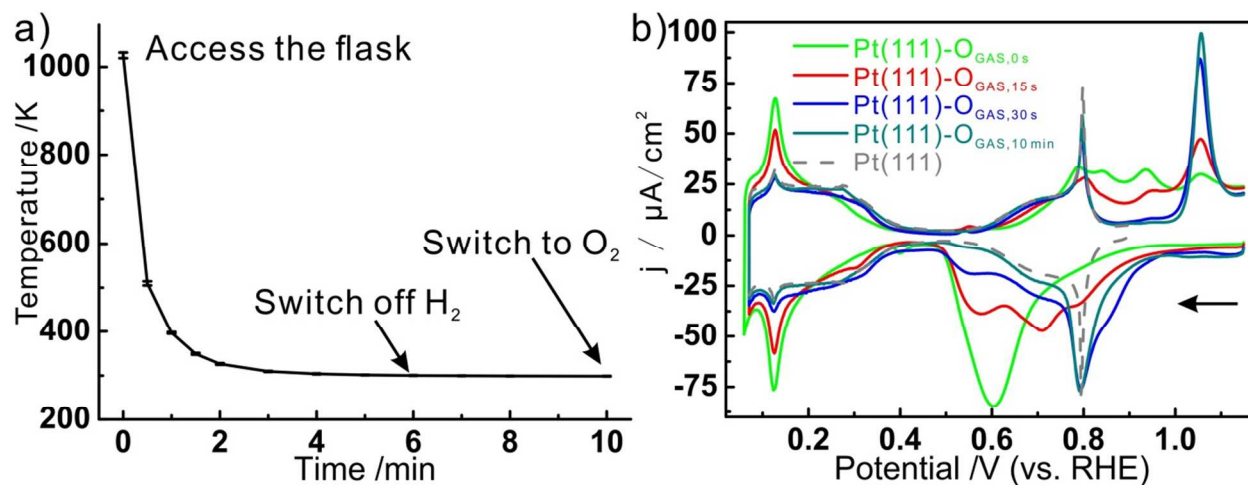


Figure S1 a) Time-dependent temperature of the bead-type Pt(111) crystal in the round-bottom flask; b) Voltammograms of Pt(111)-O_{GAS} in 0.1 mol/L HClO₄ electrolyte for different cooling times (0 s: ~1000 K; 15 s: ~500 K; 30 s; ~400 K; 10 min; 300 K). (Scan rate: 50 mV/s).

pH dependent stripping voltammogram of Pt(111)-O_{GAS} in H₂SO₄ and surface coverage of O_{GAS}

Figure S2a shows the cyclic voltammograms of Pt(111)-O_{GAS} in 0.1 mol/L HClO₄ and 0.1 mol/L H₂SO₄, and Figure S2b shows the pH dependent voltammograms of the Pt(111)-O_{GAS} in H₂SO₄ showing a pH independent cathodic peak at 0.8V on the reversible hydrogen electrode (RHE) scale, which indicates a concerted proton-coupled electron transfer reduction of Pt(111)-O_{GAS}. The peak between 0.6 and 0.4 V is due to the adsorption of bisulfate HSO₄⁻.³ Since the structure of HSO₄⁻ has been observed to be a $\sqrt{3} \times \sqrt{7}$ overlayer by STM,⁴ corresponding to a coverage of 0.218 ML, the integrated charge of this peak is helpful for estimating the coverage of the atomic oxygen O_{GAS} and the nature of the stripping peak. The integrated charges of the Area 1 and Area 2 in figure S2a and Area 3 in figure S2b are 91.2, 140.4 and 45.6 $\mu\text{C}/\text{cm}^2$, respectively. Here, we use the charge of the HSO₄⁻ desorption in pH 2.24 since the peak is deconvoluted from that of adsorbed H. These numbers show that the total charge of reduction of Pt(111)-O_{GAS} in H₂SO₄ (Area 2) and the subsequent desorption of HSO₄⁻ (Area 3) is approximately equal to the stripping of Pt(111)-O_{GAS} in HClO₄ (Area 1). The voltammograms of Pt(111)-O_{GAS} overlap in both electrolytes between 1.15 V and 0.98 V, which suggests that the interaction between Pt(111)-O_{GAS} and HSO₄⁻ is weak. Therefore, in perchloric acid we propose the following stripping reaction of Pt(111)-O_{GAS}:

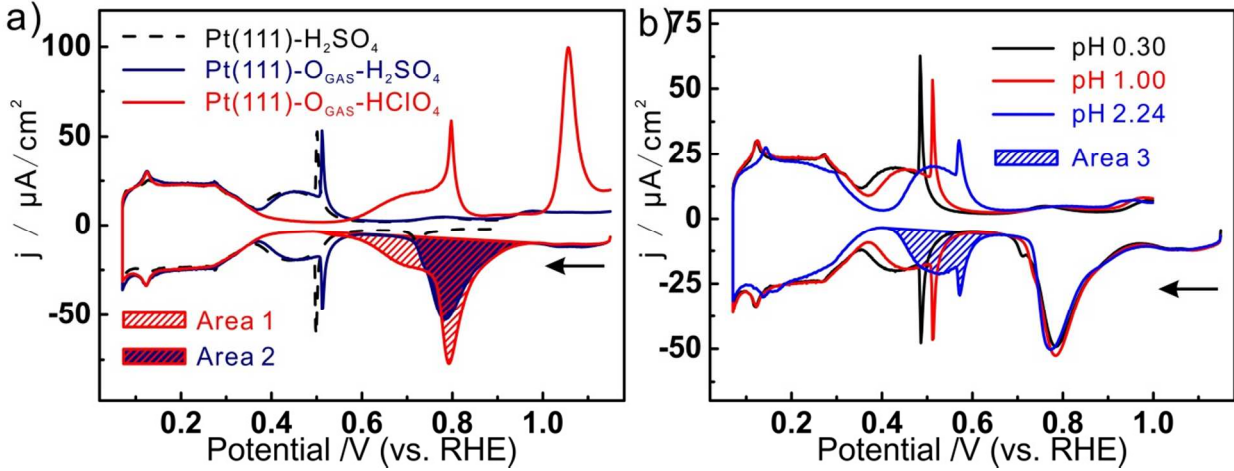
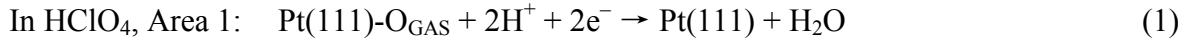
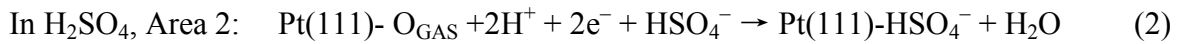


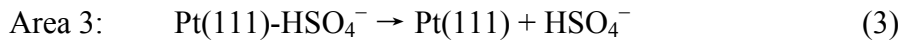
Figure S2 a) Voltammograms of Pt(111)-O_{GAS} and Pt(111) in 0.1 mol/L HClO₄ and H₂SO₄; the voltammetry of the Pt(111)-O_{GAS} starts at 1.15 V; b) pH dependent voltammograms of Pt(111)-O_{GAS} (0.1 mol/L H₂SO₄ + 0.4 mol/L HClO₄, pH 0.30; 0.1 mol/L H₂SO₄, pH 1.00; 0.01 mol/L H₂SO₄ + 0.09 mol/L Na₂SO₄, pH 2.24). (Scan rate: 50 mV/s).



In sulfuric acid, we propose a replacement by HSO₄⁻ in the stripping of O on Pt(111)-O_{GAS}:



followed by:



Based on the charge of Area 2 and Area 3 and the coverage of HSO₄⁻, the coverage of oxygen on Pt(111)-O_{GAS} is calculated to be 0.336, according to Equation 4 (where Q is the reaction charge, n is the number of transferred electrons, and θ is the coverage of adsorbate) This

coverage is reasonably consistent with the measurement of 0.4 ML on Pt(111) oxidized in 0.5 Torr O₂.⁵

$$\theta_O = \frac{Q_O}{Q_{\text{HSO}_4^-}} \times \theta_{\text{HSO}_4^-} \times \frac{n_{\text{HSO}_4^- \text{ desorption}}}{n_{\text{O-stripping}}} = \frac{140.4 \mu\text{C}/\text{cm}^2}{45.6 \mu\text{C}/\text{cm}^2} \times \frac{1}{\sqrt{3} \times \sqrt{7}} \times \frac{1}{2} = 0.336 \quad (4)$$

Stripping voltammogram of Pt(533)-O_{GAS}

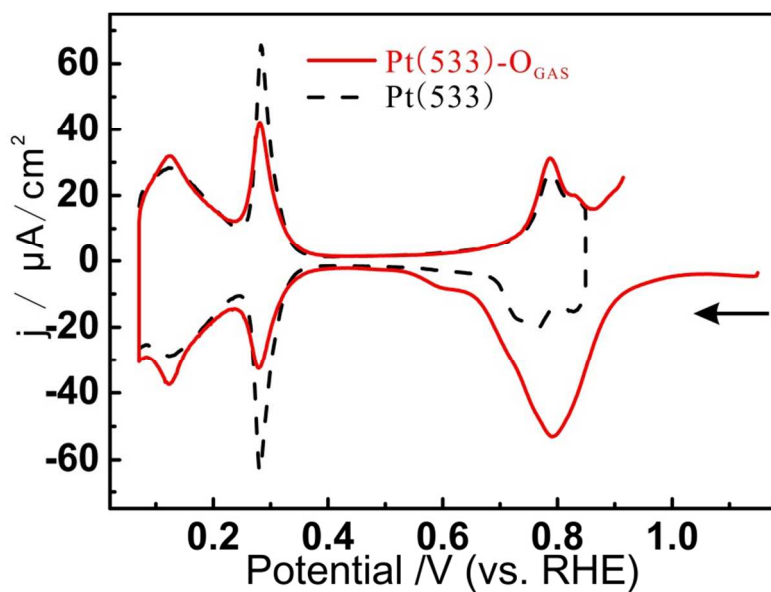


Figure S3 Stripping voltammograms of Pt(533)-O_{GAS} and Pt(533). All the measurements were performed in 0.1 M HClO₄ with a scan rate of 50 mV/s.

REFERENCES

- (1) Bashlakov, D. L.; Juurlink, L. B. F.; Koper, M. T. M.; Yanson, A. I. Subsurface Oxygen on Pt(111) and Its Reactivity for CO Oxidation. *Catal. Lett.* **2011**, *142*, 1-6.

- (2) Steininger, H.; Lehwald, S.; Ibach, H. Adsorption of Oxygen on Pt(111). *Surf. Sci.* **1982**, *123*, 1-17.
- (3) Lachenwitzer, A.; Li, N.; Lipkowski, J. Determination of the Acid Dissociation Constant for Bisulfate Adsorbed at the Pt(111) Electrode by Subtractively Normalized Interfacial Fourier Transform Infrared Spectroscopy. *J. Electroanal. Chem.* **2002**, *532*, 85-98.
- (4) Funtikov, A. M.; Linke, U.; Stimming, U.; Vogel, R. An in-situ STM Study of Anion Adsorption on Pt(111) from Sulfuric Acid Solutions. *Surf. Sci.* **1995**, *324*, L343-L348.
- (5) Miller, D. J.; Öberg, H.; Kaya, S.; Sanchez Casalongue, H.; Friebe, D.; Anniyev, T.; Ogasawara, H.; Bluhm, H.; Pettersson, L. G. M.; Nilsson, A. Oxidation of Pt(111) under Near-Ambient Conditions. *Phys. Rev. Lett.* **2011**, *107*, 195502.