Supporting Information for: Subsurface Nitrogen Dissociation Kinetics in Lithium Metal from Metadynamics

Thomas Ludwig,^{†,‡} Aayush R. Singh,^{†,‡} and Jens K. Nørskov^{*,¶}

†SUNCAT Center for Interface Science and Catalysis, SLAC National Accelerator Laboratory, 2575 Sand Hill Road, Menlo Park, California 94025, United States
‡SUNCAT Center for Interface Science and Catalysis, Department of Chemical Engineering, Stanford University, Stanford, California 94305, United States
¶Department of Physics, Technical University of Denmark, DK-2800 Kongens Lyngby,

Denmark

E-mail: jkno@fysik.dtu.dk

Density functional theory details

For the VASP Density Functional Theory (DFT) calculations, we used the setting 'PREC = Low' for the molecular dynamics and metadynamics simulations, and 'PREC = Normal' for the geometry optimization and vibrational mode calculations. The energy cutoff for the plane wave basis set used was 500 eV. The value of 'ENAUG', the plane wave cutoff for the augmentation charges, was set to 650 eV. Smearing of 'SIGMA = 0.1' was used. The calculations are not spin-polarized. A dipole correction was used to correct for the surface dipole and any resulting artificial electrostatic field; the VASP parameters 'IDIPOL=3' and 'LDIPOL=.TRUE.' were used.

Molecular nitrogen adsorption configurations

Three of the four tested molecular nitrogen configurations are displayed in Figure 1 of the main text. The other one is provided here in Figure S1:

Metadynamics parameters & sensitivity of results to pa-

rameters

An additional spreadsheet containing the complete information for the metadynamics parameters and the resulting rate constants of all sets of metadynamics simulations is included in the supporting information. A brief summary of the results is provided here in Table S1.

Table S1: Dependence of rate constant and barrier results on metadynamics parameters and use of initial bias; "width" refers to the Gaussian bias kernel standard deviation or "hill width", and the "stride" refers to the time between Gaussian bias kernel or "hill" depositions. The hill height was 0.00258 eV in all cases.

Т / К	width / Å	stride / fs	initial bias	τ / s, 90% CI	barrier / eV, 90% CI
300	0.05	20	no	[2.5, 22.6]	[0.79, 0.84]
300	0.10	40	no	[3.6, 22.6]	[0.79, 0.84]
300	0.05	120	yes	[6.4, 32.4]	[0.81, 0.85]
300	0.10	180	yes	[9.6, 32.9]	[0.82, 0.85]

The data in Table S1 indicates that the rate constant and barrier results are not very sensitive to the choice of metadynamics parameters. There is substantial overlap in the confidence intervals for rate constant and barrier among all choices of metadynamics parameters, and regardless of whether an initial bias was used or not. This provides confidence that the results would not substantially change if different values of these metadynamics parameters were chosen, or if different initial bias potentials were used. The caveat is that the initial bias, if used, must be chosen to be sufficiently low/weak enough such that the initial state is in a well defined thermodynamic equilibrium for a substantial amount of time before reacting.



Figure S1: The other molecular nitrogen adsorption configuration tested, in addition to the configurations reported in the main text. The un-corrected electronic binding energy of this configuration is $\Delta E = -1.07$; it is thus not the most stable adsorption configuration of the ones tested.

Static initial bias for refined metadynamics simulations

In order that a lower frequency can be used for more refined results, a static initial bias was used in the refined metadynamics simulations. This approach is similar to the frequencyadaptive strategy,¹ in which the metadynamics frequency is decreased after an initial rapid deposition. A natural choice for the initial bias is the accumulated bias from one of the initial simulations, at some time before the first reaction event. The accumulated bias is chosen such that the bias is still at least some multiples of $k_B T$ less than the effective free energy barrier, which is approximately 0.8 eV as shown in the main text. This ensures that the initial state exists in a thermally equilibrated state before escaping, satisfying the requirements for transition state theory, and thus Hyperdynamics,² to apply. A different initial bias potential is chosen for each temperature, taken from the corresponding initial metadynamics runs at those temperatures; this ensures that the initial bias chosen is well suited for the free energy barriers at each temperature. Thus three static initial bias potentials are used in this work; one at 300 K, 400 K, and 500 K. Those initial bias potentials are shown in Figure S2.



Figure S2: Initial bias potentials used for the refined metadynamics runs for each temperature: (a) 300 K, (b) 400 K, and (c) 500 K. The dotted vertical lines show the position of the N-N distance cutoff for the reaction event.

We provide those full initial bias potentials in the form of the sets of Gaussian kernels that they are composed of. These were provided as PENALTYPOT files to VASP; we attach the exact PENALTYPOT files for each temperature, as well as spreadsheets with the same information, as additional Supporting Information files.

To demonstrate that this procedure has the potential to improve the fits to the exponential distribution, we show the results for 300 K in Table S2.

Table S2: Comparison of initial and refined metadynamics simulation goodness-of-fit to exponential distribution

Т / К	metaD hill width / Å	metaD stride / fs	initial bias	KS test D (lower is better)
300	0.05	20	no	0.27
300	0.1	40	no	0.33
300	0.05	120	yes	0.19
300	0.1	180	yes	0.19

The Kolmogorov-Smirnov test D values are much lower in the refined simulations (those that use an initial bias and can thus use a much longer stride, or lower deposition rate). This indicates a better fit to exponential distribution. The data for the other temperatures is provided in an attached spreadsheet. With some exceptions, the general observation is that decreasing the metadynamics deposition rate led to a better fit to the exponential distribution as quantified by the KS test.

Dependence of barrier and reaction energy on simulation cell size

We calculated the reaction energy and the dissociation barrier in a cell of size 3 atoms by 3 atoms of the same surface facet. Effort was made to ensure that the final and initial states were as similar as possible to those from the smaller supercell. The same k-point density was used (we used a 2×2 Monkhorst-Pack grid for the 3×3 atom supercell, commensurate with the 3×3 Monkhorst-Pack grid for the 2×2 atom supercell used in production simulations) and all other computational parameters were kept the same. The results are displayed in Figure S3 and the barriers and reaction energies are tabulated in Table S3.



Figure S3: Free energy diagrams, in the harmonic approximation, at 400K, (a) for the 2×2 surface atom supercell and the 3×3 surface atom supercell, and showing the effect of the changes in the lithium vibrational modes on the free energies for the 3×3 (b) and 2×2 (c) supercells.

supercell	Т / К	rxn energy / eV	barrier / eV
2×2 2×2 2×2	$300 \\ 400 \\ 500$	-0.83 -0.80 -0.78	0.79 0.81 0.82
3×3 3×3 3×3	$300 \\ 400 \\ 500$	-1.18 -1.17 -1.16	$0.67 \\ 0.68 \\ 0.69$

Table S3: $N_2^* \rightarrow 2N^*$ reaction energy and barrier for 2×2 and 3×3 supercells

We found that the barrier was lower in the larger supercell, and the reaction energy was more negative. This lower barrier is also to be expected from BEP scaling; if the reaction energy becomes more negative, then the barrier is expected to be lower. Therefore the barrier we calculated in the 2×2 supercell is likely to be a slight over-estimate of the real barrier. The configurations in the initial, final, and transition states in both supercells are very similar.

Distribution of bias potentials from individual metadynamics simulations

The rate constants, and associated barriers, from the metaynamics simulations, are in this work calculated using a statistical fit of first reaction event times to an exponential distribution. In this process, the "free energy surfaces" from each individual metadynamics simulation are only indirectly used; the acceleration factor used in the calculation of the individual reaction event times depends expoentially on the free energy surface for each individual simulation. But the values of τ and k do not depend solely on the metadynamics bias itself; they also depend directly on the waiting times, since the reaction event time is the acceleration factor multiplied by the number of simulation time steps before the event occurs.

Each individual metadynamics simulation has an associated bias that accumulates until

the first reaction event. Example of these (inverted) are shown in Figure S4.



Figure S4: Metadynamics bias potentials (inverted) at the time of the first reaction events for individual metadynamics simulations at (a) 300 K, (b) 400 K, and (c) 500 K. Each shows a single example; each individual metadynamics simulation at a given temperature has a different metadynamics bias potential surface at the time of the first reaction event.

We wish to emphasize that we do not use the reconstructed metadynamics bias potentials from individual metadynamics simulations to calculate the free energy barriers by simply calculating the initial state free energy well depth at the time of the first reaction event. In fact, we show here that this procedure is not equivalent to using the acceleration factor method we describe in the main text. In particular, if the free energy barrier is calculated as the depth of the free energy well at the time of the first reaction event, then the free energy barrier is on average under-estimated. We show this in Figure S5, in which we directly compare the barriers associated with the statistical fit to reaction times to the barriers calculated from a simple reconstruction of the free energy surfaces at the first reaction time.



Figure S5: Comparison of the barriers directly reconstructed from individual metadynamics simulations (blue) and those associated with the statistical fit of reaction event times to exponential fits (dotted orange line): (a) 300 K, (b) 400 K, and (c) 500 K. The solid blue line is the mean value from the directly reconstructed barriers. The blue dotted line shows the probability density estimated by kernel density estimation.

A clear way to rationalize this is to consider the limit as the metadynamics bias deposition rate approaches zero, i.e. an unbiased simulation. In that case, the reaction event times in the simulations follow their physical exponential distribution. Although they are slow, they will in principle eventually occur. However, since in that case there is no metadynamics bias deposition, the free energy surface reconstructed from the "metadynamics bias" would be flat, and the free energy barrier calculated using this surface would be zero. This consideration underscores the importance of accounting for the waiting time in the barrier calculation. This same consideration is also true, to a lesser magnitude, at finite metadynamics deposition rates, as in our work.

Number of metal layers

3 metal layers were used for the lithium surface model in this work. The molecular nitrogen adsorption energy was calculated for a 4 surface layer model to investigate the convergence of the relevant binding energies. That data is displayed in Table S4. The difference in the adsorption energy between the 3 and 4 metal layer model is small (less than 0.1 eV);

supercell	metal layers	ΔE (N2)
3×3	3	-1.09
3×3	4	-1.17

Table S4: Benchmark of the $\rm N_2$ adsorption energy (uncorrected DFT electronic energy) vs number of metal layers.

therefore we expect that the results from the 3 metal layer model were reasonably converged with respect to the number of metal layers used.

Data from main text figures

The data for the main text figures is provided in attached supporting information spreadsheets, or in tables in the main text and supporting information.

Vibrational modes

The vibrational modes used for the harmonic approximation thermodynamics calculations are provided in an attached spreadsheet.

References

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