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Original
Across the Board: Federico Bella on Electrochemical Nitrogen Reduction / Bella, F.. - In: CHEMSUSCHEM. - ISSN 1864-564X. - ELETTRONICO. - 13:11(2020), pp. 3053-3055. [10.1002/cssc.202001051]

Publisher:
John Wiley & Sons, Inc.

Published
DOI:10.1002/cssc.202001051

Chasing electrochemistry nitrogen reduction secrets

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Today chance for 8 billion people of living in this world is closely dependent on some essential factors, among which fertilizers surely play a key role. The scientific community in the field of chemical sciences fully shares the idea that the Haber-Bosch process for the synthesis of ammonia at a large-scale allowed the demographic boom of the twentieth century, thanks to the possibility of fertilizing lands and feed people. In parallel, the use of ammonia as an intermediate for the industrial chemistry, as a product for domestic use and as a component for various processes behind the production of plastics, further highlighted the strategic role of Haber-Bosch plants at a global scale [1].

We should take into account that 170 million tons of ammonia are produced per year and, even if a hundred years of development led to an overall decrease in energy consumption and production cost, the Haber-Bosch process is responsible for ≈2% of the current world energy consumption. Considering the high temperature and pressure conditions of this process, along with the requirement of clear hydrogen and nitrogen reactant gases, it should also be kept in mind that ammonia industrial synthesis impacts for 1.44% of global CO_2 emissions (2.86 tons of CO_2 per ton of NH_3 in average). As a third critical point, Haber-Bosch plants require billions of euros of capital to be built, through an engineering project that requires several years [2].

The scientific community has recently come back to an old *Holy Grail* concept: trying to carry out ammonia synthesis under mild conditions and without the huge constrains of the Haber-Bosch large-scale (geo-localized) plants. The challenge is extremely difficult, since the aim is that of completely eliminating carbon emissions and deliver both hydrogen and required power from renewable sources [3]. This hot topic in the scientific literature (2018–) has been distributed over these research approaches: biochemical, photocatalytic, chemical looping, plasma-chemical and electrochemical.

Electrochemistry is today a leading discipline within applied chemical sciences, and the strategies developed in the last 10 years in the fields of CO_2 conversion, H_2 technologies and solar energy conversion/storage devices, seem useful to pave the way to the electrochemical nitrogen reduction reaction (E-NRR) challenge. The advantage of the electrochemical route lies on the thermodynamic force allowing a flexible control of electrochemical potentials, thus resulting in nitrogen conversion into ammonia through the addition of protons and electrons under mild conditions (25 °C, 1 atm).

The challenge of the E-NRR passes through some obstacles already known to the scientific community, but the overcoming of which is not yet close. First, the selectivity towards ammonia is hugely mined by the competitive hydrogen evolution reaction occurring at the cathodic side of cells operating in water. Second, the energy efficiency in relation to the overpotential and the system yield rate have to be effectively computed where the comparison with the Haber-Bosch process is made. Third, the real catalytic action of proposed materials must be carefully assessed, since many times the produced ammonia could come from nitrogen contamination in the electrochemical cell or decomposition of N-containing catalysts or electrolytes.

Efforts to improve the sluggish kinetics of E-NRR, due to the difficult nitrogen adsorption and N≡N cleavage, are based on precisely defined nanochemistry approaches. Xu *et al.* synthesized nanoporous palladium hydride (by dealloying and in situ hydrogen injection), achieving an ammonia yield rate of 20.4 $\mu g h^{-1} mg^{-1}$, with a Faradaic efficiency of 43.6% and a low overpotential of 150 mV [4]. The trick, defined by isotopic hydrogen labeling studies, was the involvement of hydride lattice hydrogen atoms as active hydrogen source, leading to a reduction of the energy barrier for the rate-limiting step (*i.e.*, $*N_2H$ formation); the mechanism is shown in **Figure 1A**. After that publication, hydrogenation of metals (or metal alloys) emerged as a strategy to design efficient electrocatalysts for sluggish hydrogen-involved reactions as the E-NRR one.

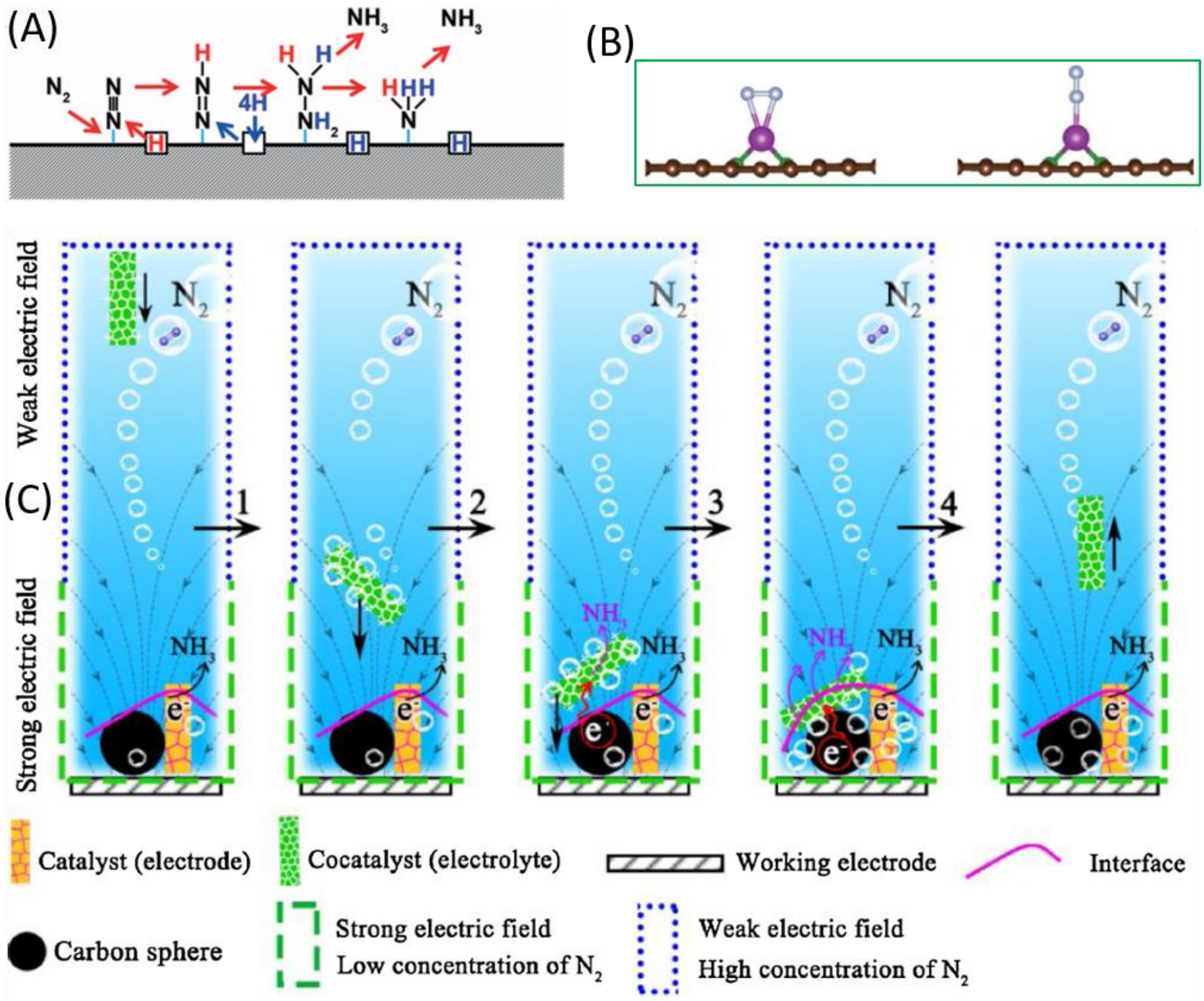

Figure 1. **A)** Proposed lattice hydrogen-involved reaction pathway for nitrogen reduction on palladium hydride. **B)** B-doped graphene with single metal atoms working for E-NRR, by a side-on (left) and end-on (right) configuration. Color code: metal in purple, B in green, C in brown and N in grey. **C)** Illustration of the catalytic mechanism of a biomimetic electrode/electrolyte design. Adapted and reprinted with permission from [4,7,5].

The low solubility of nitrogen and the competitive hydrogen production are big constrains towards the achievement of satisfying E-NRR performances. However, the structure of gas-trapping hydrophobic hair on subaquatic spiders and the function of hemocyanin in their blood was of inspiration for Liu *et al.*, who designed an aerophilic (porous Bi_5O_7I nanotubes) / hydrophilic (carbon spheres) heterostructured electrode [5]. Besides a Faradaic efficiency of 13.42% and an ammonia yield of 85.45 $mgh^{-1}\ m^{-2}$ at –0.4 V, the authors demonstrated the plastron effect in electrocatalysis (an illustrative scheme is given in **Figure 1C**).

The lack of robust design criteria for tackling the mentioned E-NRR problems requires a solid theoretical investigation within the scientific community, also including fast screening protocols. Recently, large-scale density functional theory computations by Guo *et al.* led to a descriptor-based design principle to explore the large composition space of 2D biatom catalysts, *i.e.* metal dimers supported on 2D expanded phthalocyanine [6]. By using N_2H^* adsorption energy as activity descriptor, the list of promising catalyst candidates was restricted from over 900 to less than 100, up to the identification of 3 homonuclear and 28 heteronuclear systems. Ti_2-Pc, V_2-Pc, TiV-Pc, VCr-Pc and VTa-Pc were identified as the top-5 catalysts, even able to suppress hydrogen evolution.

Theoretical chemistry approaches for electrocatalysts screening require numerous calculations in the search space, leading to a critical computational cost. As an alternative, Zafari *et al.* has recently proposed a deep neural network to predict efficient E-NRR systems among B-doped graphene single atom catalysts (see **Figure 1B**) [7]. The coordination number of the transition metal and the number of hydrogen atoms were the principal factors influencing the determining step, *i.e.* the hydrogenation of N_2 to N_2H. CrB_3C_1 was the most promising system, with a minimal overpotential of 0.13 V. This machine learning method was also able to predict free energies with an accuracy of ±0.11 eV.

A standardized set of control experiments elaborated to precisely quantify ammonia production yield and determine any source of contamination was proposed in 2019 by Andersen *et al.* [8]. Performing quantitative isotope measurements with $^{15}N_2$ gas source was highlighted as main strategy to assess E-NRR results, and the clamorous outcome of this study was that no ammonia was detected when using the most promising pure-metal catalysts proposed in several top-journals. More than in other fields, it seems that E-NRR must pass through a rigorous protocol to prevent false positives from being published and mining the already challenging research toward the discovery of alternative processes to the Haber-Bosch one. ^1H NMR spectroscopy with a solid calibration approach and based on a solvent suppression methods was later proposed by Hodgetts *et al.* as a mean for ammonium quantification [9]. The optimized method led to a rapid quantification of both $^{14}NH_4^+$ and $^{15}NH_4^+$ within 12-22 min, targeting a detection limit of 5-10 μM. The authors highlighted the importance of publishing key analysis parameters (*e.g.*, pulse program, number of scans, relaxation time, …) along with reproducibility of experimental data.

Operating ammonia synthesis in an aqueous environment and at ambient temperature and pressure is becoming an increasingly credible process, but the identification of a catalyst capable of guaranteeing a reactor able to provide high productivity is still far away. In this brief Viewpoint contribution, I listed the emerging trends in 2020, but an additional factor should also be considered. The electricity needed to conduct the electrochemical process must come from renewable sources, ideally from Sun. Low impact photovoltaic cells (even with an aqueous matrix [10]) have been recently developed and some researchers have also proposed the possibility of using ammonia as a solar fuel [11]; at a glance, ammonia could be used to produce electricity during night in an integrated home/E-NRR plant/nature scenario.

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