New membrane design allows selective and near-frictionless ion transport

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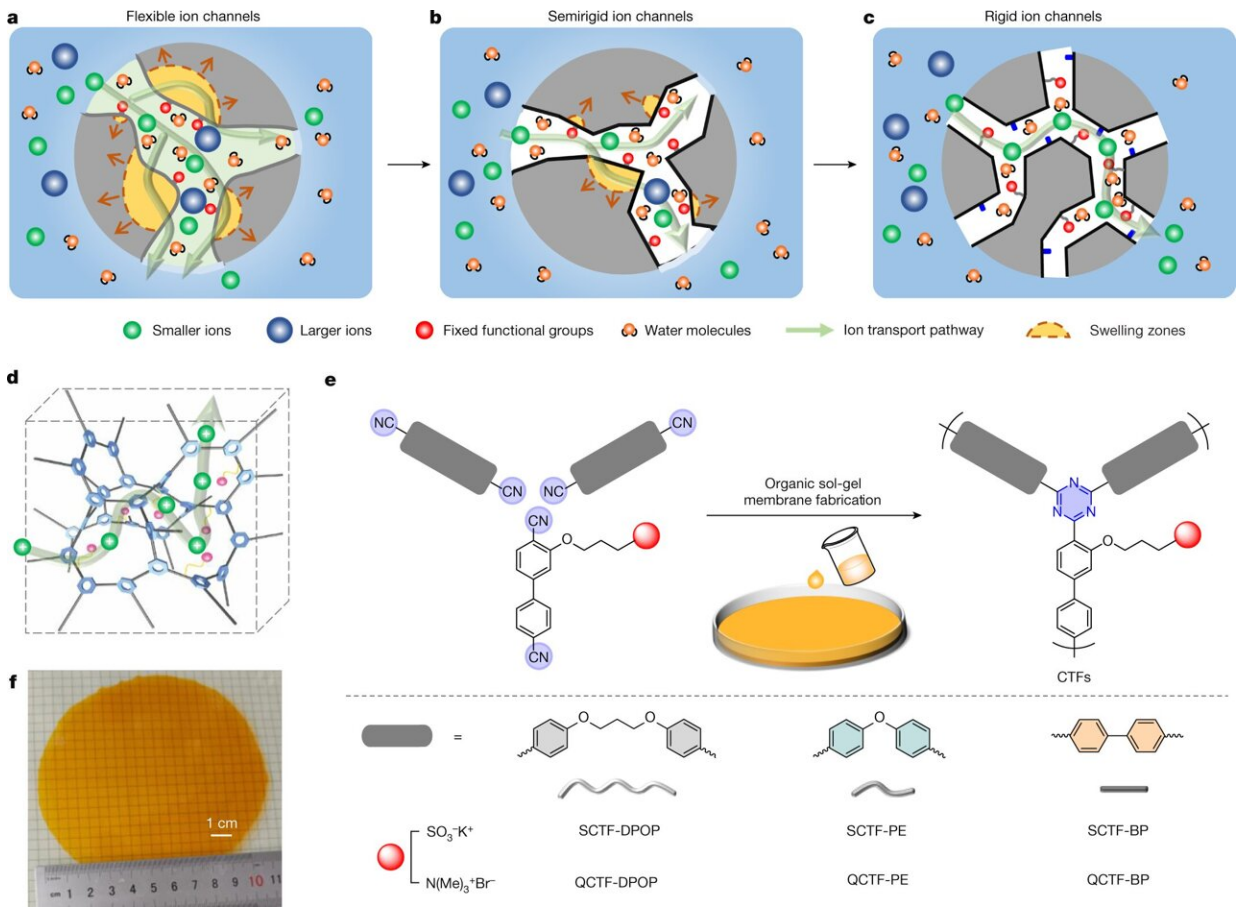

Schematic illustrations showing existing and proposed ion-selective polymer membranes with varying ion channels. a, Membranes with flexible ion channels. These contain microphase-separated morphology derived from the assembly of hydrophilic ion-conductive moieties and hydrophobic flexible-polymer backbones, represented by Nafion. b, Ion-selective microporous membranes with semirigid ion channels. The channels are formed by intrinsic micropores

resulting from inefficient polymer chain packing, represented by polymers of intrinsic microporosity and their derivatives. To render the membrane ion conductive, functional moieties are incorporated during postsynthetic modification. Membranes may age over time and swell in water. c,d, Our proposed membranes with rigid ion channels (c). These are expected to build from bottom-up synthesis and via swelling-resistant 3D polymer frameworks (d). Pore architecture and chemistry are tuned for rapid and selective ion transport. e,f, Preparation of stand-alone CTF membranes via a superacid-catalyzed organic sol-gel reaction from functional aromatic nitrile monomers (e). CTF membranes have a controlled number of ion-conductive moieties inside membrane pores and a covalent network structure. Image (f) shows a free-standing CTF membrane with a diameter of over 10 cm. Structure rigidity and microporosity of the CTF membrane can be regulated by designing variable structural units, as demonstrated at bottom right, from flexible to very rigid. Credit: *Nature* (2023). DOI: 10.1038/s41586-023-05888-x

Ion-transport membranes are vital components of clean-energy technologies, such as CO_2 electrolyzers, water electrolyzers, fuel cells, redox flow batteries and ion-capture electrodialysis. These membranes must screen out specific substances to prevent crossover while efficiently conducting specific ions.

Polymer materials have the advantages of low cost, manufacturing scalability and small footprint, and thus dominate the use of ion-transport membranes in practical modules. However, the existing polymer membranes suffer from a ubiquitous "conductivity-selectivity" trade-off: highly conductive membranes tend to exhibit low selectivity and vice versa. This trade-off presents a challenge in developing membrane materials that meet the required performance criteria.

In a study published in *Nature* on April 26, the research team led by Professor Xu Tongwen and Professor Yang Zhengjin from the

University of Science and Technology of China (USTC) of the Chinese Academy of Sciences (CAS), and their collaborators, proposed a new type of ion exchange membrane—triazine framework polymer membranes—which can break the conductivity-selectivity trade-off.

Compared to traditional materials, the triazine framework polymer membranes exhibited much enhanced capacity in both anti-swelling and anti-aging, showing an extremely low swelling ratio on water absorption. Their rigid channels ensured high selectivity from size-sieving, thus enabling extremely low permeability of active materials.

With proper control over the chemistry of rigid pore channels, the researchers observed near-frictionless ion flow within the all-rigid triazine framework polymer membrane (SCTF-BP), with the ion diffusion coefficient close to value in water. This is achieved by the robust micropore confinement within the rigid pore channels and multi-interaction between ion and membrane.

These framework membranes exhibited both extremely low permeability of active materials and ultrahigh ion diffusivity, and their advantages were exemplified as ion-conducting membranes in 2,6-dihydroxy anthraquinone / $K_4[Fe(CN)_6]$ aqueous organic redox flow batteries. The membrane delivered a neat area-specific resistance as low as 0.17 Ω cm^2, and thus enabled stable cell operation at extreme current densities, from 200 to 500 mA cm^{-2}, with both high energy efficiency and high-capacity utilization.

These data related to energy efficiency and capacity utilization far surpass those for otherwise identical cells assembled with commercial membranes and state-of-the-art ion-sieving membranes.

This work highlights the importance of secondary interactions to develop high-performing ion-transport membranes. The design strategy proposed

is believed to be broadly applicable, considering numerous options of organic reactions and functional monomers that can be utilized to construct polymer frameworks, and directs the fit-for-purpose design of membranes according to practical application demand.

More information: Peipei Zuo et al, Near-frictionless ion transport within triazine framework membranes, *Nature* (2023). DOI: 10.1038/s41586-023-05888-x

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