

Energy-Efficient Ammonia Production from Air and Water Using Electrocatalysts with Limited Faradaic Efficiency

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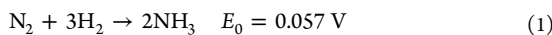
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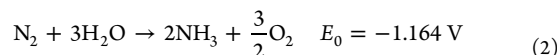
Ammonia is an industrial large-volume chemical. It is used in fertilizers and many chemical products and materials, and it pops up as a candidate green energy vector. Today, the industrial production of ammonia is dominated by the Haber–Bosch process departing from natural gas or other fossil fuel. This process is responsible for about 1.6% of the global CO₂ emissions. Electrochemical ammonia production from water and nitrogen gas using renewable electricity is a potential solution to reduce the CO₂ footprint of ammonia production. Electrocatalysts with steadily increasing Faradaic efficiency are being reported, but there seems to be a trade-off between ammonia selectivity and catalytic activity. Hydrogen gas is the main byproduct. Here we show low ammonia selectivity of electrocatalysts not to be an obstacle to energy-efficient ammonia production. The SECAM process (Solar ElectroChemical AMmonia synthesis) integrates nitrogen gas production from air, electrocatalytic ammonia synthesis, reaction product separation, and hydrogen recycling with an overall energy efficiency similar to that of the Haber–Bosch process. The electrochemical ammonia synthesis process can be powered with photovoltaics and take advantage of the day–night cycle for converting the excess hydrogen byproduct produced during the day to make additional ammonia at night. The process can be operated using electrocatalysts with Faradaic efficiencies of ammonia synthesis as low as 10%. The activity of electrocatalysts is the critical property to be improved for energy-efficient production of green ammonia.

The Haber–Bosch process for ammonia production is one of the oldest industrial catalytic processes.¹ The first ammonia plant went on stream in 1913.² In the Haber–Bosch process, N₂ gas is reduced to NH₃ using H₂ gas (eq 1):



Elevated temperatures are needed to activate the iron-based catalyst. The reaction kinetics are peculiar in the sense that the chemisorption of nitrogen gas molecules on the catalyst surface limits the reaction rate.^{3,4} The H₂ for the Haber–Bosch process is typically produced by methane steam reforming. CO₂ emission of the Haber–Bosch process amounts to up to 1.9 ton per ton of ammonia produced.⁵ In 2017, ammonia production worldwide was responsible for ca. 420 Mt of CO₂.⁶

The use of water and electricity instead of hydrogen out of methane is an alternative pathway for ammonia synthesis (eq 2).



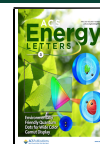
Different types of electrocatalysts performing this reaction have been reported, but they exhibit two shortcomings: low activity and low ammonia selectivity. Currently, the highest reported Faradaic efficiencies of electrochemical ammonia synthesis from water and air are in the range of 60%.^{6–8} One exception, which uses a fundamentally different process with Li-cycling, achieves a Faradaic efficiency of 88.5% at a temperature of 450 °C.⁹ Common electrochemical ammonia synthesis has hydrogen gas as the main byproduct, consuming a significant part of the invested electric energy. The SECAM process presented here uses this hydrogen gas for two purposes: (i) reaction with oxygen out of the air to prepare nitrogen gas and water to be fed to the ammonia synthesis reactor and (ii) performing electrocatalytic ammonia synthesis using H₂. The SECAM process has two modes of operation: energy-intensive production of ammonia out of nitrogen gas and water according to eq 1 (mode A, Figure 1) and an energy-extensive production of ammonia out of an N₂/H₂ gas mixture according to eq 2 (mode B, Figure 1).

In mode A (Figure 2A), air is used as a source of nitrogen. To make air suitable for ammonia production, O₂ is removed by reaction with H₂. This can be done in a fuel cell, generating electricity, or in a burner, generating heat to recover the energy. Next, the obtained gas containing already some water from the reaction of O₂ with H₂, is sent through a humidifier where additional water vapor is added. After these two steps, the hydrated nitrogen gas is fed to the electrochemical cell, where ammonia is formed on the cathode. The hydrogen evolution reaction (HER) competes with ammonia synthesis. When mode A is run such as to produce exactly the amount of

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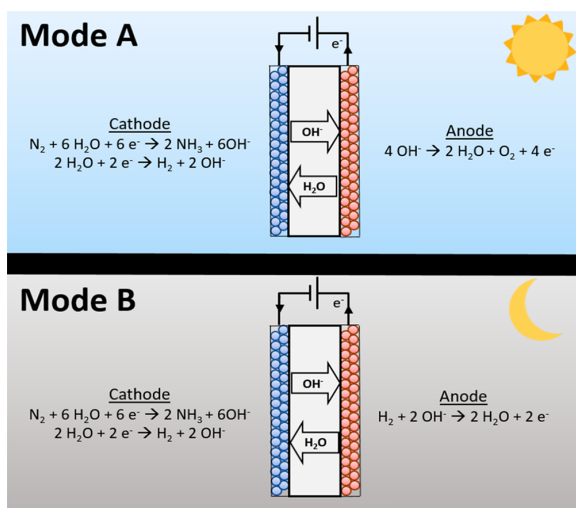


Figure 1. Overview of the half reactions occurring in the electrochemical cell, for mode A and mode B.

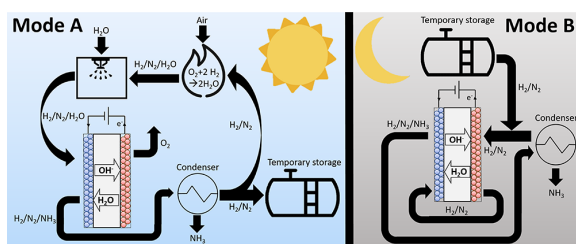


Figure 2. SECAM process for electrochemical ammonia production. (A) Energy-intensive operation mode of the electrochemical reactor, producing ammonia from water and air. (B) Energy-extensive operation mode of the electrochemical reactor, producing ammonia from an N_2/H_2 gas mixture.

hydrogen needed to eliminate the O_2 from the intake air, the electrocatalyst should have a Faradaic efficiency for ammonia production of 85%. State-of-the-art electrocatalysts have lower Faradaic efficiencies,¹⁰ and excess H_2 gas is produced. The resulting outlet gas of the cathode compartment is composed of NH_3 , H_2 , and unreacted N_2 . NH_3 is condensed out of the gas stream, resulting in a residual stream of N_2 and H_2 . Part of this stream serves the O_2 removal out of inlet air; part is stored in a tank as feed for mode B. Water is the source of H atoms and air is the source of N atoms. The molar ratio of the excess N_2/H_2 , produced in mode A, is fixed at 1/3 by tuning the air and water intake of the process.

In mode B (Figure 2B), the H_2/N_2 gas mixture from the storage vessel is sent to the anode of the electrochemical cell, where the hydrogen oxidation reaction (HOR) takes place. Next, the remaining gas is sent to the cathode, where ammonia and hydrogen gas are formed. In mode B ammonia is produced until all N_2 and H_2 gas is converted by recycling.

Modes A and B make use of the same electrochemical cell. Ammonia production in mode B consumes less than 20% of the electric power required for mode A.

Operation of SECAM according to modes A and B is dependent on the availability of electric energy. When a large amount of energy is available, for example using photovoltaics during daytime, mode A is executed. When the energy supply

is limited, for example with photovoltaics at night or on cloudy days, mode B is executed. Several SECAM reactors can run in parallel and be operated either in mode A or B to optimize the ammonia productivity according to the availability of renewable energy.

To facilitate the condensation of ammonia, the SECAM processes are operated at a pressure of 0.8 MPa. At this pressure, ammonia condenses at 20 °C.² An additional benefit of the increased pressure is a positive effect on the reaction rate by the first order kinetics.¹¹ The downside of the increased pressure is that it entails additional energy consumption and materials cost for making the reactor pressure resistant. Alternatively, the process can be run at atmospheric pressure if the produced ammonia is recovered by an extraction with water.

The energy needed for ammonia production and the share of operation modes A and B of SECAM processes with different Faradaic efficiencies at the two locations are presented in Table 1. The specifications of the process

Table 1. Comparison of the Performance of SECAM Implemented in Leuven, Belgium (Solar Energy = 158 kWh/m²·year) with an FE of 10, 50, and 85 % and in the Atacama Desert, Chile (353 kWh/m²·year) with an FE of 22.5, 50, and 85 %^a

location	process	energy consumption (MJ/mol NH_3)	mode A (h/day)	mode B (h/day)
Leuven, Belgium	SECAM 10	1.41	2.9	21.1
	SECAM 50	0.64	2.9	2.0
	SECAM 85	0.56	2.9	0.0
Atacama desert, Chile	SECAM 22.5	0.87	6.4	17.6
	SECAM 50	0.64	6.4	4.4
	SECAM 85	0.56	6.4	0.0

^aAverage energy consumption and average daily operation time of modes A and B are reported.

parameters are given in the Supporting Information. The overpotentials used for the different half reactions are according to the state of the art.^{8,12–15}

In Leuven, Belgium, a solar panel with an efficiency of 15% produces on average 430 Wh/m²·day¹⁶ with a maximal power delivery of 150 W/m². This means mode A needs 150 W peak capacity (electrochemical reactor + compressor) for every square meter of solar panel. The produced solar electricity is sufficient to operate in mode A for 2.9 h/day on average. During these 2.9 h, a reactor with a Faradaic efficiency of 10% produces enough N_2/H_2 gas mixture for mode B to run for 21.1 h. Together, this completes a day cycle of 24 h. Therefore, the minimal required Faradaic efficiency is 10% in Belgium. The highest average solar irradiation is encountered in the Atacama desert in Chile. There, a solar panel with 15% efficiency produces 967 Wh/m²·day.¹⁷ This energy is sufficient for mode A to run 6.4 h/day on average. During these 6.4 h, a reactor with a Faradaic efficiency of 22.5% produces enough N_2/H_2 gas mixture for mode B to run for 17.6 h. Therefore, the minimal Faradaic efficiency needed in Chile is higher than in Belgium, viz. 22.5%.

The energy consumption of SECAM ammonia synthesis is plotted against the Faradaic efficiency of the electrocatalysts in Figure 3. The energy consumption is highest at low Faradaic efficiency and drops rapidly when improving the Faradaic efficiency from 10% to 20%. At Faradaic efficiencies above

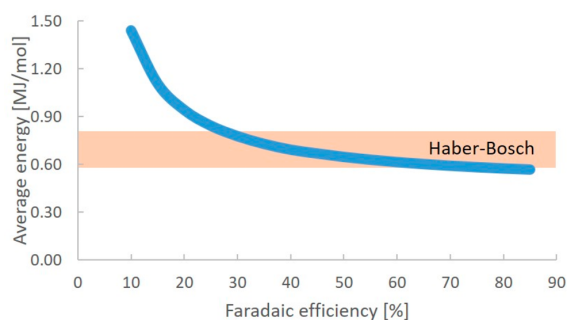


Figure 3. Average energy consumption of SECAM per mole of ammonia produced, against Faradaic efficiency of the electrocatalyst with an overpotential of 250 mV, compared to the energy consumption of the natural gas-based Haber–Bosch process.^{5,20,21}

20%, the energy needs flatten. Enhancing the Faradaic efficiency from 30% to 85% causes a gain in energy of 37%. Electrocatalyst development has been focused on enhancing Faradaic efficiency. The ARPA-E (Advanced Research Projects Agency-Energy) determined a minimal FE of 90% for the process to be economically feasible.¹⁸ However, with SECAM, ammonia synthesis could already be viable at Faradaic efficiencies of 20–30%. Therefore, the main focus of future research should be on how to increase the current density, which on state-of-the-art electrodes is still far too low for commercial ammonia production and should be raised to at least 5–10 mA/cm².

Despite the high pressures and temperatures required for the Haber–Bosch process, it is surprisingly efficient at the very large scale at which it is operated.¹⁹ The traditional natural gas-based Haber–Bosch process is reported to have an energy consumption ranging from 0.58 MJ/mol to 0.81 MJ/mol, depending on the source.^{5,20,21} SECAM is estimated to have similar energy requirements, ranging from 0.56 MJ/mol at 85% Faradaic efficiency to 0.92 MJ/mol at 20% Faradaic efficiency. As an additional advantage, SECAM allows for small-scale decentralized production, which is of interest to economically less developed parts of the world.²² With an efficient delocalized ammonia production at farms, transport costs for fertilizers can also almost be eliminated.²³ The process discussed in this Viewpoint has limited CO₂ footprint and can be operated with a fluctuating power source.

The SECAM process performs energy-efficient electrochemical ammonia production that is competitive with the Haber–Bosch process in terms of energy consumption. In contrast to the Haber–Bosch process, the discussed process is efficient at a small scale and allows a delocalized ammonia production. The process can be operated at a Faradaic efficiency as low as 20–30%. Practical implementation of SECAM processes is awaiting the development of electrocatalysts with enhanced current density even at modest Faradaic efficiency.

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■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acseenergylett.0c00455>.

Detailed information on the executed calculations and assumptions made; a graphical representation of the process streams under varying operating conditions (PDF)

■ AUTHOR INFORMATION

Complete contact information is available at:

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Notes

Views expressed in this Viewpoint are those of the authors and not necessarily the views of the ACS.

The authors declare no competing financial interest.

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