Membrane Adsorbents Comprising Self-Assembled Inorganic Nanocages (SINCs) for Super-Fast Direct Air Capture Enabled by Passive Cooling

primary project goal

The State University of New York (SUNY)–Buffalo, in collaboration with Trimeric Corporation, is developing highly porous membrane adsorbents comprising CO_2-philic polymers and self-assembled inorganic nanocages (SINCs) for rapid temperature swing adsorption using electricity-free solar heating and radiative cooling, enabling an economically viable approach for direct air capture (DAC).

technical goals

- Design and prepare membrane adsorbent based on CO_2-philic polymers and SINCs and design operation cycles with solar heating and radiative cooling for CO_2 capture from air.
- Construct and characterize a DAC prototype with the advanced sorbent and electricity-free desorption; demonstrate the 100-hour continuous operation for DAC.
- Complete the TEA using performance data from the sorbent experiments.
- Develop an understanding of breakdown pathways and confirm the revolutionary stability of the new solvent using various laboratory techniques.

technical content

The project team is developing highly porous membrane adsorbents comprising CO_2-philic polymers and SINCs with a low resistance to airflow and heat transfer for rapid temperature swing adsorption of CO_2 from the air, enabled by electricity-free solar heating and radiative cooling. The core technical activities will combine three key innovations:

1. Highly porous flat-sheet membrane adsorbents contain CO_2-philic amines that can be easily produced using a phase inversion method.
2. CO_2-philic SINCs can be easily dispersed in the polymers with great stability (compared with the metal-organic frameworks [MOFs]).
3. The adsorption and desorption are integrated with solar heating and radiative cooling for rapid continuous operation, in contrast to traditional long-cycle separate operation.

The membrane adsorbents containing amines, polymers, and SINCs can be produced using a one-step industrial process. The porous membranes coupled with porous SINCs offer low resistance for airflow and fast CO_2 sorption/desorption cycles, while the incorporation of the additional amine groups provides high CO_2 sorption capacity.

program area:

Carbon Dioxide Removal

ending scale:

Laboratory Scale

application:

Direct Air Capture

key technology:

Membranes

project focus:

Membrane Sorbents with Self-Assembled Inorganic Nanocages for DAC

participant:

State University of New York–Buffalo

project number:

FE0031960

predecessor projects:

N/A

NETL project manager:

Krista Hill
krista.hill@netl.doe.gov

principal investigator:

Haiqing Lin
State University of New York–Buffalo
haiqingl@buffalo.edu

partners:

Trimeric Corporation

start date:

10.01.2020

percent complete:

83%

Figure 1 shows the integrated membrane adsorbents and cooling technology into a single portable system to realize continuous and rapid CO_2 production. A thin sorbent membrane (e.g., 20–100 µm thick) is continuously rotated by a cylinder. The thin film at the bottom of the cylinder can reach saturation within five minutes (i.e., adsorption [A]) due to the rapid CO_2 and thermal transport within this thin film into the pores. The use of SINCs instead of MOFs enables the active sorbent sites to be highly dispersed and eliminates the need for the pore-to-pore diffusion that limits cycling time in MOFs. The CO_2 will be released at the top side of the cylinder (i.e., the desorption process [D] in the temperature range of 65–100°C), also within five minutes by the heater illuminated by a concentrated solar beam or battery-driven heater during nighttime. The obtained CO_2 may be used for algae culturing or greenhouse or further purification. Afterward, the adsorbents will be cooled by topology-optimized convection and radiative cooling structure to accelerate the cycle and improve the sorption capacity.

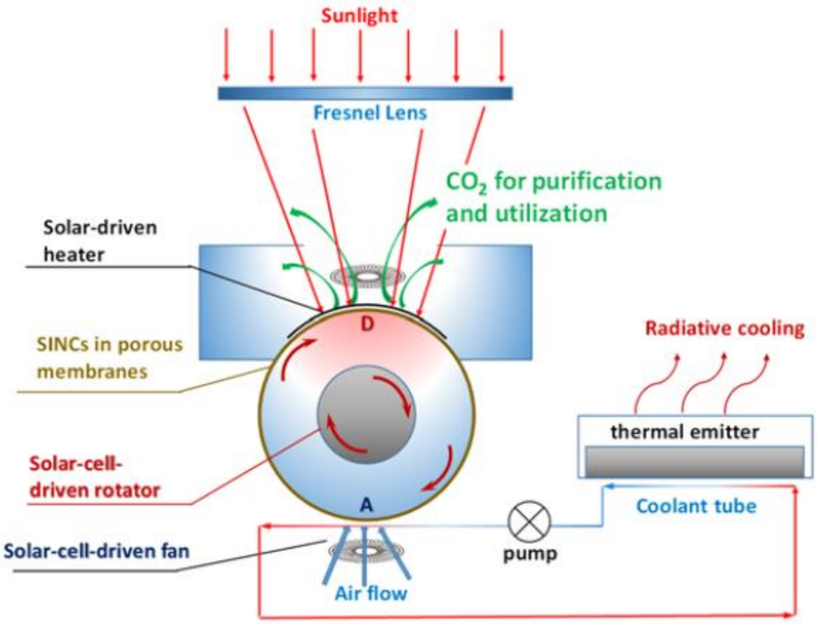

Figure 1: Integrated electricity-free radiative cooling, membrane adsorption, solar heating and desorption, and CO_2 product for further purification and utilization.

One of the key challenges for adsorption, heating, desorption, and cooling of the adsorbents is the time needed for the mass transfer and heat transfer. Ideally, the adsorbents should be embedded in a macroscopic scaffold that effectively exposes them to the air and can be easily heated for desorption. This project proposes a novel sorbent-containing, highly porous, flat-sheet membrane platform (20–100 µm) to decrease the cycle time and thus increase the capacity of CO_2 adsorption. As shown in Figure 2, the porous membranes, with a porosity of 60–95%, can contain CO_2-philic polymers such as polyethylenimine (PEI). Similar to the hollow fiber membranes (HFM)-based adsorbents, these membrane sorbents can be fabricated using existing membrane fabrication equipment and allow for similar CO_2 capture as packed bed systems while significantly reducing pressure drop and accelerating the adsorption and desorption. On the other hand, the flat-sheet platform allows easy packaging into systems with low pressure drop, and the SINCs can be well-dispersed in these highly porous polymers to further reduce mass and heat transfer resistance compared with the MOFs used in the HFM adsorbents.

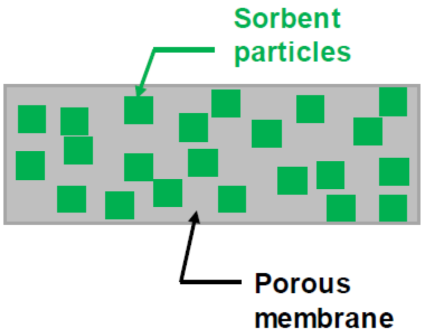

Figure 2: Flat-sheet membrane adsorbents with porosity 60–95% comprising CO_2-philic SINCs and polymers.

Figure 3 shows an example of a sorbent-containing polyvinylidene fluoride (PVDF) membrane developed by SUNY-Buffalo. PVDF membranes can be prepared using phase-inversion processes with pore sizes of 100–1,000 nm and porosity of greater than 90%, as shown in Figure 3a. More importantly, PVDF has high polarity and interactions with SINCs. Figure 3b shows that example SINCs (copper-MOF) are dispersed in the PVDF, and these nanoparticles even decrease the crystallinity of the PVDF, indicating the strong molecular interactions. Physically mixing SINCs with monomer lead to pore filling and blocking, whereas mixing SINCs with solubilized polymer and then casting films, it is possible to maintain porosity. The SINC/polymer integration can also be tailored by functionalizing the SINC ligands with short-chain oligomers to assist with solubilization into the polymer ink and increasing integration without relying on host/guest interactions into the pores.

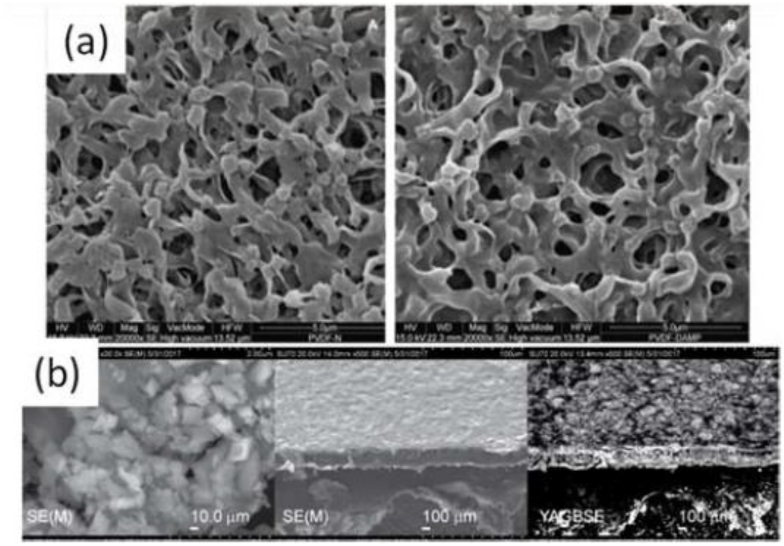

Figure 3: (a) Typical Scanning electron microscopy (SEM) photo of the surface of a porous PVDF membrane, (b) SEM of the hybrid PVDF and example SINCs (copper-MOF).

MOFs are a class of porous materials that have attracted much attention due to their permanent porosity and ability to be tuned at the molecular level through straightforward modular synthetic methods. MOFs are formed by the assembly of metal-containing nodes (metal ions or metal-based clusters) that function as structural building units and organic ligands. Carbon dioxide capture is one of the most active and attractive research areas in MOF applications. The primary challenge of MOF sorbents is their slow adsorption/desorption rate and affinity for CO_2, such that they can capture at the relatively low concentrations found in air. To overcome these challenges, SINCs are proposed as an alternative sorbent, guided by recent successes in the MOF literature. There is a growing library of MOFs that are capable of DAC, and the proposed SINC sorbent materials exploit all of their promising features (high selectivity, high uptake, long-term stability) while reducing adsorption and desorption times to a fraction of those required by frameworks. This reduction is made possible because (i) SINCs obviate the need for air/CO_2 to diffuse throughout large crystallites, and (ii) SINCs are less than 10 nm in diameter and can therefore be incorporated into ultra-thin films that enable innovations to air-capture design, as shown in Figure 4. Even when synthesized as a microcrystalline powders, MOFs range from 150–200 nm, orders of magnitude larger than SINCs. Furthermore, SINCs may be readily functionalized to either enhance mixing into polymers or for covalent incorporation into polySINCs, analogous to recently emerging polyMOFs. The use of ultra-thin porous membranes (i.e., 20–100 µm thick) increases the mass transfer of air to the sorbent sites and decreases the pressure drop, leading to super-fast sorption and desorption and lower energy.

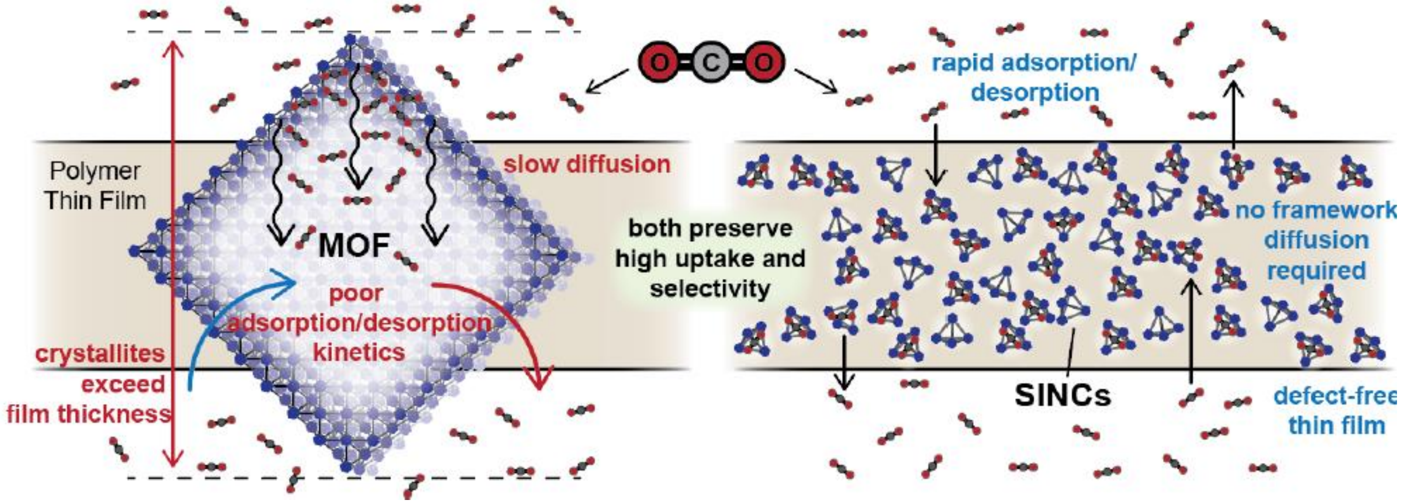

Figure 4: SINC sorbents preserve the high uptake and selectivity of MOFs for DAC while improving upon processability and the kinetics of capture and release of CO_2.

While the solar heating has been widely practiced, daytime radiative cooling has recently emerged as a promising technology to passively cool, even under direct sunlight, by combining a solar reflector with a thermal emitter. The reflector functions in the visible to the near-infrared (IR) spectral region where solar energy is concentrated. It functions as a good thermal emitter in the mid-IR spectral region where room-temperature objects emit most of their radiation energy. Such spectral mismatch is achieved by using nanoscale optical engineering. Recently, SUNY-Buffalo demonstrated electricity-free radiative cooling that operates under direct sunlight. It does not use any energy and yet can provide a cooling power of ~100 Watt/meter^2 (W/m^2) through passive radiative cooling that reaches sub-ambient temperature. It consists of layers of polydimethylsiloxane (PDMS) on an aluminum (Al) substrate with a thickness of 100 µm and 1 mm, respectively. The thermal radiation is primarily emitted by the PDMS layer, which has a near-unity emissivity for wavelengths longer than 4.5 µm due to Si–O and Si–C bond vibrations (Figure 5a), given sufficient film thickness (i.e., larger than 100 µm, as modeled in Figure 5b). Simultaneously, PDMS is transparent to sunlight, which is efficiently reflected by the Al substrate. The resulting emissivity is shown as the red line in Figure 5a.

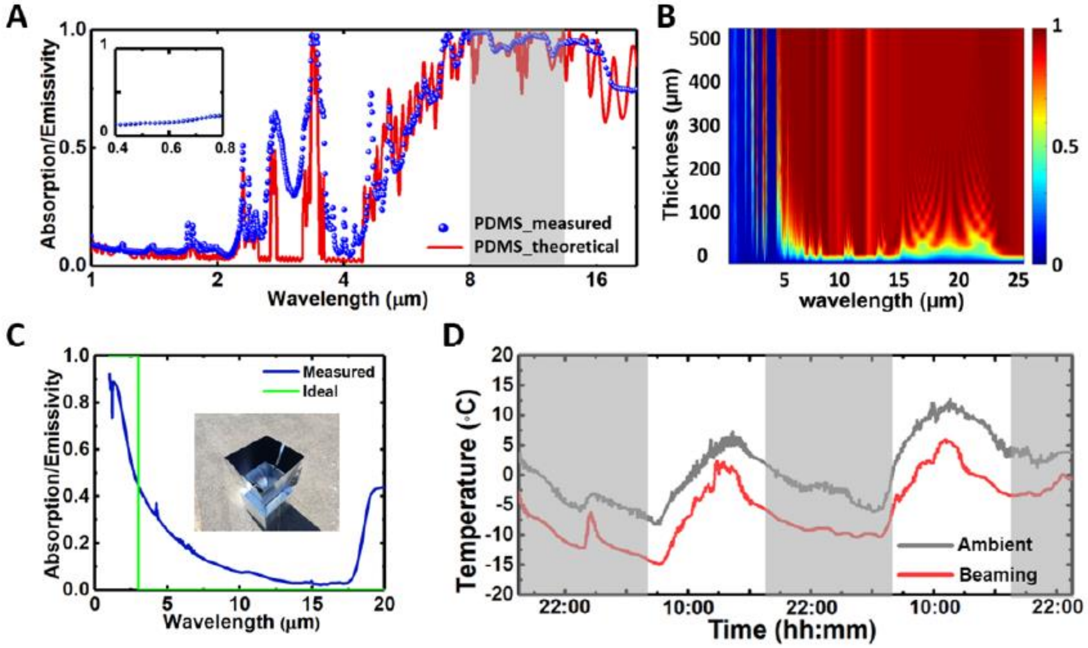

Figure 5: (a) Absorption/emissivity spectra of a planar PDMS/aluminum film with a thickness of 150 µm (solid curve shows numerical modeling and spheres represent measured data); the inset shows that the PDMS film also absorbs part of the solar irradiation in the visible and near-IR regime, (b) the modeled absorption spectra of the planar PDMS/aluminum film as the function of the PDMS film thickness, (c) absorption spectra of an ideal selective absorber (green line) and a commercial spectral selective absorber (blue line), (d) continuous 48-hour cooling test: the grey line indicates the ambient temperature and the red line is the beaming system temperature.

The emissivity of the structure is characterized using Fourier transform infrared (FTIR) spectroscopy. The daytime radiative cooler system reflects almost 96% of the solar radiation (0.3–4 µm) and emits efficiently in the mid-IR region (greater than 4 µm). The radiator was placed inside an insulating box made from polystyrene. A polyethylene film covers the opening of the box to reduce convective heat losses. In addition, a selective solar absorber was used to develop a V-shaped beam-shaping structure to guide the thermal radiation (see the photo in the inset of Figure 5c). Figure 5d compares the temperature of the system (red curve) and the ambient air (grey curve) in 48 hours. This cooler achieves a temperature reduction of about 7°C throughout the day, validating the electricity-free cooling using sunlight.

technology advantages

- Regeneration cycle achieved by solar heating.
- Electricity-free radiative cooling.
- SINCs have been found to increase CO_2 capacity of membrane sorbents.
- SINCs provide permanent pores to increase gas diffusivity and open metal sites to interact with CO_2.

R&D challenges

- Achieving sufficient radiative cooling for this application.
- Carry out radiative cooling and heating outside.

status

Studies have been completed on the influence of the substrate on CO_2 sorption using porous substrates such as fumed silica, SBA-15, gama-alumina, MIL-101(Cr), and Mg_2(dobpdc), where the fumed silica and SBA-15 with 30 wt% polyethyleneimine show the highest CO_2 capacities of 3.0 mmol/g. The SINC membrane with the lowest loading (14–16 wt% amine loading) exhibited the highest amine efficiency. A working prototype of the solar thermal porous membrane DAC sorption system has been designed, assembled, and tested. The membrane adsorbents exhibit CO_2 capacity of ~0.5 mmol CO_2/g at 400 parts per million (ppm) CO_2 in air at 22ºC. Increasing the sorption temperature from 22 to 50°C resulted in 50–100% higher CO_2 capacity and amine efficiency. Work is continuing on the synthesis of high-amine-content SINCs, and to incorporate the most promising SINCs into the membrane sorbent. Evaluation of the effect of humidity on CO_2 capacity is currently being conducted. Scale-up of the conceptual design and the development of a TEA for the pilot process is also in progress.

available reports/technical papers/presentations

Haiqing Lin, Timothy Cook, Qiaoqiang Gan, Andrew Sexton, "Membrane Adsorbents Comprising Self-Assembled Inorganic Nanocages (SINCs) for Super-fast Direct Air Capture Enabled by Passive Cooling," Project kickoff meeting presentation, Pittsburgh, PA, November 2020. *https://www.netl.doe.gov/projects/plp-download.aspx?id=11076&filename=Membrane+Adsorbents+Comprising+Self-Assembled+Inorganic+Nanocages+(SINCs)+for+Super-fast+Direct+Air+Capture+Enabled+by+Passive+Cooling.pdf*.

Haiqing Lin, "Membrane Adsorbents Comprising Self-Assembled Inorganic Nanocages (SINCs) for Super-fast Direct Air Capture Enabled by Passive Cooling," Direct Air Capture Kickoff Meeting Presentation, PA, February 2021. *https://www.netl.doe.gov/projects/plp-download.aspx?id=11074&filename=Membrane+Adsorbents+Comprising+Self-Assembled+Inorganic+Nanocages+(SINCs)+for+Super-fast+Direct+Air+Capture+Enabled+by+Passive+Cooling.pdf*.

Thien (James) Tran, "Membrane Adsorbents Comprising Self-Assembled Inorganic Nanocages (SINCs) for Super-fast Direct Air Capture Enabled by Passive Cooling," NETL Carbon Management Research Project Review Meeting, Pittsburgh, PA, August 2021. *https://netl.doe.gov/sites/default/files/netl-file/21CMOG_CDRR_Lin.pdf*