



Unintended cation crossover influences CO₂ reduction selectivity in Cu-based zero-gap electrolyzers

Received: 5 February 2023

Accepted: 21 March 2023

Published online: 12 April 2023

Check for updates

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Membrane electrode assemblies enable CO₂ electrolysis at industrially relevant rates, yet their operational stability is often limited by formation of solid precipitates in the cathode pores, triggered by cation crossover from the anolyte due to imperfect ion exclusion by anion exchange membranes. Here we show that anolyte concentration affects the degree of cation movement through the membranes, and this substantially influences the behaviors of copper catalysts in catholyte-free CO₂ electrolyzers. Systematic variation of the anolyte (KOH or KHCO₃) ionic strength produced a distinct switch in selectivity between either predominantly CO or C₂₊ products (mainly C₂H₄) which closely correlated with the quantity of alkali metal cation (K⁺) crossover, suggesting cations play a key role in C-C coupling reaction pathways even in cells without discrete liquid catholytes. Operando X-ray absorption and quasi in situ X-ray photoelectron spectroscopy revealed that the Cu surface speciation showed a strong dependence on the anolyte concentration, wherein dilute anolytes resulted in a mixture of Cu⁺ and Cu⁰ surface species, while concentrated anolytes led to exclusively Cu⁰ under similar testing conditions. These results show that even in catholyte-free cells, cation effects (including unintentional ones) significantly influence reaction pathways, important to consider in future development of catalysts and devices.