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Key parameters influencing CO₂ electrolysis performance in a zero-gap electrolyzer with acidic anolytes

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The increasing CO₂ emissions have heightened the interest in converting this gas into valuable products, with its electrochemical reduction (CO₂RR) emerging as a promising method due to the high energy efficiency and low-temperature operation. Despite advancements, zero-gap CO₂ electrolyzer configurations continue to face challenges, particularly when anion exchange membranes are used, where flow field carbonation and product/reactant crossover to the anode restrict the reactant to product carbon conversion efficiency to 50%. Cation exchange membranes with acid anolytes show potential for improved CO₂ conversion, but carbonation and electrode flooding still occur at high current densities. This study investigates the effects on the CO₂ conversion of the hydrophobic binder content (fluorinated ethylene propylene—FEPD) in the microporous layer (MPL) in the gas diffusion electrode (GDE) and the impact of hot-pressing the electrodes onto a cation exchange membrane (CEM) to form a membrane-electrode assembly (MEA).

As illustrated in Figure 1A, using commercial Pd/C as a catalyst and an anolyte composed by 0.5 M H₂SO₄ + 0.5 M K₂SO₄, results indicate that MPLs with lower FEPD content (~10% wt.) achieved slightly higher faradaic efficiency over the range of 50 to 200 mA cm⁻², (81% at 200 mA cm⁻²) and energy efficiency (35% at 200 mA cm⁻²), compared to those with 25% and 50% FEPD. Conversely, electrodes with higher FEPD content demonstrated enhanced stability, showing lower energy efficiency losses over extended operation. Hot-pressed MEAs demonstrated lower cell resistance than non-pressed assemblies, suggesting a reduction in membrane thickness. The hot-pressed MEA achieved a faradaic efficiency of approximately 63% at 200 mA cm⁻², which was lower than that of unpressed MEAs but demonstrated improved stability, with reduced losses over time in both faradaic and energy efficiency. Electrochemical analyses with an integrated reference electrode in the electrolyzer setup (Figure 1B) revealed that CO becomes the dominant product only after alkalization near the cathode surface. Conversely, at lower current densities, where the local environment is more acidic, liquid products are also observed.

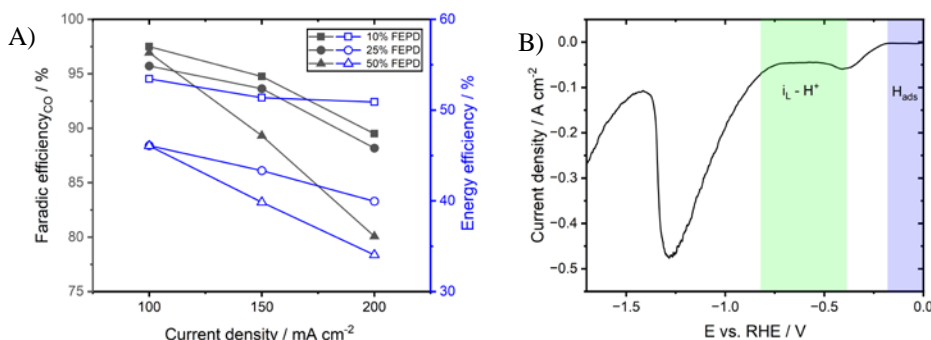


Figure 1. A) Faradaic and energy efficiencies at various current densities for MPLs with 10%, 25%, and 50% wt. FEPD. B) LSV curve for the MPL containing 25% wt. FEPD, obtained at 5 mV s⁻¹ with a CO₂ feed rate of 10 sccm.

References

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