

Supporting Information for
Effects of paramagnetic fluctuations on the thermochemistry of
MnO (100) surfaces in the oxygen evolution reaction

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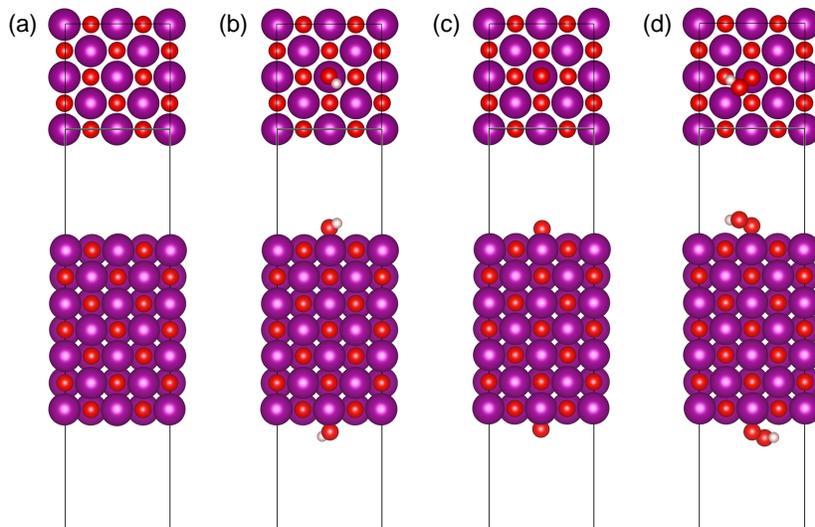


FIG. S1. Top and side views of symmetric slab models used to calculate the Gibbs free energies of intermediate states in the OER: (a) pristine surface model, and (b)-(d) surface models with OH^* , O^* , and OOH^* intermediates, respectively. The thickness of vacuum layers between slabs is about 15 Å.

To confirm the validity of our calculations, we performed two experiments with commercial MnO micropowder, which is expected to have stable surfaces. Figure S2(a) shows the polarization-corrected cyclic voltammetry (CV) curve of the MnO micropowder at pH 7. A clear additional redox reaction peak can be seen at approximately 1.6 V (vs. RHE) before the Faraday current appears. Figure S2(b) shows the *in-situ* UV-visible differential spectra of the MnO micropowder. Each differential spectrum was obtained by subtracting the reference spectrum from that obtained at each potential. As the potential increased from 1.2 V to 1.9 V, a broad peak at around 450 – 500 nm appears from 1.4 V. It has been reported previously that this feature indicates the formation of $\text{Mn}^{3+} - \text{OH}$ species on the Mn oxide surface.^{1,2} This shows that, prior to 1.9 V, i.e. at the onset potential for oxygen evolution, $\text{Mn}^{3+} - \text{OH}$ species accumulated on the surface of MnO micropowder. Both experimental results verify that a redox reaction that transforms $\text{Mn}^{2+} + \text{H}_2\text{O}$ to $\text{Mn}^{3+} - \text{OH}^*$ occurred prior to the RDS; the surface state of $\text{Mn}^{3+} - \text{OH}^*$ was maintained from 1.4 V to 1.9 V, which is consistent with our DFT results. On the other hand, the spectral signature of $\text{Mn}^{4+} = \text{O}$ species, a sharp peak at 400 nm with a broad peak at 700 nm, has not been observed in the UV difference spectra of MnO micropowders.³ This result shows that the

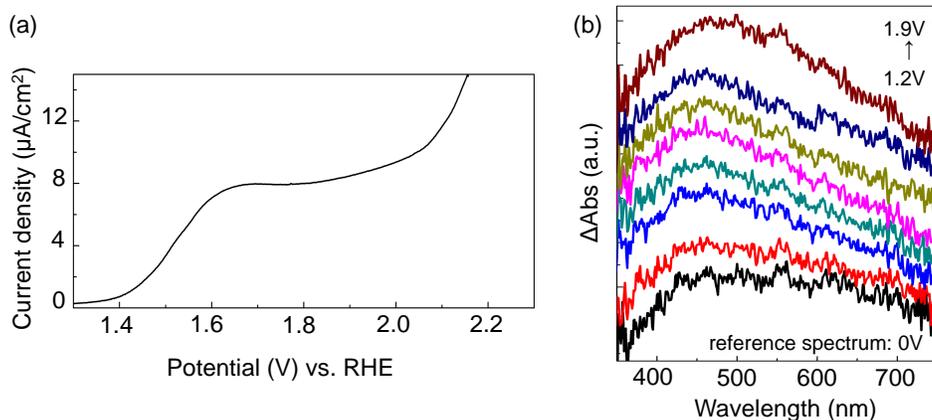


FIG. S2. Experimental evidence of the OH^* resting state for the OER in MnO micropowder. (a) Polarization-corrected CV curve of MnO powders in 0.5 M phosphate buffer at pH 7. (b) *In-situ* UV difference spectra of MnO powder with increasing potential from 1.2 V to 1.9 V. A spectrum measured at the open circuit voltage was used as the reference spectrum.

reaction step evolving from an OH^* intermediate to an O^* intermediate is the RDS for the OER on MnO micropowders. MnO micropowders are believed to be composed of low-index facets with much less structural defects than MnO nanoparticles.

REFERENCES

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