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New Polymer Becomes Wetter as Temperature Increases

Material could be used to increase the efficiency of fuel cells

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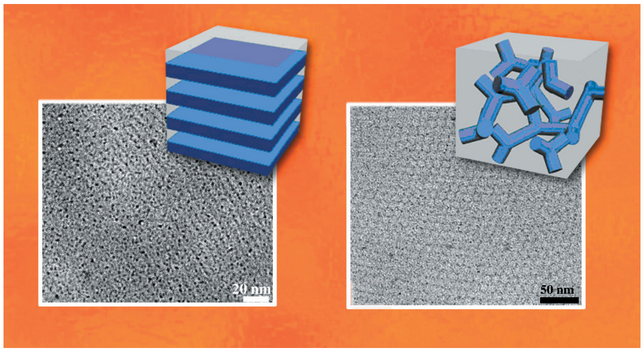
Berkeley Lab scientists have developed a polymer membrane that becomes wetter as the temperature of the surrounding air increases. This one-of-a-kind material—as unlikely as clothes that come out of the dryer wetter than when they went in—has the potential to increase the efficiency of polymer electrolyte fuel cells, which are being developed as a nonpolluting way to power cars and other applications.

“This is the first polymer membrane to increase its moisture uptake from the surrounding air as the temperature elevates, at equilibrium,” says Nitash Balsara, a polymer physicist with Berkeley Lab’s Materials Sciences Division and UC Berkeley’s Department of Chemical Engineering who led the research team that developed the material.

Other polymer membranes become drier when heated, a phenomenon seemingly as dependable as the sun rising in the east. But the polymer developed by Berkeley Lab scientists does the opposite. It sponges up more moisture from its immediate environment as the temperature rises and the relative humidity remains constant. With this unique property, the polymer could overcome a limitation common to polymer electrolyte fuel cells, which lose water as the temperature increases, and subsequently suffer a decrease in proton conductivity.



Transmission electron microscope images of the water-filled channels, which appear dark, in two block copolymer membranes. Block copolymers consist of layers of two kinds of polymer, one that attracts water and one that repels it. Channels in the block membrane on left are 2.5 nanometers thick; those on right are 4.7 nanometers thick. Schematics show architecture of the water-filled channels in the two hydrated block membranes.

“This is a big barrier because fuel cells become more efficient at higher temperatures, so they require a polymer membrane that also operates at higher temperatures,” says Balsara.

The secret to the polymer’s oddball performance is its nanoscale construction. It’s packed with water-loving pores that only measure five nanometers wide or less (one nanometer is one-billionth of a meter). For reasons not entirely understood, these extremely small pores continue to grab moisture from the air even as the thermometer rises above 90 degrees Celsius, a temperature well above the point at which other polymers stop working.

Balsara and his colleagues began developing the polymer several years ago, when they set out to fabricate a material that simply dries more slowly than usual. They hoped to capitalize on a phenomenon called capillary condensation, in which liquids spontaneously sequester inside porous materials. Scientists have known for more than 200 years that capillary condensation increases the boiling point of water adsorbed in water-loving (or hydrophilic) pores because there is more surface per unit volume to attract water molecules. In essence, the smaller the pore, the less it’s willing to relinquish its moisture as the temperature rises.

“I believed that this well-known process could be harnessed to keep water in polymer membranes, the same way the process works in nature, like in rocks,” says Balsara.

But what happens when pores approach the nanoscale? Do they hold on to moisture even more tightly? To find out, Balsara’s team conducted back-of-the-envelope calculations.

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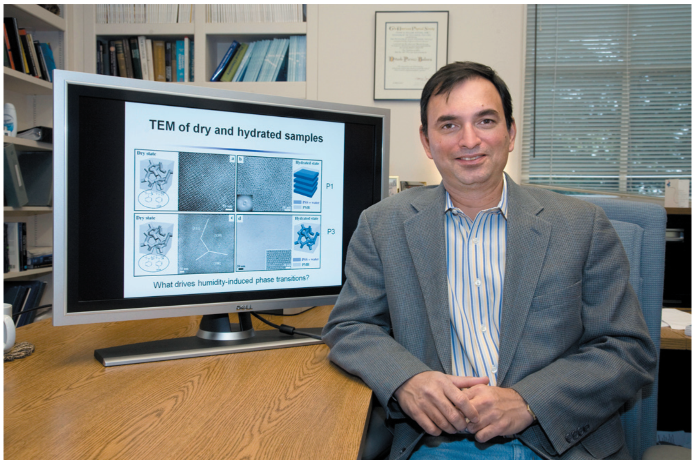
“Things got interesting as the pores approached five nanometers in width, and below that, things got really interesting,” says Balsara.

Specifically, they determined that the pressure in a pore dropped dramatically when its width is less than 5 nanometers. At this scale, pores were reluctant to give up their moisture even as the temperature increased.

To test this tantalizing result, the scientists synthesized a slew of two-phased block copolymers, so-named because they are composed of two polymers, one that repels water and another that attracts water. The hydrophilic channels in the polymers measured between two and 40 nanometers in width.

Transmission electron microscopy was used to image and measure the polymers’ hydrophilic channels in the presence of water. True to the scientists’ initial calculations, polymers with hydrophilic channels less than five nanometers wide exhibited increased water uptake, even as temperatures approached 90 degrees Celsius. These polymers also exhibited increased proton conductivity as the temperature rose.

“Our work demonstrates that the capacity of a membrane to hold water can be affected by organizing them into extremely small channels,” Balsara says. “And this is the smallest channel size in any block copolymer system ever made.”



Nitash Balsara led the research team that developed a polymer membrane that gets wetter as the surrounding air gets hotter.

Balsara can’t explain why their specially developed polymers behave the way they do. Indeed, they seem to run counter to the way the world works: on the macroscopic scale, materials dry when heated. But strange things happen at the nanoscale, and this could such an example.

“We may be tapping into a nanoscale effect that we are yet not aware of,” Balsara says. “The channels are approaching length scales in which they’re still larger than a water molecule, but not that much larger, and this could impact how the channels retain water.”

Next, Balsara hopes to optimize the mechanical properties of the polymer membranes so that they’re robust enough to survive in a fuel cell, which harness hydrogen to produce electricity without yielding greenhouse gasses and other pollutants. Their work also heralds a new method for controlling the moisture content of nanoscale materials in general, which promises to have many applications in the burgeoning field of nanotechnology.

“We did this by coupling capillary condensation with membrane physics,” says Balsara. “This enabled us to build a polymer that does much more than slow evaporation; it increases moisture uptake.”

The work was spearheaded by Moon Jeong Park of Berkeley Lab’s Materials Sciences and UC Berkeley’s Department of Chemical Engineering, who synthesized and characterized the polymer membranes. Ken Downing of Berkeley Lab’s Life Sciences Division and Andrew Minor of Berkeley Lab’s National Center for Electron Microscopy facilitated the electron microscopy work. The research was funded by the Department of Energy.

Additional information

“Increased water retention in polymer electrolyte membranes at elevated temperatures assisted by capillary condensation,” by Moon Jeong Park, Kenneth H. Downing, Andrew Jackson, Enrique D. Gomez, Andrew M. Minor, David Cookson, Adam Z. Weber, and Nitash P. Balsara, appeared in the October 26, 2007 online version of Nano Letters and is available to subscribers at http://dx.doi.org/10.1021/nl072617l

More about Nitash Balsara’s research is at http://www.cchem.berkeley.edu/npbgrp/

More about Berkeley Lab’s Materials Sciences Division is at http://www.lbl.gov/msd/