Tandem Copper - Cobalt Phthalocyanine Electrodes Enable Enhanced Electrochemical CO_2 Conversion to Ethylene

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Achieving selective multi-carbon (C_2^+) products in electrochemical CO_2 reduction (ECR) remains challenging due to competing reaction pathways. Tandem catalyst architectures have emerged as an effective strategy to address this limitation by spatially separating CO generation and subsequent C–C coupling steps [1]. Controlling reaction pathways toward multi-carbon (C_2^+) products remains a major challenge. Tandem electrode architecture has recently attracted significant attention as an effective strategy to address this challenge by spatially separating reaction steps [2]. Integrating an effective CO-generating catalyst into architecturally designed gas diffusion electrodes represents a promising pathway for improving tandem catalyst performance [3].

Electrochemical measurements of the cobalt phthalocyanine (CoPc) electrodes revealed that a higher carbon black (CB) content led to FEs of up to 90% for CO at relatively low overpotentials, corresponding to current densities between -10 and -50 mA cm^{-2} and -0.56 to -0.9 V vs. RHE, while suppressing hydrogen evolution to approximately 10%. In contrast, electrodes prepared with lower CB loading exhibited slightly reduced CO selectivity but maintained stable FEs throughout the measurements. The combination of lower CoPc loading and higher CB content likely promoted improved catalyst dispersion and greater accessibility of Co-N_4 active sites. This observation is consistent with previous reports, which attribute with decreased catalytic efficiency at higher metal phthalocyanine loadings to aggregation effects that limit active site utilization. Based on its superior CO selectivity, lower hydrogen evolution, and stable electrochemical performance, the 1 to 10 ratio of CoPc to CB was chosen for subsequent tandem electrode studies.

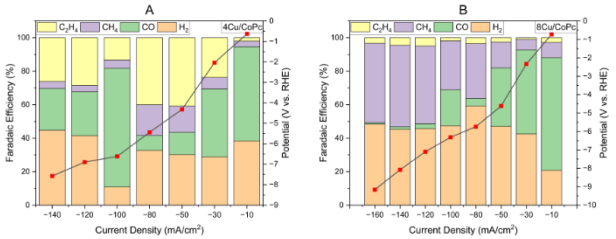


Figure 1: Different loadings of Copper - CoPc tandem electrode's FEs.

Copper electrodes were investigated following the CoPc studies to optimize sputtered copper loading, film thickness, and Nafion content for improved electrochemical performance.

The effect of copper loading and film morphology on product selectivity was subsequently evaluated to provide a reference for tandem electrode construction. Notably, lower copper loadings of 0.4 mg cm^{-2}, favored ethylene formation, achieving ethylene Faradaic efficiencies of approximately 20%. Whereas increasing the metal loading to 0.8 mg cm^{-2}, induced a transition toward methane-dominated pathways. This shift is likely associated with changes in local CO coverage and surface reaction environments that influence intermediate binding energies and proton-coupled electron transfer pathways. Based on these findings, 30 µl Nafion layered with 0.4 mg cm^{-2} copper loaded electrode was selected as the optimal platform for subsequent tandem electrode fabrication. Fabricated tandem electrode properties are given in the Table 1.

Table 1. Fabricated tandem electrodes specifications

	Cu loading (mg)	Area of Electrode (cm^2)	Nafion amount (µl)
4Cu/CoPc	0.4	1	30
8Cu/CoPc	0.8	1	30

The electrochemical results revealed clear loading dependent selectivity trends in the tandem electrodes. 4Cu/CoPc, incorporating a lower sputtered copper loading, favored ethylene formation and achieved FEs of approximately 40% at current densities of 50 and 80 mA cm^{-2} (Figure 1A). In contrast, the higher copper loading configuration (8Cu/CoPc) exhibited a pronounced shift toward methane production, with FEs exceeding 50% (Figure 1B). These findings underscore the critical role of copper loading in governing product selectivity and demonstrate the importance of catalyst design for targeting specific reaction pathways in tandem architectures.

References

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Kadir Türkmen is a researcher working on electrochemical energy conversion, with particular emphasis in electrocatalytic CO_2 reduction. He developed a strong foundation in designing and operating flow cells and flow electrolyzers during his graduate studies, where he concentrated on reaction mechanisms and catalyst performance. His research experience also includes work on H_2S splitting, contributing to a published study in this area. Türkmen is interested in advanced catalytic materials, with the goal of improving efficiency and selectivity in sustainable fuel production.
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