ELECTROCHEMICAL SYNTHESIS OF CARBOXYLIC ACIDS FROM CARBON DIOXIDE

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An immediate solution is needed to abate ramifications from global warming caused by high concentrations of atmospheric CO_2. An economically viable solution is to redefine waste CO_2 emissions as a usable feedstock via CO_2 electrolysis. CO_2 electrolysis involves using electricity to reduce CO_2 into fuels and chemical feedstocks. In particular, carboxylic acids, specifically formic acid and acetic acid, are of interest due to their compatibility in bioreactors for plastic, pharmaceutical, and food production. This dissertation is focused on improvement of electrochemical conversion of CO_2 into carboxylic acids.

In the first part of this dissertation, improvements for a tandem CO_2 to carbon monoxide to acetate system is investigated. The material properties of anion exchange membranes are connected to the resulting carbon monoxide electrolysis performance. The selectivity towards acetate is improved by up to 15% through synergistic coupling of anion exchange membranes with high ethanol crossover and partial ethanol oxidation promoting anodes. In addition, insight into the molecular design of anion exchange membranes for carbon monoxide electrolysis is investigated by comparing membranes with different pedant groups. In addition, improvements to hardware design for scale-up CO_2 and carbon monoxide electrolyzers, focused on sealing, compression, and flow dynamics, are also discussed.

In the second part of this dissertation, alternative electrolyzer architectures for high purity carboxylic acid production are discussed. First, a porous solid electrolyte architecture that utilizes a packed ionic resin interlayer for recombination of carboxylates with protons is investigated. The packed resin interlayer is redesigned into a single ionomer wafers and gasketting is redesigned to ensure uniform fluid flow for improved consistency. To determine system bottlenecks, an approach focused on key interfaces is taken to diagnose that adequate contact at anion conducting interfaces is required for low overpotential operation in deionized water. Two solutions are presented

to improve interfacial contact at anion conducting interfaces to demonstrate low overpotential operation.

Second, improvements of a perforated bipolar membrane architecture for concentrated formic acid production are presented. The formic acid removal at the anode is improved through utilization of an interdigitated flow pattern and increasing convection induced by momentum. The effluent concentration was improved from 0.1 M in the previous publication on this architecture to 3.78 M using the improved operating conditions. In addition, the reactor is scaled from 25 cm^2 to 400 cm^2 by designing a mechanically robust perforation design.

In summary, significant improvements towards electrochemical synthesis of carboxylic acids from CO_2 is demonstrated, further advancing the economic viability of this technology. A final takeaway perspective on remaining gaps in knowledge and future research opportunities in the field to develop economical CO_2 electrolyzers will be briefly discussed.