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Flexible and Scalable Microreactor Concept for the Kolbe-Electrolysis of (Biomass-Recovered) Carboxylic Acids

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PURPOSE OF THE ABSTRACT

Kolbe-Electrolysis to Reduce Carbon Footprint in Chemical Production

A renaissance of electrochemistry for the synthesis of organic compounds is observable which is driven by the search for green synthesis routes and the ambition for a direct use of sustainably generated (excess) electric current. In addition, the use of organic feedstock from biomass or fermentation contributes to the defossilation of chemical production and plays a key role in the reduction of the carbon footprint. Medium chained fatty acids (MCFA) can be recovered from biomass via hydrolysis or fermentation, representing promising platform chemicals which are used as starting materials in Kolbe-Electrolysis to synthesize valuable chemicals like solvents, fine chemicals, synthetic fuels or important monomers. Accordingly, the Kolbe process brings together the usage of electrons as reagents as well as the application of renewable generated carbon sources.[1,2]

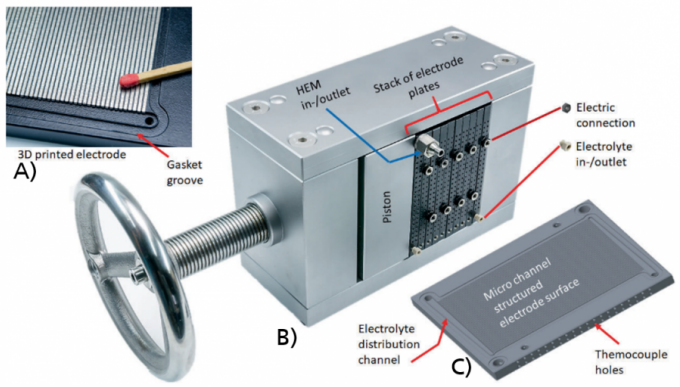
There is relevant attention on this old electrochemical reaction also considering the combination of fermentation and electrolysis. However, focus is on small lab-scale electrolysis cells operated most likely in batch mode. An electrochemical reactor, that allows higher throughputs and current densities to address industrial relevance is missing.[3,4]

Scalable and Flexible Electrochemical Microreactor Concept

Fraunhofer IMM recently developed an innovative reactor concept for continuous operation addressing especially the aspects modularity and accessibility of production scale. The plate stack designed reactor allows the operation of one electrochemical cell on a laboratory scale as well as the extension to larger numbers of electrochemical cells in view of increasing throughput. The 3-D-printed electrodes offer an active electrode surface area of 42.56 cm2 via 56 micro channels (100 mm x 0.76 mm x 0.15 mm) and a volume of 0.6 cm3 per structured plate side. Depending on the desired reaction, various electrode materials can be deposited on the reaction channels allowing a highly flexible application of the microreactor. [5]

For the Kolbe-Electrolysis electrodes are electrodeposited with platinum and n octanoic acid is used as model substance for MFCA. Electrolysis is conducted in alkaline aqueous solution where the organic product phase can be isolated constantly from the reaction mixture. In addition, it facilitates to directly electrolyze the alkaline aqueous extraction broth which is used to recover fatty acids from biomass. Parameter variation reveals a trend towards increasing productivity and decreasing energy consumption for high flow rates and moderate to high current densities. Electrolysis with two and four cells in parallel applying same conditions validated the scaling potential of the reactor concept. With further improvement of the electrode stability, electrolysis with higher applied current densities (5 kA m-2) was feasible with consistent Kolbe selectivity (95%), increasing productivity to 0.65 mol h-1 for two electrochemical cells. The development of a real continuous process with constant feed of carboxylic acid added to the recycled aqueous reaction mixture is currently under investigation.

FIGURES



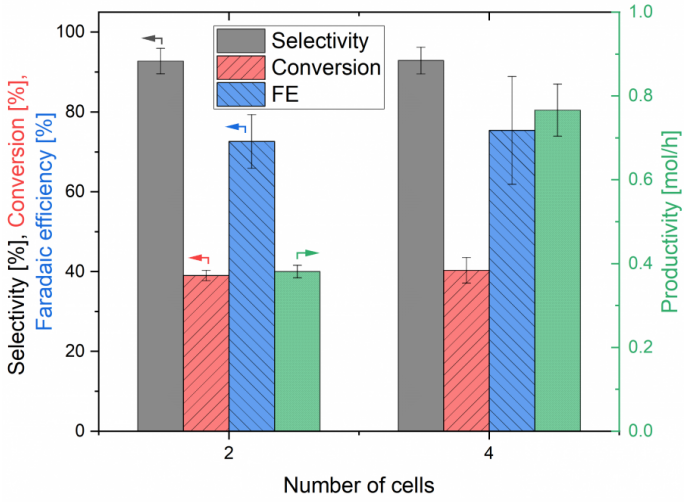


FIGURE 1

Electrochemical microreactor

Picture of micro-structured electrode with PTFE coating (A), reactor housing to assemble electrodes with in-/outlet of electrolyte and heat-exchange-medium (HEM) and electric connection (B), CAD illustration of single reactor plate.

FIGURE 2

Scaling potential

Conversion of carboxylic acid, selectivity and Faradaic efficiency (FE) for main Kolbe products (tetradecane, heptane and 1-hepten) and productivity depending on the number of electrochemical cells operated in parallel (2.6 s residence time, 3 kA m-2).

KEYWORDS

Kolbe-Electrolysis | Electrochemical microreactor | Carboxylic acid | Scaling potential

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