

Supporting Information for

**Applications of ALD MnO to Electrochemical and Photoelectrochemical
Water Splitting**

Katie L. Pickrahn,[§] Yelena Gorlin,[§] Linsey C. Seitz, Aaron Garg, Dennis Nordlund,
Thomas F. Jaramillo, and Stacey F. Bent*

Department of Chemical Engineering, Stanford University
Stanford, CA 94305-5025, USA

*sbent@stanford.edu

[§]These authors contributed equally to this work.

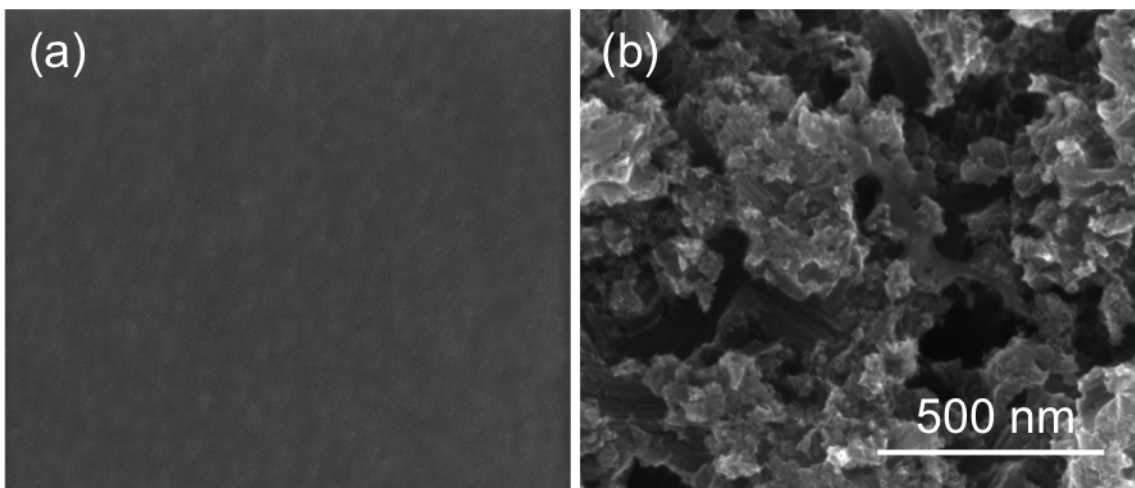


Figure S1: SEM micrograph of (a) smooth glassy carbon (s-GC) and (b) high surface area glassy carbon (HSA-GC) substrates.

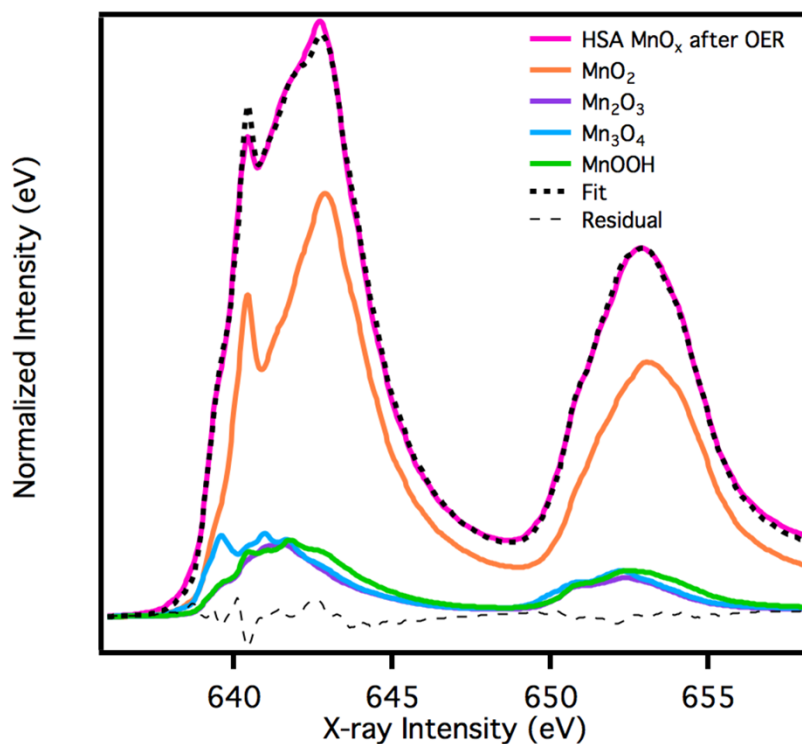


Figure S2: Plotted is a sample fitting of the Mn L-edge region XAS spectra. The sample shown is the fit of the HSA MnO_x sample after OER. The contributions of MnO₂, Mn₂O₃, Mn₃O₄, and MnOOH to the fit are also plotted.

Table S1: Comparison between other MnO_x OER Catalysts

| System | Electrolyte | U _{RHE} (j = 10 mA/cm ²) (V) | Reference |
|---|--|---|-------------|
| Ag Nanoparticles + α-MnO ₂ | 0.1 M KOH | ~1.93 | [1] |
| MnO _x | 0.1 M KPi at pH 7 | > 1.9 | [2] |
| MnO _x | 1 M KOH | > 1.9 | [3] |
| Oxidized MnO | 0.1 M KPi | > 1.86 | [4] |
| Nanostructured Mn(III) oxide | 0.1 M KOH | 1.77 | [5] |
| Electrodeposited MnO _x | Phosphoric acid, KNO ₃ , KOH. (pH 13) | ~1.75 (extrapolated from Tafel slope) | [6] |
| ALD MnO on HSA-GC | 0.1 M KOH | 1.70 | (this work) |
| Electrodeposited MnO _x on HSA-GC (~1 micron thick) | 0.1 M KOH | ~1.6 | [7] |
| Massive α-Mn ₂ O ₃ (tablet ~2 mm thick) | 1 M KOH | 1.58 | [8] |

Table S2: Comparison of MnO_x Surface Areas

| | j _{1.26 V} | j _{1.3 V} | j _{0.2 V} | Redox Feature 0.96 V |
|--|---------------------|--------------------|--------------------|----------------------|
| HSA-GC MnO _x /s-GC MnO _x | 2.5 | 2.1 | 1.8 | 3.1 |
| Annealed MnO _x /s-GC MnO _x | 1.3 | 1.3 | 1.5 | 1.1 |

The determination of the surface area is difficult for transition metal oxide systems. Here, we compare the surface area ratios of the HSA MnO_x sample to the flat GC MnO_x sample and the annealed MnO_x sample to the flat GC MnO_x sample. The first three columns are calculated from an estimate of the surface area from the capacitive currents at 1.26 V_{RHE}, 1.3 V_{RHE}, and 0.2 V_{RHE}, respectively. The final column estimates the surface area ratio from the charge passed in the redox feature in at 0.96 V_{RHE}. All measurements are for the 5th OER sweep.

Supporting Information References

1. Goh, F.W.T., et al., *Ag nanoparticle-modified MnO₂ nanorods catalyst for use as an air electrode in zinc-air battery*. *Electrochimica Acta*, 2013. **114**(0): p. 598-604.
2. Bergmann, A., et al., *Electrochemical water splitting by layered and 3D cross-linked manganese oxides: correlating structural motifs and catalytic activity*. *Energy & Environmental Science*, 2013. **6**(9): p. 2745-2755.
3. Trotochaud, L., et al., *Solution-Cast Metal Oxide Thin Film Electrocatalysts for Oxygen Evolution*. *Journal of the American Chemical Society*, 2012. **134**(41): p. 17253-17261.
4. Indra, A., et al., *Active Mixed-Valent MnO_x Water Oxidation Catalysts through Partial Oxidation (Corrosion) of Nanostructured MnO Particles*. *Angewandte Chemie-International Edition*, 2013. **52**(50): p. 13206-13210.
5. Gorlin, Y. and T.F. Jaramillo, *A Bifunctional Nonprecious Metal Catalyst for Oxygen Reduction and Water Oxidation*. *Journal of the American Chemical Society*, 2010. **132**(39): p. 13612-13614.
6. Huynh, M., D.K. Bediako, and D.G. Nocera, *A Functionally Stable Manganese Oxide Oxygen Evolution Catalyst in Acid*. *Journal of the American Chemical Society*, 2014. **136**(16): p. 6002-6010.
7. Gorlin, Y., D. Nordlund, and T.F. Jaramillo, *The Role of Heat Treatment in Enhanced Activity of Manganese Oxides for the Oxygen Reduction and Evolution Reactions*. *ECS Transactions*, 2013. **58**(1): p. 735-750.
8. Morita, M., C. Iwakura, and H. Tamura, *The anodic characteristics of modified Mn oxide electrode: Ti/RuO_x/MnO_x*. *Electrochimica Acta*, 1978. **23**(4): p. 331-335.