Electrocatalytic Conversion of Carbon Dioxide to Value-Added Chemicals

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Abstract

Carbon capture and utilization is becoming an increasingly important avenue to mitigate carbon dioxide (CO_2) emissions and levels in the atmosphere. Developing ways to utilize captured CO_2 can either partially or completely offset the cost of capturing CO_2, facilitating the implementation of carbon capture systems. One solution is to use CO_2 as a feedstock to synthesize chemicals. Currently, only a few commercially made chemicals including ethylene carbonate, salicylic acid, and urea are produced using CO_2 as a feedstock, so an opportunity exists to develop new synthetic strategies to convert CO_2 to value-added chemicals. Carboxylic acids are an ideal target in this regard because the carboxylate group is structurally similar to CO_2, and carboxylic acids are used in a wide variety of applications ranging from consumer products to pharmaceuticals. Because CO_2 is generally thermodynamically and kinetically inert, a strong driving force is required to induce reactivity. Voltage is an attractive driving force in this context because it can be sustainably generated from renewable energy and can have a profound impact on reaction kinetics. While many types of coupling partners exist for carboxylation, organic halides are particularly promising because they are widely available and can be reduced electrocatalytically at several metal electrodes, especially silver. Taken together, the electrocatalytic carboxylation of organic halides with CO_2 is a promising CO_2 utilization scheme, but improvements to this process are needed to realize its potential.

In this thesis, the sustainability and selectivity of electrocarboxylation of organic halides with CO_2 are improved via mechanistically informed design of the electrolyte. First, I develop a synthetic methodology that obviates the need for sacrificial metal anodes, which have been predominantly used for electrocarboxylation but limit the overall sustainability and practicality of the process. Sacrificial anodes produce metal cations that bind to anions in the electrolyte including the carboxylate product, preventing unwanted nucleophilic reactions with the organic halide substrate. This role of the sacrificial anode can be mimicked by adding a suitable soluble source of metal cations. With this additive, the carboxylation of a wide variety of organic halides was demonstrated with good to moderate yields that in many cases are comparable to if not better than yields obtained when using sacrificial anodes. Since the most active electrodes for carboxylation of organic halides also excel at reducing CO_2 to CO and CO_3^{2-}, precipitation of inorganic carbonates can deactivate the cathode and shutdown the electrochemical cell. However, the carboxylate anion product was shown to mitigate this passivation effect, enabling the cathode to remain active despite the presence of inorganic carbonate deposits.

Once nucleophilic side products are suppressed by the introduction of metal cations to the electrolyte, the primary remaining side reaction is hydrogenolysis of the organic halide, which can be the dominant reaction pathway for many types of organic halides. The hydrogen source for hydrogenolysis was demonstrated to come from the aprotic solvent of the electrolyte. To further elucidate the origin of hydrogenolysis, electrolysis conducted with deuterated ethanol revealed that under conditions of synthetic relevance, the hydrogenolysis product primarily forms via deprotonation of a solvent molecule. Based off of this mechanistic insight, density functional theory (DFT) calculations were used to calculate the deprotonation energies of various aprotic

solvents. These energies were shown to act as a reliable descriptor for carboxylation selectivity, providing a rational means to design and select solvents for electrocarboxylation reactions. Overall, this thesis demonstrates how proper electrolyte engineering guided by mechanistic insights is crucial for realizing sustainable and selective electrocarboxylation. These findings should guide further developments in not only electrocarboxylation but also other reductive electrosynthetic reactions.

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