ENI AWARD 2023

Energy Transition

Jeffrey Long

Winner

Cooperative Gas Capture in Metal–Organic Framework Materials

Research Description

Industrial separations of gases, including carbon dioxide capture, are often carried out using temperature or pressure swing adsorption. Here, selective uptake from the mixture occurs at low temperature or high pressure, and the pure adsorbate is then released at a higher temperature or lower pressure. Traditional adsorbents display sloping, Langmuir-type uptake that limits performance. In contrast, Prof. Jeffrey R. Long has discovered, developed, and commercialized cooperative adsorbent materials, wherein chemically selective binding at one site activates neighboring sites, leading to a step-shaped adsorption profile. This phenomenon allows a high separation capacity to be achieved with small temperature or pressure swings, dramatically reducing the energy required for a separation. Cooperative adsorption of this type was known to occur in nature—for example as the mechanism that enables the uptake and release of four dioxygen molecules simultaneously by hemoglobin—but had never been observed at high density in a porous material prior to the discovery by Long.

Long initially showed that by installing diamines at metal sites arranged in chains within a metal–organic framework (MOF), cooperative CO2 adsorption could enable the efficient, high-capacity removal of CO2 from a flue gas (Nature 2015). Here, insertion of CO2 into metal-amine bonds with concomitant proton transfer results in the reversible formation of ammonium carbamate chains, leading to a step-shaped adsorption profile. Varying the diamine can control the pressure and temperature of the step, facilitating optimization for CO2 separation from various mixtures. More recently, Long showed that by appending tetraamines, such materials could operate under extreme conditions, enabling the release of CO2 by direct contact with low-temperature steam (Science 2020). Long further developed new mechanisms that could enable this type of behavior for other gas molecules. The first success came with the design and synthesis of a MOF in which a spin transition led to the first instance of cooperative CO adsorption (Nature 2017). Here, Long created a MOF with rows of high-spin iron(II) centers that simultaneously switch to a low-spin configuration upon binding the strong-field ligand CO. Long also demonstrated how cooperative adsorption can be achieved through structural phase transitions. He showed that flexible MOFs can undergo abrupt and reversible pore-opening at certain pressures of methane, leading to unprecedented capacities and heat mitigation for natural gas storage (Nature 2015) and a mechanism for separating CO2 from natural gas. Most recently, Long demonstrated the first example of cooperative ammonia adsorption through linker displacement in a MOF, potentially enabling a more efficient means of removing ammonia from the product gas in the Haber-Bosch process (Nature 2023).

In 2014, Long co-founded Mosaic Materials. The focus of the company, which Long also directed, was to commercialize diamine-appended MOFs for the low-cost removal of CO2 from air, biogas, natural gas, and flue gases. After demonstrating that the materials could be produced inexpensively at large scale in structured forms, the company was acquired by Baker Hughes in 2022 and is now deploying the technology. The goal of this work is to rapidly increase production of the metal–organic frameworks to multi-tonne scales for incorporation in newly-designed devices for the efficient removal of CO2 from air and flue emissions. Additional technologies under development by Mosaic Materials include high-density hydrogen storage, olefin/paraffin separations, alkane isomer separations, and CO removal, all stemming from Long's discoveries. Finally, Long recently founded the Institute for Decarbonization Materials (IDMat) at Berkeley, which provides seed funding and advanced characterization facilities to support the discovery and development of new materials for mitigating global warming.