

## Ion-Conductive Porous Crystals

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**Keywords:** Ionic Conduction; Metal–Organic Framework; Covalent Organic Framework; Porous Material

Solid-state ionic conductors are important materials because of their potential applications for energy-related devices such as secondary batteries and fuel cells. Many researchers have investigated to clarify the relationship between structure and ionic conductivity using various solids. The migration of ionic carriers in solids requires some empty spaces or lattice defects for accepting the migrating ions (i.e., ion-conducting pathway). Therefore, the structural features of ionic conductors can be classified into three types.<sup>1</sup> First is the channel (porous) structure or layered structure that allows the included ionic carriers to migrate efficiently in the spaces (e.g. Na- $\beta$ -alumina). Second is the mean structure, where the ions can migrate to various lattice points, resulting in averaged occupancy of the ions on these sites (e.g.  $\alpha$ -AgI). Third is the defect structure, including some defects on the lattice point and the ions located on the neighbouring lattice point can migrate to the next position (e.g. Y-doped ZrO<sub>2</sub>).

Metal–organic frameworks (MOFs) have recently emerged as a new class of ionic conductors due to their excellent materials variety and designable pores. The porous structure of MOFs is fundamentally suitable for creating highly ion-conductive materials by constructing efficient ion-conducting pathways in the pores. Many researchers have investigated to create novel ionic conductors using various ionic carriers such as proton (H<sup>+</sup>),<sup>2</sup> hydroxide ion (OH<sup>-</sup>),<sup>3</sup> and lithium ion (Li<sup>+</sup>).<sup>4</sup> Since the ionic conductivity ( $\sigma$ ) is expressed as  $\sigma = zen\mu$  (S cm<sup>-1</sup>), where  $z$  is the valence of the ionic carrier,  $e$  is the elementary charge,  $n$  is the carrier concentration, and  $\mu$  is the mobility of the charge carrier, it is clear that the introduction of an ionic carrier into the pores of MOFs (high  $n$ ) and the construction of a suitable environment for the mobile ions in the pores (high  $\mu$ ) are the critical points to achieve high ionic conduction. One of the specific features of MOF-based ionic conductor is the guest inclusion. The guest molecules, namely ‘conducting media’, which enhance the migration of included ionic carrier, can be introduced into the remaining pores of MOFs to achieve high mobility of the ions. For example, H<sub>2</sub>O molecules adsorbed in MOFs often enhance the H<sup>+</sup> conductivity,<sup>2</sup> which is related to the specific conducting mechanism of H<sup>+</sup>, named as ‘Grotthuss mechanism’.

We have recently focused on the ionic conduction of multivalent ions such as magnesium ion (Mg<sup>2+</sup>) in MOFs. In particular, the Mg<sup>2+</sup> conductor is one of the key materials for realization of the next-generation secondary battery without the use of rare elements such as Li. However, the number of reports on highly Mg<sup>2+</sup>-conductive solids

is considerably smaller than that of Li ions. In the case of MOFs, there are a few reports on conductivity of  $\text{Mg}^{2+}$ -included MOFs.<sup>5,6</sup> However, there is a lack of direct evidence of  $\text{Mg}^{2+}$  transport and understanding of the role guest molecules for  $\text{Mg}^{2+}$  conduction in the MOFs. We recently succeeded in demonstrating that efficient  $\text{Mg}^{2+}$  transport truly occurs in the pores of MOFs and that  $\text{Mg}^{2+}$  conductivity strongly depends on the types of adsorbed guest molecules.<sup>7</sup> We prepared a MOF,  $\text{Mg-MOF-74} \supset \{\text{Mg}(\text{TFSI})_2\}_x$  ( $x \leq 0.15$ ) ( $\text{TFSI}^- = \text{bis}(\text{trifluoromethanesulfonyl})\text{imide}$ ), including only  $\text{Mg}(\text{TFSI})_2$  inside the pores (Fig. 1) and evaluated the ionic conductivity under the presence of various guests vapors (Fig. 2). The ionic conductivity, evaluated by alternating current (ac) impedance measurements, strongly depended on the guest molecules and  $\text{Mg-MOF-74} \supset \{\text{Mg}(\text{TFSI})_2\}_{0.15}$  showed superionic

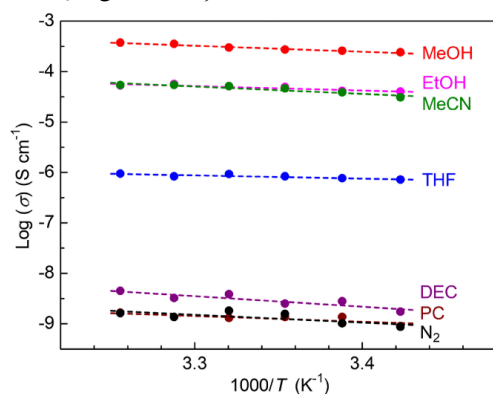


Fig. 2 Temperature dependence of the ionic conductivity of the sample of  $x = 0.15$ ,  $\text{Mg-MOF-74} \supset \{\text{Mg}(\text{TFSI})_2\}_{0.15}$ .<sup>7</sup>

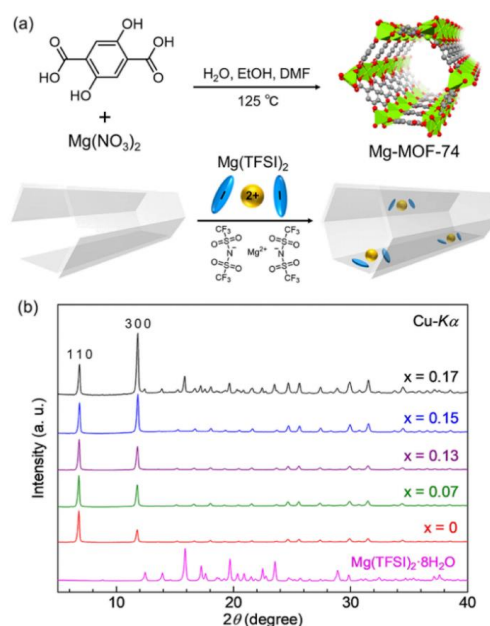


Fig. 1 (a) Schematic illustration of the introduction of only  $\text{Mg}(\text{TFSI})_2$  salts inside the pores of  $\text{Mg-MOF-74}$ . (b) XRPD patterns of  $\text{Mg-MOF-74} \supset \{\text{Mg}(\text{TFSI})_2\}_x$ .<sup>7</sup>

conductivity of  $2.6 \times 10^{-4} \text{ S cm}^{-1}$  under  $\text{MeOH}$  vapor at room temperature. Since the ac impedance measurements could not directly evaluate the  $\text{Mg}^{2+}$  conductivity in this compound because of the presence of anion,  $\text{TFSI}^-$ , we also estimated the transfer number of  $\text{Mg}^{2+}$  of the MOF by dc polarization of the cell constructed by non-blocking electrodes and confirmed the efficient  $\text{Mg}^{2+}$  conduction in the MOF ( $t_{\text{Mg}^{2+}} = 0.47$ ). The tendency that the conductivity deeply depended on the size of guest molecules is indicative that the high  $\text{Mg}^{2+}$  conduction is derived from the migration of coordinated species of  $\text{Mg}^{2+}$ .<sup>7</sup>

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