Electrocatalysis

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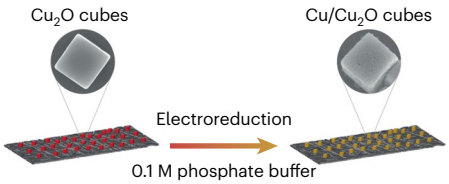
Perfecting copper catalysts



Cu-based electrocatalysts are used in many transformations, including the reduction of CO_2 to various products such as HCOOH, CO, CH_4 and C_2H_4, or the reduction of nitrate (NO_3^-) or nitrite (NO_2^-). However, the NO_3^- reduction reaction (NO_3RR) to form NH_3 is notoriously difficult, owing to the range of possible products including NO_2^-, NO, N_2 and NH_2OH, and therefore, its unsatisfactory selectivity for NH_3.

Now, writing in *ACS Catalysis*, Di Bao, Haixia Zhong, Xinbo Zhang and co-workers investigate the relationship between the oxidation state of Cu in the electrocatalyst and product selectivity, and reveal that NH_3 is preferentially produced on Cu^0 derived from Cu_2O in a neutral electrolyte. In contrast, NO_2^- formation is produced in the presence of Cu^+. "In situ Raman/infrared analysis and theoretical calculations, alongside experiments probing product selectivity based on pulsed electrolysis coupled with constant potential electrolysis, were essential tools in our investigation of the role of Cu^0 and Cu^+ in determining the selectivity of the NO_3RR," explains Zhong.

The researchers use Cu_2O cubes as catalyst precursors and first perform an electrochemical prereduction step in a neutral phosphate buffer electrolyte. In this prereduction step, the Cu_2O cubes are partially reduced to metallic Cu to produce a stable Cu/Cu_2O interface (pictured). The phosphate buffer beneficially inhibits the competitive hydrogen evolution reaction at low overpotentials.

The resultant Cu_2O-derived catalyst has the bulk structure of the Cu_2O cubes, but its surface is rougher and hence, there are more electrochemically active sites on which the NO_3RR can occur. The Cu_2O-derived catalyst has a Faradaic efficiency of 93.9% and a yield of 219.8 μmol h^{-1} cm^{-2} for NH_3 at a potential of −0.9 V versus the reversible hydrogen electrode. "This performance is superior to most Cu-based catalysts under similar reaction conditions," says Zhong. "In addition, the catalyst exhibits negligible performance degradation over seven consecutive rounds of the reaction."

"Our next step is to improve the ammonia selectivity and yield at low overpotentials by regulating electron configuration of Cu-based catalysts and structure optimization of the electrode," says Zhong. In addition, the researchers envisage replacing the H-type electrochemical cell used in the experiments with a flow cell to increase the mass transport efficiency and hence, achieve higher yields of ammonia production. "More generally, using electricity from renewable energy sources to power the electrocatalytic reduction of nitrate to ammonia has the potential to replace the energy-intensive and polluting Haber–Bosch process," concludes Zhong.

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