



High conductive, long-term durable, anhydrous proton conductive solid-state electrolyte based on a metal-organic framework impregnated with binary ionic liquids: Synthesis, characteristic and effect of anion

Hui Chen^a, Shu-Yan Han^a, Rui-Heng Liu^a, Teng-Fei Chen^a, Kai-Lun Bi^a, Jian-Bo Liang^a, Yu-Heng Deng^a, Chong-Qing Wan^{a,b,*}

^a Department of Chemistry, Capital Normal University, Beijing 100048, PR China

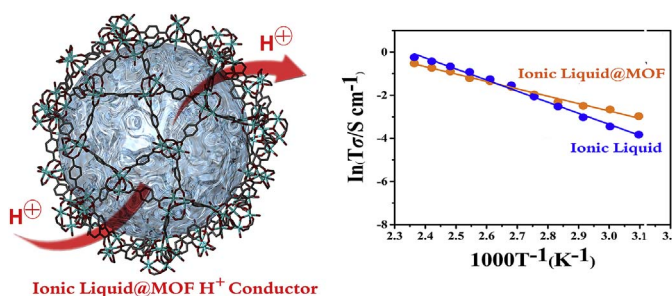
^b State Key Laboratory of Structural Chemistry, Fujian Institute of Research on the Structure of Matter Chinese Academy of Sciences, Fuzhou, Fujian 350002, PR China



HIGHLIGHTS

- Solid-state electrolyte based on MOF impregnated with ionic liquids is reported.
- High anhydrous H⁺ conductivity under high temperature is observed for the conductor.
- Counter anion in ionic liquid exhibited significant effect on the H⁺ conductivity.

GRAPHICAL ABSTRACT



ARTICLE INFO

Keywords:

Anhydrous proton conductivity
Solid-state electrolyte
Ionic liquid
High conductive
Long-term durable
Metal-organic framework

ABSTRACT

Incorporating ionic liquids (abbreviated as ILs) into porous metal-organic framework (MOF) to obtain ILs@MOF nanocomposites is documented as a feasible method to achieve new type of anhydrous proton conductor with high performance. We newly synthesized a series of ILs with different acid counter anions (R-SO₃⁻) and their ILs@MOF hybrid materials, i.e. SA-EIMS@MIL-101, MSA-EIMS@MIL-101 and PTSA-EIMS@MIL-101 (SA = sulfate acid, MSA = methanesulfonate acid, PTSA = *p*-toluenesulfonate acid, EIMS = 1-(1-ethyl-3-imidazolium)propane-3-sulfonate). Such hybrid materials displayed as anhydrous proton conduction with long-term durability even heated at 150 °C open to air. σ value of SA-EIMS@MIL-101 is up to $1.89 \times 10^{-3} \text{ S cm}^{-1}$, being in the range of the most conductive MOF-based materials. MOF support exhibited favorable proton transport and long-term retention for ILs. Anion volumes of R-SO₃⁻ displayed significant effects on the proton conductivity of such hybrid ILs@MOF materials. The smaller the van der Waals volume of R-SO₃⁻ is, the higher the conductivity of ILs@MOF is. This work suggests that the combination of a variety of the incorporated ILs and a MOF framework would afford high proton transport and gives an idea to explore the safe, anhydrous, solid-state electrolyte for high temperature proton exchange membrane fuel cell.

Abbreviations: MOF, metal-organic framework; SA, sulfate acid; MSA, methanesulfonate acid; PTSA, *p*-toluenesulfonate acid; EIMS, 1-(1-ethyl-3-imidazolium)propane-3-sulfonate; MIL-101, [Cr₃F(H₂O)₂O(BDC)₃nH₂O]

* Corresponding author. Department of Chemistry, Capital Normal University, Beijing 100048, PR China.

E-mail address: wancq@cnu.edu.cn (C.-Q. Wan).

<https://doi.org/10.1016/j.jpowsour.2017.11.089>

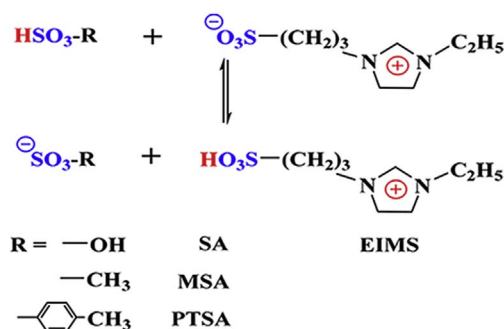
Received 30 September 2017; Received in revised form 23 November 2017; Accepted 27 November 2017

0378-7753/ © 2017 Elsevier B.V. All rights reserved.

1. Introduction

Fuel cell technology is considered to be one of the most promising way to solve the current environmental pollution and energy shortage problems [1]. Proton exchange membrane fuel cell (PEMFC) is acknowledged as one of the best candidates for the clean power source. To achieve an economically viable PEMFC with durable and easy-proton-transport properties, design and synthesis of a proton exchange membrane (PEM) with high performance is crucial because it is related to the efficiency, cost and the life of a battery [2]. However, the well-known proton conductive separator (e.g. Nafion® polymer) for PEM fuel cells requires a high hydration to maintain its high conductivity, which limits its working temperature below the boiling point of water (100 °C) because its conductivity may decline as the evaporating of water (proton carrier) at high temperature [3]. Thus, anhydrous PEM that can operate at moderate temperature (100–300 °C) received intense interest because they are high thermal stable and exhibit high performance over 120 °C [4]. Moreover, at high temperature abundant cheap oxide-based catalysts can be used to replace platinum, and poisoning of the platinum catalyst by trace amounts of carbon monoxide is thus avoided [5], and the cumbersome water management system of a PEMFC can also be dramatically simplified [1b,6]. Among significant efforts devoted to develop these high temperature anhydrous PEM, impregnating anhydrous proton carriers such as N-rich heterocycles (e.g. triazole [7], imidazole [8,9] and histamine [10]) and inorganic acids into porous metal-organic framework (MOF) [11–13] or covalent-organic framework (COF) materials has attracted enormous attentions [14,15]. MOF/COF materials can efficiently disperse the proton carriers and arrange them in order arrays through the effects of their distinct channel sizes and structures, therefore to well tune and enhance the efficient H⁺ transport [8,15a]. Notably, ionic liquids (ILs) are high thermal stable, high ionic conductive, low corrosive, nonflammable and nonvolatile [16–20], which are ideal H⁺ carrier candidate for a PEM safely working under moderate temperature. However, heterogeneously impregnating ILs into solid MOF/COF support to achieve the new type of high temperature anhydrous PEM material has remained almost unexplored till now.

Our group recently reported a novel ionic-liquid-impregnated MOF material EIMS-HTFSA@MIL-101 [21], a safe anhydrous electrolyte for H⁺ conduction over 100 °C (EIMS = 1-(1-ethyl-3-imidazolium)propane-3-sulfonate, HTFSA = *N,N*-bis(trifluoromethanesulfonyl)amide, MIL-101 = [Cr₃F(H₂O)₂O(BDC)₃nH₂O] [22] (n = 0.25, BDC = 1,4-benzenedicarboxylate). Such a soft-media-in-hard-matrix material was achieved by impregnating ionic liquid EIMS-HTFSA into solid MOF support MIL-101. Efficient dispersion of ILs over the large internal surface of MOF can lower the cost and overcomes the viscosity drawback of ILs [18], and thus endow the hybrid material with high temperature anhydrous proton conductivity over 140 °C. However, the active energy increased after the ionic liquid impregnated [21], unlike that enhanced H⁺ transport for the case of those solid proton carriers [8,15a]. With the aim to investigate acid counter anion effect of ILs and the interfacial miscibility between various ILs guests and MOF support, in this work we chosen a series of ILs with different acid counter anions (R-SO₃⁻) and obtained new ILs@MOF hybrid materials, i.e. SA-EIMS@MIL-101, MSA-EIMS@MIL-101 and PTSA-EIMS@MIL-101, and investigated their durability, temperature-dependent anhydrous H⁺ conduction (50 °C–150 °C) and the acid counter anion effects of ILs (SA = sulfate acid, MSA = methanesulfonate acid, PTSA = *p*-toluenesulfonate acid) (Scheme 1). These ILs@MOF exhibited thermal stability over 240 °C, exhibiting long-term durability even heated at 150 °C in air. Anhydrous H⁺ conductivity of SA-EIMS@MIL-101 is up to 1.89 × 10⁻³ S cm⁻¹, being in the range of the most conductive MOF-based materials [10,12b,23]. Different van der Waals volumes of the acid counter anions (R-SO₃⁻) in ILs and interfacial miscibility between such ILs and MOF support significantly influenced the conductivity of these hybrid materials. The proton conduction mechanism will also be



Scheme 1. Diagram of the Brønsted acid–base buffer and related binary ionic liquids SA-EIMS, MSA-EIMS and PTSA-EIMS in this study.

discussed.

Sulfate acid (SA) ($pK_{a1} = -2.9$), methanesulfonate acid (MSA) ($pK_a = -2.6$) and *p*-toluenesulfonate acid (PTSA) ($pK_a = -2.8$) [24] with similar acidity constant but different van der Waals volumes were selected as the proton sources, each of which was mixed with zwitterionic imidazole salt 1-(1-ethyl-3-imidazolium)propane-3-sulfonate (EIMS) in a 1:1 M ratio, respectively, obtaining the binary ionic liquids based on Brønsted acid–base buffer, namely SA-EIMS, MSA-EIMS and PTSA-EIMS (Scheme 1). Compared to the fluorinated anion such as *N,N*-bis(trifluoromethanesulfonyl)amide (HTFSA) [21], these acid counter anions (R-SO₃⁻) are less hydrophilic, and the H⁺ would be transferred within the binary ionic liquid via hopping between the adjacent –SO₃⁻ groups. Herein, MIL-101 is chosen as support. It is well known as a chemically and thermally stable MOF (up to 335 °C), featuring a mesoporous structure with two types of spherical cages ($\phi \approx 2.9\text{--}3.4$ nm) [22]. Its smallest pentagonal window (with a free opening of ≈ 1.2 nm, see ESI) is large enough to smoothly impregnate SA, MSA, PTSA (van der Waals volume, $V_{vdw} = 62.23 \text{ \AA}^3$, 70.74 \AA^3 , 143.36 \AA^3) [25] and EIMS ($V_{vdw} = 603 \text{ \AA}^3$ with $\approx 7.73 \text{ \AA}$ across) [21] into the cages. Calculated maximum number of pairs of SA-EIMS, MSA-EIMS, PTSA-EIMS to be accommodated within the large cage ($\approx 20600 \text{ \AA}^3$) reach up to 31, 30, 27 and small cage ($\approx 12700 \text{ \AA}^3$) are 19, 18, 17, respectively. The conductivity of the activated MIL-101 is negligibly (lower than 10^{-10} S cm⁻¹ at 140 °C) [21], while the ILs can serve as proton carriers, the combination of which thus can meet the protonic conductive but electronic insulative requirements to the separator for a fuel cell.

2. Experimental section

2.1. General methods and materials

All chemicals were obtained from commercial sources and used without further purification. Aqueous hydrofluoric acid (HF, Sinopharm Chemical Reagent Beijing Co. Ltd., 40%), terephthalic acid (HO₂CC₆H₄CO₂H, TCI Shanghai, 99%), chromic nitrate nonahydrate (Cr(NO₃)₃·9H₂O, Energy Chemical Company, 99%), 1-ethylimidazole (C₅H₈N₂, TCI Shanghai, 98%), 1,3-propanesultone (C₃H₆O₃S, J&K Scientific Ltd., 99%), sulfuric acid, methanesulfonic acid and *p*-toluenesulfonic acid (H₂SO₄, CH₃SO₃H, *p*-CH₃C₆H₄SO₃H, J&K Scientific Ltd.) and ethanol (C₂H₅OH, Sinopharm Chemical Reagent Beijing Co. Ltd., > 99.8%) all were used as received. MIL-101 and zwitterionic imidazole salt 1-(1-ethyl-3-imidazolium)propane-3-sulfonate [26] were obtained following the reported synthesis procedures (See ESI).

¹H NMR spectra were recorded on a Bruker AVANCE III spectrometer operating at 600 MHz in DMSO-*d*₆. Thermogravimetric measurements were obtained with a Bruker TG/DTA 2000 SA, using a heating rate of 5 °C/min from 30 °C to 800 °C under dry atmosphere. FT-IR spectra of all samples were recorded on a Bruker Equinox 55 FT-IR analyzer with dry KBr pellets within the range of 400–4000 cm⁻¹. Scanning Electron Microscope (SEM) images and Energy-dispersive X-

Download English Version:

<https://daneshyari.com/en/article/7725974>

Download Persian Version:

<https://daneshyari.com/article/7725974>

[Daneshyari.com](https://daneshyari.com)