

Electronic Supplementary Information

The Nature of Active Centers Catalyzing Oxygen Electro- Reduction at Platinum Surfaces in Alkaline Media

Yunchang Liang,^{a,(1)} David McLaughlin,^{a,(1)} Christoph Csoklich,^a Oliver Schneider,^b and

Aliaksandr S. Bandarenka^{a,c,d,}*

^a - Physik-Department ECS, Technische Universität München, James-Franck-Str. 1, D-85748
Garching, Germany.

^b - Institut für Informatik VI, Technische Universität München, Schleißheimerstraße 90a,
85748 Garching, Germany.

^c - Nanosystems Initiative Munich (NIM), Schellingstraße 4, 80799 Munich, Germany.

^d - Catalysis Research Center, TUM, Ernst-Otto-Fischer-Straße 1, 85748 Garching, Germany

⁽¹⁾ - These authors contributed equally to this manuscript.

1. Typical cyclic voltammogram (CV) of freshly prepared Pt(111) electrode in air-saturated 0.1 M KOH.

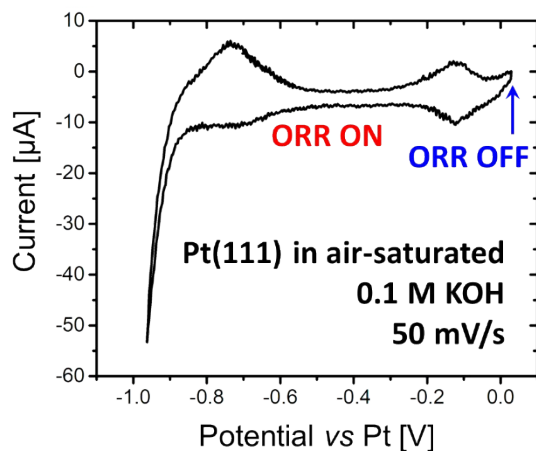


Figure S1. Typical cyclic voltammogram (CV) of freshly prepared Pt(111) electrode in air-saturated 0.1 M KOH (99.99 %, Trace Metal Basis, Sigma Aldrich) at a scan rate of 50 mV/s in the electrochemical scanning tunneling microscope (EC-STM) cell. The pseudo-reference and counter electrodes are Pt (MaTeck, 0.5 mm) wires. The potential regions for both “ORR ON” and “ORR OFF” are indicated. Spatial limitations did not permit the use of a true reference electrode and conversion of the potential scale to RHE. The electrochemical active surface area of the Pt(111) electrode determined in Ar-saturated 0.1 M HClO₄ using commercial reference electrode is $\sim 0.198 \text{ cm}^2$, which is similar to the geometric surface area of the electrode. In the EC-STM cell, due to the cell design, part of the electrode surface is covered by the sealing ring to prevent electrolyte leakage. The effective surface area of the electrode for the EC-STM measurements is $\sim 0.127 \text{ cm}^2$.

2. Typical CV of Pt(111) in air-saturated 0.1 M LiOH.

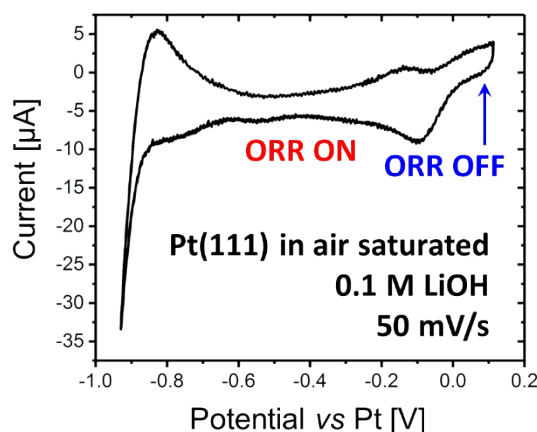


Figure S2. Typical CV of freshly prepared Pt(111) electrode in air-saturated 0.1 M LiOH (99.995%, metals basis, Alfa Aesar) in the EC-STM cell at a scan rate of 50 mV/s. Two Pt wires were used as the pseudo-reference and the counter electrodes. The potential regions for both “ORR ON” and “ORR OFF” are indicated.

3. Typical CV of Pt(111) in air-saturated 0.1 M CsOH.

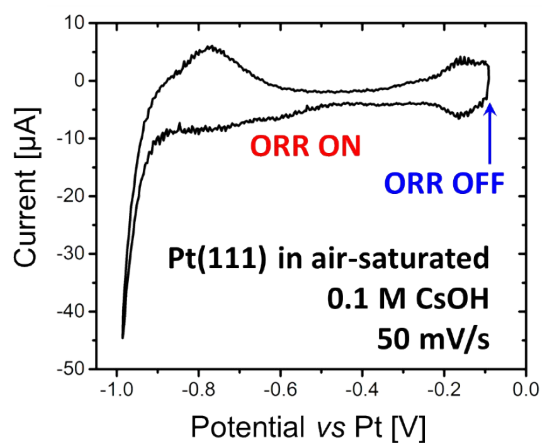


Figure S3. Typical CV of freshly prepared Pt(111) electrode in air-saturated 0.1 M CsOH (99.9%, 50 wt-% solution, Sigma Aldrich) in the EC-STM cell at a scan rate of 50 mV/s. Both the pseudo-reference and the counter electrodes were Pt wires. The potential regions for both “ORR ON” and “ORR OFF” are indicated.