Electrochemical Fingerprinting of By-products Generated During CO_2 Electroreduction

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The electrochemical conversion of CO_2 into fuels and value-added products is a promising strategy to mitigate climate change [1]. Among the approaches investigated, the electrochemical CO_2 reduction reaction (CO_2RR) stands out for its efficiency and environmental feasibility [2]. This study proposes a cyclic voltammetry-based method to identify and differentiate by-products formed during CO_2RR, aiming to clarify reaction mechanisms and improve electrocatalyst selectivity. Electrolyte solutions were prepared with 0.1 mol L^{-1} $KHCO_3$ in deionized water, containing 500 ppm of selected by-products (methanol, formate, acetate and ethanol). Samples were purged with N_2 or CO_2 to ensure saturation and oxygen removal. Cyclic voltammetry scans were initiated at positive potentials, extending into the cathodic region, and returning to the starting point. Distinct electrochemical profiles were observed for each by-product. In the case of formate, peaks were detected at -0.07 V, -0.37 V, -0.69 V and 0.02 V vs. Ag|AgCl, corresponding to platinum oxide reduction, oxidation mediated by CO, H_{ads} oxidation and strongly CO_{ads} on the platinum surface, respectively. The results demonstrate that cyclic voltammetry is a sensitive technique for monitoring CO_2RR by-products, supporting mechanism elucidation and catalyst optimization.

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References:

[1] Energy Agency, I. World Energy Outlook (2024)

[2] Badaway, I. M., Ismail, A.M.; *et al*., Scientific Reports, vol 12 (2022)