Development of sorbent materials for direct air capture of CO₂

Xiaoyang Shi, Yuanchunyu Lin, and Xi Chen*

Building a carbon–neutral world requires the removal of excess CO_2 that has already been dumped into the atmosphere. The technologies have been well established to remove carbon dioxide directly from ambient air, or "direct air capture" (DAC). DAC is still in its infancy, with many challenges remaining. Sorbents are central to the capture of CO_2 from ambient air. Many sorbents have been reported to take up CO_2, but they all have advantages and disadvantages. Recent advances in material synthesis and surface chemistry have resulted in new generations of CO_2 sorbents. Development needs to progress quickly, because global warming will not wait. We summarize recent progress on designed sorbents for CO_2 capture from ambient air. There are mainly six typical technologies for DAC, including physical sorption, sorption by strong bases, sorption by amine-modified materials, sorption by aqueous amino acid solution followed by precipitation with a guanidine compound, moisture-swing sorption, and electrochemical-swing sorption. Existing research works have put forward future perspectives and directions of sorbent materials for DAC technologies.

Introduction

The accumulation of carbon dioxide (CO_2) in the atmosphere is the primary driver of global warming. Human forcing of climate is increasing the probability of severe ecological impacts and possibly the crossing of tipping points.[1] According to scenario RCP 8.5 reported in the Intergovernmental Panel on Climate Change (IPCC), without intervention, CO_2 emissions will rise from the current 49 $GtCO_2$eq/year to between 85 and 136 $GtCO_2$eq/year by 2050.[2] The rising CO_2 concentration could cause a global mean temperature change from the pre-industrial level (1880–1900) to 2100 of 3.8–6.0°C. Moving the energy infrastructure away from fossil fuels to renewable and nuclear energy resources is a challenging task. CO_2 capture from point sources such as power plants and industrial manufacturers could reduce CO_2 emission while using fossil fuels by using localized CO_2 capture and storage (CCS) technologies.[3–5] However, the objective of stabilizing atmospheric CO_2 at 450 ppm cannot be accomplished any longer by reducing CO_2 emissions from point sources alone. This will require technologies to capture and permanently remove CO_2 directly from the air.[6]

The concept of capturing CO_2 from the air was first introduced for climate change mitigation by Lackner in 1999.[7] In the following decade, researchers put in an effort to educate the broader community that capturing CO_2 from ambient air directly is an essential and viable option for reducing greenhouse gas levels.[8,9] However, the acceptance of such technologies is still limited. Technical difficulty and cost have been raised as major concerns. Currently, the concept is broadly defined as the direct air capture (DAC) of CO_2, and the IPCC coined the term "negative emission" for such technologies.[10] In the recent report, *Special Report on Carbon Capture Utilisation and Storage* (CCUS), the International Energy Agency (IEA) has notified that carbon capture, utilization, and storage are necessary to solve the current climate change issue.[11] The feasibility of DAC technology has been demonstrated in techno-economic assessments.[12] Headline positives[13] for DAC are (1) compensating for mobile CO_2 emissions; (2) removing pipelines for CO_2 storage; (3) offering leakage insurance; (4) closing the carbon cycle (fuel from air); (5) carbon feedstock; (6) negative emissions.

The importance of DAC is also the wide range of CO_2 application scenarios in industries. The US Environmental Protection Agency has instituted a program for supplying CO_2 gas for industrial purposes. CO_2 gases captured from the air can be used to enhance oil recovery, food transportation,

Xiaoyang Shi, Earth Engineering Center, Center for Advanced Materials for Energy and Environment, Department of Earth and Environmental Engineering, Columbia University, USA;
Yuanchunyu Lin, Earth Engineering Center, Center for Advanced Materials for Energy and Environment, Department of Earth and Environmental Engineering, Columbia University, USA;
Xi Chen, Earth Engineering Center, Center for Advanced Materials for Energy and Environment, Department of Earth and Environmental Engineering, Columbia University, USA;
xichen863@hotmail.com
*Corresponding author

beverage manufacturing, indoor air purification, natural gas upgrading, low carbon cement, pulp and paper manufacturing, metal fabrication, HVAC systems, etc. CO_2 capture from the high concentration of CO_2 at the point source has geographical limitations and the regeneration process requires a large amount of heat energy, which is not suitable for all the commercial applications previously mentioned. The heart of DAC technology is the design and development of energy-efficient CO_2 sorbents. This article discusses solid sorbents that have been discovered to be useful for DAC and provides an overview of the considerations for finding new sorbent materials.

Sorbent materials for DAC

Developing sorbent materials for CO_2 sorption from ambient air is critical to alleviate climate change and close the carbon cycle. Central to most direct air capture technologies is the use of sorbent materials. There are six typical technologies for DAC, shown in **Figure 1**, including physical sorption,[14–16] sorption by strong bases,[14,17,18] sorption by amine-modified materials,[3,19–22] sorption by aqueous amino acid solution followed by precipitation with a guanidine compound,[23–28] moisture-swing sorption,[6,9,29–36] and electrochemical-swing sorption.[37–40] Different from CO_2 capture from high concentration, CO_2 is very dilute in the air. Thus, any process for capturing CO_2 must avoid spending significant amounts of energy on processing the bulk air for CO_2 removal. This rules out heating, cooling, or compressing the air. Sorbents bind CO_2 from the air without the need for energy. Indeed, the binding of the CO_2 is an exothermic reaction. However, the entropy of binding is unfavorable.

As we consider various materials and their properties, it is worth keeping in mind the properties that make a valuable sorbent for direct air capture. A promising sorbent is highly selective for CO_2; it has high binding energy that readily allows CO_2 to be removed from the atmosphere. At the same time, it can create a significant loading of the material. The process of releasing CO_2 from the sorbent must be efficient and simple. The sorbent must withstand many sorbent cycles. Finally, it must be affordable.

Physisorption materials

In the presence of physical sorbents, interactions between CO_2 and the material surface are governed by van der Waals or ion quadrupole forces. Because physisorption relies on physical interactions to bind CO_2, this process typically occurs on the surface of a sorbent.[15] This means that materials of high surface area are desirable, such as materials with high porosity or nanometer dimensions.[16] Some of these materials include zeolites, activated carbon, alumina, and metal–organic frameworks.[14]

Regeneration of solid sorbents through physisorption is energetically easy due to weak binding of CO_2. On the other hand, the thermodynamic drivers for CO_2 capture are reduced, making physisorption difficult at atmospheric CO_2 levels due to reductions in selectivity and uptake capacity. Water vapor

is ubiquitous in ambient air. Some physical sorbents, such as zeolites, exhibit a very high affinity toward water vapor; therefore, water can significantly reduce their CO_2 uptake through competitive adsorption. As for hydrophobic sorbents such as activated carbons, the negative effect of water on CO_2 uptake is not as drastic as for zeolites, particularly at low relative humidity (RH).

Zaworotko and co-workers[41,42] studied the CO_2 sorption capacities of zeolite 13X, tetraethylenepentamine-impregnated SBA-15, and microporous and ultramicroporous MOF physisorbents, as shown in **Figure 2**. The results showed that physisorbents can capture CO_2 from CO_2-rich gas mixtures, but competition and reaction with atmospheric moisture significantly reduced their DAC performance. The sorption results of CO_2 and H_2O pointed out that control of pore size and pore chemistry through crystal engineering may be a successful strategy to improve CO_2 capture performance. One advantage of physisorbents is that faster and less energy-intensive recycling of physisorbents could compensate for the lower uptake values.

Strong base materials

Chemisorption and physisorption are differentiated based on the strength of sorbate–sorbent interactions. Chemisorption occurs when a chemical bond is formed between the sorbate and sorbent. Metal hydroxides or oxides, or alkaline salts can easily scrub CO_2 from the air and convert it to metal carbonates via chemisorption.[14,17,18,43] This works well because of its high chemical binding energy. It is then possible to release a
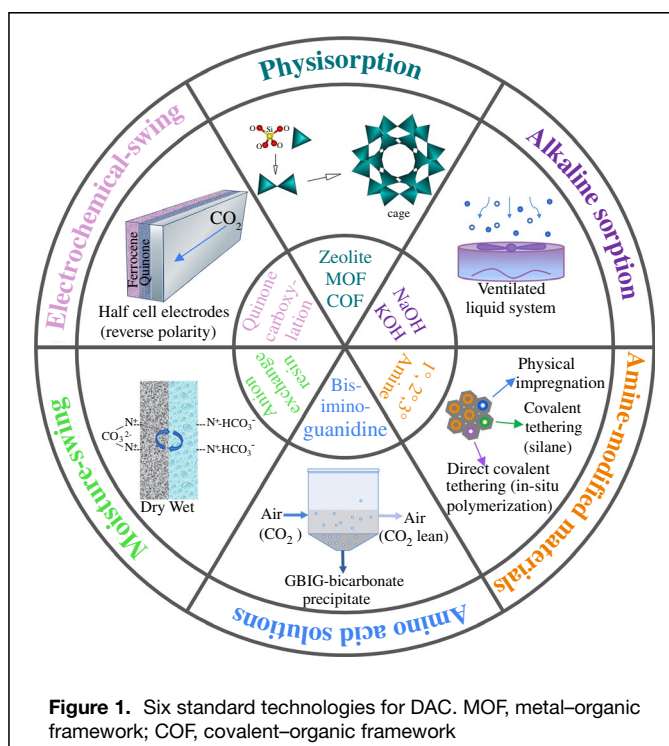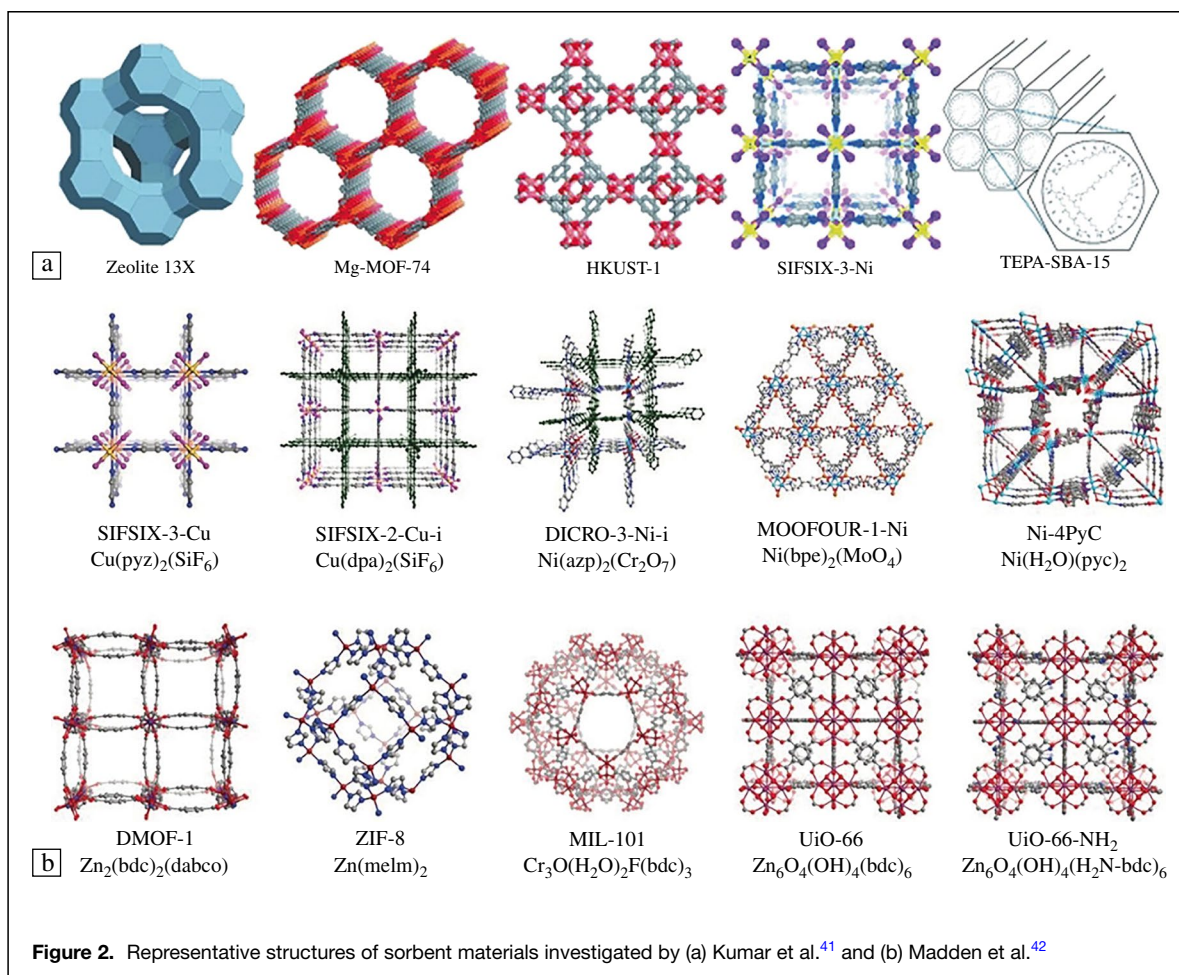

Figure 1. Six standard technologies for DAC. MOF, metal–organic framework; COF, covalent–organic framework

concentrated stream of CO_2 via a calcination step. However, calcination requires heating the material to high temperatures. Overcoming the binding energy and paying for the heat losses encountered during the heating of bulk materials to high temperatures is energy-intensive, and heat losses are difficult to avoid. However, some of this heat can be recovered through heat-integration processes. This high-energy regeneration step makes the capture with metal hydroxides or oxides or alkaline salts technically and economically difficult.[44]

One technique proposed by Lackner[45] early in this category is utilizing sodium hydroxide to uptake CO_2 from the atmosphere, forming sodium carbonate. Calcium hydroxide is then added to cause calcium carbonate to precipitate out from sodium carbonate solution. Lastly, the calcium carbonate is heated at high temperatures to form calcium oxide and CO_2, which is then compressed for storage. Baciocchi et al.[18] proposed two process designs based on this technique. The total fuel energies reported in the paper are 17 and 12 GJ/tCO_2 captured, respectively, for two different options, meaning that twice as much energy is required to remove the CO_2 emitted from a given amount of coal compared to the energy content of coal, 9 GJ/tCO_2. Energy consumption on the calcination step is too large due to the highly endothermic nature of the

reaction. Also, based on this technique, Keith et al.[46] described the process in sufficient detail in an industrial plant, including energy and materials balances, commercial engineering cost breakdown, and pilot plant data. The energy cost is 5.25 GJ/tCO_2 captured. The cost per tCO_2 from the atmosphere ranges from 94 to 232 $/$tCO_2$.
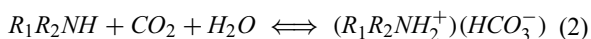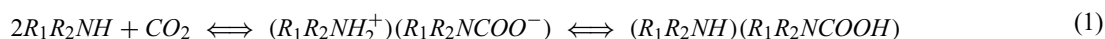
Wilcox et al.[47] detailed a land-based enhanced weathering cycle utilizing magnesite ($MgCO_3$) feedstock to repeatedly capture CO_2 from the atmosphere, shown in **Figure 3**. The work described here is germane to DAC technology. In this process, $MgCO_3$ is calcined, producing caustic magnesia (MgO) and high-purity CO_2. Researchers have investigated forming MgO with properties optimized for CO_2 capture at ambient conditions and obtained 1.4 mmol/g of CO_2 uptake capacity.[10] This MgO is spread over land to carbonate for a year by reacting with atmospheric CO_2. The authors claimed the process could cost $46–159 tCO_2^{-1} net removed from the atmosphere and has the scalable potential to remove 2–3 GtCO_2/year. Beerling et al.[48] also discussed the challenges and opportunities of enhanced rock weathering deployment. The techno-economic assessment of the potential of enhanced rock weathering to contribute DAC requires further integration of nation-by-nation quantitative analysis.

Figure 2. Representative structures of sorbent materials investigated by (a) Kumar et al.[41] and (b) Madden et al.[42]

a — Zeolite 13X — Mg-MOF-74 — HKUST-1 — SIFSIX-3-Ni — TEPA-SBA-15

SIFSIX-3-Cu $Cu(pyz)_2(SiF_6)$ — SIFSIX-2-Cu-i $Cu(dpa)_2(SiF_6)$ — DICRO-3-Ni-i $Ni(azp)_2(Cr_2O_7)$ — MOOFOUR-1-Ni $Ni(bpe)_2(MoO_4)$ — Ni-4PyC $Ni(H_2O)(pyc)_2$

b — DMOF-1 $Zn_2(bdc)_2(dabco)$ — ZIF-8 $Zn(melm)_2$ — MIL-101 $Cr_3O(H_2O)_2F(bdc)_3$ — UiO-66 $Zn_6O_4(OH)_4(bdc)_6$ — UiO-66-NH_2 $Zn_6O_4(OH)_4(H_2N-bdc)_6$

Amine-modified materials

CO_2 capture in aqueous amine solutions has long been practiced for commercial-scale CO_2 separation from the gas mixture. Monoethanolamine (MEA), diethanolamine (DEA), and methyldiethanolamine (MDEA) are the most popular for large-scale operations.[49] The major drawback of these aqueous solutions is their high heat capacities and their heat losses due to evaporation. This causes the regeneration step to become energy-intensive and costly. Toxic amine evaporation into the air is another major drawback.

To lower the energy cost, amines and polyamines on solid supports have been proposed. Amine-modified solid materials have shown significant potential for CO_2 capture from the ambient air because of their low energy consumption, chemical stability, and high reversibility. Two different sorption mechanisms are observed: (1) in dry conditions, primary and secondary amines react with CO_2 to form carbamate or carbamic acid; (2) in moist conditions, amines react with CO_2 to produce bicarbonate. Equations 1 and 2 show secondary amines R_1R_2NH react with CO_2 under dry and wet conditions, respectively

$$2R_1R_2NH + CO_2 \iff (R_1R_2NH_2^+)(R_1R_2NCOO^-) \iff (R_1R_2NH)(R_1R_2NCOOH) \tag{1}$$

$$R_1R_2NH + CO_2 + H_2O \iff (R_1R_2NH_2^+)(HCO_3^-) \tag{2}$$

The most common methods for the preparation of supported amine sorbents shown in **Figure 4** are (1) impregnation of amines on porous materials, such as silica, alumina, activated carbon, MOFs, zeolites, and clays.[50–53] For instance, Xu et al.[54] developed "molecular basket" sorbents by loading polyethylenimine (PEI) into a mesoporous molecular sieve. This first molecular basket popularized PEI-modified sorbents for CO_2 capture. To address the stability issue, Choi et al.[55] proposed a new Class 1 sorbent comprised of PEI on porous silica, which can be used as a sorbent to capture CO_2 from ultra-dilute gas streams such as ambient air. (2) Chemically grafting the amine functional group onto the surface of the supports.[56–59] Belmabkhout et al.[56] first proposed the use of tri-amine-grafted mesoporous silica, TRI-PE-MCM-41, to capture CO_2 from dry and humid air. This new sorbent showed high selectivity for CO_2 over N_2 and O_2 under both dry and humid conditions, with a 0.98 mmol/g CO_2 uptake capacity at low CO_2 concentrations (400 ppm) at 25°C. Potter et al.[60] pointed out that the use of porous alumina supports may offer potential stability advantages than porous silica, because alumina supports typically show more resilience to stream treatments than silica. (3) Other procedures such as amine tethering and ligand modification have also been used,[56–59] such as on MOFs.[61]

Class 1 sorbents have high CO_2 sorption capacity when the organic phase has low viscosity and high content of primary and secondary amine groups. However, due to the weak physical interaction of monomeric or polymeric amines and porous materials, Class 1 amines tend to deteriorate under humid conditions due to water condensation and solubilization, which reduces sorption performance.[50–52,54] Even under dry conditions, small liquid amino compounds, MEA, DEA, and diisopropanolamine (DIPA) have considerable stability problems due to their relatively low boiling point and high volatility.[50] Amines with large molecular weight are less volatile. However, a large molecular weight is not conducive to the diffusion of CO_2 in and out of the porous material. Sorption kinetics can be improved through the selection of appropriate diamines. Primary amines and moderate-to-high densities of triamine result in a balance of capacity and kinetics that can potentially be better utilized for continuous DAC processes. Future studies should further concentrate on the desorption energy demands and regeneration methods of these materials under DAC conditions.

Class 2 sorbents have amine functional groups grafted directly onto the surface of the support, making the sorbent more stable during the regeneration process than Class 1 sorbents. Though solid-supported amines have lower regeneration energies and temperatures than alkaline sorbents, they have slower sorption kinetics. Their optimum performance requires maintaining a high surface area over multiple cycles and preventing water condensation in the pores. They also tend to chemically and thermally degrade over time, especially when heated in the open air.
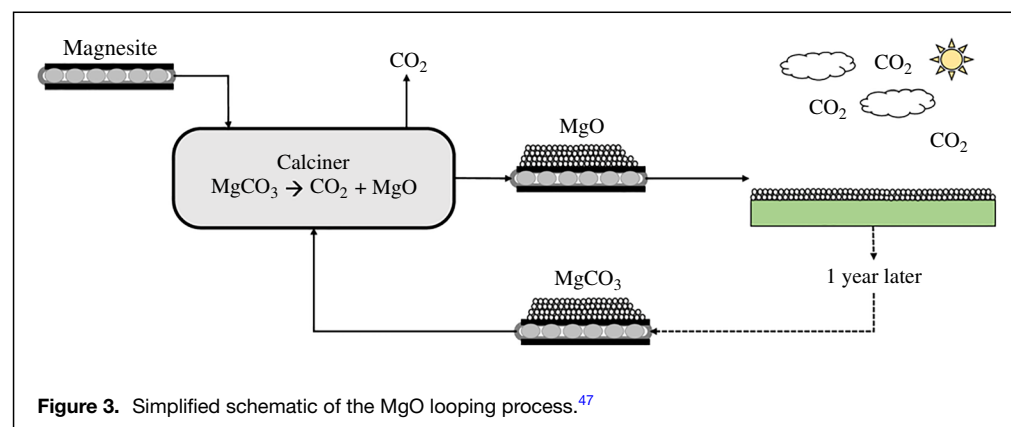
Amino acid and guanidine compound sorbents

Developing new concepts and materials that combine the best attributes of liquid and solid sorbents, and are energy efficient and cost-effective, remains a high priority in DAC research. Custelcean
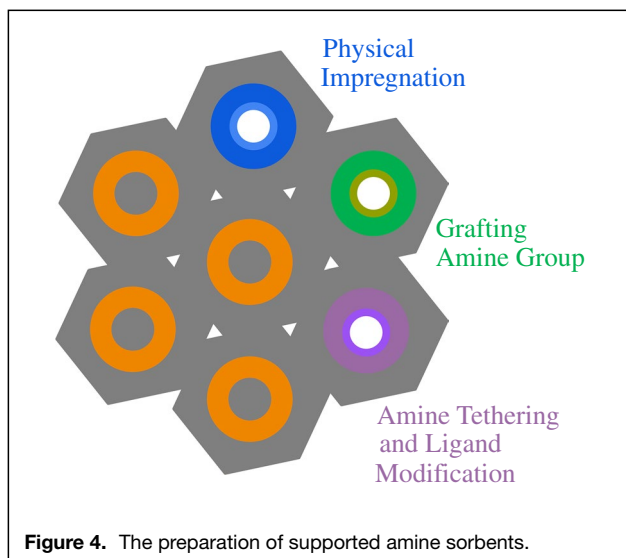

Figure 3. Simplified schematic of the MgO looping process.[47]

Figure 4. The preparation of supported amine sorbents.

et al.[23–28] report an approach to DAC mainly using off-the-shelf materials and equipment. First, CO_2 sorption is achieved with readily available and environmentally friendly aqueous amino acid solutions (glycine and sarcosine). The CO_2-loaded solutions are then reacted with a simple guanidine compound, which crystallizes as a very insoluble carbonate salt and regenerates the amino acid sorbent. Finally, effective CO_2 release and near-quantitative regeneration of the guanidine compound are achieved by relatively mild heating of the carbonate crystals using concentrated solar power. The process is shown in **Figure 5**.

The mechanism[28] and efficacy[23] of the crystallization-based approach to CO_2 separation from the air have been explained. First, the guanidine groups of the PyBIG ligand are sufficiently basic to become protonated in moderately alkaline carbonate/bicarbonate solutions (pH 8.5–10.5), thereby driving the crystallization of the bisguanidinium carbonate salt. Second, the very low aqueous solubility of crystalline $PyBIGH_2(CO_3)$ $(H_2O)_4$ facilitates its recovery from solution without the need of heating or evaporating water, which are energy-intensive. Third, the close proximity of the carbonate and guanidinium groups, hydrogen-bonded within the crystal, facilitates proton transfer among them and the formation of H_2CO_3, which then decomposes into CO_2 and H_2O with the possible assistance of the included water molecules in the crystal. Finally, as the PyBIG ligand can be quantitatively regenerated and recycled, the only chemical consumed in the overall CO_2 separation cycle is water, which could be easily recovered by condensation if desired.

The effectiveness of the CO_2 capture process depends to a large extent on a number of crystallization parameters, such as kinetics of crystallization, particle size distribution, and crystal habit, which need to be optimized as part of the technology maturation. Further work is required to accurately measure the 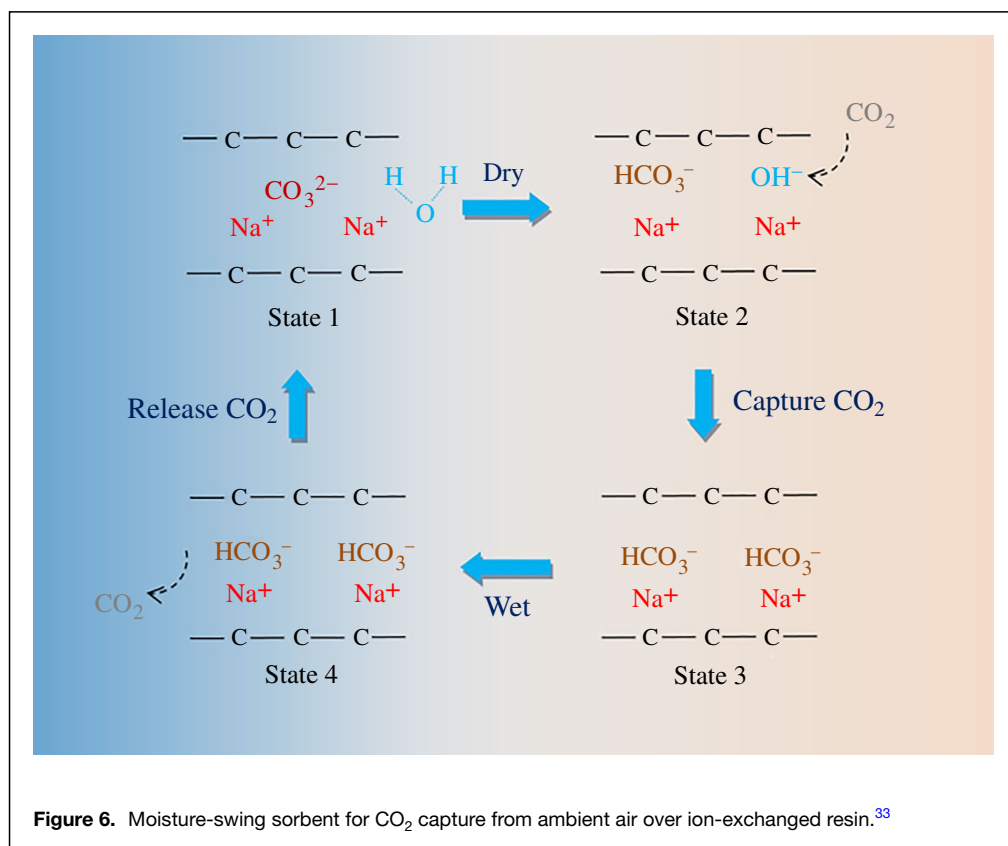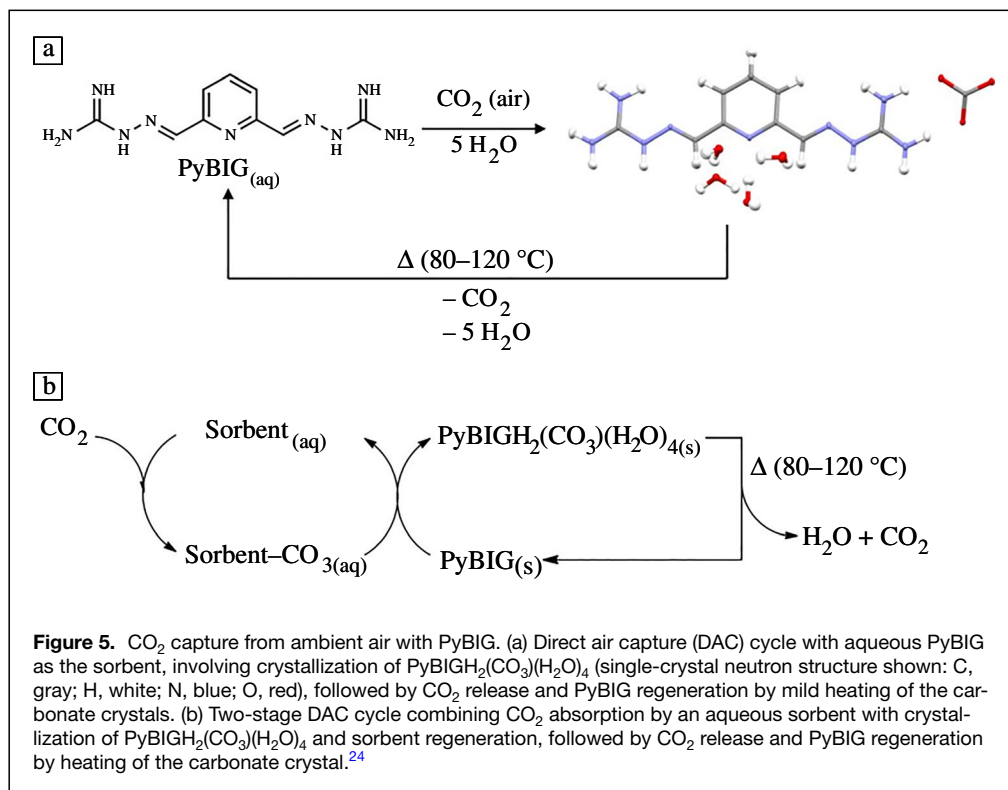kinetics of carbonate crystallization and the influence of various parameters, such as temperature, particle size, and stirring method, on the rate of sorbent regeneration. Finally, this technique that requires future consideration is how to scale up the carbonate crystallization and handle large volumes of solid.

Moisture-swing CO_2 sorbent

To overcome the high energy cost associated with amine-based sorbents, a technique to capture CO_2 from ambient air was proposed by Lackner[9] using moisture-swing sorbents. They bind CO_2 in dry surroundings and release it in the presence of moisture. Water plays a key role in the CO_2 sorption–desorption process. Such sorbents consist of an anion-exchange resin containing quaternary ammonium cations attached to a polymer network with hydroxide or carbonate anions as mobile counterions. As illustrated in **Figure 6**, for a wet resin without CO_2 loading, which Shi et al.[33] labeled State 1, the more stable carbonate anions are the dominant counterions. As the water content of the resin is reduced during drying, the carbonate ion becomes less stable and results in the splitting of one of the remaining water molecules to form a HCO_3^- ion and an OH^- ion. Due to the presence of OH^- ions, State 2 has a strong affinity to CO_2. Even at low partial pressure, the resin absorbs CO_2 from air. This results in a fully bicarbonated state, State 3. Wetting the resin leads to the full hydration of the bicarbonate ions, State 4. This results in the escape of CO_2 in the wet condition (desorption), which evolves into State 1 and the cycle is completed.

Other sorbents for moisture swing were prepared by impregnating amine-containing polymer on carbon black and further quaternization.[62] Another new moisture-swing sorbent was developed from a biomass material, chitosan, as starting material.[31] The biomass was cross-linked by poly(vinyl alcohol) in a three-dimensional network to address the water solubility of chitosan and increase the porosity of the material. Recently, Shi et al. further reported the effects of parameters of the sorbents on CO_2 capture efficiency, which can lead the way toward the optimization of sorbents for DAC in the future.[33]

The moisture-swing technology has several advantages over conventional thermal-swing or pressure-swing sorption systems[13]: (1) The swing between sorption and desorption moisture-swing sorbents can be accomplished with low-cost water instead of costly energy. (2) Water sorption and CO_2 sorption on the resin move in opposite directions; thus the energy penalties for sorption and desorption of water are eliminated. (3) The moisture swing can simplify the system design because heating and cooling units are not necessary. Much of the sorbent mass and mass of the sorbent support structure simply gain and lose sensible heat in a swing. Moisture swings also come with some disadvantages: (1) Water must be relatively clean to avoid the contamination of the resin with impurity anions. (2) Performance of the system is weather-sensitive. Humidity-swing systems perform best in hot, dry climes. A cold but moist climate could be improved by combining a moisture swing with a mild thermal swing.

Figure 5. CO_2 capture from ambient air with PyBIG. (a) Direct air capture (DAC) cycle with aqueous PyBIG as the sorbent, involving crystallization of $PyBIGH_2(CO_3)(H_2O)_4$ (single-crystal neutron structure shown: C, gray; H, white; N, blue; O, red), followed by CO_2 release and PyBIG regeneration by mild heating of the carbonate crystals. (b) Two-stage DAC cycle combining CO_2 absorption by an aqueous sorbent with crystallization of $PyBIGH_2(CO_3)(H_2O)_4$ and sorbent regeneration, followed by CO_2 release and PyBIG regeneration by heating of the carbonate crystal.[24]

Figure 6. Moisture-swing sorbent for CO_2 capture from ambient air over ion-exchanged resin.[33]

(3) The partial pressure of the released CO_2 by humidity swing is relatively low, requiring additional concentration steps before storage.

Electrochemical-swing CO_2 sorbent

Electrochemical CO_2 capture has aroused the interest of researchers[38–40] because it does not consume heat energy to release CO_2. However, a high concentration of CO_2 from 0.6 to 15%[63] is required as feeding gas during its sorption process. Capturing CO_2 directly from the air by the method of electrochemistry still requires further exploration. Recently, Hatton et al.[37] reported a novel solid-state faradaic electrochemical-swing reactive sorption system, eliminating the need for thermal energy and producing a high-purity CO_2 stream. It comprises an electrochemical cell that exploits the reductive addition of CO_2 to quinones for carbon capture. The reported device is compact and flexible, obviates the need for ancillary equipment, and eliminates the parasitic energy losses by using electrochemically activated redox carriers. An electrochemical cell with a polyanthraquinone–carbon nanotube composite negative electrode captures CO_2 upon charging via the carboxylation of reduced quinones, and releases CO_2 upon discharge. The process is shown in **Figure 7**. Hatton et al.[37] demonstrate the capture of CO_2 both in

a sealed chamber and in an adsorption bed from inlet streams of CO_2 concentrations as low as 0.6% (6000 ppm) and up to 10%, at a constant CO_2 capacity with a faradaic efficiency of >90%, and a work of 40–90 kJ per mole of CO_2 captured, with the durability of electrochemical cells showing <30% loss of capacity after 7000 cycles.
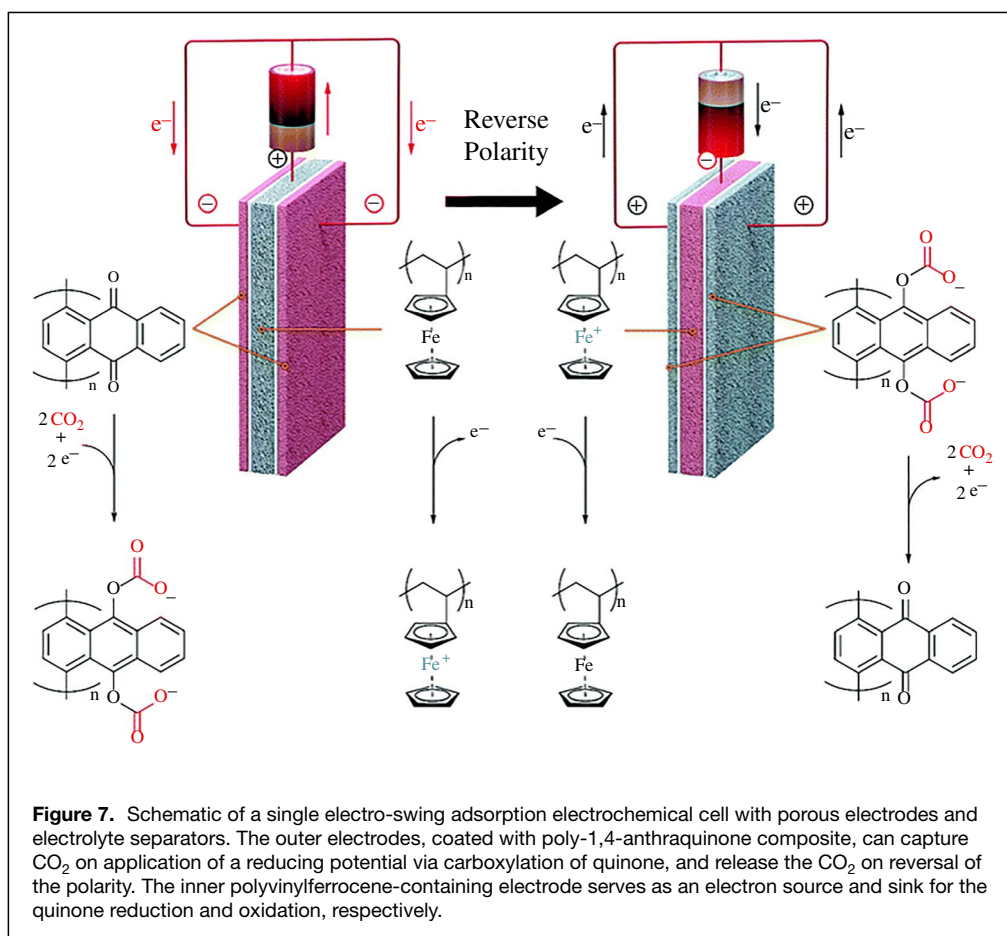
Further optimization of the electrochemical-swing sorption process can be obtained by refining the electrode chemistries and their assembly into compact adsorption devices to address a wide range of CO_2 mitigation strategies. Also, the performance of electrochemical-swing sorption for DAC needs to be further tested at 400 ppm of CO_2 under atmosphere air condition. The feed gas in the study are mixtures of nitrogen and carbon dioxide. Another question that needs to be answered is how stable quinones are during air oxidation. Also, the process of electrochemical CO_2 capture may be challenging to scale up. A very large electrode surface area is necessary for an industrial DAC application.

Performance of sorbent materials

Energy requirements for regeneration process

Energy consumption during the regeneration process is an important indicator for evaluating sorbents. Physisorption materials require the heat of adsorption from 25.5 to 56 kJ/mol.[42] They also need extra heat to release the co-adsorbed H_2O with CO_2. A Ca-based calcination process[64] and Na-based decomposition and hydrolysis[65] process require the heat of adsorption of 179 kJ/mol of CO_2 and 135 kJ/mol of CO_2, respectively, with very high regeneration temperatures. Large sensible heat transfers and the complexities of the calcinations process greatly reduce the feasibility of these technologies.

The average value of reported heat of sorption of amine-based sorbents[3,22] was estimated around 80 kJ/mol of CO_2 based on the average value of reported heat of sorption of CO_2 by amine solution.[3]

Figure 7. Schematic of a single electro-swing adsorption electrochemical cell with porous electrodes and electrolyte separators. The outer electrodes, coated with poly-1,4-anthraquinone composite, can capture CO_2 on application of a reducing potential via carboxylation of quinone, and release the CO_2 on reversal of the polarity. The inner polyvinylferrocene-containing electrode serves as an electron source and sink for the quinone reduction and oxidation, respectively.

(See figure on next page.)

Figure 8. There are five categories of materials displayed: (1) amine-modified materials, (2) moisture-swing sorbents, (3) amino acid with guanidine, (4) strong base materials, and (5) physisorption materials. Electrochemical-swing sorbents are not shown in this figure, as there is a lack of standardized measurement. Capacities of sorbents are shown as columns at the top. The kinetics of sorbents are labeled with numbers at the bottom. Blank spaces are used when the kinetics data of the sorbent are not available. Stabilities are shown as dots at the bottom. All data can also be found from Tables I to V in the Supporting Information.

Extra energy is also required to heat the support materials of sorbents and to evaporate the co-adsorbed water during the regeneration. The water adsorption at humid conditions is between 2.7 and 3.7 mol of H_2O per mole of CO_2 with the heat of water adsorption between -53 and -47 kJ mol^{-1} of H_2O. This will cause an additional energy consumption of 140–170 kJ mol^{-1} of CO_2.

The overall enthalpy of CO_2 release from $PyBIGH_2(CO_3)$ $(H_2O)_4$ is about 223 kJ/mol of CO_2.[24] The enthalpy includes 148 kJ/mol of dehydration of the carbonate salt, and 75 kJ/mol of CO_2 release from the anhydrous carbonate salt. The series of endothermic events are between 80ºC and 140ºC. While a large fraction of the heat required to release the CO_2 is spent on water evaporation, some of the waste heat could be recovered by process modifications that involve water condensation steps in which the resulting heat is collected and reused via heat exchangers.[24]

The energy use of electrochemical-swing sorbent for CO_2 capture is from 20 to 80 kJ/mol of CO_2.[37] When the energy use is about 43 kJ/mol, 60% fraction of CO_2 can be released from the electrode; when the energy use is about 80 kJ/mol, 95% fraction of CO_2 can be released from the electrode.[37]

The energy consumption of moisture-swing sorbent has been reported about 50 kJ/mol of CO_2 compared to other sorbents.[29] Unlike in a thermal swing, which unavoidably heats the bulk material, in a moisture swing of an intrinsically hydrophobic resin, the water consumption scales with the CO_2 loading rather than the mass of the resin. This eliminates a major source of energy consumption.

Stability, kinetics, and capacity of sorbents

Challenges facing sorbent design are sorbent stability, sorbent kinetics, and sorbent capacity. Stability or longevity, and sorbent cycle duration data are scarcely available in the literature. A summary of sorbent stability, sorbent kinetics, and sorbent capacity for DAC is presented in **Figure 8**. The existing data typically report capacity variations after less than tens of consecutive cycles, although air capture sorbent needs to undergo tens of thousands of cycles. The stability of sorbents needs to be improved. Fast sorbent loading and unloading cycles are important for reducing costs and for building lightweight collectors. Kinetics are affected by binding energies and also by diffusion into porous materials and by the geometry of sorbent materials. Improved kinetics can lower costs. These

types of optimizations have not yet been considered in detail. Large sorbent capacity can reduce the cost of CO_2 capture. To improve the capacity of amine sorbents, the different molecular weights of amines can be prepared in the different pore sizes of porous materials. This can improve the functionality of amines.

Summary and outlook

Some reports claim conventional technologies for DAC are uneconomical.[66] DAC costs will fall as a result of the learning-by-doing from deployment, with each iteration on the technology becoming increasingly more economical, similar to the technologies of light disk and solar PV panel.[12] With the possible carbon taxes on CO_2 emitting industries, DAC is an indispensable tool to stop global warming.[13] DAC technologies represent a myriad of options: the development of all of these options is critical in reaching mid-century climate goals of 1.5℃.

Solid sorbents are central to the capture of CO_2 from ambient air. Direct air capture is still at its early stage, with many challenges remaining. Many sorbents rely on a thermal swing. The energy requirement is often very large, because of the large bulk mass that is being heated and the coevolution of steam. The energy cost of thermal regeneration is further exacerbated by the presence of binders or other support materials that keep the sorbent in place. These materials add heat capacity without contributing directly to CO_2 capture. Thin coatings of sorbents with fast heat and mass transfer can reduce energy losses into the support structure by keeping regeneration times shorter. There have been reports that show ultrahigh CO_2 permeance in gas separation membranes, and thus membrane separation could be a potential new technology for DAC in addition to sorbent-based CO_2 capture.

The moisture-swing concept is different from other ways of loading and unloading a sorbent. Although some achievements on the moisture-swing technique have been made, materials employed thus far are limited to a few polymer resins, and novel nanomaterials with functional groups and gas diffusion channels need to be developed in the future. CO_2 capacity of current moisture-driven CO_2 sorbents will decrease gradually with the increase of humidity level. This is one major issue because the implementation of CO_2 capture device is limited to locations where the environment is dry. Designing new materials that can capture a comparable amount of CO_2 in either dry or wet conditions is essential.
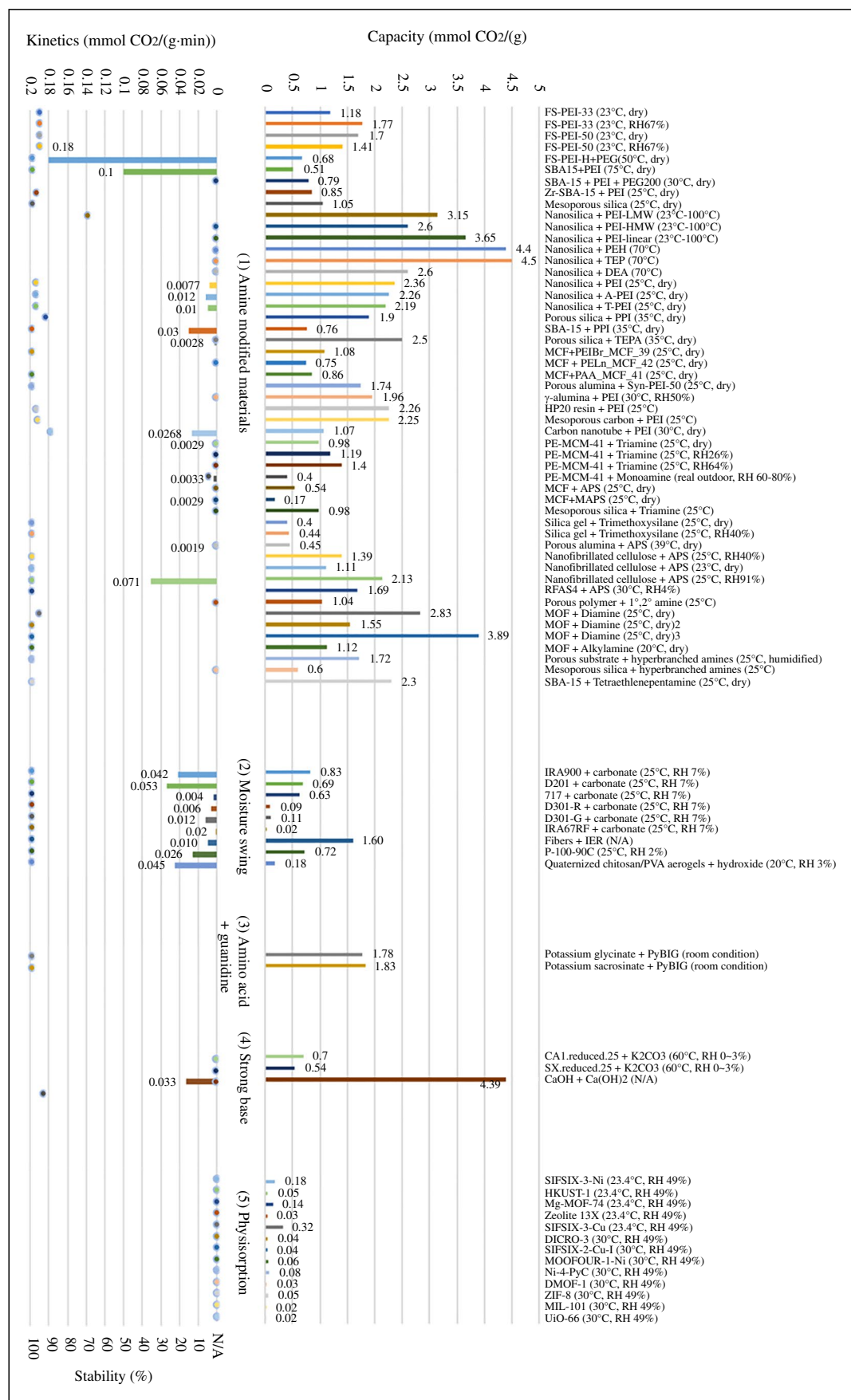
Fully loaded sorbents should release CO_2 out in liquid water but not in a relatively wet condition. Researchers can adjust pore size, spacing of cations, and surface hydrophobicity of the sorbents to improve their performance. The construction of nanoscale-ordered channels in moisture-swing materials is also crucial to enhancing material exchange efficiency during CO_2 sorption/desorption processes. Material engineering strategies can improve kinetics during the sorption/desorption process, including *in situ* growth and template synthesis method. Sorbents do not require prohibitively expensive feedstock or have large energy demands during synthesis.

In conclusion, sorbents are critical to the success of DAC and there remains much room for their improvement. Development needs to progress quickly, because climate change is an urgent crisis. Many studies focus on the development of sorbents for high sorption capacity and fast kinetics. However, studies on practical factors and sorption processes are also necessary for engineering applications. For example, the sorption process of a sorbent for DAC should be conducted in an actual ambient air condition (78% N_2, 21% O_2, 1% Inert gases, and water vapors, under different humidity conditions). In future studies, all sorbents for DAC should be assessed in all facets, such as sorbent stability, sorption kinetics, sorption capacity, selectivity, regeneration energy penalty, and cost. Energy-efficient and low-cost CO_2 sorbents must be developed to solve the issue of global climate change.

Acknowledgments

Conflict of interest
All authors declare no competing interests.

Data availability
All data generated or analyzed during this study are included in this published article (and its supplementary information files).

Supplementary Information
The online version contains supplementary material available at https://doi.org/10.1557/s43577-022-00320-7.

References
1. T.F. Stocker, A. Schmittner, *Nature* **388**, 862 (1997). https://doi.org/10.1038/42224
2. R.K. Pachauri, *Climate Change 2014: Synthesis Report. Contribution of Working Groups I, II and III to the Fifth Assessment Report of the Intergovernmental Panel on Climate Change* (IPCC, Geneva, 2014)
3. S. Choi, J.H. Drese, C.W. Jones, *ChemSusChem* **2**, 796 (2009). https://doi.org/10.1002/cssc.200900036
4. Y. Xu, C. Luo, H. Sang, B. Lu, F. Wu, X. Li, L. Zhang, *Chem. Eng. J.* **435** (Pt. 2), 134960 (2022). https://doi.org/10.1016/j.cej.2022.134960
5. Y. Xu, C. Shen, B. Lu, C. Luo, F. Wu, X. Li. L. Zhang, *Carbon Capture Sci. Technol.* **1**, 100015 (2021). https://doi.org/10.1016/j.ccst.2021.100015
6. X. Shi, H. Xiao, H. Azarabadi, J. Song, X. Wu, X. Chen, K.S. Lackner, *Angew. Chem. Int. Ed.* **59**(18), 6984 (2020). https://doi.org/10.1002/anie.201906756
7. K. Lackner, H.-J. Ziock, P. Grimes, *Carbon Dioxide Extraction from Air: Is It An Option?* (Los Alamos National Lab, New Mexico, 1999)
8. D.W. Keith, M. Ha-Duong, J.K. Stolaroff, *Clim. Change* **74**, 17 (2006). https://doi.org/10.1007/s10584-005-9026-x
9. K.S. Lackner, *Eur. Phys. J. Spec. Top.* **176**, 93 (2009). https://doi.org/10.1140/epjst/e2009-01150-3
10. V.A. Tuan, C.H. Lee, *Vietnam J. Chem.* **56**, 197 (2018). https://doi.org/10.1002/vjch.201800013
11. International Energy Agency (IEA), *Special Report on Carbon Capture Utilisation and Storage, CCUS in Clean Energy Transitions* (IEA, Paris, 2020). https://www.iea.org/reports/ccus-in-clean-energy-transitions
12. K.S. Lackner, H. Azarabadi, *Ind. Eng. Chem. Res.* **60**, 8196 (2021). https://doi.org/10.1021/acs.iecr.0c04839
13. K.S. Lackner, S. Brennan, J.M. Matter, A.-H.A. Park, A. Wright, B. van der Zwaan, *Proc. Natl. Acad. Sci. U.S.A.* **109**(33), 13156 (2012). https://doi.org/10.1073/pnas.1108765109
14. O. Shekhah, Y. Belmabkhout, Z. Chen, V. Guillerm, A. Cairns, K. Adil, M. Eddaoudi, *Nat. Commun.* **5**, 4228 (2014). https://doi.org/10.1038/ncomms5228
15. M. Oschatz, M. Antonietti, *Energy Environ. Sci.* **11**, 57 (2018). https://doi.org/10.1039/C7EE02110K
16. V. Presser, J. McDonough, S.-H. Yeon, Y. Gogotsi, *Energy Environ. Sci.* **4**, 3059 (2011). https://doi.org/10.1039/C1EE01176F
17. D.W. Keith, M. Ha-Duong, J.K. Stolaroff, *Clim. Change* **74**, 17 (2006)
18. R. Baciocchi, G. Storti, M. Mazzotti, *Chem. Eng. Process.* **45**, 1047 (2006)
19. W. Chaikittisilp, H.-J. Kim, C.W. Jones, *Energy Fuels* **25**, 5528 (2011)
20. S.A. Didas, A.R. Kulkarni, D.S. Sholl, C.W. Jones, *ChemSusChem* **5**, 2058 (2012)
21. M.A. Sakwa-Novak, C.W. Jones, *ACS Appl. Mater. Interfaces* **6**, 9245 (2014)
22. A. Holewinski, M.A. Sakwa-Novak, C.W. Jones, *J. Am. Chem. Soc.* **137**, 11749 (2015). https://doi.org/10.1021/jacs.5b06823
23. C.A. Seipp, N.J. Williams, M.K. Kidder, R. Custelcean, *Angew. Chem. Int. Ed.* **56**, 1042 (2017). https://doi.org/10.1002/anie.201610916
24. F.M. Brethomé, N.J. Williams, C.A. Seipp, M.K. Kidder, R. Custelcean, *Nat. Energy* **51**, 23338 (2018)
25. R. Custelcean, *Chem. Sci.* (2021). https://doi.org/10.1039/D1SC04097A
26. R. Custelcean, K.A. Garrabrant, P. Agullo, N.J. Williams, *Cell Rep. Phys. Sci.* **2**, 100385 (2021). https://doi.org/10.1016/j.xcrp.2021.100385
27. R. Custelcean, N.J. Williams, K.A. Garrabrant, P. Agullo, F.M. Brethomé, H.J. Martin, M.K. Kidder, *Ind. Eng. Chem. Res.* **58**(51), 23338 (2019). https://doi.org/10.1021/acs.iecr.9b04800
28. N.J. Williams, C.A. Seipp, F.M. Brethomé, Y.-Z. Ma, A.S. Ivanov, V.S. Bryantsev, M.K. Kidder, H.J. Martin, E. Holguin, K.A. Garrabrant, R. Custelcean, *Chemistry* **5**(3), 719 (2019). https://doi.org/10.1016/j.chempr.2018.12.025
29. T. Wang, K.S. Lackner, A. Wright, *Environ. Sci. Technol.* **45**, 6670 (2011). https://doi.org/10.1021/es201180v
30. X. Shi, Q. Li, T. Wang, K.S. Lackner, *PLoS One* **12**, e0179828 (2017). https://doi.org/10.1371/journal.pone.0179828
31. J. Song, J. Liu, W. Zhao, Y. Chen, H. Xiao, X. Shi, Y. Liu, X. Chen, *Ind. Eng. Chem. Res.* **57**(14), 4941 (2018). https://doi.org/10.1021/acs.iecr.8b00064
32. X. Shi, H. Xiao, X. Chen, K.S. Lackner, *Chem. Eur. J.* **22**, 18326 (2016)
33. X. Shi, H. Xiao, K. Kanamori, A. Yonezu, K.S. Lackner, X. Chen, *Joule* **4**(8), 1823 (2020). https://doi.org/10.1016/j.joule.2020.07.005
34. J. Song, L. Zhu, X. Shi, Y. Liu, H. Xiao, X. Chen, *Energy Fuels* **33**(7), 6562 (2019). https://doi.org/10.1021/acs.energyfuels.9b00863
35. M. Armstrong, X. Shi, B. Shan, K. Lackner, B. Mu, *AIChE J.* **65**, 214 (2019). https://doi.org/10.1002/aic.16418
36. X. Shi, H. Xiao, X. Liao, M. Armstrong, X. Chen, K.S. Lackner, *J. Chem. Phys.* **149**, 164708 (2018). https://doi.org/10.1063/1.5027105
37. S. Voskian, T.A. Hatton, *Energy Environ. Sci.* **12**, 3530 (2019). https://doi.org/10.1039/C9EE02412C
38. P. Singh, J.H. Rheinhardt, J.Z. Olson, P. Tarakeshwar, V. Mujica, D.A. Buttry, *J. Am. Chem. Soc.* **139**(3), 1033 (2017). https://doi.org/10.1021/jacs.6b10806
39. D.H. Apaydin, M. Gora, E. Portenkirchner, K.T. Oppelt, H. Neugebauer, M. Jakesova, E.D. Głowacki, J. Kunze-Liebhäuser, M. Zagorska, J. Mieczkowski, N.S. Sariciftci, *ACS Appl. Mater. Interfaces* **9**, 12919 (2017). https://doi.org/10.1021/acsami.7b01875
40. J.H. Rheinhardt, P. Singh, P. Tarakeshwar, D.A. Buttry, *ACS Energy Lett.* **2**, 454 (2017). https://doi.org/10.1021/acsenergylett.6b00608
41. A. Kumar, D.G. Madden, M. Lusi, K.-J. Chen, E.A. Daniels, T. Curtin, J.J. Perry IV, M.J. Zaworotko, *Angew. Chem. Int. Ed.* **54**(48), 14372 (2015)
42. D.G. Madden, H.S. Scott, A. Kumar, K.-J. Chen, R. Sanii, A. Bajpai, M. Lusi, T. Curtin, J.J. Perry, M.J. Zaworotko, *Philos. Trans. R. Soc. A* **375**, 20160025 (2017)
43. N. Masoud, G. Bordanaba-Florit, T. van Haasterecht, J.H. Bitter, *Ind. Eng. Chem. Res.* (2021). https://doi.org/10.1021/acs.iecr.1c01229

44. J. Wang, H. Huang, M. Wang, L. Yao, W. Qiao, D. Long, L. Ling, *Ind. Eng. Chem. Res.* **54**(19), 5319 (2015). https://doi.org/10.1021/acs.iecr.5b01060

45. K.S. Lackner, P. Grimes, H. Ziock, *SourceBook-The Energy Ind. J. Issues* **57**, 6 (1999)

46. D.W. Keith, G. Holmes, D. St. Angelo, K. Heidel, *Joule* **2**, 1573 (2018). https://doi.org/10.1016/j.joule.2018.05.006

47. N. McQueen, P. Kelemen, G. Dipple, P. Renforth, J. Wilcox, *Nat. Commun.* **11**, 3299 (2020). https://doi.org/10.1038/s41467-020-16510-3

48. D.J. Beerling, E.P. Kantzas, M.R. Lomas, P. Wade, R.M. Eufrasio, P. Renforth, B. Sarkar, M.G. Andrews, R.H. James, C.R. Pearce, J.-F. Mercure, H. Pollitt, P.B. Holden, N.R. Edwards, M. Khanna, L. Koh, S. Ouegan, N.F. Pidgeon, I.A. Janssens, J. Hansen, S.A. Banwart, *Nature* **583**, 242 (2020). https://doi.org/10.1038/s41586-020-2448-9

49. K.A. Mumford, Y. Wu, K.H. Smith, G.W. Stevens, *Front. Chem. Sci. Eng.* **9**, 125 (2015). https://doi.org/10.1007/s11705-015-1514-6

50. A. Goeppert, S. Meth, G.S. Prakash, G.A. Olah, *Energy Environ. Sci.* **3**, 1949 (2010)

51. M.B. Yue, L.B. Sun, Y. Cao, Y. Wang, Z.J. Wang, J.H. Zhu, *Chem. A Eur. J.* **14**(11), 3442 (2008)

52. S. Choi, M.L. Gray, C.W. Jones, *ChemSusChem* **4**, 628 (2011). https://doi.org/10.1002/cssc.201000355

53. Y. Belmabkhout, R. Serna-Guerrero, A. Sayari, *Ind. Eng. Chem. Res.* **49**, 359 (2010). https://doi.org/10.1021/ie900837t

54. X. Xu, C. Song, J.M. Andresen, B.G. Miller, A.W. Scaroni, *Energy Fuels* **16**, 1463 (2002)

55. S. Choi, M.L. Gray, C.W. Jones, *ChemSusChem* **4**, 628 (2011)

56. Y. Belmabkhout, R. Serna-Guerrero, A. Sayari, *Chem. Eng. Sci.* **65**, 3695 (2010)

57. J.A. Wurzbacher, C. Gebald, A. Steinfeld, *Energy Environ. Sci.* **4**, 3584 (2011)

58. C. Gebald, J.A. Wurzbacher, P. Tingaut, T. Zimmermann, A. Steinfeld, *Environ. Sci. Technol.* **45**, 9101 (2011). https://doi.org/10.1021/es202223p

59. M.A. Sakwa-Novak, S. Tan, C.W. Jones, *ACS Appl. Mater. Interfaces* **7**, 24748 (2015). https://doi.org/10.1021/acsami.5b07545

60. M.E. Potter, K.M. Cho, J.J. Lee, C.W. Jones, *ChemSusChem* **10**, 2192 (2017). https://doi.org/10.1002/cssc.201700115

61. B. Wang, R.-B. Lin, Z. Zhang, S. Xiang, B. Chen, *J. Am. Chem. Soc.* **142**, 14399 (2020). https://doi.org/10.1021/jacs.0c06473

62. H. He, W. Li, M. Lamson, M. Zhong, D. Konkolewicz, C.M. Hui, K. Yaccato, T. Rappold, G. Sugar, N.E. David, K. Damodaran, S. Natesakhawat, H. Nulwala, K. Matyjaszewski, *Polymer* **55**(1), 385 (2014). https://doi.org/10.1016/j.polymer.2013.08.002

63. L. Legrand, O. Schaetzle, R.C.F. de Kler, H.V.M. Hamelers, *Environ. Sci. Technol.* **52**, 9478 (2018). https://doi.org/10.1021/acs.est.8b00980

64. M. Mahmoudkhani, D.W. Keith, *Int. J. Greenh. Gas Control* **3**, 376 (2009). https://doi.org/10.1016/j.ijggc.2009.02.003

65. V. Nikulshina, N. Ayesa, M.E. Gálvez, A. Steinfeld, *Chem. Eng. J.* **140**, 62 (2008). https://doi.org/10.1016/j.cej.2007.09.007

66. K.Z. House, A.C. Baclig, M. Ranjan, E.A. van Nierop, J. Wilcox, H.J. Herzog, *Proc. Natl. Acad. Sci. U.S.A* **108**(51), 20428 (2011)

67. A. Goeppert, M. Czaun, R.B. May, G.K. Surya Prakash, G.A. Olah, S.R. Narayanan, *J. Am. Chem. Soc.* **133**(50), 20164 (2011). https://doi.org/10.1021/ja2100005

68. S. Meth, A. Goeppert, G.K.S. Prakash, G.A. Olah, *Energy Fuels* **26**, 3082 (2012). https://doi.org/10.1021/ef300289k

69. X. Wang, X. Ma, V. Schwartz, J.C. Clark, S.H. Overbury, S. Zhao, X. Xu, C. Song, *Phys. Chem. Chem. Phys.* **14**, 1485 (2012). https://doi.org/10.1039/C1CP23366A

70. Y. Kuwahara, D.-Y. Kang, J.R. Copeland, P. Bollini, C. Sievers, T. Kamegawa, H. Yamashita, C.W. Jones, *Chem. Eur. J.* **18**(52), 16649 (2012)

71. S.H. Pang, L.-C. Lee, M.A. Sakwa-Novak, R.P. Lively, C.W. Jones, *J. Am. Chem. Soc.* **139**, 3627 (2017). https://doi.org/10.1021/jacs.7b00235

72. S.H. Pang, R.P. Lively, C.W. Jones, *ChemSusChem* **11**, 2628 (2018). https://doi.org/10.1002/cssc.201800438

73. D. Brilman, R. Veneman, *Energy Procedia* **37**, 6070 (2013)

74. W. Chaikittisilp, R. Khunsupat, T.T. Chen, C.W. Jones, *Ind. Eng. Chem. Res.* **50**, 14203 (2011)

75. Z. Chen, S. Deng, H. Wei, B. Wang, J. Huang, G. Yu, A.C.S. *Appl, Mater. Interfaces* **5**(15), 6937 (2013). https://doi.org/10.1021/am400661b

76. L. Keller, B. Ohs, J. Lenhart, L. Abduly, P. Blanke, M. Wessling, *Carbon* **126**, 338 (2018). https://doi.org/10.1016/j.carbon.2017.10.023

77. Y. Miao, Z. He, X. Zhu, D. Izikowitz, J. Li, *Chem. Eng. J.* **426**, 131875 (2021). https://doi.org/10.1016/j.cej.2021.131875

78. A. Sayari, Y. Belmabkhout, *J. Am. Chem. Soc.* **132**, 6312 (2010)

79. C. Gebald, J.A. Wurzbacher, A. Borgschulte, T. Zimmermann, A. Steinfeld, *Environ. Sci. Technol.* **48**, 2497 (2014). https://doi.org/10.1021/es404430g

80. L. He, M. Fan, B. Dutcher, S. Cui, X. Shen, Y. Kong, A.G. Russell, P. McCurdy, *Chem. Eng. J.* **189–190**, 13 (2012). https://doi.org/10.1016/j.cej.2012.02.013

81. W. Lu, J.P. Sculley, D. Yuan, R. Krishna, H.-C. Zhou, *J. Phys. Chem. C* **117**, 4057 (2013)

82. W.R. Lee, S.Y. Hwang, D.W. Ryu, K.S. Lim, S.S. Han, D. Moon, J. Choi, C.S. Hong, *Energy Environ. Sci.* **7**, 744 (2014)

83. S. Choi, T. Watanabe, T.-H. Bae, D.S. Sholl, C.W. Jones, *J. Phys. Chem. Lett.* **3**, 1136 (2012)

84. P.-Q. Liao et al., *Chem. Sci.* **7**, 6528 (2016). https://doi.org/10.1039/C6SC00836D

85. H. Li, K. Wang, D. Feng, Y.-P. Chen, W. Verdegaal, H.-C. Zhou, *ChemSusChem* **9**(19), 2832 (2016). https://doi.org/10.1002/cssc.201600768

86. S. Choi, J.H. Drese, P.M. Eisenberger, C.W. Jones, *Environ. Sci. Technol.* **45**, 2420 (2011)

87. W. Chaikittisilp, J.D. Lunn, D.F. Shantz, C.W. Jones, *Chem. A Eur. J.* **17**, 10556 (2011)

88. X. Wang, J. Song, Y. Chen, H. Xiao, X. Shi, Y. Liu, L. Zhu, Y.-L. He, X. Chen, *Ind. Eng. Chem. Res.* **59**(38), 16507 (2020). https://doi.org/10.1021/acs.iecr.0c03189 ☐

Xiaoyang Shi received his Ph.D. from Earth and Environmental Engineering at Columbia University in 2017 with Klaus S. Lackner for studies on the mechanism of humidity-swing CO_2 sorbents. Currently, he is working as a Post-doctoral Scholar at the Center for Advanced Materials for Energy and Environment, Columbia University. His research focuses on the synthesis of materials for CO_2 capture from ambient air and modeling of ion hydration reactions.
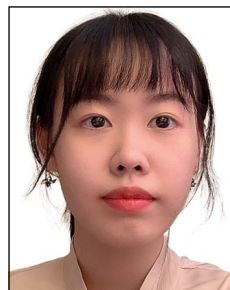
Yuanchunyu Lin received her BS from Columbia University and MS from Earth and Environmental Engineering at Columbia University. Currently She is a PhD candidate in the Department of Earth and Environmental Engineering at Columbia University. Her research interests mainly focus on the synthesis of sorbent materials for DAC of CO_2 and CO_2 conversion using Dual Functional Materials (DFM).

Xi Chen is a Professor of Earth and Environment Engineering at Columbia University. He is the Director of the Earth Engineering Center (EEC), and the Center for Advanced Materials for Energy and Environment(CAMEE)at Columbia University. He received his PhD from Harvard University in 2001 and joined Columbia in 2003. He has received numerous awards including the NSF CAREER Award, the Presidential Early Career Award for Scientists and Engineers(PECASE), ASME Sia Nemat-Nasser Early Career Award, and the SES Young Investigator Medal.