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Boosting Nitrate-to-NH_3 Efficiency on Co_3O_4/Cu_xO_y Electrode by Tailoring Electrochemical Surface Activation

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Ammonia (NH_3) production is a process of high scientific, technological and commercial interest due to its wide range of applications, such as fertilizers and fuels. The Haber-Bosch industrial process consists of the reaction of N_2 and H_2 gases under high temperature (~500°C) and pressure (200-300 atm) conditions and, due to the high energy demand, it consumes 1-2% of the total energy produced worldwide annually.[1] Electrochemical nitrate reduction (NO_3RR) emerges as a promising alternative, as the energy required can be supplied in the form of electricity and produced by renewable sources.[2] Cobalt/Copper-based dual site electrocatalysts have shown promising results for NO_3RR, such as high efficiency, selectivity and stability.[3] In order to establish its applicability in a multitude of electrochemical setups, the Co_3O_4/Cu_xO_y electrocatalyst was developed through a three-step process: i) electrodeposition of metallic cobalt on copper, ii) electrodeposition of cobalt oxalate and iii) calcination of the resulting material in atmospheric air. SEM/EDX revealed Cu_xO_y porous agglomerates (1.7 to 3.2 µm) and Co_3O_4 nanowires (~0.4 µm diameter) homogeneously distributed over the catalyst surface. F_{2g}, E_g and A_{1g} vibrational modes of Co_3O_4 and A_g of CuO were found in the Raman spectra. XRD patterns identified the presence of Cu_2O and Co_3O_4 cubic phases and planes of monoclinic CuO. The electroactivity was evaluated by slow CV of 1 mV s^{-1}, which shows the onset for NO_3RR at 0.20 V_{RHE} and a multi-step reaction to NH_3. Aiming to boost nitrate-to-NH_3 efficiency, two electrochemical surface activation protocols were applied in NaOH 1.0 mol L^{-1}: i) 10 CV cycles from 0.15 to -0.40 V_{RHE} at 20 mV s^{-1} (CV-activated) and 1-h chronoamperometry at -0.30 V_{RHE} (CA-activated). At -0.2 V_{RHE}, CA-activated enhanced the FE (and YR) of NH_3 to 94.4 ± 3.1% V_{RHE} (43.4 ± 3.2 µmol h^{-1} cm^{-2}) *versus* 38.8 ± 6.9% (26.8 ± 9.2 µmol h^{-1} cm^{-2}) of the CV-activated. Surface (XPS) and structural characterization (*in situ* XAS) suggest that the increased performance and selectivity is due to the formation of Cu^0/Cu^+ and $Co_3O_4/Co(OH)_2$ active sites favored by the chronoamperometric pre-treatment. The dissolution process during electrochemical activation was evaluated by *on line* ICP-MS. Overall, the dissolution of Cu and Co in negative potentials were observed, however, much less pronounced in CA-activated method which clearly indicates the preservation of the active sites. Identification of the reaction intermediates was assessed by *in situ* FTIR and *on line* DEMS, converging to the idea that NH_3 was mainly formed by sequential hydrogenation of NO instead of the decomposition of hydroxylamine while N_2 and N_2H_4 were found to be byproducts.

References

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