LETTER

Electrochemical Ammonia Synthesis: The Energy Efficiency Challenge

Yuanyuan Zhou,[†] Xianbiao Fu,[†] Ib Chorkendorff,* and Jens K. Nørskov*

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ABSTRACT: We discuss the challenges associated with achieving high energy efficiency in electrochemical ammonia synthesis at near-ambient conditions. The current Li-mediated process has a theoretical maximum energy efficiency of ∼28%, since Li deposition gives rise to a very large effective overpotential. As a starting point toward finding electrocatalysts with lower effective overpotentials, we show that one reason why Li and alkaline earth metals work as N_2 reduction electrocatalysts at ambient conditions is that the thermal elemental processes, N_2 dissociation and NH_3 desorption, are both facile at room temperature for these metals. Many transition metals, which have less negative reduction potentials and thus lower effective overpotentials, can dissociate N_2 at these conditions but they all bind NH_3 too strongly. Strategies to circumvent this problem are discussed, as are the other requirements for a good N_2 reduction electrocatalyst.
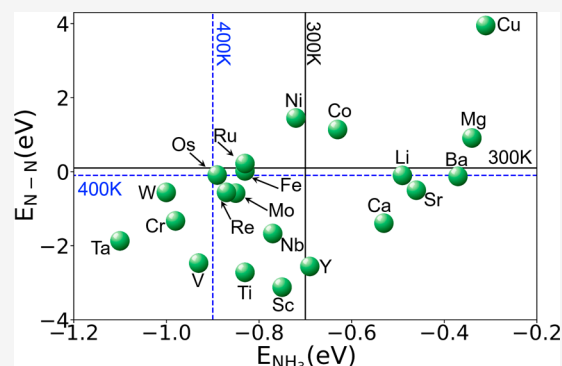
The electrochemical nitrogen reduction reaction (eNRR) is an attractive alternative to the Haber−Bosch process for making ammonia. An electrochemical process can readily use green electricity from solar or wind together with water and nitrogen from the air to form ammonia with no CO_2 emissions. Apart from the importance of ammonia as fertilizer, ammonia is an excellent energy carrier.[1,2] The only electrochemical system so far that produces large amounts of ammonia is the Li-mediated process first proposed by Fichter in the 1930s[3] and later investigated by Tsuneto et al. in the 1990s.[4] In this process, Li deposited at the cathode acts as the catalyst in an organic solvent with a Li salt and a few percent of ethanol added as proton carrier. Recently it was shown rigorously that the process is indeed nitrogen reduction, and after that, several strategies have been proposed to improve the ammonia faradaic efficiency (FE) and stability by potential-cycling, adding additional oxygen, and using ionic liquid as proton carrier.[5−7] Very recently, the field has developed substantially reporting a selectivity (or Faradaic efficiency, FE) toward N_2 reduction of more than 90% and current densities approaching 1 A/cm² all using sacrificial agents for proton donors.[5−9] This was improved recently by implementing a scalable continuous-flow cell and using hydrogen[10−12] as the proton source. Most recently it has been shown that calcium can replace lithium.[13] Additionally, novel metal-N_2 batteries have found promising applications in the eNRR field.[14]

One of the main challenges with the Li (Ca)-mediated process is that the maximum theoretical energy efficiency is ∼28%, since Li (Ca) needs to be electrodeposited as a metal at the cathode, and this requires a very negative potential below −3.0 V_{SHE} (−2.9 V_{SHE}). This severely limits the technical usefulness of the process. The US Department of Energy (DOE) REFUEL program[15] suggests a minimum target for a technical system of 60% energy efficiency. For comparison, the Haber-Bosch process can be operated at ∼75% efficiency.[16,17] If we could find catalysts that do not require very negative potentials to be stable, one could increase the energy efficiency of the electrochemical ammonia synthesis process significantly, see also ref.[18,19] We note that the advantage of near-ambient conditions and delocalized ammonia synthesis may to some degree compensate for a lower energy efficiency.[20]
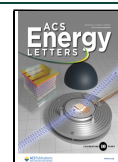
In this work, we point to an important reason why only cathode electrocatalysts like Li and Ca have so far been able to produce ammonia at ambient conditions by identifying two facile thermal elemental processes: N_2 dissociation and NH_3 desorption. On the basis of this insight, we discuss the possibility of using catalysts that do not require very negative

potentials to be stable and hence could increase the energy efficiency of the electrochemical ammonia synthesis process significantly.

The electrochemical ammonia synthesis over reactive surfaces consists of N_2 dissociation followed by consecutive addition of protons and electrons to adsorbed N to form ammonia, which subsequently desorbs. All electrochemical steps in the hydrogenation of adsorbed N can be made fast by lowering the cathode potential, and potentials much less negative than needed to deposit Li (Ca) are usually sufficient for that purpose.[19] If the two thermal processes, N_2 dissociation, and NH_3 desorption, are fast, then the rate and selectivity become controlled by the transport of protons to the reactive surface. The proton transport rate, in turn, is given by the rate of transport through the organic electrolyte and, most importantly, the transport rate through the solid electrolyte interface (SEI) layer that forms when very reactive Li (or Ca) reacts with the organic electrolyte.[21−24] This is completely analogous to the situation in Li-ion batteries. A model based on the transport properties of protons and Li and the transport and dissociation of N_2 has been successful in explaining, qualitatively, the dependence of the selectivity and rate on the concentration of proton carriers, nitrogen pressure, and oxygen content.[5] An important insight is that a good selectivity toward ammonia is only possible when the proton flux matches the N_2 dissociation rate.[10] That means, for instance, that using water as a solvent is difficult since water is a proton carrier and the proton flux will be way too large.[25]

In the transport-limited model, the success of the Li-mediated process at ambient conditions must be ascribed to the fact that the Li-SEI layer has just the right proton transport properties to give a high selectivity. While the SEI layer determines the proton flux together with the concentration of proton carriers, the cathode catalyst determines the N_2 dissociation rate and the NH_3 desorption rate. The N_2 dissociation rate is given by the transition state energy for N_2 dissociation, E_{N-N}, while the NH_3 desorption rate is given by its adsorption energy, E_{NH_3}. We base this discussion on a model where the reactions take place at the three-phase boundary between the cathode electrocatalyst, organic electrolyte (with limited ammonia solubility), and the gas phase N_2 and NH_3. In Figure 1 we plot the two energies as a function of each other for a range of metal catalysts. Note that they need not correlate. The chemical bond of the N−N transition state to the surface is similar to that of adsorbed N, which is why they correlate, but the bond of NH_3 to the surface has a quite different nature.[27] A good cathode catalyst has a low E_{N-N} (low barrier) and a high E_{NH_3} (weak bond). A free energy barrier of the order 0.7 eV gives a rate of the order 1/s at 300 K according to absolute rate theory. This means that E_{N-N} should be below ∼0.1 eV, since there is an entropic barrier toward N_2 adsorption of the order 0.6 eV at room temperature.[28] Similarly, E_{NH_3} should be above ∼ −0.7 eV. For the desorption rate, the entropy of the transition state is assumed to closer to that of the adsorbed state other than the gas phase. Two lines, E_{N-N} = 0.1 eV and E_{NH_3} = −0.7 eV, have been added to Figure 1, and good eNRR catalyst candidates should be in the lower right quadrant relative to these lines. Clearly, Li and the alkaline earth metals stand out here. This goes a long way toward explaining why Li[29−31] and Ca[13] are the only metals observed so far with high selectivity at room temperature. This may also explain the very recent observation that Mg can
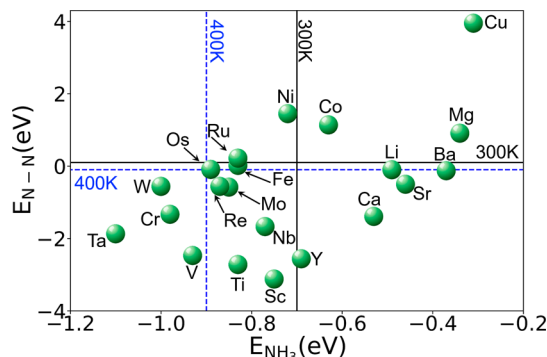

Figure 1. Two-descriptor map for eNRR on the alkali, alkaline earth, and transition metals. E_{NH_3} is the adsorption energy of NH_3 and E_{N-N} is the adsorption energy of the N_2 transition state (N−N). E_{NH_3} determines the rate of NH_3 desorption, while E_{N-N} determines the rate of N_2 dissociation. The most stable crystal is adopted for each metal at ambient conditions. The data of transition metals with bcc(111), fcc(211), or hcp(11$\bar{5}$) and alkali, alkali earth metals with fcc(111) and bcc(110) are illustrated. Only if both processes are facile at a given temperature will the eNRR process be fast. The solid lines indicate the energies where both elementary processes will proceed with a rate constant of 1/s at 300 K. The dashed lines indicate the same at 400 K. Details of the DFT method used to calculate the adsorption energies are outlined in the SI. We note that our calculated enthalpy at low coverage on Fe(111) (−0.83 eV) agrees well with the value extracted from thermal desorption experiments (−0.84 eV).[26] See also Figure S1 for the coverage-dependent adsorption energies.

electrochemically make ammonia.[32] The effect of the applied potential is estimated in Tables S3−5, indicating the analysis in Figure 1 should be still valid by the potential change. Previous works have also reported that NH_3 desorption is one of the key steps for the single atom catalysts[33] and $Fe_2Mo_6S_8$ complex surface.[34] It is also shown that enhancing electron transport speed could also help for a rapid hydrogenation reaction in eNRR.[35]

All the transition metals, if capable of activating N_2, appear to be ammonia-poisoned at room temperature. Different facets of the same transition metal may behave differently. For instance, the bcc(111) facet of Fe (E_{N-N} = 0.02 eV < 0.1 eV) could dissociate N_2 molecule with a rate around 1 s^{-1} at 300 K, but suffers from the ammonia-poisoned problem E_{NH_3} = −0.83 eV < −0.7 eV at room temperature. The bcc(210) facet of Fe E_{NH_3} = −0.63 eV > −0.7 eV can desorb ammonia at ambient conditions but hardly dissociate N_2 molecules at ambient conditions (E_{N-N} = 0.54 eV > 0.1 eV).

Notice that, on one hand, energy efficiency is a critical metric in evaluating the viability of any ammonia synthesis process. On the other hand, it is not the sole determinant of the overall feasibility and economic competitiveness of a technology. The final cost of ammonia is influenced by a multitude of factors beyond energy efficiency alone, including production scale, operational conditions, infrastructure requirements, storage, transportation, and the ability to integrate with decentralized and renewable energy sources. For instance, the ammonia production price varies with the production scale.[36] At a production scale of 2000 ton$_{NH_3}$ day^{-1}, a single-stage electrochemical ammonia synthesis system with N_2 and H_2O as reactants will produce ammonia at a cost of 750 \$ ton^{-1}. The Haber-Bosch process produces ammonia at a cost of 159

$ ton^{-1}. But at the production scale of 30 kg$_{NH3}$ day^{-1}, the cost of electrochemical approaches is much cheaper than the Haber-Bosch process. Therefore, the cost advantage of electrochemical ammonia synthesis lies in small-scale ammonia production. In the case of the Li (Ca)-mediated process, although the theoretical maximum energy efficiency is lower than that of the Haber−Bosch (HB) process, this process offers other advantages, such as the potential to operate under near-ambient conditions and the possibility for localized, small-scale ammonia production.

One way to shift transition metals like Fe or Ru to the right in Figure 1, would be to add promoters which can reduce the NH$_3$ adsorption energy. Adsorbed alkali metals are known to do that,[37] but as discussed above they would not be stable except at very negative potentials. The repulsive interaction between adsorbed alkali atoms and adsorbed NH$_3$ is electrostatic in nature—adsorbed alkalis transfer electrons to the surface and adsorbed NH$_3$ has an electric dipole in the same direction. There may be other electropositive additives with a less negative reduction potential.[38] Such electropositive additives may induce an electric dipole by transferring electron density to the catalytic surface. The induced electric field stabilizes the N−N transition state by attractive interaction with the slightly negative dipole moment of N−N species and destabilizes the NH$_x$ species due to the repulsive interaction between the field and the dipole moments of the NH$_x$ species.

Another option is to increase the temperature. This is illustrated in Figure 1 by the dashed lines indicating the energies where the dissociation and desorption rate constants are 1/s at 400 K. note that the TS energy hardly changes since the free energy barrier is mostly entropic in nature. Several transition metals now move into the right quadrant, including Fe. As shown in Table S2, the required temperature to alleviate the ammonia-poisoning issue for possible transition metals is around 400−500 K. However, the conventional liquid electrolytes are often not stable in this temperature range. There are a few proton conductors that works at the very high temperature (>600 K), and the challenge is to find suitable proton-conducting electrolytes which could work with the right proton conductivity at relatively low temperature.

In summary, we have presented the energy efficiency challenge for eNRR and possible solutions. By revisiting the mechanism of the Li/Ca-mediated process, we identified that besides the suppression of proton flux by the SEI-layer and the proton carrier, the N$_2$ dissociation rate (E_{N-N}) and NH$_3$ desorption rate (E_{NH_3}) are two thermal descriptors which explain why Li and Ca work for eNRR at ambient conditions. We found that all the transition metals, if capable of activating N$_2$, appear to be ammonia-poisoned at room temperature. We also discussed additives besides alkali and temperature could help alleviate the ammonia-poisoning issue at ambient conditions for transition metals binding nitrogen very strongly, which provides more options for cathodic catalysts except Li and Ca. The possible cathodic candidates e.g., Fe and Mo can be reduced at much less negative potentials than Li and Ca which could help improve the energy efficiency of eNRR. We note that there are several additional requirements for a metal to be a good eNRR electrocatalyst. It needs to be able to form a suitable SEI layer or alternatively one needs to be able to synthesize a suitable overlayer with controllable proton flux, perhaps in the form of a solid electrolyte. We further notice that many of the interesting metals are quite oxophilic. Thus,

the metal must also need to be reducible in the presence of trace amounts of water. The oxophilic nature of the possible metal candidates may have an effect on the selectivity for eNRR and alter the reaction mechanism[39] or simply block the active sites for nitrogen dissociation on the catalytic surface.

■ ASSOCIATED CONTENT

Data Availability Statement

For additional information see the Supporting Information.

ⓈSupportingInformation

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsenergylett.4c02954.

Materials and Methods, Supplementary Text, Tables S1−S5, and Figure S1 (PDF)

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Author Contributions

[†]Y.Z. and X.F. contributed equally to this work. Conceptualization: J.K.N., I.C., Y.Z., and X.F. Data curation: Y.Z. Formal analysis: Y.Z., X.F., I.C., and J.K.N. Investigation: Y.Z., X.F. Methodology: Y.Z, J.K.N. Visualization: Y.Z. The project was supervised by J.K.N and I.C. The original draft was written by Y.Z. and J.K.N. The manuscript was reviewed and edited by Y.Z., X.F., I.C., and J.K.N.

Notes

The authors declare no competing financial interest.

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