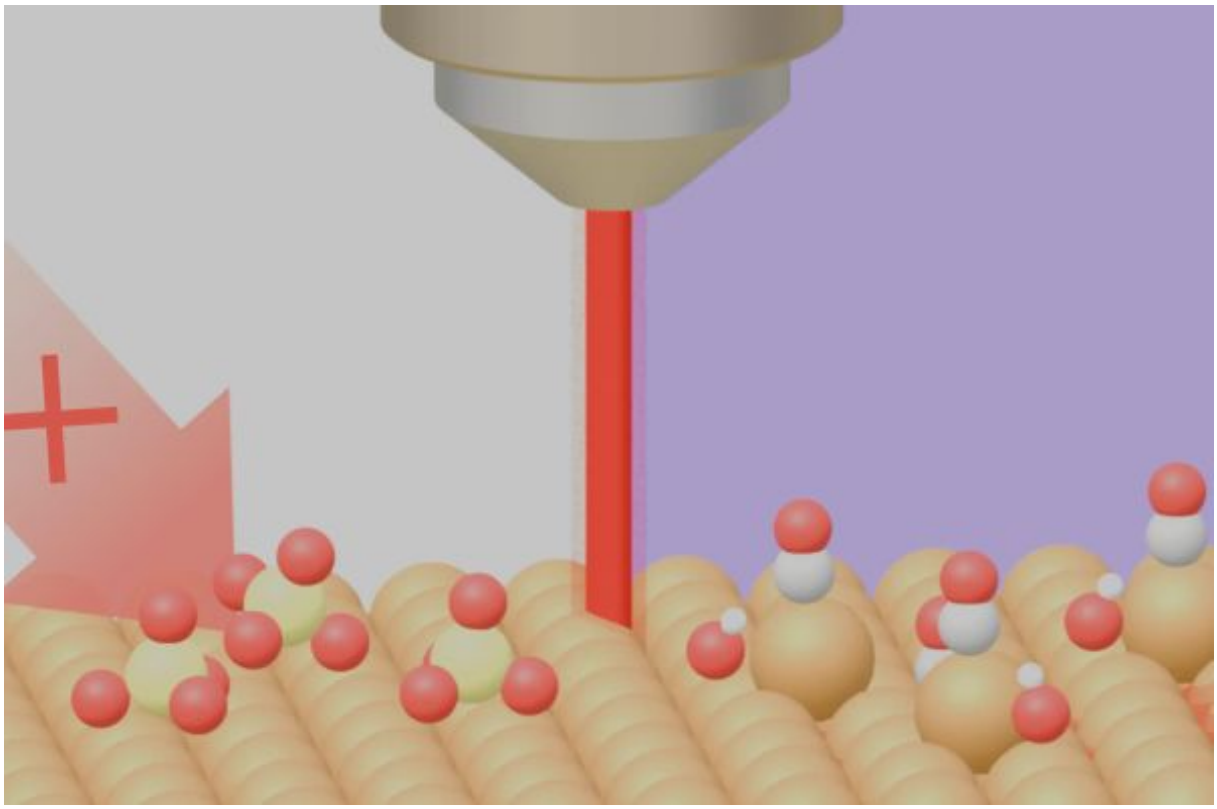

The dual role of anions in acidic CO? conversion

The role of anions (negatively charged particles) in the conversion of carbon dioxide (CO2) into useful chemicals in an acidic environment has been traditionally underexplored. In a JACS publication, researchers from ICFO and ICIQ have now demonstrated that anions actively influence CO2 electroreduction, hindering the production of the desired compounds at low electrical currents while progressively stabilizing the key intermediates for their formation as the current increases.

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Carbon dioxide (CO2) is widely known as one of the most common greenhouse gases. Several actions have been proposed to reduce it and even to convert it into useful chemicals, with the aim of mitigating the greenhouse effect while also taking advantage of the CO2 surplus to generate industrially relevant chemicals.

Electrochemical CO2 reduction (CO2R) in acidic media has recently emerged as a promising

strategy. This intricate reaction depends on many environmental factors and involves several intermediate chemicals, both positively and negatively charged. Cations, such as potassium and caesium, have been extensively studied, and most experts now agree that they play a crucial role in the successful progression of the reaction. **Anions**, although also present in the form of sulfates and hydroxyls, have not attracted as much attention, and their role remains poorly understood.

Yet emerging evidence suggests that anions are far from being passive species and can actively modulate CO2R performance. ICFO researchers, **Adrian Pinilla-Sanchez**, **Dr. Barbara Polesso**, **Prathama Haldar**, **Ranit Ram**, **Dr. Anku Guha**, led by **Prof. F. Pelayo Garcia de Arquer**, have now built on this knowledge, further revealing how these negatively charged particles influence CO2 conversion in acidic media and under industrially relevant conditions. The study, published in the Journal of the American Chemical Society and conducted in close collaboration with the Institute of Chemical Research of Catalonia (ICIQ), combined in situ surface-enhanced Raman Spectroscopy with computational simulations (Grand Canonical Density Functional Theory).

The joint experimental and theoretical strategy has unequivocally shown that the role of anions depends on both the pH (demonstrating that the higher acidic conditions, the more intense the observed effects) and how much electrical current flows through the electrochemical cell.

At **low currents**, sulfates and hydroxyls strongly attach to the surface of the electrode, **blocking the active sites** where CO2 would normally bind and begin its conversion process. But **at higher currents**, the increased negative charge on the electrode surface repels the anions, especially the sulfates. This **weakens the binding strength of sulfates**, causing them to eventually move away from the active sites. Instead, early-stage intermediates and **carbon monoxide** (*CO), a key intermediate for the formation of multicarbon products, become adsorbed, allowing CO2 reduction to start happening. At the same time, many hydroxyls, generated in situ by the ongoing reactions and being less affected by the electrostatic repulsion due to their lower negative charge, remain near the electrode. Their presence **stabilizes *CO**, thereby facilitating the chemical reactions that ultimately produce the desired compounds.

Overall, this research sheds light on how **anions**, largely unexplored until now, affect CO2R, revealing that they **are strategic rather than passive actors**. According to the team, these insights could guide the design of the acidic CO2R systems that have yet to be developed.

Reference:

Adrian Pinilla-Sanchez, Suraj Panja, Barbara Polesso, Prathama Haldar, Ranit Ram, Ranga Rohit Seemakurthi, Anku Guha, Nuria Lopez, and F. Pelayo Garcia de Arquer, Interfacial Adsorbate Competition Regulates Intermediate Stabilization and Onset Potential in Acidic CO2 Electroreduction, Journal of the American Chemical Society **2026** 148 (9), 10026-10036

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