Insights into Efficient Electrochemical Nitrate Reduction to Ammonia: Reaction Environment and Metal Electrode

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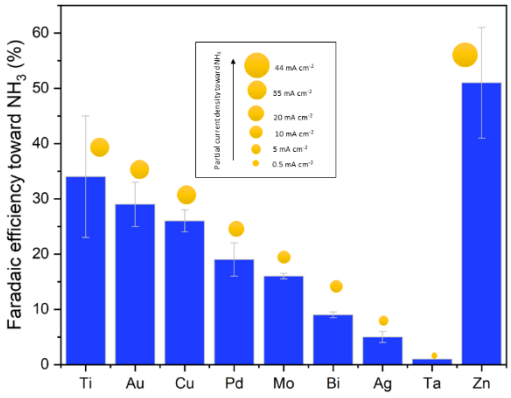
The ammonia economy is mainly driven by the inorganic fertilizer demand. Around 70% of worldwide ammonia production is used as feedstock for fertilizers. The global ammonia production is about 176 Mt per year, and it is expected to increase by 40% by 2050. [1,2] However, the actual ammonia economy seriously pollutes the air, soil, and water, contradicting climate neutrality goals. Pollution comes from different parts of the ammonia value chain, from its production to its transformation as fertilizers. While fertilizers are essential in providing sufficient food to feed our planet, they have been the main cause of water pollution. Fertilizers are the source of nitrogen nutrients (nitrates, NO_3^-), which allow crops to grow. However, less than 50% of the applied nitrates nurture crops, while the rest inevitably leaches to the groundwater, polluting water. A high level of nitrates makes water unsuitable to drink and harms the natural environment, particularly via eutrophication.[3] Therefore, it is of vital importance to develop sustainable technologies that allow treating water from nitrates. Electrocatalysis is a promising technology for such a challenge.

Electrocatalysis could not only eliminate nitrates from water, but also conveniently convert them back into ammonia, generating an added value apart from nitrogen remediation. Although electrocatalytic nitrogen reduction to ammonia is promising, its practical application is hindered by the lack of an electrocatalyst that simultaneously can show high stability, activity, and selectivity. For instance, some transition metal-based electrocatalysts (e.g., Rh, Pt, Cu, Ir) have shown appreciable

activity, but not simultaneously selectivity towards ammonia in acidic or alkaline media.[4,5] Clearly, the development of a “champion electrocatalyst” for such a reaction is not trivial. Our primary research focus is to tailor electrocatalyst properties for nitrates to ammonia rationally by identifying active sites favorable for efficient ammonia evolution and understanding the effect of the reaction environment (nitrate concentration, pH, applied voltage, and presence of other ions) on activity and selectivity.

As the initial phase of our research, the electrochemical investigation was carried out using metal foil electrodes (Ti, Ag, Au, Cu, Bi, Pd, Zn, Ta, and Mo). We observed that in a reaction environment rich in protons (i.e., pH 1), selectivity towards ammonia increases with nitrate concentration. In such an acidic media, the highest faradaic efficiencies (FE) to NH_3 were reached at an applied potential of -1V versus RHE for most of the tested metal foils. For example, Ti reached a faradaic efficiency of 34% with a current partial density to ammonia of -36 mA cm^{-2} using 0.4M [NO_3^-] at pH 1. Because an acid media of pH 1 with a high concentration of nitrated (0.4 M) favored the formation of ammonia, the intrinsic activity of the metals was investigated at such conditions at -1V vs. RHE, Figure shown. Ti, Au, and Cu showed the highest efficiency with notable corrosion resistance. The effect of higher pH was also investigated, showing Cu, Au, Ti, and Ag can also catalyze ammonia formation in specific pH conditions.



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