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Carbon capture and utilisation

Binding and release in balance

Integrating CO_2 capture and electrochemical conversion may lower energy use relative to the separated processes, but scale-up is limited by low carbon conversion and energy-intensive solvent regeneration. New research shows that piperazine, alongside a Ni single-atom catalyst, allows effective, stable CO_2 capture, and conversion to CO in a low-energy process.

Federico Dattila

Carbon capture and utilization (CCU) technologies separate CO_2 from point sources or the air and use it as a feedstock, with the aim of mitigating greenhouse gas emissions and generating useful products. To capture CO_2, amine solvents are typically employed because they bind CO_2 strongly; so strongly, in fact, that substantial amounts of energy (usually thermal) are required to release the captured CO_2 for subsequent conversion. Therefore, to avoid the energy-intensive solvent regeneration step, researchers have sought to integrate the capture and conversion steps by performing direct electroreduction of CO_2-loaded capture agents.[1] This approach has the further advantage that these amine-CO_2 adducts (termed carbamates) feature CO_2 in an activated, bent configuration, which lowers the overpotential required for its reduction. Nevertheless, good capture agents still bind CO_2 too strongly, inhibiting its release and limiting the overall carbon conversion efficiency. Thus, so far, integrated CCU process still requires thermal solvent regeneration steps to reach acceptable carbon utilization.[2,3]

Now, writing in Nature Energy, Ziyun Wang, Tianyi Ma and co-workers in Australia, New Zealand, Republic of Korea and China report that piperazine (a cyclic molecule with two amine groups) is an excellent medium for integrated carbon capture and conversion, and show that its adduct with CO_2 can be directly reduced to CO using a nickel single-atom catalyst, even at room temperature.[4]

The researchers began by considering whether an amine with optimal carbamate formation energy exists. An extremely exergonic Gibbs free energy of carbamate formation would imply excessive stability of the CO_2 adduct, preventing its reduction. Endergonic values would instead lead to hydrolysis of the carbamate to bicarbonate, again hindering any useful CO_2 conversion. Using density functional theory (DFT) calculations, Wang, Ma and colleagues show that piperazine has a mild carbamate formation energy, yet maximum CO_2 capture activity. The team calculated the CO_2 capture activity by taking the product of the amine mass-normalized CO_2 capture capacity (quantified *via* ^{13}C nuclear magnetic resonance, NMR) and the CO_2 adsorption rate (taken from literature).

Wang, Ma and colleagues then carried out process simulations to determine whether carbamates form in CO_2-loaded piperazine aqueous solutions. The simulations predicted that the protonated carbamate zwitterion (H^+PZCOO^-) was the most concentrated species in bulk solution for a CO_2 loading higher than 0.5 mol per mol of amine. Indeed, using ^{13}C NMR spectroscopy, they observe carbamates for loadings beyond 0.8 mol/mol and its concentration increased with increasing CO_2 loading. These findings were validated by *in situ* infrared spectroscopy and DFT.[5]

With the capture step successfully accomplished, the researchers then considered the greater challenge: could carbamates accumulate at the cathode and undergo reduction? Previous research has shown that a different amine-based molecule, monoethanolamine, is a candidate for integrated capture and conversion of CO_2.[2] However, while being an excellent capture agent, reduction of the monoethanolamine carbamate is relatively poor because of limited mass transfer to the cathode and too strong CO_2 binding; alkali cations and 60°C were needed to prevent poisoning by amine cations and force CO_2 release, respectively. In turn, piperazine showed itself to be a better candidate than monoethanolamine. According to estimations by ^{13}C NMR, H^+PZCOO^- has comparable diffusion properties to (bi)carbonate, yet a higher diffusion coefficient than protonated piperazine ions; thus, carbamates could accumulate at the electrode surface.

The last challenge left was CO_2 reduction. In line with DFT predictions, Wang, Ma and colleagues report greater than 40% selectivity to CO when using a Ni single-atom catalyst during linear sweep voltammetry up to −1.6 V vs RHE (the reversible hydrogen electrode) in 1.5 M piperazine at 100% CO_2 loading, room temperature and pressure. The researchers also found a positive reaction order between CO partial current density and carbamate concentration, validating the long-debated hypothesis of carbamate as a CO_2 electrolysis precursor (in line with a recent report of carbamate reduction to methane on Ni).[6]

To test the system in a more practical setup, CO_2 electrolysis was carried out in a membrane electrode assembly (using an anion-exchange membrane and geometric device area of 5 cm^2 area) with current densities between 10 and 100 mA cm^{-2}. The researchers report CO selectivity up to 75% at 50 mA/cm^2 and 60°C, decreasing to 16-38% at room temperature. Without further supply of CO_2 to the electrolyte after the initial loading, the electrolyser functioned for 26 hours: up to 75.6% carbon was converted in the process, with 23.3% energy stored in carbon bonds. Through appropriate recycling of CO_2, the operation was prolonged to 100 h at 100 mA cm^{-2}.

While this integrated capture-conversion unit capable of room temperature CO_2 reduction at pre-industrial rates (100 mA cm^{-2}) is certainly promising, there is still much work to be done in the

future. This proof-of-concept should now be confirmed on other standard catalysts employed for CO_2 reduction (e.g. Ag, Bi, Cu), which may be affected by poisoning,[2] or unable to trigger carbamate reduction. This could allow a broader range of molecules to be produced, beyond carbon monoxide shown already. Higher applied current density (> 100 mA cm^{-2}) and longer operating times are also required to assess the possible scale-up of the process. The next challenge is to enhance product selectivity (here limited to < 80%) by optimizing amine or applied temperature, but at the same time ensuring that the overall energy efficiency is not reduced.

Given the limited size of the market for CO_2-derived products in comparison to the CO_2 mitigation challenge,[7] CCU is clearly just one aspect of decarbonisation and must be implemented alongside carbon sequestration and emissions reduction strategies. Nevertheless, the findings of Wang, Ma and colleagues bring us one step closer to developing low energy CCU units able to capture and convert CO_2 in an integrated, stand-alone process.

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Competing interests

The author declares no competing interests.

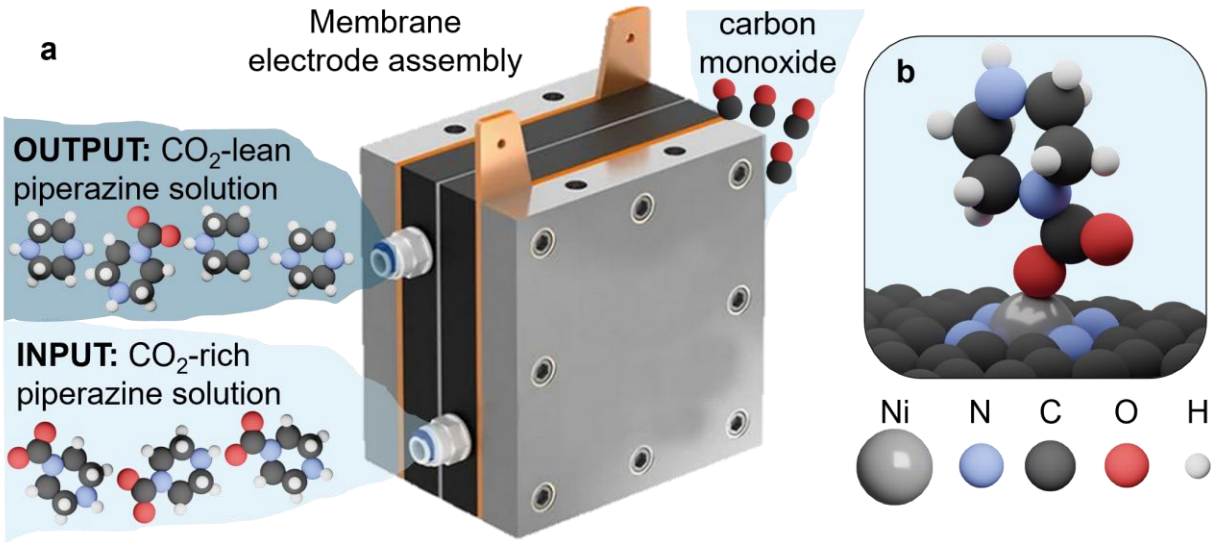


Figure 1. The potential of room-temperature piperazine-based carbamate reduction. (a) In a typical setup, CO_2-rich piperazine solution enters the membrane electrode assembly at the electrolyte inlet, carbamate reduction to carbon monoxide occurs on the Ni-N_4 catalyst, and CO_2-lean piperazine solution exits at the outlet. Carbon monoxide is produced in the process. (b) An illustration of the Ni-N_4 catalyst with bound carbamate.

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