Electrochemical Ammonia Synthesis - The Selectivity Challenge

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1 Main Text

The N_2 molecule is particularly inert; the N-N triple bond is one of the most stable in all of chemistry, and, in addition, the molecule has no dipole moment and a very low polarizability. Therefore, one of the major challenges in chemistry today is to find new ways to activate N_2. Industrially, N_2 reduction to NH_3 is performed via the Haber Bosch process at high temperature and pressure.[1–5] The process uses hydrogen from natural gas or other fossil resources and the production of ammonia, mainly for fertilizers, accounts for more than 1% of the total fossil energy consumption on Earth.[6] The development of an efficient electrochemical process to reduce N_2 to NH_3 under ambient conditions and using energy from solar or wind sources would enable a sustainable process for making fertilizers and energy carriers. An additional advantage of such a process would be that it could be implemented at the point of fertilizer use, avoiding the distribution infrastructure that is currently absent in less developed parts of the world.[7] NH_3 produced from electrochemical N_2 reduction may also be used as a carbon-free fuel.[8,9]

There are two major problems associated with electrochemical N_2 reduction. From a thermodynamic perspective, electrochemical reduction is possible, but all attempts so far have found a large overpotential (low rates) and very low selectivity towards NH_3;[10–13] most protons and electrons go towards evolving H_2. We suggest that, while it would be a clear advantage to find catalysts with a smaller overpotential, the main problem is the low selectivity. An estimate of the power needed to make enough ammonia for a typical field (100 kg of NH3/hectare/yr)[14] suggests that at an overpotential of 1V and a selectivity towards NH_3 of 100% it would take of the order 145 W/hectare, assuming that the process runs all of the time under 100% faradaic efficiency. Accounting for the intermittent nature of solar power,[15] this corresponds to a typical solar cell area of 5 m^2 (0.05% of the hectare) or to a small, residential scale wind turbine.[16] Doubling the overpotential means increasing the solar cell area by 45%, but a selectivity of 10^{-2} (at the very high end of what is possible today)

means increasing the area to 500 m^2 (5% of the hectare), which is prohibitively expensive [Supporting Information].

Molecular catalysts and enzymes often have better selectivity towards ammonia production,[17–19] although they are fragile and provide few turn-overs. The question is: what are the fundamental issues that prevent us from using a solid electrocatalyst? In principle, solid catalysts offer the advantage of larger current density by not having to shuttle electrons to the catalyst, better stability, and a considerably easier separation of products from the catalyst. These properties are particularly important to decentralized ammonia synthesis, which must be simple and stable.

In the present viewpoint, we discuss a qualitative analysis that may shed some light on the problem of H$_2$/NH$_3$ selectivity and point to strategies to circumvent the problem.

Consider the following simple model of the electrochemical N$_2$ reduction process:

$$\mathrm{H^+ + e^- + *} \; \overset{K_H}{\longleftrightarrow} \; \mathrm{*H} \tag{R1}$$

$$\mathrm{N_2 + *} \; \overset{K_N}{\longleftrightarrow} \; \mathrm{*N_2} \tag{R2}$$

$$\mathrm{H^+ + e^- + *N_2} \; \overset{k_N}{\longrightarrow} \; \mathrm{*N_2H} \tag{R3}$$

$$\mathrm{H^+ + e^- + *H} \; \overset{k_H}{\longrightarrow} \; \mathrm{H_2 + *} \tag{R4}$$
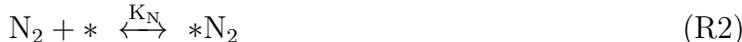
Here a * signifies an active site on the catalyst, capital K's denote equilibrium constants, and small k's are rate constants. For electrochemical steps, these constants depend expo-

nentially on the applied potential. We assume that the first hydrogenation step of N_2 is rate-determining, i.e. the rate of (R3) determines the rate of ammonia production. There is some evidence that this is the case.[20–23] (R1) is generally known to be faster than (R4).[21] Therefore, the first two adsorption reactions are in equilibrium at the potentials of interest. We neglect the backward reactions of (R3) and (R4), so that the considerations in the following are only valid far from equilibrium (low conversion). Experiments to date seem to be well into that regime. We have neglected Tafel and surface hydrogenation pathways in this analysis, since electrochemical steps will dominate at the very negative potentials needed for N_2 reduction.[23] We also neglect adsorbate-adsorbate interactions, which tend to be insignificant for adsorbed hydrogen, the dominant surface species in the relevant potential regime, as we will show below. An implication of (R3) being both rate-determining and irreversible is that N_2 is the primary nitrogen based reducible species competing with H for surface sites in our model. This assumption is reasonable for our qualitative analysis of selectivity because an appreciable build-up of later intermediates (NH_x) at steady state would require a high selectivity of N_2 adsorption with respect to H adsorption.

Under these assumptions, the coverages of H and N_2 are given by simple Langmuir isotherms:

$$\theta_H = \frac{K_H \tilde{c}_+ \tilde{c}_-}{1 + K_H \tilde{c}_+ \tilde{c}_- + K_N \tilde{c}_{N2}} \tag{1}$$

$$\theta_{N2} = \frac{K_N \tilde{c}_{N2}}{1 + K_H \tilde{c}_+ \tilde{c}_- + K_N \tilde{c}_{N2}} \tag{2}$$

where $\tilde{c}_+$ and $\tilde{c}_{N2}$ are the concentrations of protons and N_2 near the catalyst surface. Assuming equilibrium between bulk and near-surface concentrations, $\tilde{c}_+$ and $\tilde{c}_{N2}$ are given by $\tilde{K}_H c_+$ and $\tilde{K}_N c_{N2}$, respectively, where c_+ and c_{N2} are bulk concentrations and the $\tilde{K}$'s are the bulk-to-near-surface equilibrium constants. The inclusion of both bulk and near-surface concentrations as parameters in the model allows us to distinguish changes in bulk species

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concentrations (e.g. a switch from protic to aprotic solvents) from situations that alter species transfer from the bulk to the surface (e.g. the addition of a proton diffusion barrier). We include a "concentration of electrons, $\tilde{c}_-$", which is not meant to indicate a physical concentration but to account for cases where the electron transfer rate, k_t, is limiting. For instance, in (R1), K_H is the ratio of the forward and backwards rate constants of (R1), $K_H = \frac{k_H}{k_{H-}}$, and $\tilde{c}_-$ represents the reduced forward rate when electrons are transferred to the active site with a certain rate less than the proton transfer rate, $k_t < k_H$. When $k_t <<$ k_H, we have $\tilde{c}_- = \frac{k_t}{k_H}$ since the total rate is then given by the electron transfer rate. The calculation of k_t for an electrochemical system requires knowledge of the appropriate redox potential and properties of the system.[24] For a metal surface, $\tilde{c}_- = 1$, since electrons are always available at the Fermi level.

At negative enough potentials, (R1) will always win over (R2), since (R1) is driven by a potential, whereas (R2) is not. The potential, U_S (vs. RHE), at which H adsorption becomes favorable depends on the N_2 and H adsorption free energies, ΔG_H^0 and ΔG_{N2}^0, at zero potential:

$$U_S = -\frac{1}{e}\left(\Delta G_H^0 - \Delta G_{N2}^0\right) \tag{3}$$

ΔG_H^0 scales with ΔG_{N2}^0 with a slope less than 1 for different transition metal surfaces,[21] meaning that U_S becomes more negative for increasingly reactive catalysts. Thus, we expect that N_2 competes most favorably with H for active sites on the most reactive catalysts; however, the limiting potential, U_L, at which all steps in N_2 reduction are exergonic, is consistently more negative than U_S.[23] Therefore, the surface will be covered by hydrogen at relevant potentials.

At potentials more negative than U_S, $K_N << K_H$, and we have

$$\theta_{\mathrm{H}} \simeq 1 \tag{1a}$$

$$\theta_{\mathrm{N2}} \simeq \frac{\mathrm{K_N}\tilde{c}_{\mathrm{N2}}}{\mathrm{K_H}\tilde{c}_{+}\tilde{c}_{-}} \tag{2a}$$

and the rate of ammonia and hydrogen production can be written

$$\mathrm{r_N} = \mathrm{k_N}\theta_{\mathrm{N2}}\tilde{c}_{+}\tilde{c}_{-} \simeq \mathrm{k_N}\frac{\mathrm{K_N}}{\mathrm{K_H}}\tilde{c}_{\mathrm{N2}} \tag{4}$$

$$\mathrm{r_H} = \mathrm{k_H}\theta_{\mathrm{H}}\tilde{c}_{+}\tilde{c}_{-} \simeq \mathrm{k_H}\tilde{c}_{+}\tilde{c}_{-} \tag{5}$$

At relevant potentials (more negative than the limiting potential for N_2 reduction), $K_N <<$ K_H due to the exponential dependence of K_H on potential. Under these conditions, the driving force for H_2 production is large[23] and thus k_H is likely to be larger than k_N. We expect that the ratio $\frac{k_N}{k_H}$ remains relatively constant across electrolyte systems with varying proton transfer kinetics as both steps are essentially proton addition to adsorbed species and are therefore likely to have energetics that scale with each other. Even under the conservative assumption that k_N and k_H are comparable, $\frac{r_N}{r_H}$ scales as $\frac{K_N}{K_H}$ and hydrogen evolution should always dominate at normal proton concentrations outside a metal surface. We suggest this to be one of the fundamental reasons for the very low selectivity usually encountered in ambient condition electrochemical N_2 reduction over metal surfaces.

We note that for the most reactive surfaces, N_2 may not adsorb associatively. In that case, the selectivity challenge can be framed in terms of the competition between the binding energies of N and H. It may also be necessary to compare the chemical transition state barrier for N_2 dissociation with the electrochemical transition state barrier for H^+/e^- transfer to the surface to determine the likely surface coverage.[25]

Eq. (4) and (5) show r_N to be zeroth order in the electron and proton concentrations, while r_H is first order in both. Therefore, a strategy for increasing the NH_3 selectivity could be to (substantially) lower the accessibility of electrons, protons or both. This strategy would slow down the hydrogen evolution while keeping the ammonia synthesis rate roughly the same.

The physical picture we suggest is the following: when an active site opens up after desorption of H_2 or NH_3, it can be replaced by either N_2 or H (from the recombination of H^+ and e^-). If there are protons and electrons around at a potential below U_S, hydrogen will dominate both thermodynamically and kinetically at the active site, and hydrogen evolution results. If, on the other hand, there are no protons or electrons around, then N_2 will adsorb, and when the protons and electrons are provided, they may preferentially attack the bound N_2.

This picture is in agreement with the successful strategy taken in the reduction of N_2 by Mo complexes in solution, where the proton source and the reductant are added slowly to an aprotic solvent in order to obtain a high selectivity.[26] It may also provide part of the explanation for why the nitrogenase enzyme has a high selectivity (on the order of 75% faradaic efficiency). Here electron transfer is coupled to the hydrolysis of ATP and one of the steps associated with this process is rate limiting.[27,28] The analysis above suggests a number of possible approaches to improve NH_3 selectivity in solid electrocatalytic systems.

At a metal surface in ohmic contact with an external circuit, it is impossible to control the access to electrons (the chemical potential of the electrons can be controlled, but not availability). For an electrochemical process over a metal surface catalyst to be selective towards ammonia, one would therefore need to severely limit the access to protons. We

note that in aqueous base, there will still be a substantial source of protons from water. An aprotic (or extremely alkaline) solvent with very few proton donors (water or other) would be a possible way to hinder proton transfer thermodynamically. Another solution would be to surround the catalyst by an aprotic, hydrophobic protection layer that kinetically slows down proton transfer while allowing N_2 to pass through. These possibilities are illustrated in Figure 1a and 1b. There are attempts in the literature to suppress hydrogen evolution for a range of applications, both via reducing the number of proton donors [29,30] and through the use of a protection layer to hinder proton transport. [31–33] It may also be possible to reduce the effective proton concentration near the surface ($\tilde{c}_+$), without changing the number of proton donors, through a solvent with slow proton transfer kinetics from the bulk. It has been shown, for example, that more sterically bulky proton donor molecules exhibit considerably slower proton transfer in non-aqueous electrolytes. [34] The use of such a proton donor could allow N_2 to more easily compete with H for surface active sites.

A metal-insulator-catalyst electrode could provide a possibility to control the electron tunneling from the electrode through the insulator to the catalyst metal overlayer, [35] hence controlling the selectivity through Eq. (4) and (5), see Figure 1c. A photochemical process provides interesting possibilities for controlling the electron flow (Figure 1d). If the rate of electron generation and/or transfer becomes the slowest step, the possibility again opens up for a more selective process. There are several reports in the literature of photochemical N_2 reduction. [36–39] We suggest that the improved NH_3 selectivity seen in these studies could be related to the suppression of hydrogen evolution that results when electron transfer becomes rate-limiting.

From Eq. (4), we note that increasing the bulk concentration of N_2 in solution (c_{N2}) would also increase N_2 reduction selectivity to NH_3. Based on the fact that most organic solvents have an N_2 solubility only one or two orders of magnitude higher than that of wa-

ter,[40] however, we expect that it would be challenging to manipulate c_{N2} enough to obtain the several orders of magnitude improvement in selectivity we need for electrochemical N_2 reduction to become feasible.

In conclusion, our qualitative model of electrochemical N_2 reduction suggests that limiting either proton or electron availability at the surface is a promising way to improve selectivity to NH_3. This enhancement may allow electrochemical processes to compete more favorably with thermochemical processes for NH_3 production, especially in distributed settings. The above discussion may also have bearing on the electrochemical reduction of other very stable, weakly interacting molecules such as CO_2.

Acknowledgement

Supporting Information Available

The supporting information contains power calculation details for a typical hectare of farmland. This material is available free of charge via the Internet at `http://pubs.acs.org/`.
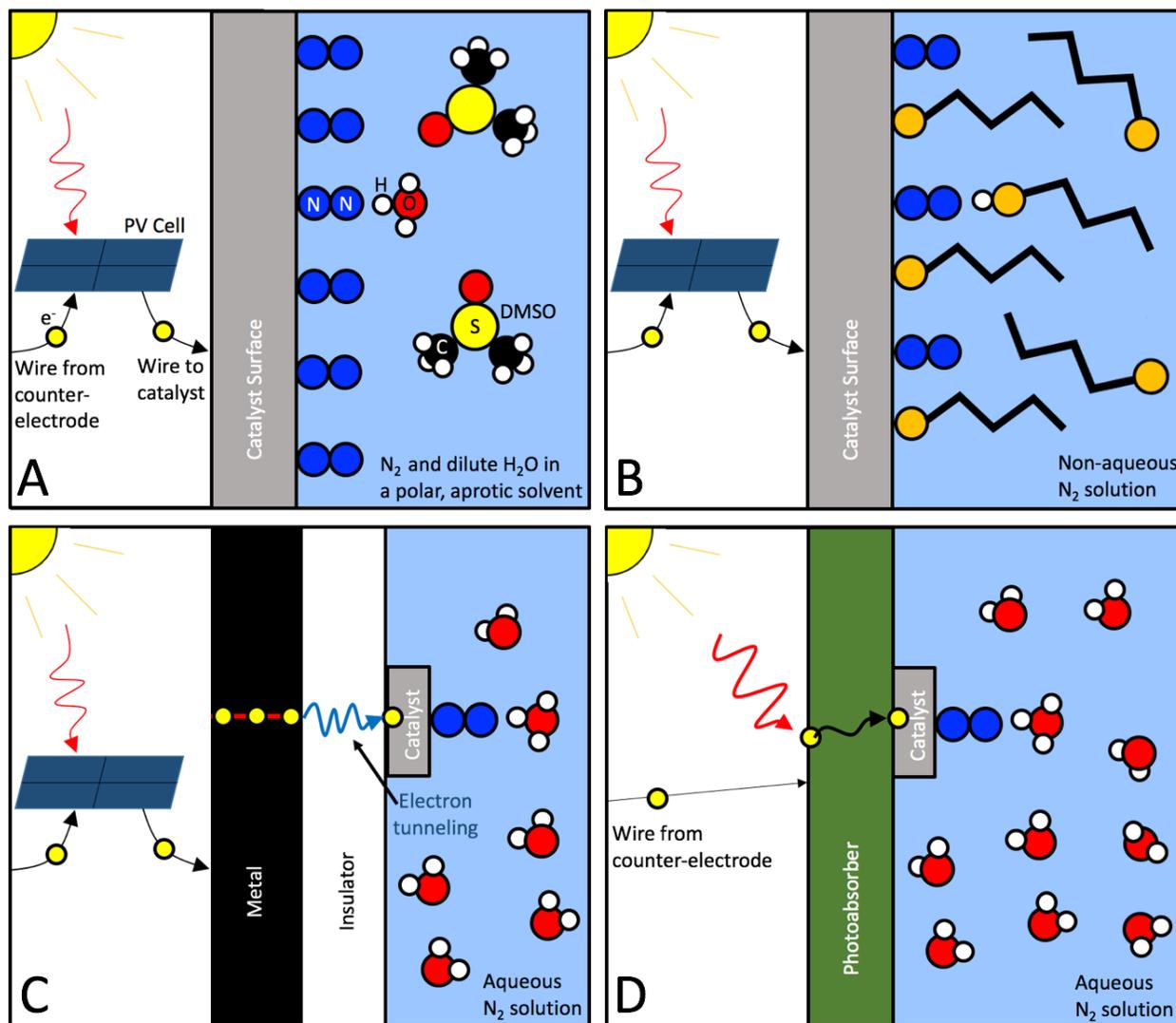
Figure 1: Strategies to improve selectivity in electrochemical ammonia synthesis: A) Limit the proton transfer rate by reducing the concentration of protons in the bulk solution. B) Limit the proton transfer rate by increasing the barrier for proton transfer to the surface. C) Limit the electron transfer rate by requiring electrons to tunnel through a thin insulator, taking care to prevent electron thermalization. D) Limit the electron transfer rate by using photoabsorbers to supply a slow stream of electrons.

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