Upscaling electrochemical reduction of CO_2

In situ separation of formic acid in three compartment cell

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Introduction

The electrochemical reduction of CO_2 is a potentially important field of study that directly addresses concerns regarding both energy consumption and climate change. The main challenges are the poor selectivity due to the competing hydrogen evolution reaction, the high overpotential and the low current efficiency.

These challenges can be overcome in part by using gas diffusion electrodes in a flow cell where the tin catalyst is deposited on a carbon support. Tin catalysts have been shown to be selective for the production of formate ions under alkaline conditions which subsequently need to be transformed to formic acid.

Here we propose an *in situ* separation concept comprising of a three compartment electrochemical cell. We built a mass transport model which can be used to evaluate the scaling up of the electrochemical conversion and separation to formic acid.

Anode: $H_2O \rightarrow \frac{1}{2}O_2 + 2H^+ + 2e^-$ $\quad E^0 = -1.23$ V

Cathode: $CO_2 + H_2O + 2e^- \rightarrow HCOO^- + OH^-$ $\quad E^0 = -0.2$ V

Overall: $CO_2 + H_2O \rightarrow HCOO^- + H^+ + \frac{1}{2}O_2$

Three compartment cell separation concept

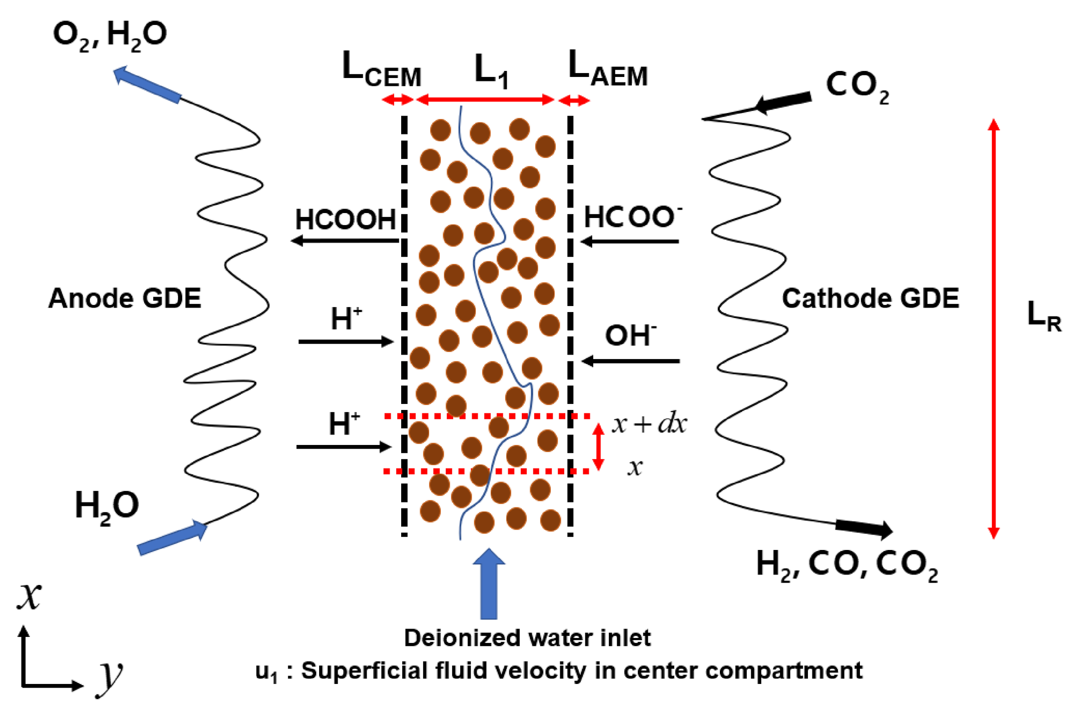

Figure 1. Schematic representation of the three compartment cell for the in situ separation of formic acid

The overall reaction consists of CO_2 and water reacting to form formic acid and oxygen.
When an electrolyzer is used for this reaction, formate ions are produced at the cathode and protons are produced at the anode. They need to recombine to form formic acid.

Gas diffusion electrodes can be used to effectively separate the electrolyte from the gaseous reactant (CO_2). In this way, the electrolyte can be highly alkaline as it is required for the reaction to occur with a high selectivity and current density.

The formate ions are directly synthesized electrochemically from CO_2 when tin is used as a catalyst on the cathode. At the anode, the water oxidation reaction occurs having as main product O_2 gas and H^+.

By using ion selective membranes, a middle compartment can be created as depicted in Figure 1. There, formate ions from the catholyte can cross the anion exchange membrane, the proton from the anolyte can cross the cation exchange membrane and they together can recombine to form formic acid aqueous solution. The formic acid product can thus be extracted from the reactor.

Results and outlook

Model validation with experimental results

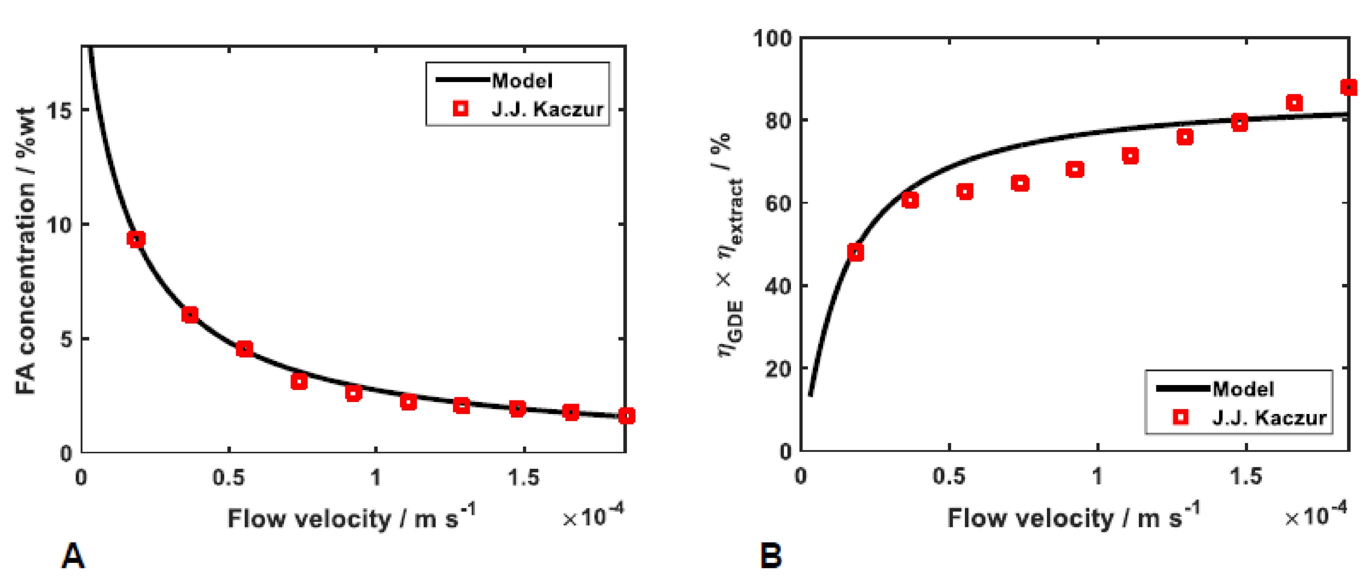

Figure 3. Formic acid Faradaic efficiency as a function of center flow velocity and catholyte inlet concentration of $HCOO^-$ depicted by the black continuous lines. Experimental data depicted by the red points.

The mass transport model is validated using experimental results published by Kaczur et al.* Figure 2 shows a good agreement between the model and the experimental data.

*H. Yang, J. J. Kaczur, S. D. Sajjad, and R. I. Masel, "Electrochemical conversion of CO2 to formic acid utilizing Sustainion™ membranes," *Journal of CO_2 Utilization,* vol. 20, pp. 208-217, 2017/07/01.

The main goal of our research is to develop a concept that allows a technical and economical viable upscaling of the process.

Model prediction of electrolyzer scale up

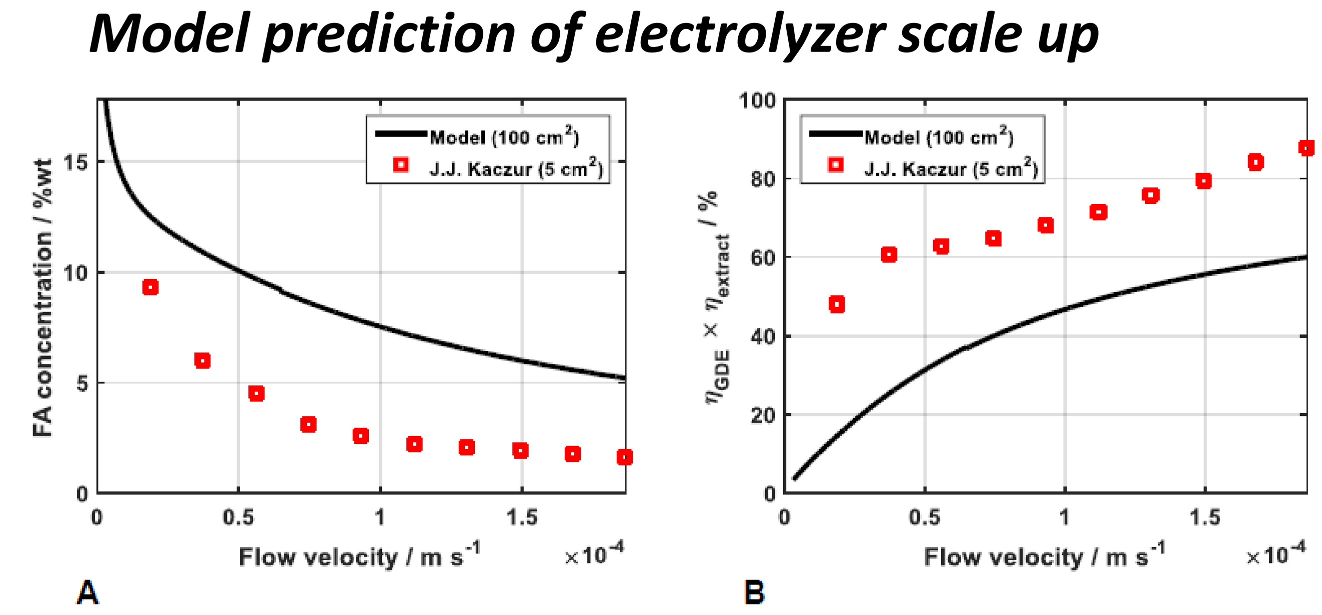

Figure 3. Formic acid Faradaic efficiency as a function of center flow velocity and catholyte inlet concentration of $HCOO^-$ depicted by the black continuous lines representing a 100cm^2 electrode. Experimental data depicted by the red points representing a 5cm^2 electrode.

The validated mass transport model is used to predict the behavior of the electrolyzer upon scaling up. Figure 3 shows how increasing the cathode surface are from 5cm^2 to 100cm^2 leads to an increase in formic acid concentration and decrease in overall efficiency.

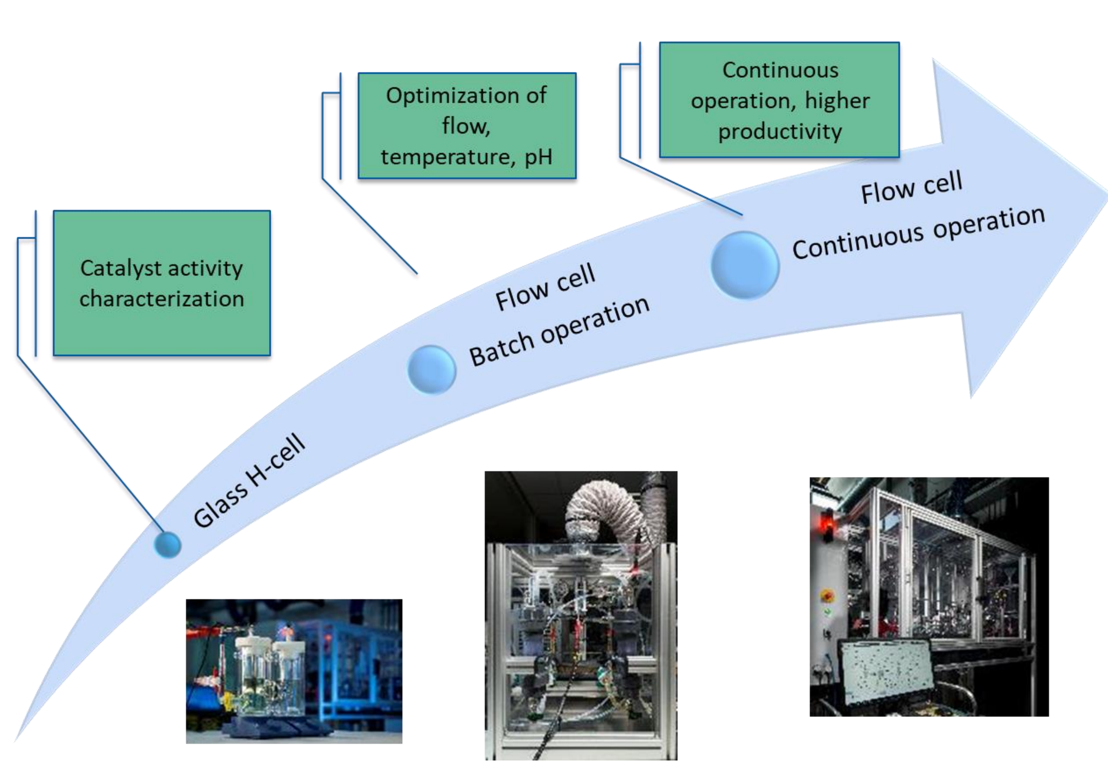

Figure 4. The route to scaling up the electrochemical reduction of CO_2

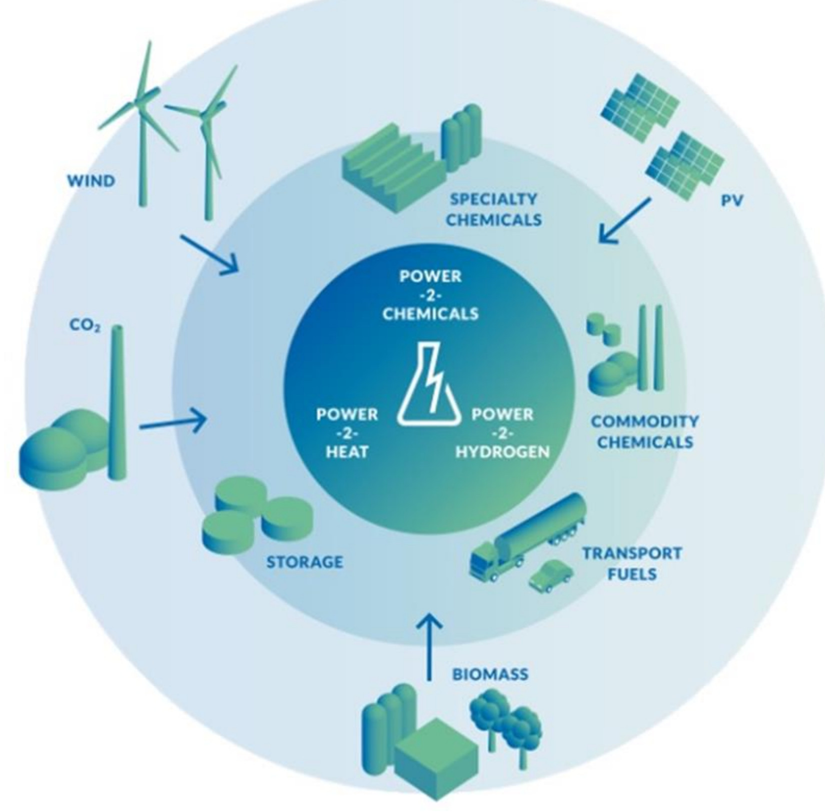

Figure 5. Voltachem program. Electrification of the chemical industry

Figure 6 Electrolyser system (1600 cm^2) developed at TNO for continuous electrochemical production.

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