

Why nitrogen favors oxygen reduction on graphitic materials

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Methods

Using numerical basis sets¹ under the PBE functional,² periodic DFT calculations under neutral charge conditions were performed running Dmol^{3,3}. All the electrons were explicitly considered in the calculations under a spin unrestricted approach. Explicit water molecules in addition to the COSMO⁴ continuum solvation model were included in the calculations as solvation effect treatment. The results were corrected for dispersion forces using the Tkatchenko and Scheffler method.⁵ The effects of non-zero dipole moments in the supercells were cancelled by means of external fields.⁶ Free energy profiles were obtained by correcting DFT total energies for zero point vibrational energies and entropies. Potential effects were incorporated into the free-energy profiles by means of the computational hydrogen electrode formalism.⁷

For energy profile calculations, a single water molecule was explicitly included in each adsorbent/adsorbate model, in addition to the COSMO continuum solvation model, as solvation effect treatment. Moreover, 0.21 eV per significant non-explicitly modeled hydrogen bond was applied as correction. Only when the solvation effect was sufficiently captured the total free-energy estimated for the whole of the ORR reaction -4.93 eV was in

excellent agreement with the theoretical value -4.92 eV, corresponding to the standard electrode potential of 1.23 V. The correct alignment of the free-energy profiles is essential to directly compare experimental and computational results.

Free energy profiles were obtained correcting DFT energies for zero point vibrational energies and entropies, using the expression:

$$\Delta G = \Delta E_{DFT} + \Delta E_{ZPVE} - T\Delta S$$

where ΔE_{DFT} , ΔE_{ZPVE} and ΔS are differences in DFT total energies, zero point vibrational energies and entropies, respectively.

Potential effects were incorporated into the free-energy profiles by means of the computational hydrogen electrode formalism, using the relation:

$$\Delta G(E) = \Delta G^o - nFE$$

where ΔG^o is the total free energy for the redox reaction, n is the number of electrons exchanged, F is the Faraday constant and E the electrode potential.

Optimal adsorbent/adsorbate configurations were searched for using numerical basis sets of double-numerical quality. For this phase of the calculations, the optimization convergence thresholds were set to 2.0×10^{-5} Ha for the energy, 0.004 Ha/Å for the force, and 0.005 Å for the displacement. The SCF convergence criterion was set to 1.0×10^{-5} Ha for the energy. Assuming the previously optimized configurations, energies were estimated using numerical basis sets of double-numerical quality plus polarization. In this case, the SCF convergence criterion was set to 1.0×10^{-6} Ha for the energy.

Orbital cutoffs radius of 3.1, 3.7, 3.4 and 3.3 Å were always used in the numerical basis set for H, C, O and N atoms, respectively. Brillouin zones were always sampled, under the Monkhorst-Pack method, using grids corresponding to distances in the reciprocal space of the order of 0.04 1/Å. Convergence was always facilitated introducing 0.002 Ha of thermal smearing, though total energies were extrapolated to 0°K . The value 78.54 was taken, as

dielectric constant for water, in the continuous solvation model.

In addition to the free-energy profiles, a stability descriptor of the OOH_{ads} state, for each adsorbent configuration for which this parameter could be relevant, was estimated regarding the discussion of the undesirable production of hydrogen peroxide. This descriptor was calculated as the energy difference between the adsorbent/adsorbate complex completely relaxed and that corresponding to the same complex with the active carbon-proximal oxygen distance constrained to a significant larger distance. To better capture the hydrogen peroxide ion solvation effect, a more complete first shell of solvation, formed by four explicit water molecules, was included in the model.

Table S1. Free-energy profiles in eV for the complete ORR on different NG configurations.

Reaction	Configuration											
	G0-2	G1-2	Z0-1	Z0-2	Z1-2	Z2-1	A0-1	A0-2	A1-a	A1-2	A2-1	
OO (1)	-4.93	-4.93	-4.93	-4.93	-4.93	-4.93	-4.93	-4.93	-4.93	-4.93	-4.93	-4.93
OO_{ads} (2)			-5.16			-4.81			-4.99	-5.53	-5.24	
OOH_{ads} (3) (stability)		-4.48	-3.96		-5.72	-4.23 (0.44)	-5.48		-3.68	-4.62	-4.08	
O_{ads} (4)	-3.84	-2.41	-2.17			-1.21			-1.77	-2.30	-1.82	
OH_{ads} (5)	-2.67	-1.20	-0.65	-2.65	-2.47	-0.85	-2.06	-2.43	-0.43	-1.12	-0.78	

Table S2. Free-energy profiles in eV for the ORR to hydrogen peroxide n different NG configurations

Reaction	Configuration												
	G0-2*	G1-2*	Z0-1*	Z0-2*	Z1-2*	Z2-1*	A0-1*	A0-2*	A1-a*	A1-2*	A2-1*	Z0-1	
OO (1)	-1.39	-1.39	-1.39	-1.39	-1.39	-1.39	-1.39	-1.39	-1.39	-1.39	-1.39	-1.39	-1.39
OO_{ads} (2)		-1.56	-1.41			-1.31			-1.15	-1.44	-1.42	-1.51	
OOH_{ads} (3)	-1.22	-1.01	-0.78		-1.32	-0.86	-1.15		-0.75	-1.04	-0.87	-0.78	

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