## The cactus effect

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This bioinspired approach ... is able to overcome the challenge of conserving water in the bulk membrane while not hindering ion transport Polymer membranes are used in many different energy-related settings, including proton-exchange fuel cells and reverse electrodialysis. For such applications, the membrane must permit water-mediated ion transport but retain sufficient water in the bulk of the membrane to achieve high conductivity.

Many techniques developed to maintain the hydration of polymer membranes rely on the addition of external, and bulky, water management systems or require the fabrication of polymers with specific morphologies. For applications of a smaller size, external systems are not viable and the fabrication of specific morphologies often

requires complex fabrication procedures.

Hence, Michael Guiver, Young Moo Lee and an international team of co-workers have taken inspiration from the cactus plant to design coated membranes that respond to surrounding humidity, retain water, and demonstrate high conductivity in model fuel cell and reverse electrodialysis experiments. "This bioinspired approach involving thin, hydrophobic layers with very narrow nanocracks, which open in humidifying conditions, is able to overcome the challenge of conserving water in the bulk membrane while not hindering ion transport," says Lee.

The cactus plant has stomata that remain closed during the day when its surroundings are hot but open at night when the conditions are cooler and more humid, thus allowing the plant to retain and retrieve as much

water as possible. In a similar way, the hydrophobic coating of these polymer membranes forms nanometre-sized cracks in humid conditions, but on dehydration these cracks partially close. The result is a polymeric membrane that can regulate its water content and exhibit improved electrochemical performance compared with non-coated membranes when used as part of a single fuel cell, and that can enhance ionic selectivity when used as cation- or anion-exchange membranes for reverse electrodialysis. "Additionally, this nanocrack-patterned thin coating can provide a protective barrier against strong acid and base, as well as reactive radicals, which leads to the drastic enhancement of ion-exchange membrane stability," says Lee.

The membrane is made from sulfonated poly(arylene ether sulfone) and the hydrophobic coating is achieved by atmospheric plasma treatment of the surface — a process that requires only 15 minutes. Atomic force microscopy analysis reveals that there are no visible nanocracks on the membrane surface directly after fabrication. However, when the coated membrane is placed in distilled water, the membrane swells and cracks appear on the surface. On removal from the water and reduction of the humidity to 35-45%, the cracks partially close, allowing retention of the water inside the bulk membrane. Lee and co-workers also show that this technique can be used to achieve similar self-humidifying behaviour for other hydrocarbon polymer membranes.

"Although this technique provides a water-retention effect without disturbing ion transport, optimization of the control of nanocrack formation depending on various polymer materials with different water-swelling properties will be required for mass production using plasma treatment conditions," explains Lee. This optimization will be crucial to introduce the application of these coatings in other technologies, including their use as drug delivery vehicles, artificial muscles, membrane sensors, and in membrane distillation and 4D printing systems. Generally, the long-term stability of hydrocarbon membranes, such as the one used in this study, has stalled their commercial application in fuel cells compared with perfluorosulfonic acid membranes; further tests are required to determine if this coating can overcome these stability issues. Alison Stoddart

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