Centre for Sustainable & Circular Technologies

Centre for Sustainable and Circular Technologies; University of Bath

Project Title:	Powering the future: understanding mechanistic pathways in electrocatalytic CO_2 reduction
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Industrial Partner:	Catalytic Innovations

Project Summary

The electro-catalytic reduction of CO_2 and H_2O to CO, formaldehyde, formic acid, MeOH or higher alcohols holds great potential to give access to key chemical building blocks with much reduced carbon footprint compared to traditional processes based on fossil resources. When powered by renewable electricity from wind, tidal or solar the process mimics natural photosynthesis that not only saves fossil resources but actively consumes anthropogenic CO_2. Because the reaction is not dependent on industrial infrastructures or geologically confined resources, it also offers the prospect of small-to-medium scale decentralised chemical and fuel production. The development of efficient electrocatalysts is key to tuning the selectivity of the reaction and increase its efficiency so that real-world application may become viable.

Promising advances in catalyst design have recently been made, but our understanding of their mode of action is still based on empirical optimisation, *ex-situ* characterisation and computational modelling. A general complication for detailed *in-situ* studies of electrocatalysts is that the electrochemical responses are difficult to match with independent characterisation of the chemical transformations occurring in the electrolyte under reaction conditions. An accurate mapping of what products are generated over time at different pH values and potentials applied would greatly enhance our understanding of their electrochemical signatures, and allow distinguishing concentred versus consecutive product formation pathways that help to understand the overall mechanism. This is especially important in the case of CO_2 reduction, as in addition to the various reduced carbon species that may form, competition with proton reduction to give H_2 is crucial to improving the efficiency of the process. Currently no methods exist to capture all of these events under meaningful working conditions.

Bath's Dynamic Reaction Monitoring (DReaM) Facility offers a unique combination of complementary *operando* techniques currently comprising multi-nuclear FlowNMR, head-space MS, liquid phase MS, UV-vis, and HPLC. All of these are part of a fully integrated and computer-controlled system that is able to track reaction intermediates and products in real time to give comprehensive insight into complex reaction networks. We have successfully demonstrated *in-situ* analysis of reactions under similar conditions to electrocatalytic CO_2 reduction, and have established the quantitative detection of all relevant reaction products in aqueous solution including H_2, CO, H_2CO, HCOOH, H_3COH and higher alcohols. Fast 2D techniques can complement the ^1H NMR analysis, and the use of $^{13}CO_2$ will make direct ^{13}C NMR monitoring possible. Cross-over experiments with unlabelled CO or CO_2

will give further insights into the sequence of higher product formation. This would be the first demonstration of real-time *in-situ* analysis of an electrocatalytic reaction by high-resolution FlowNMR spectroscopy, and the ability to freely modulate the electrochemical conditions during the analysis will provide unprecedented insights into the reaction network, paving the way to the rational design of improved catalysts and optimized reaction conditions.

The project will be conducted in the CSCT and in partnership with Catalytic Innovations and their partner Air Co. They have developed some highly active Cu-based CO2 reduction catalysts and proprietary electrochemical flow cell designs that are well suited for interfacing with our flow setup at Bath. Their launch of “the world’s first carbon-negative vodka” recently made international news. Based in MA with offices in RI and NY (USA), they have been industrial partner of the DReaM Facility since its foundation in 2016.

Sustainability issues addressed

This project has the potential to give access to key chemical building blocks with much reduced carbon footprint compared to traditional processes based on fossil resources.