

## Supplementary Materials for

### Solvated Proton and the Origin of the High Onset Overpotential

#### in the Oxygen Reduction Reaction on Pt(111)

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**There are six supplementary figures, including**

**Figure S1. 2D MTD results for O<sub>2</sub>\* dissociation and O<sub>2</sub>\* association at  $q=0.0$ , with  $d_{OO}$  and  $d_{OH}$  as the variables.**

**Figure S2. 2D MTD results for O\* hydrolysis at  $q=0.0$ .**

**Figure S3. 2D MTD results for O\* hydrolysis at  $q=+0.5$ .**

**Figure S4. 2D MTD results for O\* protonation at  $q=-0.5$ .**

**Figure S5. The relationship between the charge  $q$  on our Pt(111)|HBr|water model and the shift in the electrode potential as calculated from the double reference method.**

**Figure S6. 1D MTD results for OH\* protonation at  $q=0.0$  and  $q=+0.5$ .**

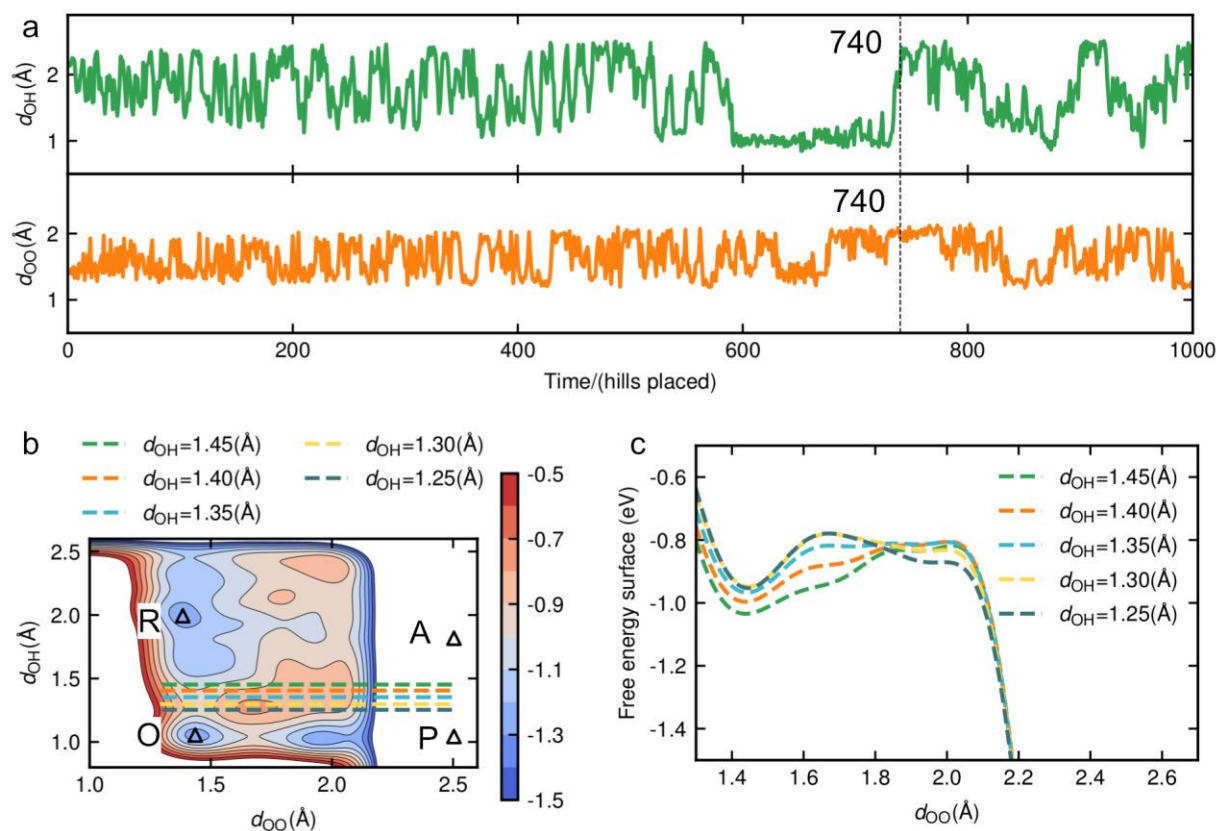


Figure S1. 2D MTD results for O<sub>2</sub>\* dissociation and O<sub>2</sub>\* association at  $q=0.0$ , with  $d_{OO}$  and  $d_{OH}$  as the variables. (a)  $d_{OH}$  and  $d_{OO}$  plotted against the accumulated number of hills added to the system during MTD simulation. While  $d_{OO}$  fluctuated back and forth frequently, it took 740 hills for  $d_{OH}$  to sample the O–H bond region and came back to the original O...H hydrogen bond distance. The duration was therefore  $740 \times 25 = 18,500$  time steps (22.2 ps), for the data collection to produce the 2D FES. (b) Horizontal lines cut through 2D free energy surface, with  $d_{OH} = 1.25$ , 1.30, 1.35, 1.40, and 1.45 Å, respectively, and (c) the free energy changes along these lines show that elongation of  $d_{OO}$  along these lines is facile, with a barrier between 0.16~0.2 eV.

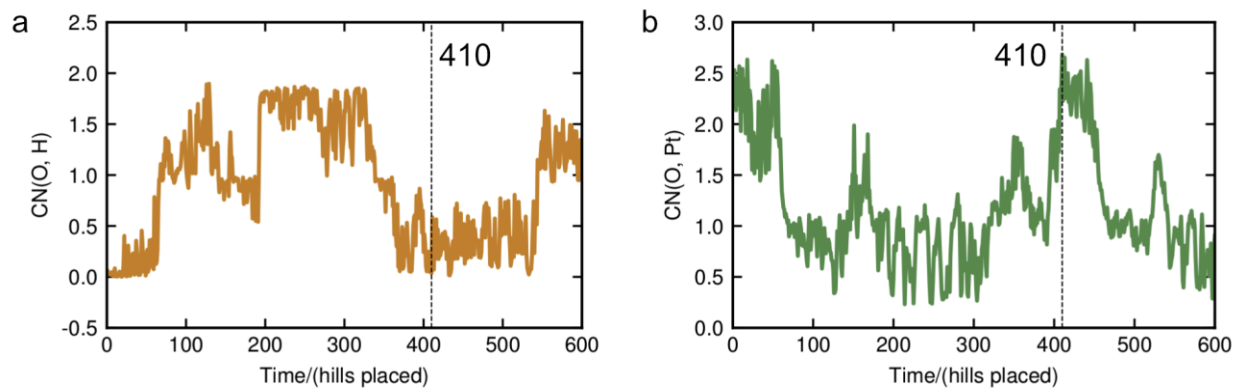


Figure S2. Two-dimensional metadynamics results for  $O^*$  hydrolysis at  $q=0.0$ . The two variables  $CN(O, H)$  and  $CN(O, Pt)$  are plotted against the accumulated number of hills added to the system during MTD simulation. The data collection for the 2D FES, shown in Figure 2 of our paper, was from the 1<sup>st</sup> hill to the 410<sup>th</sup> hill, when both variables were returned to their initial values.

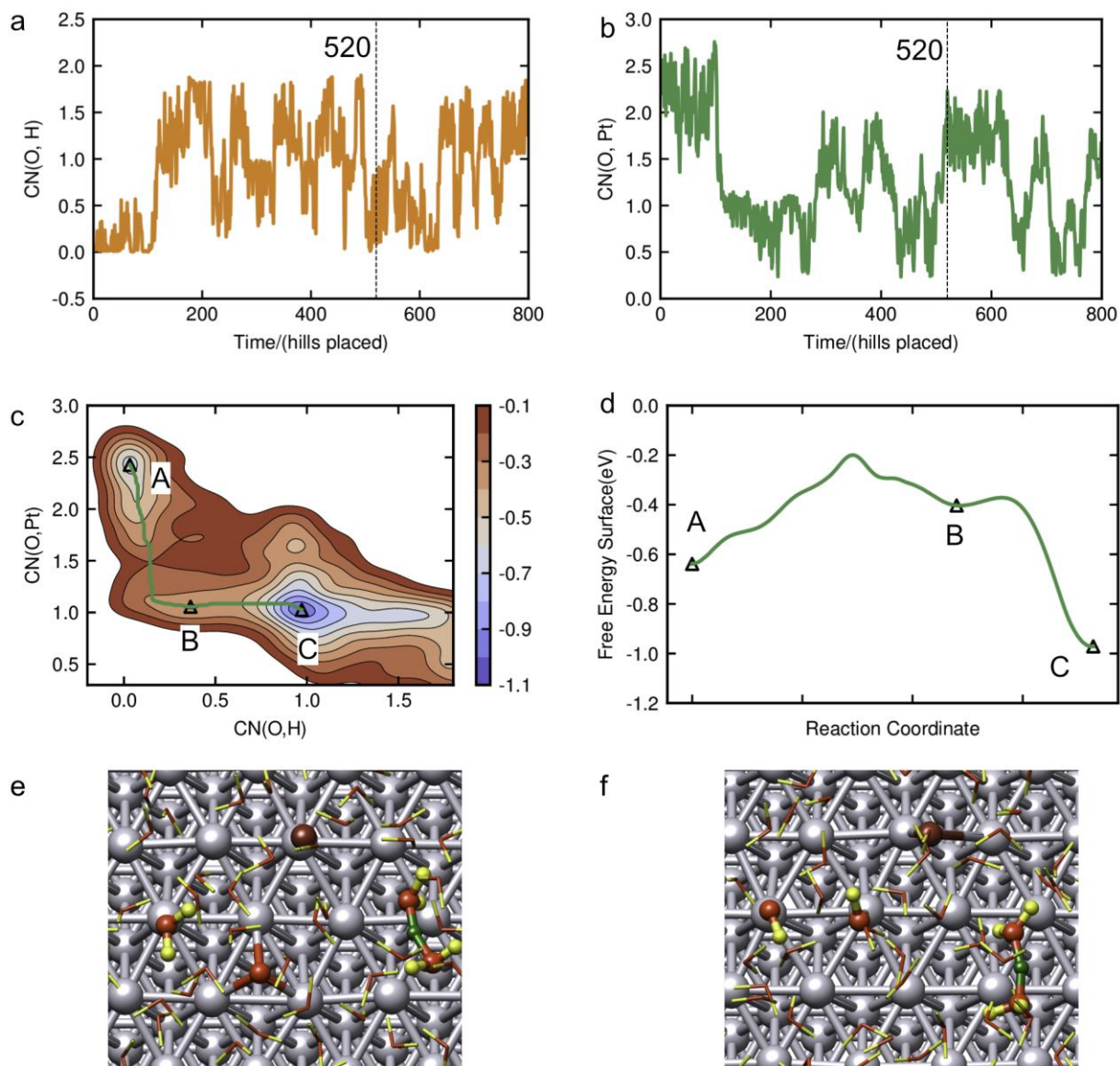


Figure S3. 2D MTD results for  $O^*$  hydrolysis at  $q=+0.5$ . The variables are  $CN(O, H)$  and  $CN(O, Pt)$ . One bias Gaussian potential was added at  $CN(O, H) = 2.0$  to prevent the formation of  $H_2O^*$ , and another at  $CN(O, Pt) = 0.1$  to prevent the desorption of  $O^*$ . (a) and (b) show the evolution of  $CN(O, H)$  and  $CN(O, Pt)$ , respectively, plotted against the number of potential hills added to the system. Both variables evolved back to their original values at the 520<sup>th</sup> hills, which was also the total number of hills collected in the 2D FES plot shown in (c) and 1D reaction profile shown in (d). The top view for the beginning reactant A is shown in (e), and that for the hydrogenation product is shown in (f). The presence of two  $OH^*$  indicates it went through the hydrolysis channel.

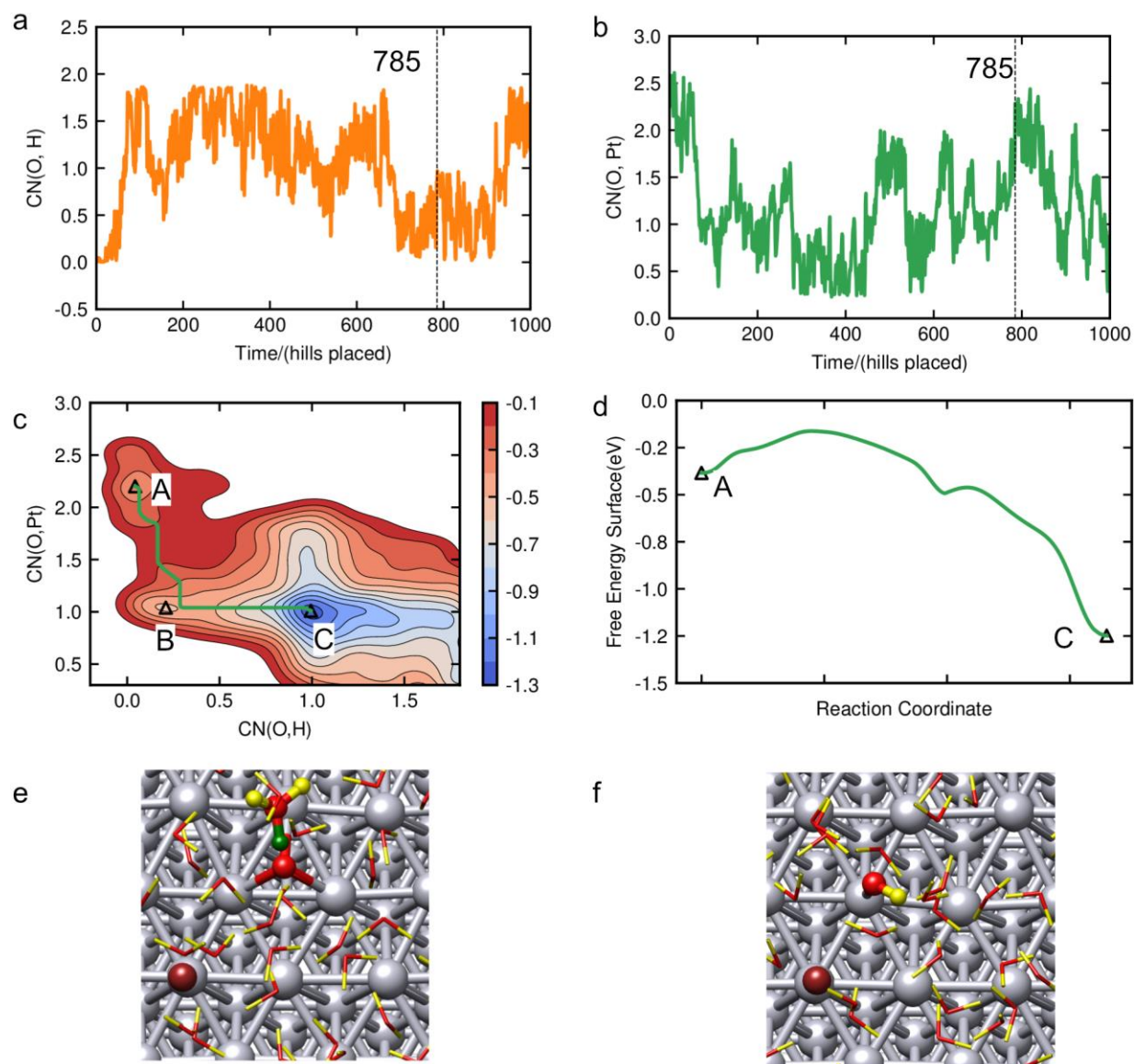


Figure S4. 2D MTD results for O\* protonation at  $q = -0.5$ . The two variables are  $CN(O, H)$  and  $CN(O, Pt)$ . One bias Gaussian potential was added at  $CN(O, H) = 2.0$  to prevent the formation of  $H_2O^*$ , and another at  $CN(O, Pt) = 0.1$  to prevent the desorption of O\*. (a) and (b) show the evolution of  $CN(O, H)$  and  $CN(O, Pt)$ , respectively, plotted against the number of potential hills added to the system. Both variables evolved back to their original values at the 785<sup>th</sup> hills, which was also the total number of hills collected in the 2D FES plot shown in (c) and 1D reaction profile shown in (d). The top view for the beginning reactant A is shown in (e), and that for the hydrogenation product is shown in (f). The presence of only one OH\* indicates it went through the protonation channel, in contrast to the hydrolysis channel in Figure S3.

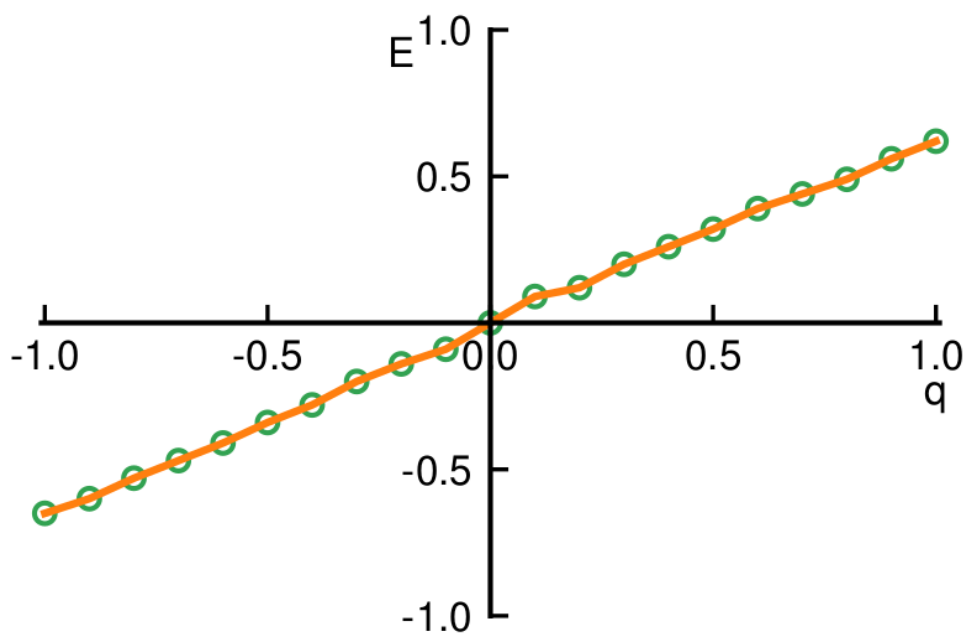


Figure S5. The relationship between the charge  $q$  on our Pt(111)|HBr|water model and the shift in the electrode potential as calculated from the constant charge double reference method.<sup>1-2</sup>

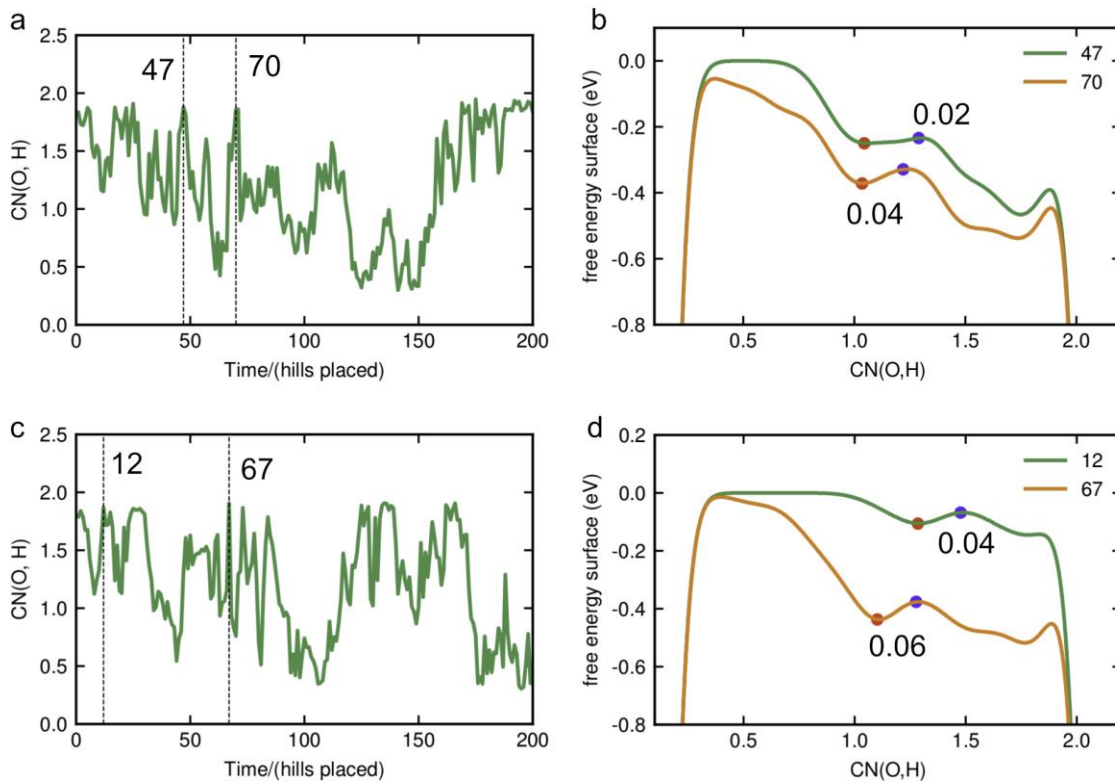


Figure S6. 1D MTD results for OH\* protonation at  $q=0.0$  and  $q=+0.5$ . The variable is CN(O, H), with two additional bias potentials, one at CN(O, H) = 2.2 to prevent the desorption of H<sub>2</sub>O\* and one at CN(O, H) = 0.0 to prevent the formation of O\*. (a) and (b) for  $q=0.0$ ; (c) and (d) for  $q=+0.5$ . By ~70<sup>th</sup> hills, the variable has already evolved at least twice between OH\* and H<sub>2</sub>O\*. In both cases, the reaction free energy is exergonic.

## References:

1. Taylor, C. D.; Wasileski, S. A.; Filhol, J. S.; Neurock, M., First principles reaction modeling of the electrochemical interface: Consideration and calculation of a tunable surface potential from atomic and electronic structure. *Phys. Rev. B* **2006**, *73* (16), 16.
2. Filhol, J. S.; Neurock, M., Elucidation of the electrochemical activation of water over Pd by first principles. *Angew. Chem. Int. Ed. Engl.* **2006**, *45* (3), 402-6.