

The Oxygen Hydration Mechanism for the Oxygen Reduction Reaction at Pt and Pd Fuel Cell Catalysts

Yao Sha[†], Ted H. Yu[†], Boris V. Merinov[†], Pezhman Shirvanian[§] and William A. Goddard

III^{†}*

[†]Materials and Process Simulation Center, California Institute of Technology, MC 139-
74, Pasadena, California 91125

[§]Ford Motor Co., Research & Advanced Engineering, 2101 Village Rd, Dearborn,
Michigan 48104

Supporting Information

The estimation for the barrier of the hydrogen reduction reaction



The reaction at 0.00V relative to normal hydrogen electrode (NHE) is exothermic electrode is barrierless¹. At 0.8eV, however, with lower electrode work function (e becomes more stable by 0.8eV), the reaction becomes endothermic. The reaction enthalpy can be estimated by the hypothetical cycle developed by Norskov etc. ²



At 0.00eV relative to NHE, the reaction enthalpy for the first step is 0.00eV. At 0.80eV (ORR condition), it becomes 0.8eV endothermic. The second step can be estimated by

$$E = 1/2(\text{binding energy of H}_2) - (\text{binding energy of H}_{\text{ad}} \text{ to Pt surface})$$

$$= 2.31\text{eV} - 2.86\text{eV} \text{ (3.00eV for Pd)}$$

$$= -0.55\text{eV} \text{ (-0.69eV for Pd)}$$

So, for 0.0V vs NHE, the reaction is exthothermic with reaction enthalpy $E = -0.55\text{eV}$. At 0.8V vs NHE, the reaction is endothermic with enthalpy $E = 0.25\text{eV}$. Given the fact that the reaction is likely to have the same reaction pathway and transition state regardless of the potential, a good estimate of the barrier at 0.8V vs NHE would be $E_a(\text{Pt}) = 0.25\text{-}0.30\text{eV}$. The corresponding estimation for Pd would be $E_a(\text{Pd}) = 0.11\text{-}0.16\text{eV}$. The estimated barrier is much lower than the RDS in all mechanisms involved in our paper, so it doesn't affect our discussion. The overall potential energy surface is shown in Figure 1.

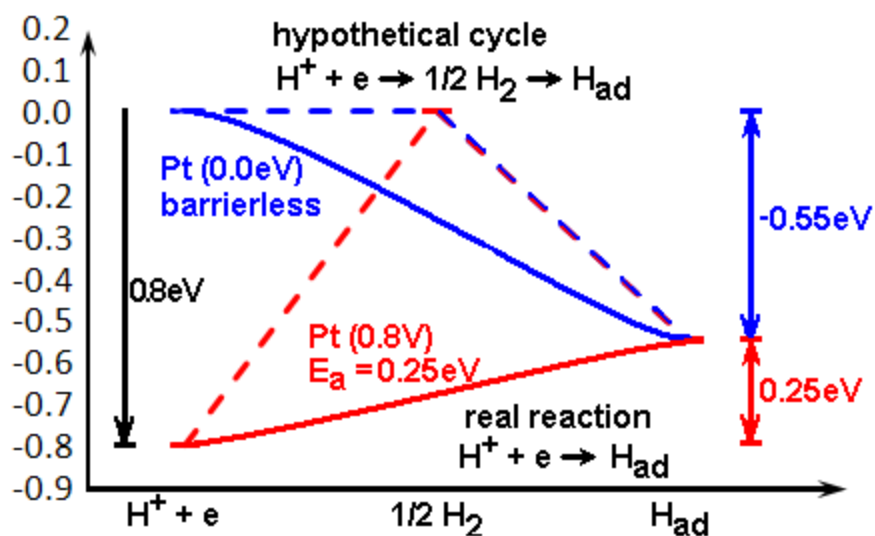


Figure 1. Calculation of reaction enthalpy for reaction (1) using cycle (2). Reaction (1) is exthothermic by 0.55eV at 0.0V vs NHE and 0.25 endothermic at 0.8V vs NHE.

(1) Anderson, A. B.; Sidik, R. A.; Narayanasamy, J.; Shiller, P. Theoretical calculation of activation energies for $\text{Pt} + \text{H}^+_{(\text{aq})} + \text{e}^{(-)}(\text{U}) \rightleftharpoons \text{Pt-H}$: Activation energy-based symmetry factors in the marcus normal and inverted regions. *J. Phys. Chem. B* 2003, *107*, 4618-4623.

(2) Norskov, J. K.; Rossmeisl, J.; Logadottir, A.; Lindqvist, L.; Kitchin, J. R.; Bligaard, T.; Jonsson, H. Origin of the overpotential for oxygen reduction at a fuel-cell cathode. *J. Phys. Chem. B* 2004, *108*, 17886-17892.