A Systematic Study of Metal-Supported Boron Nitride Materials for the Oxygen Reduction Reaction

Supporting Information

Ralph Koitz, Jens K. Nørskov, and Felix Studt

Error Estimation for Electrochemical Reactions

BEEF-vdW ensemble energies are determined for all species participating in a particular reaction. Each ensemble contains 2000 non-selfconsistent energies, E_i. An energy difference for the reaction, ΔE_i, is calculated for each member i of the ensemble. For the simple case of *h*-BN adsorption on Ni(111), ΔE_i is given as:

$$\Delta E_i = E_i(h\text{-BN/Ni}) - E_i(h\text{-BN}) - E_i(\text{Ni}),$$

yielding a set of 2000 energy differences, $\{\Delta E_i\}$. The error bars on the calculated DFT energy are then computed as the standard deviation over all elements in this set.

The same procedure is applied to computing the ensemble of ORR overpotentials. For each ensemble member, potential differences are calculated for individual ORR steps.

$U1_i = 1.23\ \text{V} - [\Delta G_i(\text{O}_2\text{*}) - \Delta G_i(\text{OOH*})]$,
$U2_i = 1.23\ \text{V} - [\Delta G_i(\text{OOH*}) - \Delta G_i(\text{O*})]$,
$U3_i = 1.23\ \text{V} - [\Delta G_i(\text{O*}) - \Delta G_i(\text{OH*})]$,
$U4_i = 1.23\ \text{V} - [\Delta G_i(\text{OH*}) - \Delta G_i(\text{*})]$,

where $\Delta G_i = \Delta G + \Delta E_i$. ΔG is the free energy of a species and ΔE_i is the associated non-selfconsistent energy difference from the BEEF-vdW ensemble as defined above. The overpotential for a particular member of the ensemble is then given as

$$U_i = max(U1_i, U2_i, U3_i, U4_i),$$

and the set $\{U_i\}$ can then be analyzed and visualized using a histogram. Note that due to the *max*() function, the resulting $\{U_i\}$ does not follow a normal distribution any more as $\{U1_i\}$, $\{U2_i\}$… do.

We employ a BEEF-vdW ensemble optimized for chemisorption energies, as described in ref. 48 of the main text.

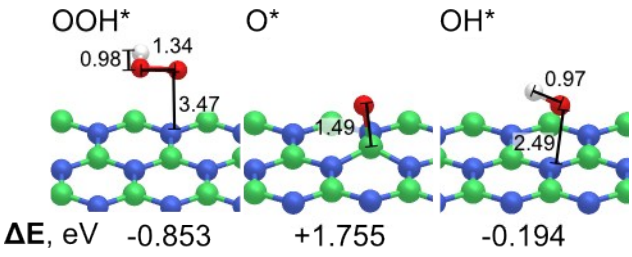

Figure S1: Adsorbed ORR intermediates on free-standing *h*-BN with interatomic distances (Angstrom) and adsorption energies.

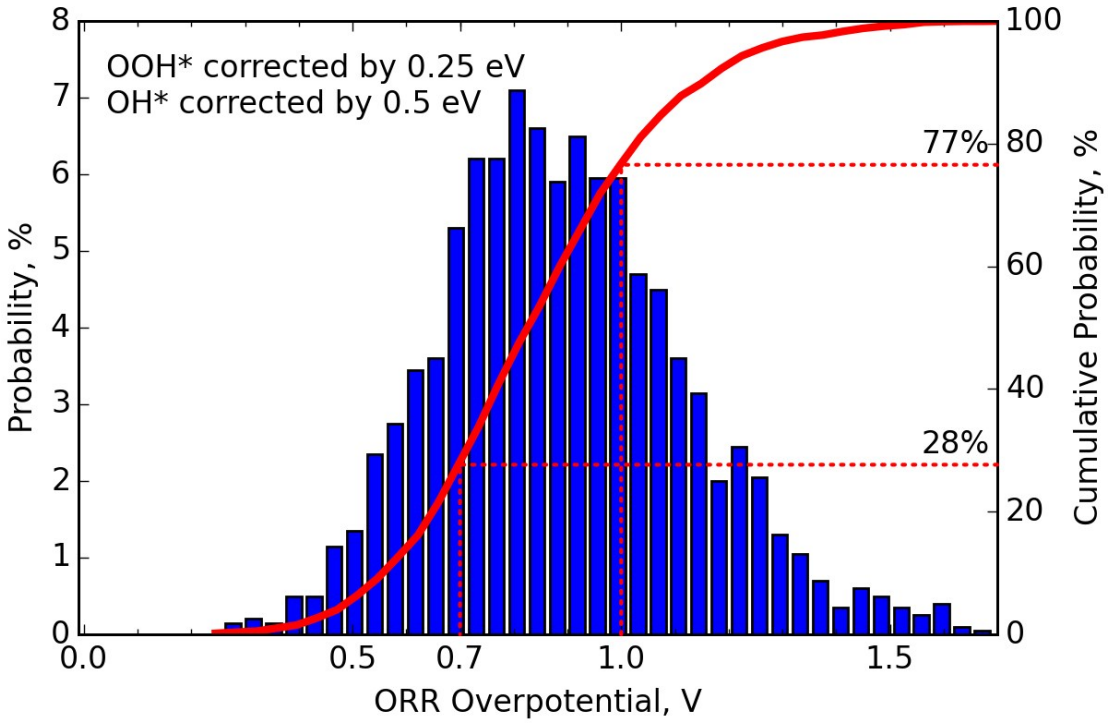

Figure S2: Overpotential for the ORR on h-BN/Cu(111) when taking into account a 0.25 eV correction for ΔG(OOH*) and 0.50 eV for ΔG(OH*) due to solvation effects at the metal surface. Red curve indicates cumulative probability (secondary y axis), i.e. 77% of calculated overpotentials are smaller than 1.0 V.

Table S1: Interaction energies ΔE_{int} for h-BN on Ni, Cu, and Co. This quantity is calculated as the energy difference of the frozen optimized BN and metal subsystems, relative to the optimized energy of the full heterostructure.

		Ni(111)	Cu(111)	Co(0001)
ΔE_{int}	$N_{top}B_{fcc}$	-0.062	-0.075	-0.242
	$N_{top}B_{hcp}$	-0.042	-0.075	-0.228
	$N_{fcc}B_{hcp}$	-0.078	-0.072	-0.082
	$B_{top}N_{fcc}$	-0.078	-0.071	-0.082
	$B_{top}N_{hcp}$	-0.077	-0.072	-0.082
	$B_{fcc}N_{hcp}$	-0.079	-0.072	-0.082

Table S2: Entropy contributions to the free energy of ORR steps on metal-supported *h*-BN, relative to *h*-BN/Metal + O_2 + $2H_2$, in analogy to free energy profiles in the main text.

	h-BN/Ni(111)	*h*-BN/Co(0001)	*h*-BN/Cu(111)
Δ*S*(OOH*), eV	-0.694	-0.704	-0.737
Δ*S*(O*), eV	-0.450	-0.401	-0.404
Δ*S*(OH*), eV	-0.587	-0.587	-0.593
Δ*S*(2 H_2O), eV	-0.272	-0.272	-0.272