ELECTROCHEMICAL AMMONIA SYNTHESIS

Aprotic is the key

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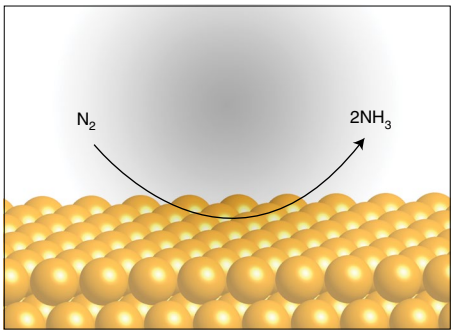

The industrial production of ammonia via the Haber–Bosch process has undoubtedly been one of the major breakthroughs of the twentieth century. The process, however, requires harsh temperature and pressure conditions (>500 °C, >100 bar), which are a direct consequence of the hurdle of activating the N≡N triple bond. Massive efforts are currently devoted toward finding alternative routes to synthesize ammonia under mild conditions. The electrochemical reduction of N_2 has emerged among the alternatives as a potentially green process that could be powered by solar or wind energy. The main challenge is to design electrocatalysts that deliver high ammonia rate and high Faradaic efficiency. Despite the current intensive research in N_2 electroreduction, Faradaic efficiencies have barely reached 15%. This is due to the more favourable competing hydrogen evolution reaction in aqueous electrolyte. One strategy to achieve values as high as 60% has been the use of aprotic solvents, albeit at the expense of low ammonia rate.

Now, Douglas MacFarlane and co-workers show that the rate of ammonia production and its Faradaic efficiency can be balanced by means of an aprotic electrolyte design strategy. The authors use a highly fluorinated ionic liquid salt in a fluorinated ether solvent as electrolyte. Core–shell α-Fe/Fe_3O_4 nanorods grown on carbon fibre paper are employed as the catalyst, with the outer oxide shell acting as a passivation layer. By optimizing the mole fraction of the ionic liquid in the electrolyte and the amount of water (at the ppm range), the authors achieve an ammonia rate one-order-of-magnitude higher than previous works on aprotic N_2 electroreduction, still maintaining a remarkable 31% Faradaic efficiency. Further research and optimization is necessary and there is still a long way to go, but the field is certainly moving forward.

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