Kinetic barriers and reaction energetics of oxygen evolution reaction on nitrogen-doped carbon nanotubes

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Abstract:

We have investigated kinetic barriers and reaction energetics for the oxygen evolution reaction (OER) on singly and doubly nitrogen-doped single-walled carbon nanotubes (NCNTs). Our calculations combine DFT with the climbing image nudged elastic band (CI-NEB) method. Solvent effects have been included by a 45 water molecule droplet model. The sites for the CI-NEB calculations were chosen based on a simple thermodynamic model, which ignored both solvent effects and kinetic barriers [1]. One of these sites was located on a singly nitrogen-doped CNT, and the other was on a doubly-doped CNT. According to the thermodynamic model, the two sites were approximately equally suitable for OER. However, our reaction barrier calculations revealed a clear difference in the rate-determining *OOH formation step between the two systems, with barrier heights differing by more than 0.4 eV. Thus, the thermodynamic model may be insufficient for identifying optimal OER sites. Of the remaining three reaction steps of the four-step OER process, the two H_2O forming ones were barrierless in all cases. We also performed solvent-free barrier calculations on NCNTs and undoped CNTs. Substantial differences were found in the energies of the intermediates when the solvent was present. The low activation energy barriers observed for these reactions corroborate both theoretical and experimental research findings of the utility of NCNTs for OER catalysis.

References:

[1] Rossmeisl, J.; Logadottir, A.; Nørskov, J. K. Chem. Phys. 2005, 319, 178 - 184.