## Why membranes matter: Influence of the ion exchange membrane in holistic process optimization of electrochemical CO<sub>2</sub> reduction

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## **Abstract:**

Carbon neutrality of the chemical industry requires a drastic decrease in CO<sub>2</sub> emissions of its production processes. Additionally, innovative technologies based on renewable feedstock must be developed to replace fossil fuel-based production. The conversion of CO2 and water to valuable chemicals, e.g., carbon monoxide and syngas, by co-electrolysis is a promising and heavily discussed strategy to approach this challenge. Although research on this process has vastly progressed, one essential question is not yet fully answered: Which ion exchange membrane is best suited for electrochemical CO<sub>2</sub> reduction in terms of economics? In this work, we developed a process model for holistic optimization of electrochemical production of CO and syngas, including downstream processing of the respective product gases with membrane gas permeation. The model considers state-of-the-art experimental data to describe the electrolyzer performance and optimizes the flowsheet design and process operation in order to minimize production costs. Our findings demonstrate that CO<sub>2</sub> electrolyzers with an anion exchange membrane and those with a bipolar membrane show competitive production costs for CO and syngas, respectively. Most surprisingly and against the often-ascribed detriment, the CO<sub>2</sub> pumping effect in the AEM electrolyzer does not significantly impair the economics of the process. Quite the contrary, the release of CO2 at the anode and the subsequent separation and recycling using gas permeation offers an efficient indirect regeneration of carbonate and bicarbonate species in the electrolyte. The holistic optimization also reveals that electrochemical membrane reactors for CO<sub>2</sub> reduction to CO need to be optimized for the selective synthesis of CO and not for the co-electrolysis to syngas. Moreover, our results highlight membrane gas permeation as a suitable separation technology for downstream processing in electrochemical CO<sub>2</sub>-to-CO conversion. Thus, in the future CO<sub>2</sub> electrolysis offers broad applicability for membrane technology in the up-and downstream processing.

**Keywords**: carbon utilization, holistic process optimization, electrochemical CO<sub>2</sub> reduction, techno-economic assessment

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