

CO<sub>2</sub> UTILIZATION

## Breaking down hidden barriers

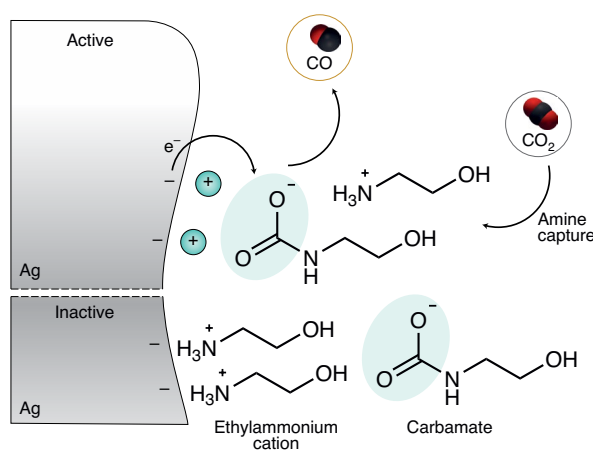
CO<sub>2</sub> capture and its electrochemical conversion to valorized products are energy-intensive processes. Now, researchers report that judicious control of the electrode interface and reactant transport unlock a lower energy pathway allowing direct conversion of CO<sub>2</sub> from the captured state to CO.

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Electrochemical upgrading of carbon dioxide to value-added chemicals or fuels has been a long-sought target, but is energy-intensive<sup>1</sup>. An upstream process is also needed to capture and separate the CO<sub>2</sub> from flue gas emissions to yield a concentrated, purified stream for use in electrochemical reactors. Today's capture is based on aqueous amine chemisorption<sup>2</sup>; while the CO<sub>2</sub> absorption step is energetically downhill, large energy barriers arise from the need to regenerate the CO<sub>2</sub>-saturated solution by thermal or pressure-swing desorption. This step involves breaking the nitrogen–carbon bond formed between amine and CO<sub>2</sub> during capture and can consume up to 30% of a plant's power<sup>3</sup>.

To address these pitfalls, an attractive possibility is to do away with the intervening regeneration step and conduct electrochemistry directly on CO<sub>2</sub> 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 CO<sub>2</sub>, electrons drive further reaction of CO<sub>2</sub> to products while freeing the amine for further CO<sub>2</sub> uptake. Prior efforts have demonstrated the feasibility of electrochemical N–C bond cleavage upon reduction in amine–CO<sub>2</sub> systems<sup>4,5</sup>. However, these proof-of-concept studies used non-aqueous electrolytes, where CO<sub>2</sub>-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 CO<sub>2</sub> to a valorized chemical, carbon monoxide, in aqueous solution, exhibiting Faradaic yields up to 72% at high areal currents<sup>6</sup>.

During classical capture reactions, CO<sub>2</sub> reacts with a primary alkylamine, forming negatively charged carbamate anions alongside an equimolar amount of alkyl ammonium cations. It is the carbamate containing the CO<sub>2</sub> that Sargent and colleagues target for electrochemistry (Fig. 1).



**Fig. 1 | Modulating the electrode–electrolyte interface unlocks reactivity of captured CO<sub>2</sub>.**

The inclusion of compact ions such as K<sup>+</sup>, Rb<sup>+</sup> or Cs<sup>+</sup> alongside amine-derived ions — carbamate anions and ethylammonium cations — leads to improved and more-compact structuring of the electrode–electrolyte interface. This enables facile electron transfer to the CO<sub>2</sub>-containing carbamate anion with high Faradaic yields of a valorized product, carbon monoxide.

The generated ions act as an electrolyte but, depending on the 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 (MEA) bound to CO<sub>2</sub>, 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 caesium. These cations were found to displace the alkylammonium ions and form a more-dense electrochemical double layer. This enabled closer carbamate approach, unlocking its electrochemical

activity. With caesium 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 cm<sup>-2</sup> 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 CO<sub>2</sub> can be lowered somewhat in the integrated system. Sargent and colleagues' approach needs 23 kJ per tonne of product, compared to 29 kJ per tonne, for state-of-the-art alkaline flow cells or membrane electrode assembly cells. More significantly, an improvement in overall CO<sub>2</sub> utilization is achieved using amines, yielding more attractive economics compared to the above counterparts, where CO<sub>2</sub> is more readily lost to parasitic processes.

These findings mark a new step in CO<sub>2</sub> capture and utilization, showing the feasibility of creating formally reduced products from amine–CO<sub>2</sub> solutions for the first time. Importantly, the results confirm that amines can act more generally — now in aqueous, in addition to non-aqueous, environments — as a facilitator for CO<sub>2</sub> 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 of exceeding 90% FE for conventional CO<sub>2</sub> reduction to CO (ref. 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–CO<sub>2</sub> reduction warrants further fundamental research. In addition, deeper insights into the complex interactions between amine, CO<sub>2</sub>, salt cations and anions, and water at the electrochemical interface will support the 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 CO<sub>2</sub>

(refs. 8,9), indicating an emerging era of research at the intersection of two previously disparate fields with the potential to lower critical energy barriers and cost. □

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#### Competing interests

The author declares no competing interests.