Supplementary Information

Free energies of molecules are estimated from the standard thermodynamic data[1-3] (ΔG_f^0 and S^0 at 298K, 1bar) and the calculated free energy of O_2 and H_2 gas.

$$G(H_2(g)) = E_{DFT} - TS^0_{H_2(g)}$$
$$G(O_2(g)) = E_{DFT} - TS^0_{O_2(g)}$$

$$\frac{1}{2}H_2(g) \longrightarrow H(g) \quad ; \ \Delta G_f^o = 2.11eV \quad \Rightarrow G(H(g))$$
$$\frac{1}{2}O_2(g) \longrightarrow O(g) \quad ; \ \Delta G_f^o = 2.40eV \quad \Rightarrow G(O(g))$$
$$H_2(g) + \frac{1}{2}O_2(g) \longrightarrow H_2O(l) \ ; \ \Delta G_f^o = -2.46eV \quad \Rightarrow G(H_2O(l))$$
$$H_2(g) + O_2(g) \longrightarrow H_2O_2(aq) \ ; \ \Delta G_f^o = -1.39eV \quad \Rightarrow G(H_2O_2(aq))$$

Together with the above free energies, the following standard reversible potential[4] (U^0) and the change of Gibbs free energy (ΔG) from experiments[5] are used to estimate the ΔG for each reaction step.

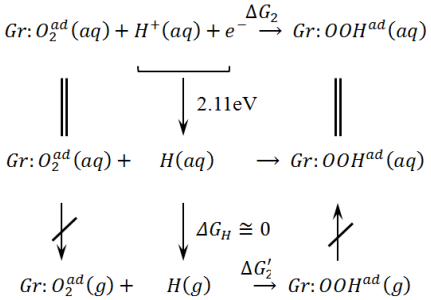
$$H^+(aq) + e^- \rightleftharpoons H(aq) \quad ; \ U^0 = 2.11V$$
$$OOH(aq) + H^+ + e^- \rightleftharpoons H_2O_2(aq) \quad ; \ U^0 = 1.436V$$
$$O_2(g) + H^+ + e^- \rightleftharpoons OOH(aq) \quad ; \ U^0 = -0.046V$$
$$OH^-(aq) + H^+(aq) \longrightarrow H_2O(l) \quad ; \ \Delta G = -0.92eV$$
$$OOH^-(aq) + H^+(aq) \longrightarrow H_2O_2(aq) \quad ; \ \Delta G = -0.69eV$$

Free energy change (ΔG_H) from H(aq) to H(g) also calculated from above thermodynamic data and it is assumed as zero in following calculations.

$$H(aq) \longrightarrow H(g) \quad ; \ \Delta G_H = 0.004eV$$

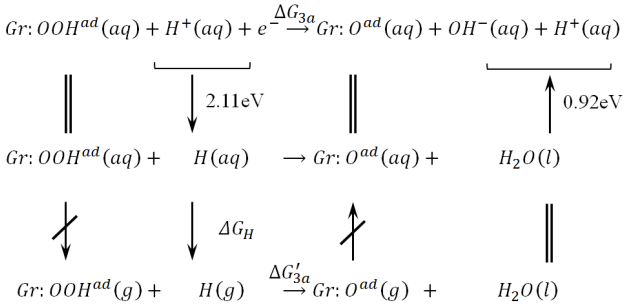
In this method we also assumed that the volumetric and entropic contributions to the free energy for the bulky reactant and product approximately cancel each other and are negligible.

Reaction (2)



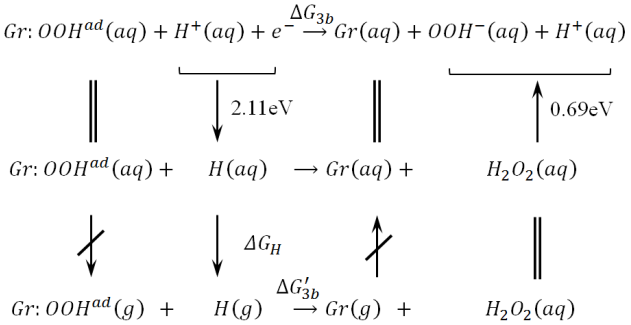
$$\Delta G_2' = G(Gr:OOH^{ad}) - G(Gr:O_2^{ad}) - G(H(g))$$
$$\Delta G_2 = 2.11 + \Delta G_2'$$

Reaction (3a)



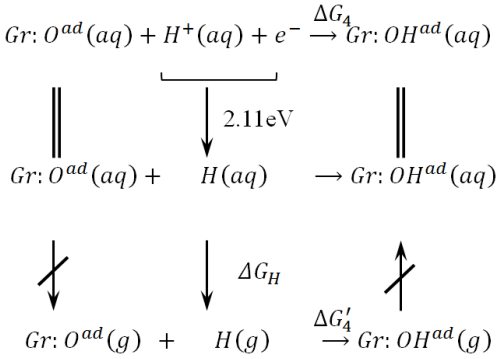
$$\Delta G_{3a}' = G(Gr:O^{ad}) + G(H_2O(l)) - G(Gr:OOH^{ad}) - G(H(g))$$
$$\Delta G_{3a} = 2.11 + \Delta G_{3a}' + 0.92$$

Reaction (3b)



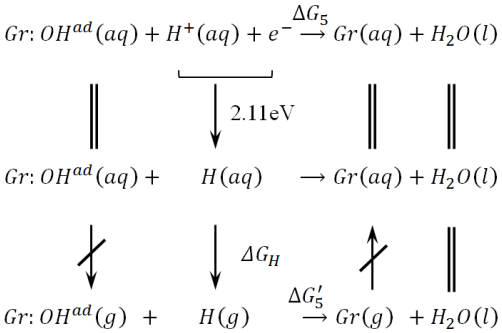
$$\Delta G_{3b}' = G(Gr) + G(H_2O_2(aq)) - G(Gr:OOH^{ad}) - G(H(g))$$
$$\Delta G_{3b} = 2.11 + \Delta G_{3b}' + 0.69$$

Reaction (4)



$$\Delta G_4' = G(Gr:OH^{ad}) - G(Gr:O^{ad}) - G(H(g))$$
$$\Delta G_4 = 2.11 + \Delta G_4'$$

5 Reaction (5)



$$\Delta G_5' = G(Gr) + G\left(H_2O(l)\right) - G(Gr{:}\,OH^{ad}) - G(H(g))$$
$$\Delta G_5 = 2.11 + \Delta G_5'$$

10 The adsorption barriers and the subsequent processes can be affected by the temperature and solvent as shown in platinum surface.[6] As mentioned in the main text, we did not consider these effects explicitly, however, the reversible potentials are calculated from the experimental data in aqueous solution at 15 room temperature, we can assumed that these additional effects are somewhat considered.

References

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