AMMONIA SYNTHESIS

Electrifying the Haber–Bosch

Joule <https://doi.org/10.1016/j.joule.2019.10.006> (2019)

Credit: Elsevier

The Haber–Bosch process, where nitrogen and hydrogen molecules react to form ammonia ($\text{N}_2 + \text{H}_2 \rightarrow \text{NH}_3$), accounts for 1.4% of global carbon dioxide emissions and consumes 1% of the world's total energy production. Hydrogen is produced onsite via methane steam reforming ($\text{CH}_4 + \text{H}_2\text{O} \rightarrow \text{CO} + 3\text{H}_2$) in combination with the water–gas shift reaction ($\text{CO} + \text{H}_2\text{O} \rightarrow \text{CO}_2 + \text{H}_2$). Nitrogen and hydrogen combine in a high-pressure reactor with the aid of an iron-based catalyst. Given the energy- and carbon-intensive requirements of the process, alternatives must be sought to fulfil the enormous global demand for ammonia through a significantly greener approach.

Now, Vasileios Kyriakou and colleagues have designed a protonic ceramic membrane reactor that consists of Ni–BaZr_{0.7}Ce_{0.2}Y_{0.1}O_{3–x} and VN–Fe porous electrodes, respectively as the anode and cathode, separated by a BaZr_{0.8}Ce_{0.1}Y_{0.1}O_{3–x} solid electrolyte membrane. The reactor operates at ambient pressure and temperatures between 550 and 650 °C. In the anode compartment the CH₄ + H₂O reactant mixture is converted to CO₂ and H⁺. The latter is transported to the cathode compartment through the membrane, where it reacts with lattice nitrogen from the cathode to form NH₃ via a

Mars–van Krevelen mechanism — nitrogen vacancies are healed with N₂ gas. The researchers achieve a maximum ammonia rate of 68 mmol_{NH₃} h⁻¹ m⁻² at 0.63 V and 600 °C, with a Faradaic efficiency to ammonia of 5.5%. Higher Faradaic efficiencies up to 14% are obtained at lower currents, at the expense of lower NH₃ rates.

The protonic ceramic membrane reactor is combined with a protonic ceramic fuel cell, fed with the leftover H₂ from the reactor plus ambient air at 550 °C, which recovers part of the electricity consumed in the synthetic process and furthermore purifies N₂ for its use in the reactor. The researchers conclude by performing energy consumption and CO₂ emissions analyses to explore the viability of their overall process. They find that at 0.3 V, the cathode catalyst's Faradaic efficiency to NH₃ must increase to at least 35% to consume less energy than a conventional Haber–Bosch plant (500 kJ mol_{NH₃}⁻¹). CO₂ emissions could be cut by half at Faradaic efficiencies higher than 75%.

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Published online: 12 December 2019
<https://doi.org/10.1038/s41929-019-0414-4>