

Electrochemical Production and Application of Formic Acid / Formate by Low Temperature H₂O,CO₂-Co-Electrolysis

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Abstract

Electrochemical CO₂ reduction by low temperature H₂O,CO₂-Co-Electrolysis is a way to valorize CO₂ as a feedstock to produce valuable chemicals and/or to store excess renewable electricity as chemical energy. Depending on pH and electrocatalyst, formic acid or formate is formed which is a favorable target product to reach both of these objectives and to contribute to the sector coupling. Even though, to date, its application in industry is rather limited, formic acid / formate shows large potential for a greener chemistry. As energy storage chemical, formate has benefits in terms of handling and storage, whereas in contrast pure formic acid has a much higher volumetric energy density. For both of them, the electricity can easily be recovered either in direct fuel cells (Direct Formate Fuel Cell or Direct Formic Acid Fuel Cell), or by highly selective heterogeneously catalysed decomposition to hydrogen which is supplied to a PEM fuel cell. With the intention of producing chemicals of even larger added value, formic acid / formate can also be used as reactant in consecutive reaction processes. Examples would be the use in fermentation with formatotrophic bacteria to produce higher hydrocarbons such as isobutene which is currently investigated in the EU project eForFuel ([1], www.eformuel.eu) or the use as a transportable precursor for local synthesis gas / CO production in hydroformylation or carbonylation processes. A related idea would be the decentralized production of formic acid / formate and the centralized conversion into synthesis gas and subsequent Fischer Tropsch synthesis. However, the electrochemical production of formic acid / formate suffers from two major issues to be solved for an industrial application. One of those is the low energetic efficiency, resulting from poor reaction kinetics even with the use of a state-of-the-art catalyst, which is currently subject of intense research. Besides improving the reaction kinetics, optimization of reactor and electrode design as well as electrolyte is crucial to minimize potential losses. The other issue is the limitation in current density caused by the low solubility of CO₂ in aqueous media and, thus, by severe mass transport limitation. The most promising solution, to date, is the use of gas diffusion electrodes (GDE) [2,3]. These electrodes comprise a highly porous structure, which is partly wetted by electrolyte while retaining open pores for CO₂ transport. Our research focuses on a certain type, the Single Layer GDE. In contrast to multilayered GDEs, much higher current densities up to several hundred mA/cm² are achievable [4]. This is due to the hierarchical porosity and distinct hydrophobicity of the electrode leading to a comparatively large three-dimensional three phase boundary, but with the downside of a lower stability. Increasing the mechanical stability, as well as the three phase boundary inside the GDE is subject of our current research.

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