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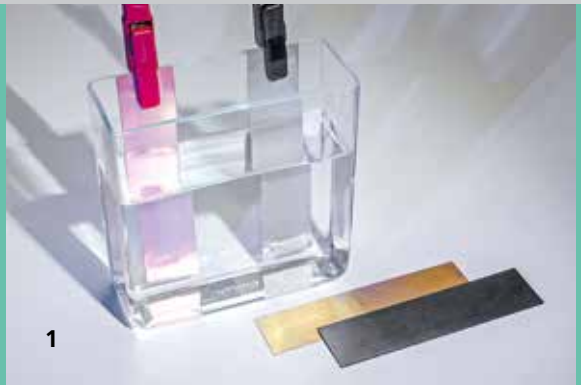

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1 *Electrodes - central elements of electrochemical cells*
2 *Reactor plate with microstructured electrode (Pt coated) and integrated heat exchanger*

PRODUCTION OF CHEMICALS BY ELECTROCHEMICAL MICROREACTORS

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There is currently a renaissance of electrochemistry for the synthesis of organic compounds observable. It is driven by the search for „green" synthesis routes and by the emergence of novel synthesis strategies. But also the ambition for a direct use of sustainably generated (excess) electric current plays a role. So, organic electrochemistry is considered as future technology for the environment-friendly production of chemical compounds. Nevertheless, there are still challenges and problems linked to electrosynthesis and there is also a need for flexible reactor concepts.

Advantages of electrochemical microreactors

Electrochemical microreactors contribute to a resolution of these issues. Fraunhofer IMM has a long track in developing and realizing electrochemical microreactors characterized by small electrode distances and great surface-to-volume-ratios as key features [1].

These thin-gap electrochemical microreactors disclose the following advantages:

- Attainment of high current densities over the whole electrode surface
- Reduction of the amount of required conducting salts or even conducting salts free operation
- Large surface areas for electrode reactions
- The integrated heat exchanger structures remove reaction heat efficiently and avoid in consequence hot spots decreasing reaction yield
- Low voltage drop by low Ohmic resistance
- Enhanced selectivity by constant and uniform current density distribution, homogeneous flow and defined residence times

Novel, flexible reactor concept

In order to meet current needs in electrosynthesis, Fraunhofer IMM developed a novel innovative reactor concept addressing especially the aspects modularity, flexibility,

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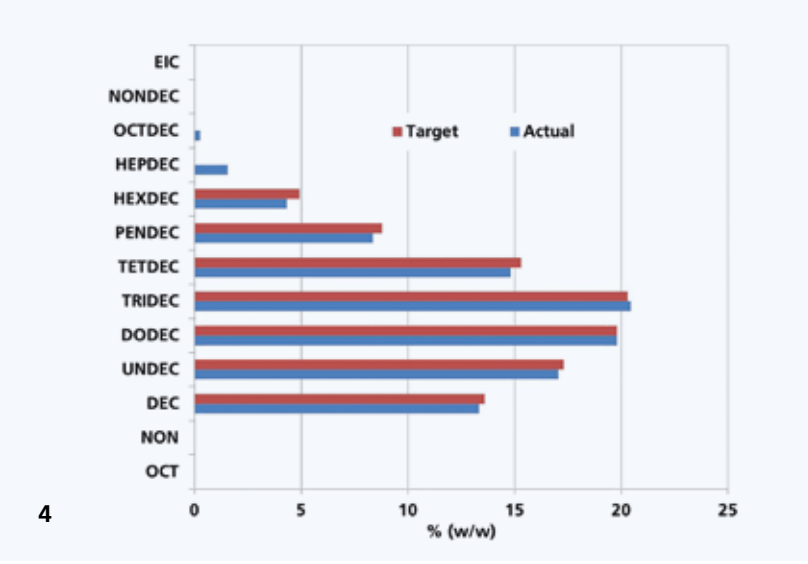

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high pressure operation and accessibility of production scale.
This new reactor is designed as plate stack reactor as fundament for a flexible reactor concept. The plates bear the structured electrodes typically on both sides and are equipped with an integrated heat exchanger. A combination of additive manufacturing to realize the base plates with their complex fluid structures, surface coating (e.g. with PTFE) of the plates for electric insulation, milling to create the micro channels on the plates surface and electroplating to deposit different electrode materials are used to realize the versatile electrochemical microreactor.

The basic reactor plates are characterized as follows:

- Electrode outer dimension: 100 mm x 118 mm
- Active electrode surface per structured plate side: 53.6 cm^2 provided via 67 micro channels
- Channel dimensions: 800 µm in width, 100 µm in depth and 100 mm in length
- Channel volume per structured plate side amounts to 0.5 cm^3

The reactor is designed for operation conditions up to 200 °C and up to 100 bar, for electrolyte flow rates up to 100 mL min^{-1} and for coolant flow rates up to 50 mL min^{-1} per electrode assembly. The reactor concept allows a multitude of operation possibilities:

- Use of 1 to 9 electrode assembly units in the overall reactor housing
- Operation of the electrode assemblies as mono or bipolar cells
- Operation of the electrode assemblies as undivided or divided cell (by use of diaphragmas or ion exchange membranes (e.g. PEM))
- Parallel, serial or mixed operation of the electrode assemblies. Therewith, numbering-up and scale-up possibilities are also given.
- Individual designation of electrode assemblies is feasible when using a multichannel galvanostat

As electrode materials / electrode coatings stainless steel, platinum and boron doped diamond (BDD) are already in place. Materials as e.g. nickel, graphite, glassy carbon, lead or lead oxide are in principle also feasible as electrode materials.

Application possibilities and examples

In general, electrochemical procedures are broadly applicable from water treatment, hydrogen peroxide production to a multitude of electroorganic synthesis like the oxidation of alcohols, phenols, aldehydes, halogenation of aromatics, alkoxylation reactions, synthesis of aromatic aldehydes, C-C cross coupling reactions and reduction of nitro groups to name of few.
An evolving application focus for Fraunhofer IMM is the cation pool and cation flow method as modern organic synthesis approach. In the field of the Kolbe electrolysis Fraunhofer IMM already collected considerable experience [2].
The Kolbe electrolysis is formally a decarboxylative dimerization of two carboxylic acids or carboxylate ions.
Radical intermediates are formed which then mainly react by C-C-coupling to dimer products. In case that a mixture of different carboxylates is used, all combinations of them are generally seen as product. Depending on electrolysis conditions further oxidation of the radicals to cation intermediates and follow-up products can occur.

Kolbe electrolysis in context of industrial production of fuels from fatty acids had been economically not attractive due to the high costs of reactants, the high electric power demand, but also the requirement of cells with >100 µm thick Pt-electrodes. Changed boundary conditions (potential availability of fatty acids from renewable resources or even waste streams, use of renewable energy from wind and photovoltaic) led to a revived interest. Application of an electrochemical microreactor with a stainless steel electrode with a thin (only 5 µm) Pt-coating by Fraunhofer IMM yielded a reduction of material costs and improved productivity. Precise control of the process conditions furthermore prevented follow-up processes. By this, precise alkane product composition (e.g. resembling jet fuel) can be attained when using rightly chosen carboxylates mixtures.

References

[1] A. Ziogas et al., J. Appl. Electrochem. 39 (12) (2009) 2297-2313.
[2] A. Ziogas et al., WO 2016/70075 A1.

3 *Assembled flexible electro chemical microreactor with four reactor plates*

4 *Kolbe electrolysis: Comparison target (jet fuel composition) and achieved results*