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Helping Membranes Perform Under Pressure

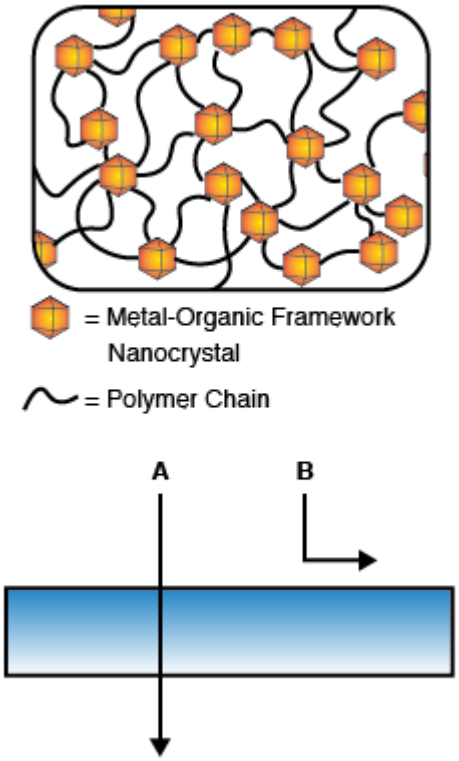
Synergy between polymers and tiny crystals creates more robust membranes

Stephen Meckler

Chemistry enables our modern way of life, from the fuels powering our grid to the materials making up our cars, computers and clothing. Good chemistry requires pure chemicals. As a result, up to 15 percent of all the energy humans use goes towards chemical

separations. Technologies to make these separations more efficient and environmentally friendly could go a long way towards a greener economy.

Polymer membranes for gas separations, which work like sheets of plastic that let some gases pass through while blocking others, are a promising technology in this field. However, in some cases, these membranes lose the ability to discriminate between different chemicals when the gases being separated are at high pressure. This is unfortunate because many important separations run best under such conditions. Techniques to make polymers resistant to these high-pressure gases exist but typically reduce membrane permeability, meaning less gas can be purified in a given amount of time.



(Bottom) Schematic of a membrane for gas separations. Gas A permeates quickly through the membrane, but gas B is largely blocked from traversing the membrane. (Top) Metal-organic framework nanocrystals dispersed in the polymer matrix increase the membrane performance and reduce plasticization. *Image courtesy of Stephen Meckler, CGS EFRC*

Researchers at the Center for Gas Separations Relevant to Clean Energy Technologies (CGS), an Energy Frontier Research Center, have developed an exciting new solution to this problem. By embedding very small porous particles into high-performing polymer membranes, they have developed a method to combat performance loss at high pressures without sacrificing membrane permeability. In fact, in some cases, performance gains over the unmodified polymer are observed over a large range of pressures. This signals a rare accomplishment in membrane science: a win-win scenario in which the membrane scientist can “have her cake and eat it too,” so to speak.

Plasticization and membrane tradeoffs. Polymers are large organic molecules made up of repeating units bonded together, and they make up all of the plastics you use on a daily basis. These materials comprise nearly all commercially available membranes for several important reasons: they are easy to scale up, they are easy to process into different shapes and they have excellent performance. However, they suffer from a few key drawbacks. One is their tendency to plasticize. This means that certain important gases, including carbon dioxide and ethylene, will dissolve into the polymer and cause it to swell. When this happens, the polymer loses its ability to discriminate between different chemicals, reducing the membrane’s selectivity. This detrimental effect is at its worst at the high pressures where many membrane separations are performed. One

common method to combat plasticization is cross-linking, in which individual polymer strands are bound together with small organic molecules to prevent them from swelling. However, this process is known to reduce the gas flux through the membrane, lowering the productivity of the separation.

Robust membranes from synergy. The porous crystals used in these membranes are metal-organic frameworks (MOFs), and they are kind of like molecular sponges made of metal centers linked by small organic molecules. Their uniform pores are highly selective for certain molecules, making them fascinating targets for applications in separations. Pure MOF membranes have excellent performance but are fragile and difficult to produce. Mixing nanoscale MOF crystals into a polymer membrane is far easier and can improve permeability and selectivity versus the pure polymer.

The CGS researchers discovered something exciting about their MOF-polymer blends. When the MOF and polymer chemical structures are compatible, the nanocrystals appear to bind the polymer chains together, similar to the way a molecular cross-linker would. But unlike traditional cross-linked polymers, their MOF-polymer composite membranes often perform better than the pure polymer owing to the MOF's porosity and selectivity for certain gases. The MOFs used in these studies, known as M_2(dobdc), helped resist plasticization in films of various polyimide polymers, a scientifically exciting and industrially relevant class of polymer. This synergy between the two materials extends the high membrane performances recorded in ideal laboratory conditions to conditions far more applicable to real-world separations.

Outlook. In their research, the CGS scientists identify two key separations in which this technology could make a significant difference. As natural gas is gradually adopted as a cleaner, domestically sourced alternative to oil, removing carbon dioxide contaminants from the fuel is an increasingly costly endeavor because of the plasticization of traditional polymer membranes. Similarly, in the production of chemicals, the separation of very similar small organic molecules such as ethane and ethylene is very costly. In both these cases, the MOF-polymer membranes discovered by the CGS researchers could make these separations more efficient and, therefore, more environmentally friendly.

Acknowledgments

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More Information

Bachman JE, ZP Smith, T Li, T Xu, and JR Long. 2016. "Enhanced Ethylene Separation and Plasticization Resistance in Polymer Membranes Incorporating Metal-Organic Framework Nanocrystals." *Nature Materials* 15:845-849. DOI: 10.1038/nmat4621

Bachman JE and JR Long. 2016. "Plasticization-Resistant Ni_2(dobdc)/Polyimide Composite Membranes for the Removal of CO_2 from Natural Gas." *Energy and Environmental Science* 9:2031-2036. DOI: 10.1039/C6EE00865H

About the author(s):

Stephen Meckler is a graduate student in the chemistry department at the University of California, Berkeley. He is a member of the Center for Gas Separations Relevant to Clean Energy Technologies (CGS) Energy Frontier Research Center. His research focuses on developing and studying porous materials for gas separation membranes, including porous polymers, metal-organic frameworks and composites thereof.

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