

Metal cations drive carbon dioxide's chemical reduction

Experimental evidence confirms one long-standing hypothesis: Positively charged metal ions stabilize the reaction's intermediate molecules.

The industrial production of ammonia, cement, and other compounds generates carbon dioxide as a byproduct. Those processes add some 1.3 gigatons of carbon emissions to the atmosphere per year. That's about two-thirds of the annual emissions associated with transportation.¹ A more sustainable system would redirect that industrial CO₂ waste stream to be an input for the synthesis of methanol, biofuels, and other useful chemicals.

One approach dissolves the CO₂ in an aqueous electrolyte solution and strips one of its electrons by using a metal catalyst and an applied current between two electrodes. If the catalyst is gold or silver, then the intermediate anion CO₂⁻ reacts with a proton from a water molecule to form carbon monoxide. Copper and other catalysts drive reactions that produce ethylene, ethanol, and other chemicals. The reaction could also be used to recycle the CO₂ from power-plant emissions.

To better understand the electrochemical reduction of CO₂, PhD candidate Mariana Monteiro at Leiden University in the Netherlands, her adviser Marc Koper, and their colleagues investigated how metal cations, such as cesium, in the electrolyte solution affect the reaction. Previous research hinted that they generate a local electric field near the electrode that boosts the reaction's effectiveness.²

The researchers have now found that the metal cations not only accelerate the reaction but are indispensable to it. Without them, the reaction doesn't yield the expected CO product.³

A simple solution

The most common way to improve the effectiveness of electrochemical CO₂ reduction, or any surface reaction, is to tune the catalyst. Tweaking a gold cata-

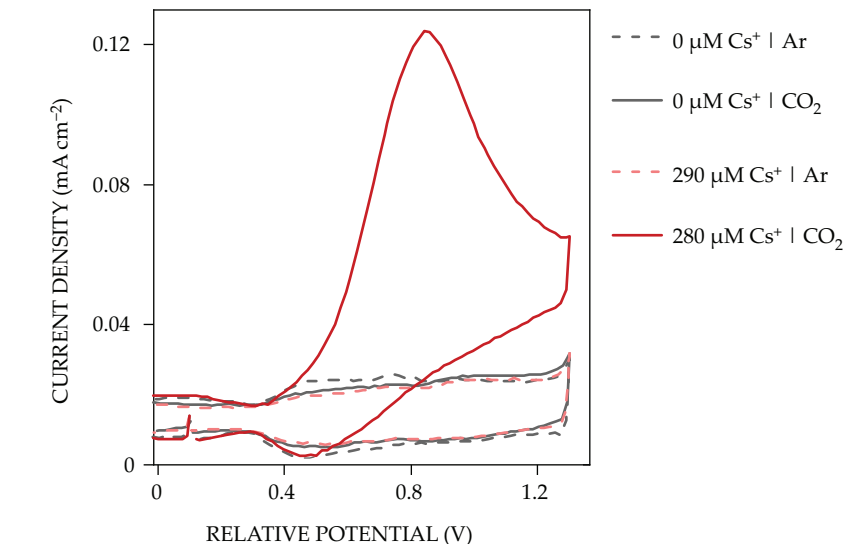


FIGURE 1. ELECTROCHEMICAL MEASUREMENTS of current density as a function of a gold electrode potential indicate that the reduction of carbon dioxide to carbon monoxide can proceed only with cesium or other metal cations in solution (solid red line). Baseline measurements in an argon atmosphere (dashed red and black lines) yielded no CO product, as expected. But the experiment without metal cations and a CO₂ atmosphere (solid black line) also failed to produce CO. (Adapted from ref. 3.)

lyst's crystalline structure, for example, changes the availability and nature of its active sites. Tuning can increase the catalyst's activity and selectivity—a measure of the formation of desired products relative to undesired ones. In 1959 Russian chemist Alexander Frumkin found that the specific composition of the electrolyte solution also affects the reaction's effectiveness.⁴

Since then, various studies have identified three possible mechanisms related to how metal cations, such as cesium and other alkali metals, in an electrolyte solution affect the reaction. One proposes that the cations drive the reaction by adsorbing to the surface of the electrode and generating a steep gradient in the electric potential between the electrode surface and the electrolyte bulk. The second possibility is that metal cations interact with water molecules close to the electrode and act as a buffer that regulates the pH to conditions more favorable for CO₂ reduction. The third hypothesis asserts that metal cations interact with nearby negatively charged intermediate molecules and electrostatically stabilize them long enough for the reaction to proceed.

Despite the progress in understanding CO₂ electrocatalysis, researchers still hadn't determined the primary contribution of the cations in the reaction when Monteiro and her colleagues started their research in 2019. To figure it out, they ran the reaction with and without metal cations in the electrolyte. "Everyone was surprised that no one had done this," she says. "I started super-complicated, with various species and mixtures. Then I came to my senses and thought, 'What if we remove the cation from the equation?'"

The researchers chose a polycrystalline gold electrocatalytic system for their experiments because of its stability and simplicity. In that system, CO and molecular hydrogen are the only two products formed from the reaction of CO₂ and water. Monteiro and her colleagues tested for the cation effect by running the reduction reaction with and without Cs⁺ or other dissolved alkali metals in the electrolyte.

An aqueous electrolyte is, by definition, a solution with water, cations, and anions. The experiment without metal cations used a dilute electrolyte solution

of sulfuric acid, whose only cations were hydrogen ions. But any impurities in the electrolyte could lead the researchers to misinterpret the results. Monteiro says that “everything you put in the experiment has to be ultraclean.” That meant she had to carefully clean the glassware before every experiment. To remove any contaminants from the electrode surface, the researchers heated it to just below its melting point. All told, the cleaning and other preparations for each lab experiment took about half a day.

Sticking together

“All the main theories to explain the cation effect up to now were related to an electric-field effect,” says Monteiro. The gold electrode in the electrocatalytic system is negatively charged. The metal cations in solution, the thinking goes, may produce an electric field near the electrode that helps nudge the CO_2 to undergo a reduction reaction. Even if the cations are removed, the electrode surface is still negatively charged. In principle, the reaction should therefore proceed.

However, the experimental results plotted in figure 1 clearly show that CO was generated only with metal cations in solution. Increasing the concentration of Cs^+ yielded more CO. The case with a CO_2 atmosphere and no metal cation in solution was statistically indistinguishable from the control experiments with an argon-only atmosphere.

The researchers also measured the effect of alkali metal ions lighter than Cs. The largest cation, Cs^+ , showed the highest activity for CO_2 reduction, followed by progressively smaller cations, an observation that agrees with previous studies.

To uncover what the cations were up to, coauthors Federico Dattila, Rodrigo García-Muelas, and Núria López of the Institute of Chemical Research of Catalonia in Tarragona, Spain, modeled the experimental system using density functional theory and *ab initio* molecular dynamics simulations. Their calculations clarified that the Cs^+ pushes CO_2

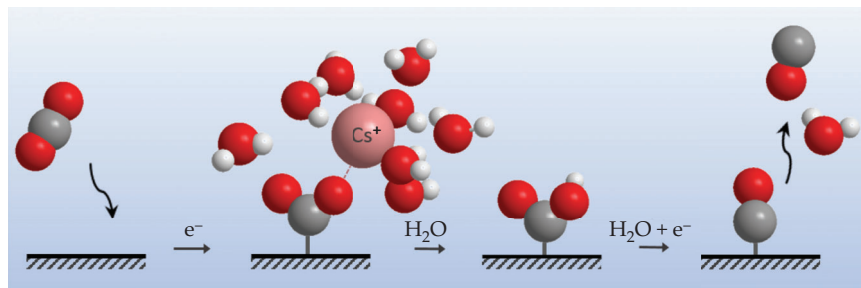


FIGURE 2. A CESIUM CATION in the electrolyte hosts several water molecules in its vicinity. Because of cesium's large ionic radius, each water molecule consequently has a weak attraction to the cation. That property allows Cs^+ to move close enough to the surface of an electrode and interact with an intermediate molecule in the reduction reaction of carbon dioxide to carbon monoxide. The interaction stabilizes the adsorbed molecule and is critical for the reaction to proceed to completion. (Adapted from ref. 3.)

to adsorb to the electrode surface and explicitly interacts with the adsorbed intermediate molecule CO_2^- , as illustrated in figure 2. The interaction stabilizes CO_2^- and allows for the next reaction steps to take place, which yield CO.

Compared with other alkali metals, Cs^+ is the most effective. The ion is large and has only a +1 charge. Therefore, the water molecules from the electrolyte don't interact with it too strongly. With such a property, Cs^+ easily reaches the electrode surface unimpeded and stabilizes CO_2^- .

An engineering problem

Monteiro and her colleagues found that systems with copper and silver electrodes also need metal cations to enable the reduction of CO_2 to CO. That finding means that metal cations like Cs^+ are critical for reducing CO_2 in a wide range of electrocatalytic systems and for generating different chemical products besides CO.

The other two hypothesized mechanisms of the cations—increasing the electric gradient and regulating the pH—may still have some effect on the reaction. To achieve any future commercial applications, engineers of electrocatalytic systems should therefore consider not only the catalyst but also the electrolyte and the metal cations in it. Other species sim-

ilar to Cs^+ , such as multivalent cations and specialized surfactants, may have an even more pronounced stabilizing effect on the CO_2 reduction reaction.

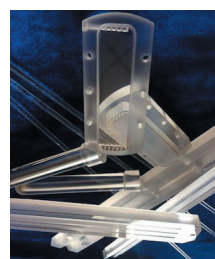
The next step to recycling CO_2 via electrocatalysis is to further optimize the reaction for commercial settings. Several previous efforts have studied approaches in neutral pH conditions. In another paper, Monteiro, Koper, and two other colleagues from the chemical technology company Avantium in Amsterdam demonstrated a proof of concept for the first step in CO_2 electrochemical reduction in an acidic solution and at conditions similar to those of an industrial setting.⁵ The laboratory-scale system demonstrated a 30% improvement in energy efficiency compared with a neutral pH system. According to Monteiro, “To scale it up to a real industrial scale is more of an engineering problem now than a chemistry one.”

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