Electrochemical Plasma-Activated CO_2 Reduction at a Plasma-Water Interface

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Abstract: In this work, we investigate how the use of plasma-activated carbon dioxide at a water interface impacts electrochemical product generation. We design a novel non-thermal plasma electrode to discharge carbon dioxide plasma into water in an electrochemical cell with a Cu nanoparticle electrocatalyst. The plasma-water CO_2 electrocatalysis enhances generation of high-value multicarbon products compared to electrocatalysis alone.

1. Introduction

Electrochemical carbon dioxide reduction enables a sustainable pathway to harness renewable energy sources and upgrade recovered CO_2 to value-added carbon-based C_1 and C_2 chemical products, but its ability to generate more valuable and energy-dense higher order carbon products has been limited [1]. Non-thermal carbon dioxide plasma can be generated at ambient temperature and pressure and contains energetic excited oxygen and carbon species [2] that, when introduced to an electrocatalyst, could participate in reaction pathways that have higher activation barriers and lead to the generation of higher order carbon species. Further, plasma discharges over water in an electrochemical cell generate plasma-activated water, introducing solvated electrons and secondary reactive oxygen species [3] that may participate in electrocatalytic reactions towards a wider variety of possible products.

Here we demonstrate the novel combination of plasma pre-activation of CO_2 at the electrolyte surface of an electrochemical cell and subsequent electrocatalytic upgrading into valuable higher order products.

2. Methods

A 12 W CO_2 DC plasma jet is discharged in the air gap between a stainless rod and a grounded electrolyte surface containing 0.1 M $KHCO_3$. A Cu nanoparticle electrocatalyst is positioned in the electrolyte, and experiments with varying electrochemical current density are conducted. Online gas chromatography is used to analyze gaseous products, and ion chromatography and nuclear magnetic resonance are used to measure products in the electrolyte.

3. Results and Discussion

Plasma activation did not significantly affect C_1 partial current density at low current densities (Figure 1). At 15 and 20 mA cm^{-2}, though, the partial current density for C_1 products generated with plasma on fell below that for plasma off. Similarly, C_2 product generation was not affected by plasma at low current densities, but at 15 mA cm^{-2}, the C_2 partial current density became much larger with plasma off than with plasma on (Figure 1b).

Conversely, plasma activation enhanced the partial current density for C_3 and C_4 products with plasma on compared to plasma off (Figures 1c-1d). The only C_4 product detected, n-butane, was only detected for plasma on experiments.

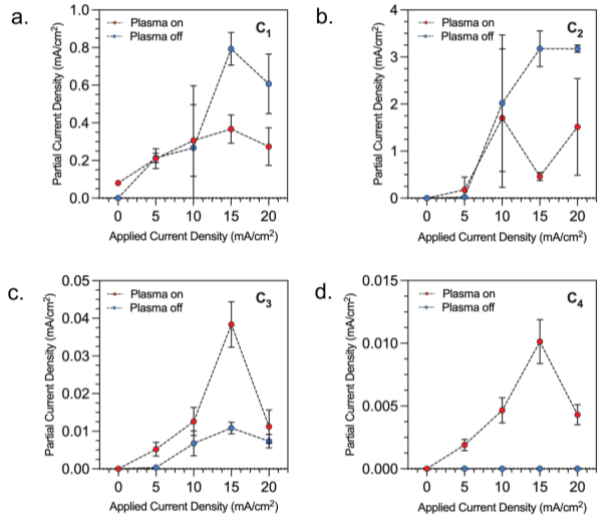

Fig. 1. Partial current density for plasma on and plasma off electrocatalytic CO_2 reduction to organic products by carbon number: a) C_1, b) C_2, c) C_3, and d) C_4.

4. Conclusion

We demonstrate improved generation of higher order, valuable chemical products using plasma pre-activation in CO_2 electrocatalysis. We conduct further experiments that interrogate how plasma gas activation and plasma-liquid interactions contribute to changes in product formation.

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References

[1] Saravan. A et al, Chem. Eng. Sci., **236**, 116515 (2021)
[2] George, A et al, Renew. Sustain. Energy Rev., **135** (2021)
[3] Rumbach, P et al, J. Electrochem. Soc., **163** (10) (2016)