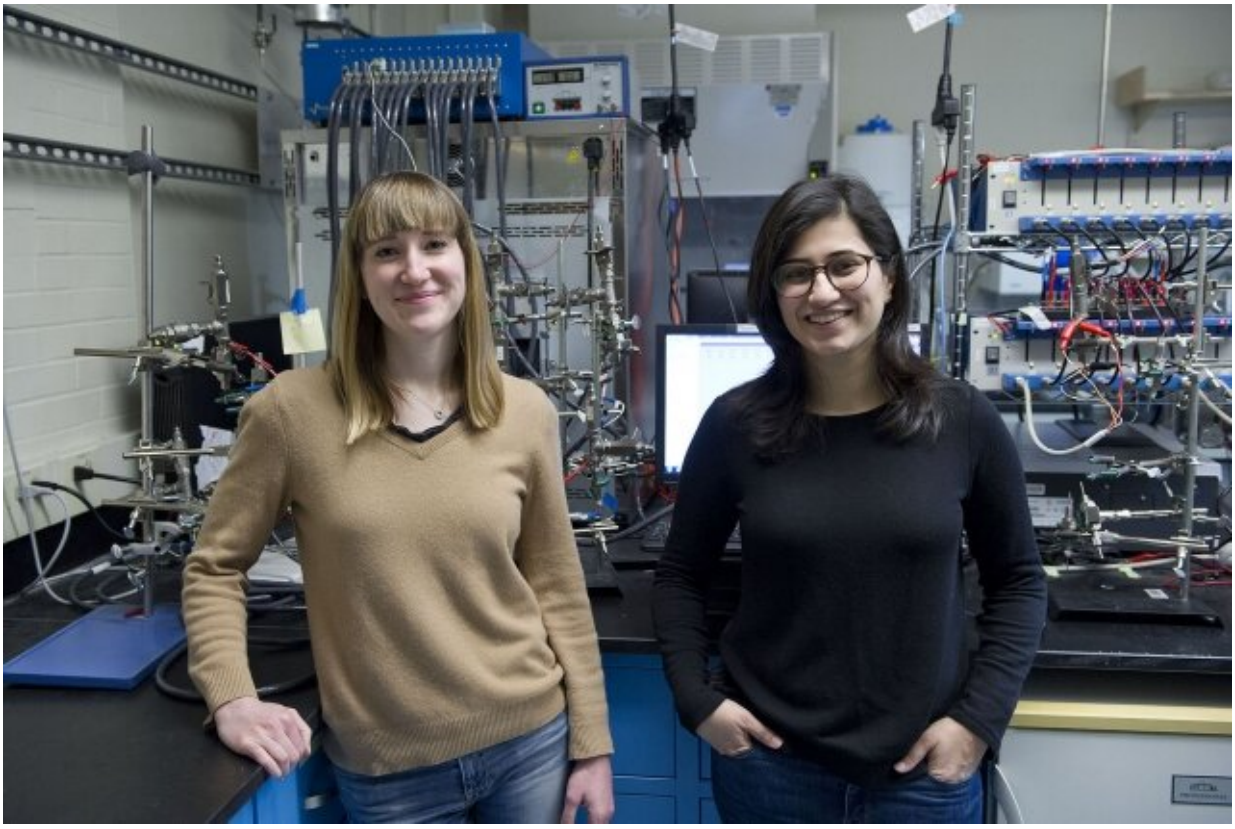
# Removing carbon dioxide from power plant exhaust

July 30 2019, by Nancy W. Stauffer



MIT Assistant Professor Betar Gallant (left) and graduate student Aliza Khurram are developing a novel battery that could both capture carbon dioxide in power plant exhaust and convert it to a solid ready for safe disposal. Credit: Stuart Darsch

Reducing carbon dioxide ($CO^2$) emissions from power plants is widely considered an essential component of any climate change mitigation plan. Many research efforts focus on developing and deploying carbon capture and sequestration (CCS) systems to keep $CO_2$ emissions from power plants out of the atmosphere. But separating the captured $CO_2$ and converting it back into a gas that can be stored can consume up to 25 percent of a plant's power-generating capacity. In addition, the $CO_2$ gas is generally injected into underground geological formations for long-term storage—a disposal method whose safety and reliability remain unproven.

A better approach would be to convert the captured $CO_2$ into useful products such as value-added fuels or chemicals. To that end, attention has focused on electrochemical processes—in this case, a process in which chemical reactions release electrical energy, as in the discharge of a battery. The ideal medium in which to conduct electrochemical conversion of $CO_2$ would appear to be water. Water can provide the protons (positively charged particles) needed to make fuels such as methane. But running such "aqueous" (water-based) systems requires large energy inputs, and only a small fraction of the products formed are typically those of interest.

Betar Gallant, an assistant professor of mechanical engineering, and her group at MIT have therefore been focusing on non-aqueous (water-free) electrochemical reactions—in particular, those that occur inside lithium-$CO_2$ batteries.

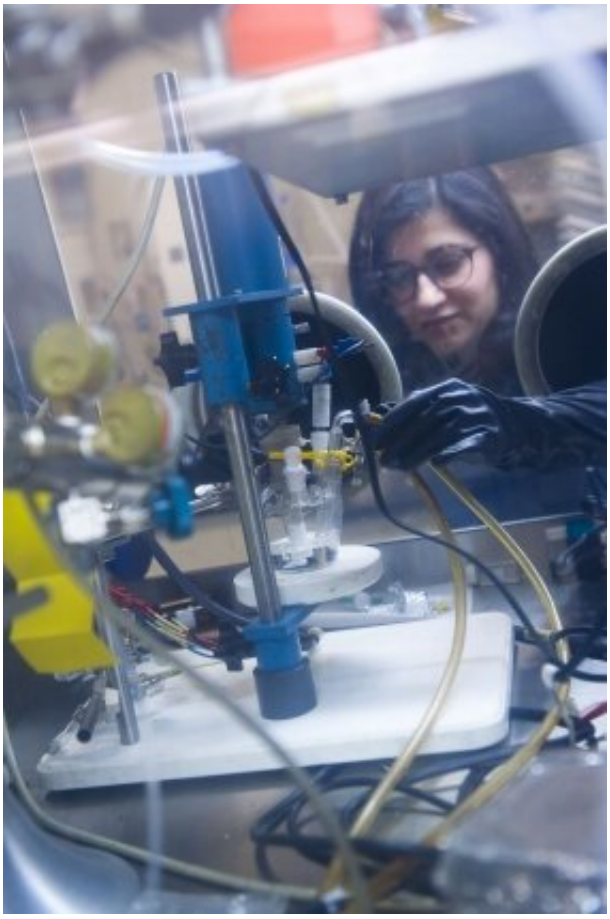
Research into lithium-$CO_2$ batteries is in its very early stages, according to Gallant, but interest in them is growing because $CO_2$ is used up in the chemical reactions that occur on one of the electrodes as the battery is being discharged. However, $CO_2$ isn't very reactive. Researchers have tried to speed things up by using different electrolytes and electrode materials. Despite such efforts, the need to use expensive metal catalysts

to elicit electrochemical activity has persisted.

Given the lack of progress, Gallant wanted to try something different. "We were interested in trying to bring a new chemistry to bear on the problem," she says. And enlisting the help of the sorbent molecules that so effectively capture $CO_2$ in CCS seemed like a promising way to go.

## Rethinking amine

The sorbent molecule used in CCS is an amine, a derivative of ammonia. In CCS, exhaust is bubbled through an amine-containing solution, and the amine chemically binds the $CO_2$, removing it from the exhaust gases. The $CO_2$—now in liquid form—is then separated from the amine and converted back to a gas for disposal.



Graduate student Aliza Khurram prepares for experiments by pumping carbon dioxide through an electrochemical cell consisting of lithium and carbon electrodes plus a specially designed electrolyte. Credit: Stuart Darsch

In CCS, those last steps require high temperatures, which are attained using some of the electrical output of the power plant. Gallant wondered whether her team could instead use electrochemical reactions to separate the $CO_2$ from the amine—and then continue the reaction to make a solid, $CO_2$-containing product. If so, the disposal process would be simpler than it is for gaseous $CO_2$. The $CO_2$ would be more densely packed, so it would take up less space, and it couldn't escape, so it would be safer. Better still, additional electrical energy could be extracted from the device as it discharges and forms the solid material. "The vision was to put a battery-like device into the power plant waste stream to sequester the captured $CO_2$ in a stable solid, while harvesting the energy released in the process," says Gallant.

Research on CCS technology has generated a good understanding of the carbon-capture process that takes place inside a CCS system. When $CO_2$ is added to an amine solution, molecules of the two species spontaneously combine to form an "adduct," a new chemical species in which the original molecules remain largely intact. In this case, the adduct forms when a carbon atom in a $CO_2$ molecule chemically bonds with a nitrogen atom in an amine molecule. As they combine, the $CO_2$ molecule is reconfigured: It changes from its original, highly stable, linear form to a "bent" shape with a negative charge—a highly reactive form that's ready for further reaction.

In her scheme, Gallant proposed using electrochemistry to break apart

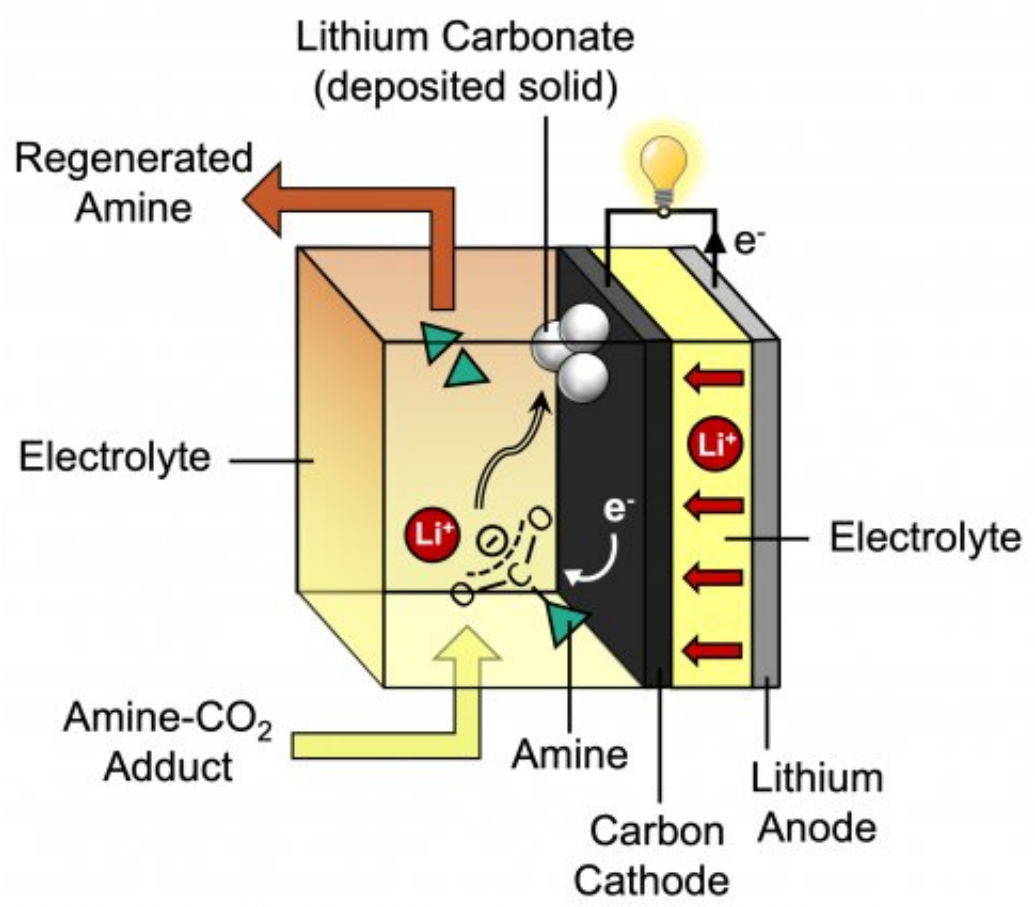
the $CO_2$-amine adduct—right at the carbon-nitrogen bond. Cleaving the adduct at that bond would separate the two pieces: the amine in its original, unreacted state, ready to capture more $CO_2$, and the bent, chemically reactive form of $CO_2$, which might then react with the electrons and positively charged lithium ions that flow during battery discharge. The outcome of that reaction could be the formation of lithium carbonate ($Li_2CO_3$), which would deposit on the carbon electrode.

At the same time, the reactions on the carbon electrode should promote the flow of electrons during battery discharge—even without a metal catalyst. "The discharge of the battery would occur spontaneously," Gallant says. "And we'd break the adduct in a way that allows us to renew our $CO_2$ absorber while taking $CO_2$ to a stable, solid form."

## A process of discovery

In 2016, Gallant and mechanical engineering doctoral student Aliza Khurram began to explore that idea.

Their first challenge was to develop a novel electrolyte. A lithium-$CO_2$ battery consists of two electrodes—an anode made of lithium and a cathode made of carbon—and an electrolyte, a solution that helps carry charged particles back and forth between the electrodes as the battery is charged and discharged. For their system, they needed an electrolyte made of amine plus captured $CO_2$ dissolved in a solvent—and it needed to promote chemical reactions on the carbon cathode as the battery discharged.




This diagram depicts the process during discharge of the new lithium-CO2 battery developed by MIT Assistant Professor Betar Gallant and her group. The researchers' proposed battery consists of a lithium anode plus a carbon cathode that is surrounded by a special electrolyte that incorporates lithium ions (Li+) and amine. Credit: Massachusetts Institute of Technology

They started by testing possible solvents. They mixed their $CO_2$-absorbing amine with a series of solvents frequently used in batteries and then bubbled $CO_2$ through the resulting solution to see if $CO_2$ could be dissolved at high concentrations in this unconventional chemical environment. None of the amine-solvent solutions exhibited observable changes when the $CO_2$ was introduced, suggesting that they might all be viable solvent candidates.

However, for any electrochemical device to work, the electrolyte must be spiked with a salt to provide positively charged ions. Because it's a lithium battery, the researchers started by adding a lithium-based salt—and the experimental results changed dramatically. With most of the solvent candidates, adding the salt instantly caused the mixture either to form solid precipitates or to become highly viscous—outcomes that ruled them out as viable solvents. The sole exception was the solvent dimethyl sulfoxide, or DMSO. Even when the lithium salt was present, the DMSO could dissolve the amine and $CO_2$.

"We found that—fortuitously—the lithium-based salt was important in enabling the reaction to proceed," says Gallant. "There's something about the positively charged lithium ion that chemically coordinates with the amine-$CO_2$ adduct, and together those species make the electrochemically reactive species."

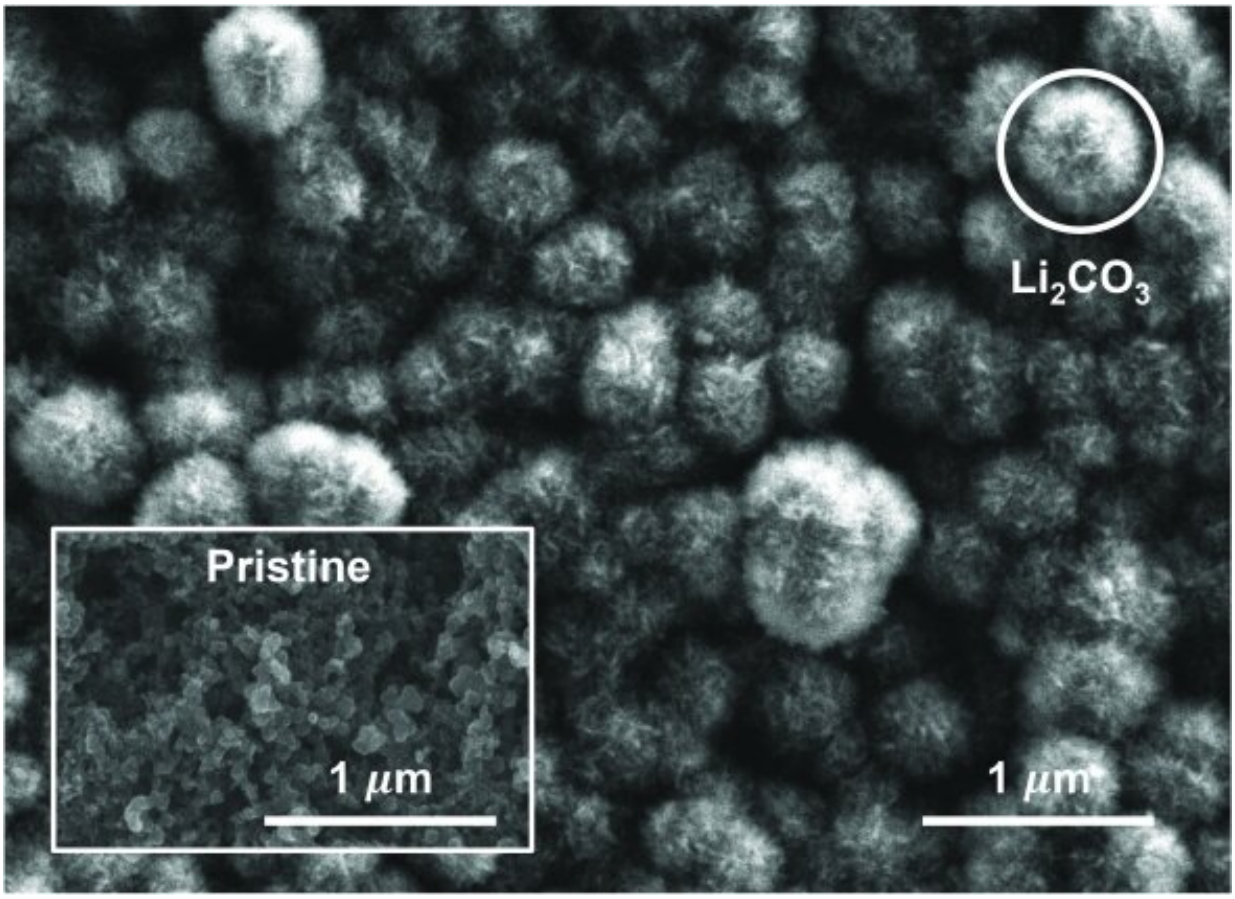
## Exploring battery behavior during discharge

To examine the discharge behavior of their system, the researchers set up an electrochemical cell consisting of a lithium anode, a carbon cathode, and their special electrolyte—for simplicity, already loaded with $CO_2$. They then tracked discharge behavior at the carbon cathode.

As they had hoped, their special electrolyte actually promoted discharge reaction in the test cell. "With the amine incorporated into the DMSO-based electrolyte along with the lithium salt and the $CO_2$, we see very high capacities and significant discharge voltages—almost three volts," says Gallant. Based on those results, they concluded that their system functions as a lithium-$CO_2$ battery with capacities and discharge voltages competitive with those of state-of-the-art lithium-gas batteries.

The next step was to confirm that the reactions were indeed separating the amine from the $CO_2$ and further continuing the reaction to make

$CO_2$-derived products. To find out, the researchers used a variety of tools to examine the products that formed on the carbon cathode.




This scanning electron microscope (SEM) image shows the cathode from the researchers' lithium-carbon dioxide system after discharge. Analysis of the spherical structures confirms that they are composed of Li2CO3. The inset shows an SEM image of the carbon cathode before discharge. Absence of the spheres confirms they were formed during discharge. Credit: Massachusetts Institute of Technology

In one test, they produced images of the post-reaction cathode surface using a scanning electron microscope (SEM). Immediately evident were

spherical formations with a characteristic size of 500 nanometers, regularly distributed on the surface of the cathode. According to Gallant, the observed spherical structure of the discharge product was similar to the shape of $Li_2CO_3$ observed in other lithium-based batteries. Those spheres were not evident in SEM images of the "pristine" carbon cathode taken before the reactions occurred.

Other analyses confirmed that the solid deposited on the cathode was $Li_2CO_3$. It included only $CO_2$-derived materials; no amine molecules or products derived from them were present. Taken together, those data provide strong evidence that the electrochemical reduction of the $CO_2$-loaded amine occurs through the selective cleavage of the carbon-nitrogen bond.

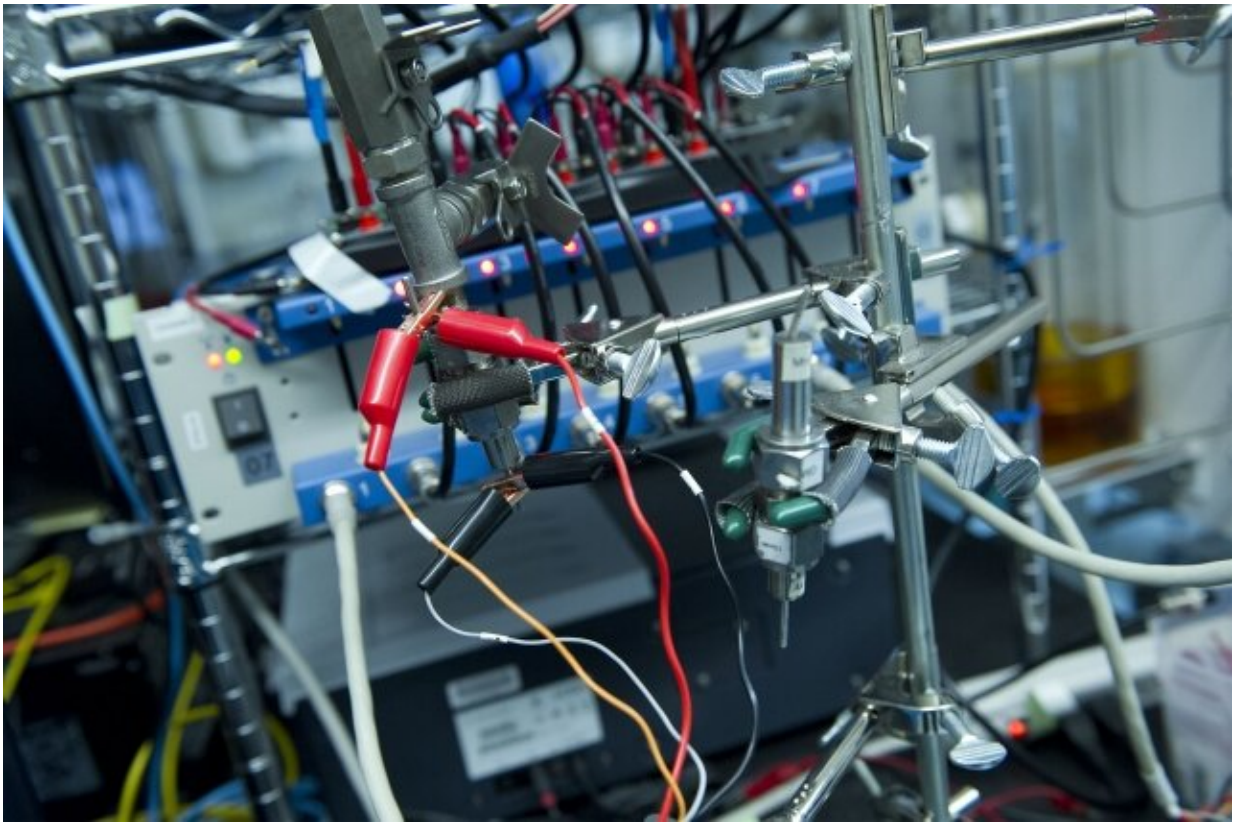
"The amine can be thought of as effectively switching on the reactivity of the $CO_2$," says Gallant. "That's exciting because the amine commonly used in $CO_2$ capture can then perform two critical functions. It can serve as the absorber, spontaneously retrieving $CO_2$ from combustion gases and incorporating it into the electrolyte solution. And it can activate the $CO_2$ for further reactions that wouldn't be possible if the amine were not there."

## Future directions

Gallant stresses that the work to date represents just a proof-of-concept study. "There's a lot of fundamental science still to understand," she says, before the researchers can optimize their system.

She and her team are continuing to investigate the chemical reactions that take place in the electrolyte as well as the chemical makeup of the adduct that forms—the "reactant state" on which the subsequent electrochemistry is performed. They are also examining the detailed role of the salt composition.

In addition, there are practical concerns to consider as they think about device design. One persistent problem is that the solid deposit quickly clogs up the carbon cathode, so further chemical reactions can't occur. In one configuration they're investigating—a rechargeable battery design—the cathode is uncovered during each discharge-charge cycle. Reactions during discharge deposit the solid $Li_2CO_3$, and reactions during charging lift it off, putting the lithium ions and $CO_2$ back into the electrolyte, ready to react and generate more electricity. However, the captured $CO_2$ is then back in its original gaseous form in the electrolyte. Sealing the battery would lock that $CO_2$ inside, away from the atmosphere—but only so much $CO_2$ can be stored in a given battery, so the overall impact of using batteries to capture $CO_2$ emissions would be limited in this scenario.



The researchers use this setup to test the storage capacity and discharge voltage of their batteries. Credit: Stuart Darsch

The second configuration the researchers are investigating—a discharge-only setup—addresses that problem by never allowing the gaseous $CO_2$ to re-form. "We're mechanical engineers, so what we're really keen on doing is developing an industrial process where you can somehow mechanically or chemically harvest the solid as it forms," Gallant says. "Imagine if by mechanical vibration you could gently remove the solid from the cathode, keeping it clear for sustained reaction." Placed within an exhaust stream, such a system could continuously remove $CO_2$ emissions, generating electricity and perhaps producing valuable solid materials at the same time.

Gallant and her team are now working on both configurations of their system. "We don't know which is better for applications yet," she says. While she believes that practical lithium-$CO_2$ batteries are still years away, she's excited by the early results, which suggest that developing novel electrolytes to pre-activate $CO_2$ could lead to alternative $CO_2$ reaction pathways. And she and her group are already working on some.

One goal is to replace the lithium with a metal that's less costly and more earth-abundant, such as sodium or calcium. With seed funding from the MIT Energy Initiative, the team has already begun looking at a system based on calcium, a material that's not yet well-developed for battery applications. If the calcium-$CO_2$ setup works as they predict, the solid that forms would be calcium carbonate—a type of rock now widely used in the construction industry.

In the meantime, Gallant and her colleagues are pleased that they have found what appears to be a new class of reactions for capturing and

sequestering $CO_2$. "$CO_2$ conversion has been widely studied over many decades," she says, "so we're excited to think we may have found something that's different and provides us with a new window for exploring this topic."

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Provided by Massachusetts Institute of Technology