

Bread from air (and electricity): producing ammonia at the interface of porous carbons and room-temperature salt melts

The importance of ammonia seems to escape public notice, yet its role for the prosperity of mankind cannot be overestimated.



As one of the most important commodity chemicals, produced on the scale of more than a hundred million tons per year, it is a starting point for further synthetic products such as fertilizers and is even discussed as a carrier molecule for the hydrogen economy. In fact, just to emphasise its role as a precursor for fertilizers, it is sufficient to consider that almost half of the global population is currently sustained thanks to the existence of a technological process to artificially produce ammonia in large quantities, called the Haber-Bosch-process after two of its inventors Fritz Haber and Carl Bosch.

All plants, including agricultural ones, strictly require nitrogen-containing compounds for their growth, usually provided in the chemical form of nitrate salts. In the natural nitrogen cycle, atmospheric nitrogen is transformed into ammonium ions, a chemically stable form of ammonia in solution, by specific bacteria and fungi, which is then further converted into nitrate compounds by other bacteria. These compounds are finally taken up by plants via their roots and incorporated into the plant body, where they become part of the food chain, serving as the nutrition basis for higher organisms. In the end, the nitrogen bound in these plants returns to its atmospheric dinitrogen state, ready to participate in the nitrogen cycle again. This highly selective and energy-efficient process, which reached perfection over an evolutionary timespan escaping human imagination, is not fast enough to sustain an ever-growing population. This was realised in the late nineteenth century. Even the classical approaches of agriculture, such as fertilizing soil with animal dung or compost and efficient crop rotation, were not sufficient to provide enough food. Several South-American states, especially Chile with its abundant deposits of Chilean saltpetre, a natural form of nitrates, and guano, a nitrate-rich mineral formed from seabird excrements, became key suppliers of fertilizer for the global population. Even wars were waged over the distribution of these resources and access to them. Since nitrogen in the form of N_2 or dinitrogen is the main constituent of the atmosphere,

it was obvious that a technological solution to the problem had to be found. The main problem, however, was that the N_2 molecule is very unreactive and, therefore, difficult to convert to any further chemical, usually requiring very harsh reaction conditions. During this time, the idea of 'bread from air' was born and research activities on how to convert atmospheric nitrogen into essential chemicals picked up pace.

As a result of these efforts, two relevant industrial-scale processes for the production of bioavailable nitrogen compounds were developed, the Frank-Caro and the Birkeland-Eyde processes. Unfortunately, both of them suffered from an extremely high amount of required energy per mass of nitrogen converted. Hence, none was ever considered widely commercially viable. Between 1904 and 1908, Fritz Haber conducted his research on ammonia synthesis from the elements nitrogen and hydrogen. Haber recognised that although the reaction was extremely slow, it was still possible to yield ammonia on an industrially relevant scale at very high pressures, temperatures around 300 °C, and in the presence of a suitable catalyst, a substance capable of accelerating a chemical reaction without being consumed itself. After the patent for this process was granted in 1911, the technical obstacles, most importantly the development of reactor materials capable of withstanding the reaction conditions, were successfully tackled in close cooperation with Carl Bosch. The way for the seemingly limitless synthetic production of ammonia had been paved. However, the procedure still requires high energy input to achieve the necessary temperatures and pressures and, perhaps even more importantly, a suitable hydrogen source. Contrary to the ubiquitous nitrogen, hydrogen does not occur in the atmosphere in its elemental form and has to be produced from other compounds. In the beginning, hydrogen generated as a byproduct of chlorine production was used to generate various chemicals. Later, it was obtained from a reaction between coal and water at high temperatures on the industrial scale. With decreasing prices for oil and gas, especially after World War II, and

the development of efficient procedures, hydrogen production was increasingly realised by employing these starting materials.

Apart from the optimisation of reactor components, catalysts and procedures, the main concept of the Haber-Bosch process remained essentially the same for more than 100 years, despite the ever-growing demand for ammonia. Consequently, this process alone accounts for about 2 per cent of the global industrial energy consumption and 1 per cent of the world's greenhouse gas emissions. This is, of course, mainly due to the fact that today natural gas is the main source of hydrogen. This leads to the second key drawback of the Haber-Bosch process, its centralisation. Haber-Bosch ammonia plants are usually few yet huge production sites that are situated close to natural gas reserves to assure short transport paths and high energy efficiency by coupling the facilities to other energy-intensive processes. However, the locations of ammonia fertilizer use are rarely the same as where it is produced. The fertilizer is distributed over the whole globe, leading to immense costs to the end users due to transportation difficulties. Remote and impoverished regions have to face a potentially precarious situation regarding their food supply. Disconnecting ammonia production from fossil-resource demand, particularly from geologically restricted deposits of starting materials, is therefore of utmost urgency, especially in view of the increasing threat of climate change.

In regions where energy from renewable sources is abundant and cheap, e.g. hydrothermal energy in Norway or Iceland, or solar energy in the Mediterranean areas, hydrogen can be generated by splitting water into hydrogen and oxygen, using electricity. This hydrogen can then be used in conventional Haber-Bosch plants, which already means a significant drop in carbon-dioxide emissions and possibly increased decentralisation. The overall energy efficiency of this approach is already close to that of classical Haber-Bosch-synthesis, but again, due to the high temperatures and pressures required for the reaction itself, it can hardly be considered sustainable.

Perhaps the most elegant way to synthesise ammonia is the direct combination of water splitting and ammonia production in one and the same electrochemical cell driven by renewable energy sources. In this case, hydrogen would be supplied in the form of protons and electrons rather than in its elemental form. Water could be directly reacted with atmospheric nitrogen to yield ammonia, without intermediate products, at high energy utilisation and without the dependence on fossil resources. Fertilizers could be produced directly at the site, where they are required most, using only sunlight, water and air. Furthermore, excess energy generated at peak hours of sunlight, wind or tides could be used to produce ammonia, which can be used as fuel for transportation, heating and electricity generation. This would enable society to develop an 'ammonia-economy', similar to the popularly and often discussed hydrogen economy.

In principle, the electrochemical reaction of protons and electrons with nitrogen

to yield ammonia is possible. However, the dinitrogen molecule's chemical inertness is also a major hurdle in this case. This means that both the binding to the catalyst surface and the further reaction with protons and electrons are strongly impeded. Typically, attempts to resolve this involved designing catalysts to attract the nitrogen molecule and change the binding situation within so that further conversion becomes more favourable. Still, in most cases of the current state of the art, the reaction requires the expenditure of a surplus of energy to overcome the reluctance of nitrogen to bind to the catalyst surface and to accept a hydrogen atom, the so-called overpotential. Frequently, the overpotential needed is so high that other reactions, e.g. the decomposition of the electrolyte solvent, are triggered rather than the desired ammonia synthesis. It becomes clear that new concepts in electrocatalysis, beyond catalyst design and optimisation, are needed to drive electrochemical ammonia synthesis at reasonable space-time yields and selectivities.

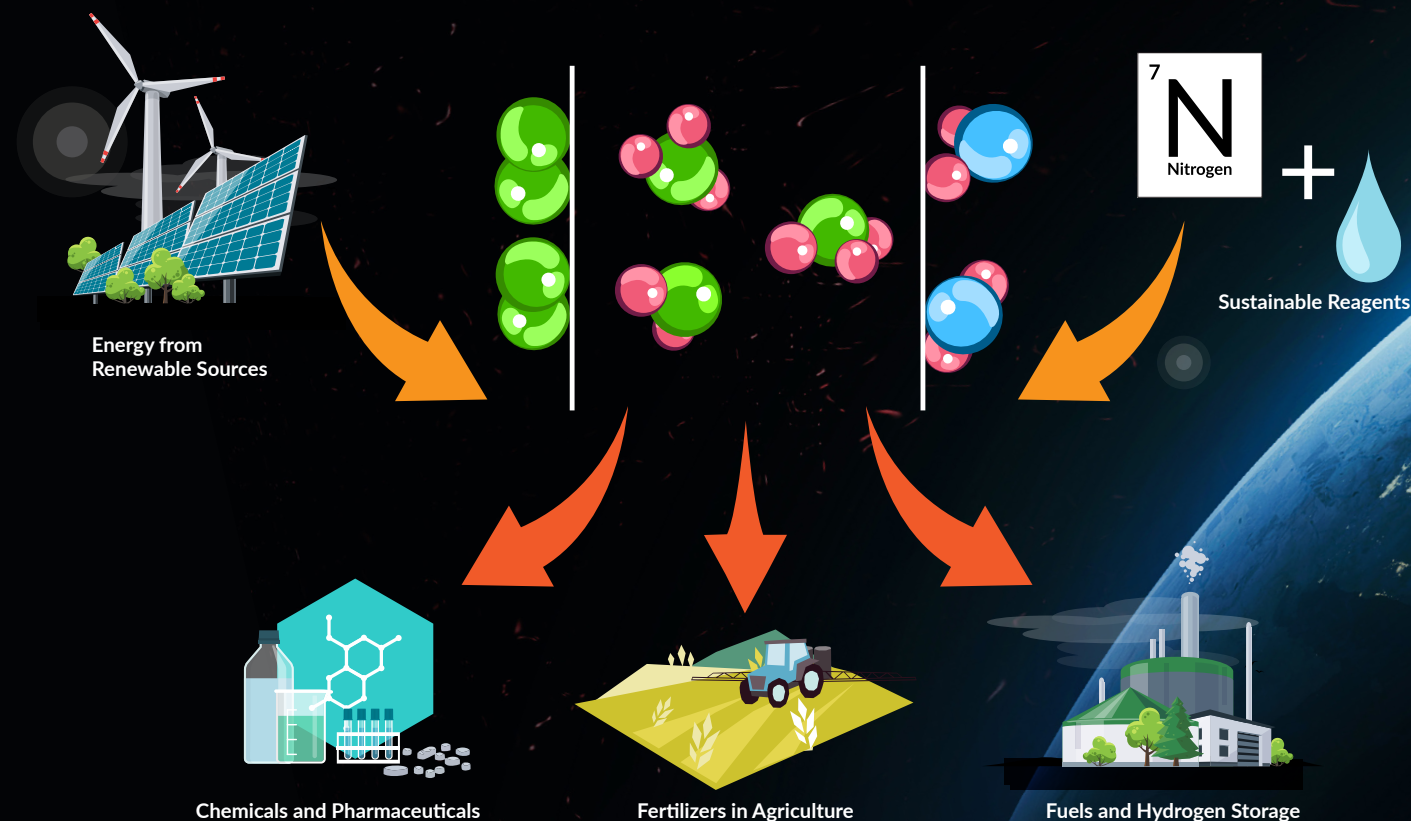
Using salts, which already melt at room temperature, so-called room-temperature ionic liquids (RTILs), as the solvent has been shown to be stable under the reaction conditions and provide an environment on the nanoscale, which can distort the electronic structure of the nitrogen molecule in a way that it becomes more likely to participate in chemical reactions.

The idea of the ERC-funded project CILCat is to move this system into an activated carbon pore, a cavity of the size of only several molecules. Due to the special interaction of the pore walls with the ionic liquids, together with the high pressures exerted on the nitrogen molecule within, the molecule will be enabled to not only adsorb to the carbon surface but also to become energetically destabilised in a way that further reaction to ammonia will be facilitated. In this way, the project strives to accomplish a leap forward in the pursuit of a next-generation, emission-free and delocalised ammonia synthesis for the sustainable future of the chemical industry and food supply.

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Electrocatalytic Ammonia Synthesis CILCat



PROJECT NAME

Nanocarbon-Ionic Liquid-Interfaces for Catalytic Activation of Nitrogen - CILCat

PROJECT SUMMARY

The ERC Starting Grant project "Nanocarbon-Ionic Liquid-Interfaces for Catalytic Activation of Nitrogen" (CILCat) aims to establish a novel principle in catalysis that holds holistic perspectives for the activation of small molecules within electric double-layers formed between ionic liquids and nanostructured carbon materials. The electrocatalytic nitrogen fixation will serve as a model reaction at the beginning.

PROJECT PARTNERS

The CILCat project is hosted at the Institute of Technical Chemistry and Environmental Chemistry at the Friedrich-Schiller University Jena. The project members collaborate with the members of the Center for Energy and Environmental Chemistry Jena (CEEC Jena). Other major collaboration partners are located at the Max-Planck-Institute of Colloids and Interfaces in Potsdam and at the Helmholtz-Zentrum Berlin (HZB).

PROJECT LEAD PROFILE

Prof. Dr. Martin Oschatz obtained his PhD at the Technische Universität Dresden in 2015 with summa cum laude. After a postdoctoral stay at Utrecht University, he became a group leader for nanocarbon materials at the Max-Planck-Institute of Colloids and Interfaces. Since 2021 he has been a full professor for the chemistry of materials for energy applications at the Friedrich-Schiller University Jena and a member of the Center for Energy and Environmental Chemistry Jena (CEEC Jena).

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