

## Impacts of Unintended Cation Crossover through Anion Exchange Membranes on the Operation of Zero-gap Cu-based CO<sub>2</sub> Electrolysers

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CO<sub>2</sub> electroreduction (CO<sub>2</sub>ER) in gas-fed membrane electrode assemblies enable CO<sub>2</sub>ER at industrially relevant rates, and hence provide a promising strategy to scale-up this technology for future practical applications. Electrolysers based on anion exchange membranes (AEMs) have been introduced as a strategy for preventing undesired H<sub>2</sub> evolution at the cathode during CO<sub>2</sub>ER under zero-gap, catholyte-free conditions. One expects that the anolyte concentration should not significantly impact the performance of AEM-based CO<sub>2</sub> cathodes, since the (an)ion conduction direction is presumed to be from cathode to anode, maintained mainly by CO<sub>3</sub><sup>2-</sup> and HCO<sub>3</sub><sup>-</sup> derived from CO<sub>2</sub>. In contrast to this expectation, we observed that varied anolyte concentrations have substantial effects on the behaviors of zero-gap Cu-based cathodes. When using pure water or dilute alkaline anolytes, CO was produced as dominant product, while concentrated anolytes (>0.1M) directed the selectivity towards C<sub>2</sub>+ products. The parasitic H<sub>2</sub> evolution reaction was also influenced, being more suppressed for the dilute anolytes. Typically, selectivity trends for Cu-based catalysts are correlated to surface speciation (e.g. Cu oxidation states) and/or morphological changes during CO<sub>2</sub>ER. To control for these possibilities, we assessed both aspects as a function of anolyte employed. Using an adapted electrochemical reactor with X-ray transparent window, we conducted operando X-ray absorption spectroscopy (XAS) to track the catalyst in the zero-gap cell under true operation conditions. The results indicate complete reduction of the oxidized Cu surface occurs for all the investigated anolytes. Additionally, ex-situ XRD and SEM characterization revealed no obvious structural or morphological changes between samples tested with different anolytes. These observations suggest the varied selectivities we see are not simply explainable by composition or morphological/structural effects. Interestingly, under certain conditions, the unintended but significant migration of K<sup>+</sup> cations from the anolyte to the cathode surface was observed. The amount of K<sup>+</sup> detected at the cathode depends on the anolyte concentration, with a threshold concentration of approx. 0.1 M KOH required before significant amounts of K<sup>+</sup> crossover occurs, correlating with the selectivity switching from CO to C<sub>2</sub>+ products. This strongly suggests the absence or presence of cations can be a major influencer of CO<sub>2</sub>ER selectivity, even in catholyte-free configurations using AEMs. Moreover, cations were found to crossover even under open circuit, and therefore may be diffusing spontaneously along with water uptake by the membrane.

