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Breaking down hidden barriers

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CO₂ utilization

Breaking down hidden barriers

CO₂ capture and its electrochemical conversion to valorized products are energy-intensive processes. Now, researchers report that judicious control of the electrode interface and reactant transport unlock a lower-energy pathway allowing direct conversion of CO₂ from the captured state to CO.

Betar M. Gallant

Electrochemical upgrading of carbon dioxide to value-added chemicals or fuels has been a long-sought target, but is energy-intensive.¹ An upstream process is also needed to capture and separate the CO₂ from flue gas emissions to yield a concentrated, purified stream for use in electrochemical reactors. Today's capture is based on aqueous amine chemisorption;² while the CO₂ absorption step is energetically downhill, large energy barriers arise from the need to regenerate the CO₂-saturated solution by thermal or pressure-swing desorption. This step involves breaking the nitrogen-carbon bond formed between amine and CO₂ during capture and can consume up to 30% of a plant's power³.

To address these pitfalls, an attractive possibility is to do away with the intervening regeneration step and conduct electrochemistry directly on CO₂ in the captured state. This would rely on electrons supplied at an electrode, rather than heat, to cleave the N-C bond; instead of regenerating CO₂, electrons drive further reaction of CO₂ to products while freeing the amine for further CO₂ uptake. Prior efforts have demonstrated the feasibility of electrochemical N-C bond cleavage upon reduction in amine-CO₂ systems^{4,5}. However, these proof-of-concept studies used nonaqueous electrolytes, where CO₂-derived products such as carbonates are produced rather than formally-reduced gases or liquids. Writing in *Nature Energy*, Edward Sargent and co-workers at the University of Toronto and Seoul National University now report conversion of amine-bound CO₂ to a valorized chemical, carbon monoxide (CO), in aqueous solution, exhibiting Faradaic yields up to 72% at high areal currents.⁶

During classical capture reactions, CO₂ reacts with a primary alkylamine, forming negatively-charged carbamate anions alongside an equimolar amount of alkyl ammonium cations. It is the carbamate containing the CO₂ that Sargent and colleagues target for electrochemistry (Figure 1).

The generated ions act as an electrolyte but, depending on amine structure, can be bulky, which affects how they behave under applied potential.

The researchers found that when electrochemical reduction is conducted directly on solutions of monoethanolamine bound to CO₂, low Faradaic efficiencies (FE, <5%) of CO were attained. Spectroscopy experiments revealed that the positively-charged, sterically-hindering ammonium cations preferentially adsorbed in the electrode double layer under negative polarization. Here they act as a barrier, effectively blocking the desired electron transfer to the carbamate.

Building upon these insights, the researchers found that the blocking interface was disrupted by including a supporting electrolyte salt containing compact cations such as potassium, rubidium or cesium. These cations were found to displace the alkylammonium ions and form a denser electrochemical double layer. This enabled closer carbamate approach, unlocking its electrochemical activity. With cesium ions, the Faradaic efficiency increased up to 30%. Further gains were attained by operating at elevated temperatures of 60 °C in a flow-cell configuration, which helped overcome mass transport limits associated with the bulky reactants and also provided thermal activation of the N-C bond. Even with less-active potassium ions, up to 70% FE to CO was attained at 50 mA/cm² by using the improved configuration.

Using the obtained FE, the researchers showed that the projected energy needed from point of emission to electrochemical conversion of CO₂ can be lowered somewhat in the integrated system. Sargent and colleagues' approach needs 24 kJ/ton of product, compared to 30 and 29 kJ/ton, for state-of-the-art alkaline flow cells and membrane electrode assembly cells, respectively. More significantly, an improvement in overall CO₂ utilization is achieved using amines, yielding more attractive economics compared to the above counterparts, where CO₂ is more readily lost to parasitic processes.

These findings mark a new step in CO₂ capture and utilization, showing the feasibility of creating formally-reduced products from amine-CO₂ solutions for the first time. Importantly, the results confirm that amines can act more generally — now in aqueous, in addition to nonaqueous, environments — as a facilitator for CO₂ electrochemistry, opening broader areas of study across an expanded range of electrolyte media.

However, several aspects of the current system will benefit from continued research before practicality can be fully assessed. The high FEs were achieved using a Ag catalyst, which is already known to be a good electrocatalyst capable exceeding 80% FE for conventional CO₂ reduction to CO ⁷ — higher than achieved so far using amines. Notably, on carbon electrodes without Ag, the researchers reported that only hydrogen was formed. More efforts are needed to understand the catalyst's role and examine whether amines can attain benchmark FE performance, or whether there are limitations inherent to the modified reaction pathways.

In addition, while up to ten cycles of capture-reduction were demonstrated indicating a potential for amine re-use, the conditions – 30 °C, with less-active potassium ions – corresponded to the lower end of reported FEs of ~20%. Thus, it remains to be seen whether high efficiencies and durability can be combined.

The work also shines a light on numerous variables that are ripe for further study and optimization. The researchers focused on a single amine, MEA; the role of the amine structure in the thermodynamics, kinetics, products and FE of amine-CO₂ reduction warrants further fundamental research. In addition, deeper insights into the complex interactions between amine, CO₂, salt cations and anions, and water at the electrochemical interface will support pursuit of pathways to further-reduced products, if such pathways exist. Excitingly, new groundwork is being laid that expands the toolbox of known molecular-electrochemical means to manipulate CO₂,^{8,9} indicating an emerging era of research at the intersection of two previously-disparate fields with potential to lower critical energy barriers and cost.

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The author declares no competing interests.

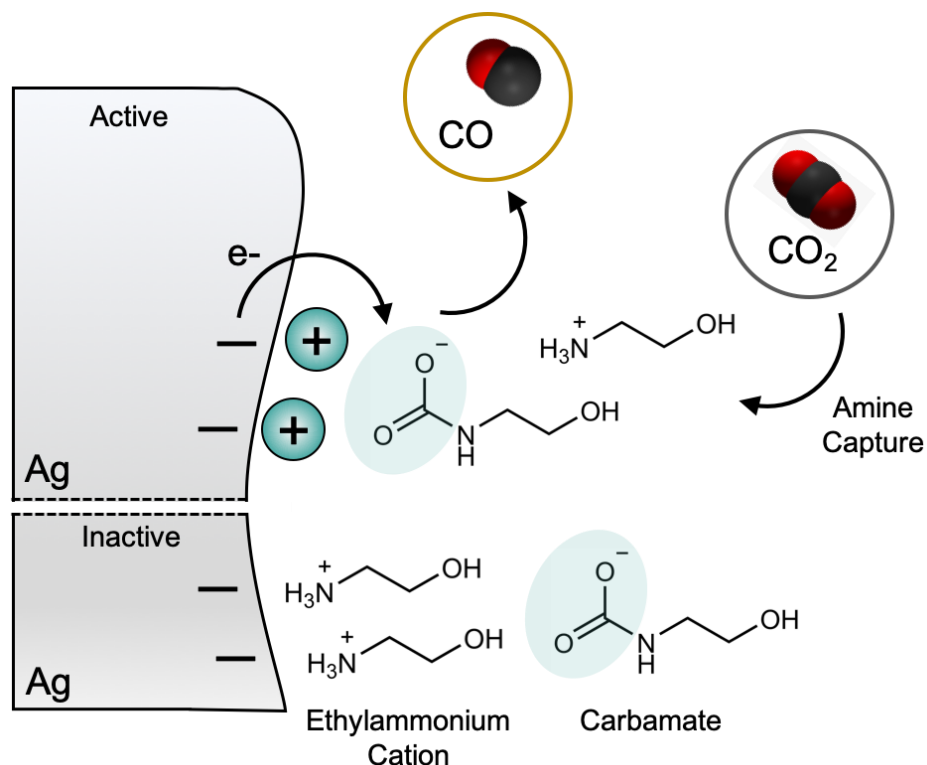


Figure 1. Modulating the electrode-electrolyte interface unlocks reactivity of captured CO_2 .

The inclusion of compact ions such as K^+ , Rb^+ , or Cs^+ alongside amine-derived ions — carbamate anions and ethylammonium cations — in the electrolyte leads to improved and more-compact structuring of the electrode-water interface. This enables facile electron transfer to the CO_2 -containing carbamate anion with high Faradaic yields of a valorized product, carbon monoxide.

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