Short Communication

Influence of Supporting Electrolyte on the Electrocatalysis of CO₂ Reduction by Cobalt Protoporphyrin

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The electrochemical conversion of CO₂ into high-value fuels is a promising technique to reduce CO₂ emission and relieve the crisis of fossil fuel depletion. Here we report the influence of supporting electrolyte on the electrochemical reduction of carbon dioxide catalyzed by cobalt protoporphyrin. Phosphate anion strongly coordinates to the cobalt center leading to the positive movement of Co^{III}/Co^{II} redox peak and the difficulty formation of carbon monoxide. Alkali cations, such as Li⁺, Na⁺ and K⁺, exhibit different catalytic activity and product selectivity. The efficiency of the hydrogen evolution reaction from direct proton (H⁺) reduction is increasing with the increase of the cation size. That is because the smaller cations preserve larger hydration number of water leading to geometrical hindrance, which hinders the diffusion of H⁺ to the electrode surface. On the contrary, the formation of CO and CH₄ is decreasing with increasing of the cation size. This is resulted from the coordination of alkali cations to the oxygen atom of the key intermediate of CO₂ electrochemical reduction, CO₂^{•-} anion, through ion-pairing. The smaller the cation size is, the stronger the ion-pairing is, helping the cleavage of one of the C-O bond. The deeper insight into the ionic effects and reaction mechanism of the electrochemical reduction of CO₂ suggest new strategies for the utilization of CO₂.

Keywords: Cobalt protoporphyrin, CO₂ electrochemical reduction, alkali cations, phosphate

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