Proton Conduction with Metal-Organic Frameworks

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Science 26 Jul 2013:
Vol. 341, Issue 6144, pp. 354-355
DOI: 10.1126/science.1239872

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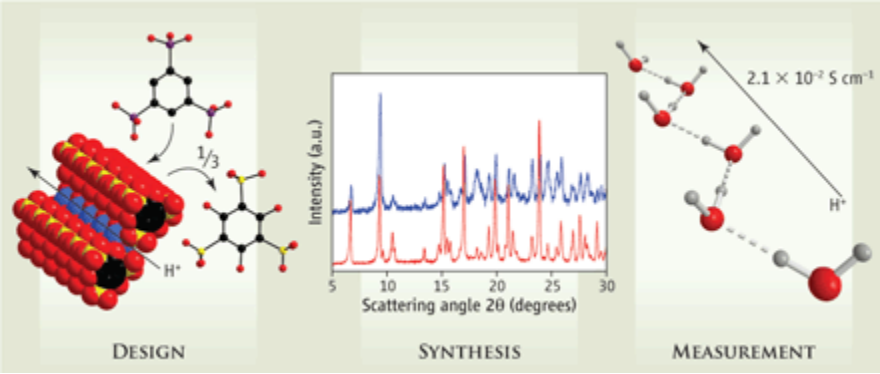
Proton-exchange membrane fuel cells (PEMFCs) generate electricity because the electrons generated by the reaction of hydrogen and oxygen must travel through an external circuit; the membrane electrolyte only transfers protons. The membrane materials of choice have been ionomeric polymers, such as sulfonated fluoropolymers (Nafion), that achieve proton conductivities of up to 1 S cm−1, but the requirement to keep these materials hydrated limits their operating temperature and efficiency. Metal-organic frameworks (MOFs), in which inorganic assemblies are joined by organic linkers, have inherent porosity that could be exploited for the development of proton-conducting membranes. Among recent studies of experimental proton-conducting MOFs [e.g., (1)], two general targets for PEMFC operation have emerged: developing better materials for operations under humid conditions (below 100°C), and developing efficient anhydrous proton conductors that could unlock the cost efficiencies enabled by humidity-independent operation above 100°C.



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Improving proton conductors.

The molecular structure of PCMOF2½, which can conduct protons along a molecular chain. Improvements in measured proton conductivity can be enabled through execution (as depicted by the x-ray diffraction peaks that provide structural information) to design new frameworks for further evaluation.

Efficient ion conduction requires the facile movement of charge through a material. Proton conduction can be envisaged as best occurring through a pathway of sites of equal proton affinity separated by an energy barrier that is as small as possible. Beyond protonation and deprotonation, this arrangement of donor and acceptor sites must open transport pathways, so any design must also encompass supramolecular considerations.

The improvement of materials is facilitated when changes in properties can be directly related to changes in structure. Unlike polymers, MOFs are crystalline, and x-ray techniques provide atomic-level

structures. Progress requires an iterative cycle of design, synthesis and characterization, and functional assessment (see the figure). The crystallinity of MOFs, coupled with the many options for structural modification, enables molecular-level design and hence structural optimization. Porosity, which in itself can facilitate unwanted fuel crossover in a PEMFC, can be used to advantage by filling pores with water or a nonvolatile proton carrier.

The field of proton-conducting MOFs has its roots in layered metal phosphonates (2). These materials can show exceptional proton conductivities (>10−2 S cm−1) but also are prone to swelling in humid atmospheres, which may cause unwanted mechanical stress during PEMFC operation. Kitagawa and co-workers expanded the proton-conducting realm to traditional coordination polymers more broadly [see (3) and references therein], especially for the temperature regime from 20° to 75°C. In 2009, Hurd et al. (4) and Kitagawa and co-workers (5) incorporated amphiprotic heterocycles into MOFs as proton carriers to obtain conductivities in the 10−4 S cm−1 range at temperatures above 100°C.

The ability to “decorate” parent MOF structures allows for incorporation of acidic groups with spatial predictability, such as a sulfonated MIL-53 analog (6). Several MOF structures have now been reported that conduct at 10−3 S cm−1 or higher by incorporating phosphonate groups (7), or secondary ions such as polycarboxylates (8) or ammonium (9), as proton transfer sites. The highest degrees of proton conductivity in MOFs were both reported in the past year and are both greater than 10−2 S cm−1 for PCMOF2½ (10), a mixed sulfonate-phosphonate MOF that exploits isomorphous replacement, and for MIL-101 loaded with a mixture of H2SO4 and H3PO4 (11).

The latter example also shows the potential stability of MOFs, which need to be robust to address challenges of practical proton conductors. Taylor et al. reported a MOF that retained proton conductivity greater than 10−3 S cm−1 after immersion in boiling water for 1 week (12). With the ever-increasing number of robust MOF scaffoldings available for derivatization, finding materials that are stable in the presence of water and over the required temperature range for fuel cell operation should not be an insurmountable hurdle.

From a broader perspective, even a MOF that is not highly robust can, because of its crystallinity, help establish structure-activity relations—for example, by direct visualization of a proton transfer pathway because of confinement of carriers in pores (13) or as a calibration tool for modeling studies. Horike et al. recently reported an anhydrous MOF with a crystallographically located proton transfer pathway of turnstile-like hydrogen phosphate and imidazolium ions (14). The authors refer to the solid as a “plastic crystal” because of the ability of components to reorient in the solid state. This study touches on perhaps the most intriguing prospect for MOFs regarding ion conduction: that they can exhibit dynamic behavior in the solid state (15) with reversibility and often with retention of crystallinity.

Although advances in absolute conductivity and robustness have been made, there are still substantive challenges for MOF proton conductors. With respect to the MOF itself, even better conductors can be envisaged that balance robustness and dynamics in a framework with three-dimensional proton transfer pathways. For incorporation in an engineered membrane electrode assembly (MEA), the brittleness of MOF materials will need to be addressed. A mixed-matrix polymer would stabilize the MOF mechanically while offering conduction pathways through the polymer, the MOF, and the interfaces, depending on the extent of loading. Wu et al. (16) and Liang et al. (17) have recently reported promising results in this direction. Compatibility with the electrode components is an issue for any electrolyte; optimizing the interfaces in MEAs is itself a large domain of research. Given that MOFs are being studied for a broad

expanse of electrochemical applications beyond electrolytes (18, 19), if one were to conjure a boldly optimistic scenario, MOFs could be used for all parts of a fuel cell (electrolytes, electrodes and catalyst supports, and gas-diffusion layers) where variations on a framework could yield different components with appropriate choice of metals, linkers, and guest catalyst loadings.

References

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M. Yoon,

K. Suh,

S. Natarajan,

K. Kim

, Angew. Chem. Int. Ed. 52, 2688 (2013).

FIND IT SFX Check for full textCrossRefWeb of Science

↲

G. Alberti

et al

., Solid State Ionics. 58, 339 (1992).

FIND IT SFX Check for full textCrossRefWeb of Science

↲

T. Yamada,

M. Sadakiyo,

H. Kitagawa

, J. Am. Chem. Soc. 131, 3144 (2009).

FIND IT SFX Check for full textCrossRefMedlineWeb of Science

↲

J. A. Hurd

et al

., Nat. Chem. 1, 705 (2009).

FIND IT SFX Check for full textCrossRefMedline

↲

S. Bureekaew

et al

., Nat. Mater. 8, 831 (2009).

Check for full textCrossRefMedlineWeb of Science

↲

M. G. Goesten

et al

., J. Catal. 281, 177 (2011).

Check for full textCrossRefWeb of Science

↲

R. M. P. Colodrero

et al

., Dalton Trans. 41, 4045 (2012).

Check for full textCrossRefMedlineWeb of Science

↲

M. Sadakiyo

et al

., J. Am. Chem. Soc. 131, 9906 (2009).

Check for full textCrossRefMedlineWeb of Science

↲

E. Pardo

et al

., J. Am. Chem. Soc. 133, 15328 (2011).

Check for full textCrossRefMedlineWeb of Science

↲

S. Kim,

K. W. Dawson,

B. S. Gelfand,

J. M. Taylor,

G. K. H. Shimizu

, J. Am. Chem. Soc. 135, 963 (2013).

Check for full textCrossRefMedlineWeb of Science

↵

V. G. Ponomareva

et al

., J. Am. Chem. Soc. 134, 15640 (2012).

Check for full textCrossRefMedlineWeb of Science

↵

J. M. Taylor,

K. W. Dawson,

G. K. H. Shimizu

, J. Am. Chem. Soc. 135, 1193 (2013).

Check for full textCrossRefMedlineWeb of Science

↵

S. C. Sahoo

et al

., J. Am. Chem. Soc. 133, 17950 (2011).

Check for full textCrossRefMedlineWeb of Science

↵

S. Horike

et al

., J. Am. Chem. Soc. 134, 7612 (2012).

Check for full textCrossRefMedlineWeb of Science

↵

S. Horike,

S. Shimomura,

S. Kitagawa

, Nat. Chem. 1, 695 (2009).

Check for full textCrossRefMedlineWeb of Science

↲

B. Wu

et al

., Chem. Commun. 49, 143 (2013).

Check for full textCrossRefWeb of Science

↲

X. Liang

et al

., Chem. Sci. 4, 983 (2013).

Check for full textCrossRef

↲

A. Morozan,

F. Jaouen

, Energy Environ. Sci. 5, 9269 (2012).

Check for full textCrossRefWeb of Science

↲

S.-I. Li,

Q. Xu

, Energy Environ. Sci. 6, 1656 (2013).

Check for full textCrossRefWeb of Science