CO_2 REDUCTION

A framework for forming formate

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With the help of a catalyst, CO_2 can be electrochemically reduced to fuels and energy carriers, such as formate (HCO_2^-). One of the major issues to consider when designing catalysts to effect this conversion is how to direct the reaction to yield the desired product. For instance, under typical conditions, the competing hydrogen evolution reaction can also occur, which results from the electrochemical reduction of protons (H^+) and lowers the selectivity of the catalytic process to the desired carbon-containing molecules. Now, Bianca Ceballos and Jenny Yang of the University of California, Irvine, have constructed a thermodynamic framework to identify selective CO_2 reduction catalysts, and provide experimental validation.

The researchers recognize that during the catalytic cycles that result in formation of either formate or hydrogen, the catalyst typically must form a metal hydride intermediate. Therefore, they evaluate the reactivity of metal hydrides with protons, which would lead to hydrogen production, and to CO_2, which would lead to formate production. To do this, they calculate the free energy of product formation — either hydrogen or formate — as a function of the acid strength of the proton donor (pK_a) in the reaction solution and the hydride donor strength (hydricity) of the metal hydride intermediate. Through this approach they map out a window in which formate is favoured over hydrogen generation. Given that hydricity values are known for a wide variety of compounds and can be tuned predictably through molecular design, appropriate catalysts that give access to this region can be targeted for selective CO_2 reduction. To validate the framework, the researchers test $Pt(dmpe)_2(PF_6)_2$ and find that it is a highly selective electrocatalyst, reducing CO_2 to formate at >90% Faradaic efficiency.

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