High Li and Mg conductivity in a Cu-azolate metal-organic framework

Elise M. Miner, Sarah S. Park, and Mircea Dinca

J. Am. Chem. Soc., Just Accepted Manuscript • DOI: 10.1021/jacs.8b13418 • Publication Date (Web): 18 Feb 2019

Downloaded from http://pubs.acs.org on February 19, 2019

Just Accepted

“Just Accepted” manuscripts have been peer-reviewed and accepted for publication. They are posted online prior to technical editing, formatting for publication and author proofing. The American Chemical Society provides “Just Accepted” as a service to the research community to expedite the dissemination of scientific material as soon as possible after acceptance. “Just Accepted” manuscripts appear in full in PDF format accompanied by an HTML abstract. “Just Accepted” manuscripts have been fully peer reviewed, but should not be considered the official version of record. They are citable by the Digital Object Identifier (DOI®). “Just Accepted” is an optional service offered to authors. Therefore, the “Just Accepted” Web site may not include all articles that will be published in the journal. After a manuscript is technically edited and formatted, it will be removed from the “Just Accepted” Web site and published as an ASAP article. Note that technical editing may introduce minor changes to the manuscript text and/or graphics which could affect content, and all legal disclaimers and ethical guidelines that apply to the journal pertain. ACS cannot be held responsible for errors or consequences arising from the use of information contained in these “Just Accepted” manuscripts.
High Li\(^+\) and Mg\(^{2+}\) conductivity in a Cu-azolate metal-organic framework

Elise M. Miner, Sarah S. Park, and Mircea Dincă*

Department of Chemistry, Massachusetts Institute of Technology, 77 Massachusetts Avenue, Cambridge, Massachusetts 02139, United States

Supporting Information

ABSTRACT: A Cu-azolate metal-organic framework uptakes stoichiometric loadings of Group 1 and 2 metal halides, demonstrating efficient reversible release and reincorporation of immobilized anions within the framework. Ion pairing interactions lead to anion-dependent Li\(^+\) and Mg\(^{2+}\) transport in Cu\(_3\)(ttpm)\(_2\)-0.6CuCl\(_2\), whose high surface area affords a high density of uniformly distributed mobile metal cations and halide binding sites. The ability to systematically tune the ionic conductivity yields a solid electrolyte with a Mg\(^{2+}\) ion conductivity rivaling the best materials reported to date. This MOF is one of the first in a promising class of frameworks that introduces the opportunity to control the identity, geometry, and distribution of the cation hopping sites, offering a versatile template for application-directed design of solid electrolytes.

INTRODUCTION

Since the emergence of the first rechargeable galvanic cell in 1860,\(^1\) rechargeable batteries have become an enabling technology for a range of critical processes in modern life. Although old in a sense, rechargeable battery technologies represent an important field of modern research, spurred by the scale and variety of applications stemming from an inevitable transition to renewable and clean energy technologies. Among the various possible technologies, metal and metal-ion batteries are particularly versatile in serving a range of applications especially in consumer electronics, where they offer a combination of high volumetric capacity and ~1000-cycle lifetime that is well suited for such devices.\(^2\) However, despite significant advances there is much room for improvement in efficiency, lifetime, and safety of metal and metal-ion batteries. All these could be improved by transitioning from liquid electrolytes, the current industry standard, to solid ion conductors. Liquid electrolytes exhibit relatively narrow potential stability windows, cation transference numbers of \(<\ 0.4\) that lead to lifetime-limiting polarization effects, and little control over the uniformity of Li plating during charging.\(^2\) Non-uniform plating can cause dendrite formation, which may result in piercing the battery separator and leakage of the flammable organic liquid electrolyte, or if contact is made with the other electrode, circuit shorting. Efforts to address these challenges have included development of solid-state electrolytes.\(^3\)–\(^7\) Although solid electrolytes exhibit higher potential stability windows, higher transference numbers, and are safer by virtue of their reduced flammability and increased mechanical stability, they can suffer from low conductivity and poor interfacial contact between the electrodes and the electrolyte.\(^8\) An ideal system would combine the lower transport and interfacial resistance of liquid electrolytes with the safety and enhanced stability features of solid electrolytes.

One class of materials that may provide clues to addressing these challenges is metal-organic frameworks (MOFs). The high surface area of MOFs offers the ability to install a high density of charged species in a small geometric volume. This allows for closely packed cation hopping sites, which could minimize activation energy for ion transport and increase ion conductivity. Additionally, the ordered porosity of MOFs could aid in controlling the uniformity of cation plating at the anode during charging, thus preventing dendrite formation. Many MOFs present metal sites whose coordination spheres are initially occupied by solvent molecules. Removing the solvent molecules exposes coordinatively unsaturated cationic sites onto which anions can be docked. The coordinated anions require charge-balancing cations that become the only mobile charge carriers, thus maximizing cation transference numbers. Finally, altering the lability and/or valency of the metal centers, changing pore polarity by ligand functionalization, and enlarging the pore diameter by extending the ligand length offer multiple tunable variables for systematic optimization of electrolyte performance. Indeed, several MOFs have been explored as solid-state electrolytes, and have featured many of the benefits listed above.\(^8\)–\(^12\) Although promising, many of these MOFs require additional salt content in excess of what would be expected based on the number of available anion binding sites. This necessarily implies that not only cations, but also anions will be mobile, which in turn reduces the cation transference numbers. Additionally, activation energies in such materials are sometimes higher than is desired, as ion pairing between anions and cations is still strong. Some of the reported MOF-based electrolytes have also shown poor stability to electrochemical cycling, eliminating their viability for rechargeable batteries. To expand upon current MOF electrolytes, we took advantage of a Cu-azolate material, Cu\(_3\)(ttpm)\(_2\) (H\(_4\)ttpm = tetrakis(4-tetrazolylphenyl)methane)\(^24\)
that presents multiple anion binding sites, a key feature that enabled ionic conductivity in another MOF electrolyte previously reported by our group.\textsuperscript{8} This abundance of anionic binding sites in Cu(ttpm)\textsubscript{3} leads to high mobile Li\textsuperscript{+}, Mg\textsuperscript{2+}, and Al\textsuperscript{3+} density. The ability to reconstitute this MOF in various types of metal salts allowed for modulation of the ion pairing strength, as evidenced by conductivity and activation energy values that change as a function of anion identity.

**EXPERIMENTAL METHODS**

Complete experimental methods are provided as Supporting Information.

**RESULTS AND DISCUSSION**

**Preparation of MOF-MX\textsubscript{n}**

The anionic parent material, Cu[(Cu\textsubscript{3}Cl)(tttpm)]\textsubscript{2}·CuCl\textsubscript{2}, and the neutral framework, Cu(ttpm)\textsubscript{3}·0.6CuCl\textsubscript{2}, were synthesized according to a reported procedure.\textsuperscript{24} It was previously shown that Cu(tetrazole)\textsubscript{3} secondary building units (SBUs) in the original material feature 5 possible halide binding sites, a portion of which can be made available for anion binding by Soxhlet extraction with methanol (Scheme 1).\textsuperscript{24} Importantly, some of these sites bear bridging halides, which opens the possibility of reducing their ion pairing with mobile cations because electron density on the bridging halides would be screened by multiple Cu\textsuperscript{2+} ions. Reconstitution of Cu\textsubscript{n}(tttpm)\textsubscript{2}·0.6CuCl\textsubscript{2} in saturated THF solutions of various Group I and 2 metal halide salts (i.e., LiCl, LiBr, MgCl\textsubscript{2}, MgBr\textsubscript{2}) afforded anionic structures balanced with alkali and alkaline earth metal cations (Scheme 1). The resulting materials were washed with propylene carbonate (PC), a commonly used dielectric that solvates the metal cations and can improve inter-particle conductivity.\textsuperscript{19,20} Inductively-coupled plasma-mass spectrometry (ICP-MS) and quantitative \textsuperscript{1}H NMR spectroscopy of digested samples (Figures S1-S6) provided the Group I and 2 metal content and propylene carbonate content, respectively, for the final electrolyte formulations (Table 1). Soaking the MOF in solutions of LiCl, LiBr, MgCl\textsubscript{2}, or MgBr\textsubscript{2} installed approximately 2 equivalents of halide per Cu SBU. Stoichiometric reincorporation of immobilized anions promoted by appropriate equivalents of open metal sites within the host provides the potential to maximize cation transference numbers and modulate the ionic transport properties of the electrolyte by altering the identity of the immobilized anion.

That the coordination mode of the halides can be defined within the crystallographic parameters of the MOF as opposed to random dispersion of the salts within the electrolyte matrix was evidenced by powder X-ray diffraction (PXRD) and scanning electron microscopy-energy dispersive X-ray spectroscopy (SEM-EDS). Soxhlet-extracting the anionic

**Table 1.** Formulas of MOF-MX\textsubscript{n}, including metal ratios as determined by ICP-MS and propylene carbonate (PC) content from \textsuperscript{1}H NMR spectroscopy. Refer to Table S1 for weight percentages of M\textsuperscript{n+} in the electrolytes.

<table>
<thead>
<tr>
<th>Sample name</th>
<th>Cu</th>
<th>M\textsuperscript{n+} (M\textsuperscript{n+} = Li\textsuperscript{+}, Mg\textsuperscript{2+})</th>
<th>X (X = Cl\textsuperscript{−}, Br\textsuperscript{−}, I\textsuperscript{−})</th>
<th>Formula</th>
</tr>
</thead>
<tbody>
<tr>
<td>MOF-LiCl</td>
<td>2.5</td>
<td>1.0</td>
<td>1.0</td>
<td>Cu\textsubscript{4}(tttpm)\textsubscript{2}(CuCl\textsubscript{2})\textsubscript{0.6}(LiCl)\textsubscript{1.8}19PC</td>
</tr>
<tr>
<td>MOF-LiBr</td>
<td>2.4</td>
<td>1.0</td>
<td>1.0</td>
<td>Cu\textsubscript{4}(tttpm)\textsubscript{2}(CuCl\textsubscript{2})\textsubscript{0.6}(LiBr)\textsubscript{1.8}20PC</td>
</tr>
<tr>
<td>MOF-LiI</td>
<td>4.5</td>
<td>1.0</td>
<td>1.0</td>
<td>Cu\textsubscript{4}(tttpm)\textsubscript{2}(CuCl\textsubscript{2})\textsubscript{0.6}(LiI)\textsubscript{1.8}20PC</td>
</tr>
<tr>
<td>MOF-MgCl\textsubscript{2}</td>
<td>6.1</td>
<td>1.0</td>
<td>2.0</td>
<td>Cu\textsubscript{4}(tttpm)\textsubscript{2}(CuCl\textsubscript{2})\textsubscript{0.6}(MgCl\textsubscript{2})\textsubscript{1.8}17PC</td>
</tr>
<tr>
<td>MOF-MgBr\textsubscript{2}</td>
<td>6.4</td>
<td>1.0</td>
<td>2.0</td>
<td>Cu\textsubscript{4}(tttpm)\textsubscript{2}(CuCl\textsubscript{2})\textsubscript{0.6}(MgBr\textsubscript{2})\textsubscript{1.8}21PC</td>
</tr>
<tr>
<td>MOF-MgI\textsubscript{3}</td>
<td>7</td>
<td>1.0</td>
<td>2.0</td>
<td>Cu\textsubscript{4}(tttpm)\textsubscript{2}(CuCl\textsubscript{2})\textsubscript{0.6}(MgI\textsubscript{3})\textsubscript{1.8}15PC</td>
</tr>
</tbody>
</table>

**Scheme 1.** Synthesis of Cu[(Cu\textsubscript{3}Cl)(tttpm)]\textsubscript{2}·CuCl\textsubscript{2}, Cu\textsubscript{4}(tttpm)\textsubscript{2}·0.6CuCl\textsubscript{2}, and the target MOF-MX\textsubscript{n}, where M = Li\textsuperscript{+} or Mg\textsuperscript{2+}, X = Cl\textsuperscript{−} or Br\textsuperscript{−}, and n = 1 or 2. H atoms have been omitted for clarity.
Cu[(Cu,Cl)(ttpm),CuCl2 resulted in almost total disappearance of the [110] reflection at 2θ ≈ 8°, which has electron density from both axial Cl− and bridging μ3-Cl− as major contributors (Figure S7). PXRD patterns of the MOF-MXn samples showed a reemergence of this reflection, consistent with immobilized halides having a crystallographically distinct coordination mode within the Cu4 SBU (Figure 1, Figure S8).

PXRD also confirmed that the MOF retains its structure both during the treatment with halide salts, and during electrochemical cycling. However, treating the MOF with LiI or MgI2 resulted in major reduction of crystallinity with the former and total destruction of the MOF structure with the latter (Figure S8). This is not unexpected, as I− is readily oxidized by Cu2+ and CuI2 itself is unstable to disproportionation.25−28 In line with redox activity at the MOF Cu2+ sites, iodide-treated samples exhibit faradaic events that are not observed with the other halides (Figure S9).

![Figure 1. Representative PXRD pattern showcasing the disappearance and reemergence of the [110] reflection at 2θ ≈ 8° (largely contributed by the halide electron density), as well as stability of the MOF to electrochemical cycling. See Supplementary Figure S8 for PXRD patterns of the other analogues.](image)

Further evidence for homogeneous incorporation of halides in the MOF-MXn electrolytes came from SEM-EDS (Figure Sio). The homogeneity of chloride as well as copper distribution in the spectra confirmed that no amorphous MXn phase had aggregated within the electrolyte matrix. Additionally, reduction of the average crystallite size by approximately two orders of magnitude during the halide soak was consistent with the MXn salts penetrating the crystals themselves rather than residing in grain boundaries or other more kinetically accessible locations (Figure Sio).

**Conductivity measurements with MOF-MXn.** To ensure that the parent Cu4(ttpm),0.6CuCl2 was sufficiently electrically insulating to prevent short-circuiting, a 100 V potential (from −50 V to 50 V) was applied to a pressed pellet and the resulting current was measured. The generated I-V curve yielded an electrical conductivity of 5.08×10−12 S cm−1, confirming that Cu4(ttpm),0.6CuCl2 is an electrical insulator and a suitable host as a solid electrolyte (Figure Sii).29

To measure ionic conductivity, MOF-MXn powders were loaded into a test cell and subjected to electrochemical impedance spectroscopy (EIS) from 1 MHz to 1 Hz. Fitting the resulting EIS spectra to the circuit shown in the Methods section (see Supporting Information) gave Li+ conductivities ranging from 2.4×10−5 S cm−1 (MOF-LiCl) to 1.1×10−4 (MOF-LiI) at 25 °C for the MOF-LiX samples (Figure 2, Table 2). Excitingly, this data highlighted the ability to systematically tune the conductivity by modulating the softness of the anion, in turn altering the ionic strength of the Li-halide interaction. Additional utility of this modular structure was showcased in the activation energies. Variable-temperature EIS (Figure Siz) and fitting the corresponding Arrhenius plots gave activation energies which also varied as a function of anion softness (Ea = 0.34 eV for MOF-LiCl to 0.24 eV for MOF-LiI) (Table 2). These low
activation energies of < 0.4 eV are on-par with those of superionic conductors.30

**Li⁺ transference numbers for MOF-LiX.** To evaluate the contribution of Li⁺ ions to the ionic current, Li⁺ transference numbers were calculated for MOF-LiX (Figures S3–S5). MOF-LiCl yielded a high Li⁺ transference number of 0.69, indicating that almost 70% of the current passed resulted from mobile Li⁺ ions as opposed to other mobile, charged species.30 This transference number is competitive with many solid electrolytes and a marked improvement upon liquid electrolytes, which typically exhibit Li⁺ transference numbers of only 0.3–0.4.30,31 In the latter, the current is dominated by other mobile ions which can migrate to the electrodes and cause polarization effects that decrease battery lifetime. Ironically, the modularity of the anion identity here produces both quantifiable improvements in terms of conductivity and activation energy of the electrolytes, as well as challenges following these same trends. Thus, Li⁺ transference numbers for the MOF-LiBr and MOF-LiI samples were only 0.42 and 0.34, respectively (Table 2). This is likely due to the fact that in addition to ion pairing strength between the Li⁺ and the anions decreasing with increasing anion softness, the Coulombic forces immobilizing the anions close to the Cu²⁺ centers also weaken with increasing anion softness.30 Thus, upon application of electrochemical bias, a higher percentage of Br⁻ and I⁻ ions migrate to the opposite electrode compared to Cl⁻ ions. One possible solution could involve utilizing anions of enhanced steric bulk so that their mobility is more limited compared to those of monatomic anions. A caveat with this approach may be that significantly increasing the anion size could result in lower loading of the desired metal salt, due to pore volume constraints within the MOF.

**Durability studies with MOF-LiX.** Electrochemical cycling experiments revealed good durability for the MOF-LiX electrolytes. Over 200 cycles, MOF-LiCl and MOF-LiBr retained reversible stripping and plating of Li, with only slight increase in overpotential (Figure S6). Additionally, the crystallinity of the structures was retained during extended electrochemical measurements (Figure S8). Interestingly, MOF-LiCl showed an increase in anodic current between cycles 1 and 30, after which time the current then decreased with progressing cycles. This may be due to slower kinetics observed in MOF-LiCl, consistent with the lower conductivity compared to that of MOF-LiBr. MOF-LiBr passed the maximum faradaic current during the first cycle, and current decreased over subsequent cycles. As expected, these cycling measurements also highlighted the instability of MOF-LiI, which lost all faradaic current after only 78 cycles.

As another measure of robustness, the MOF-LiX electrolytes showed large potential stability windows. In particular, MOF-LiCl exhibits a potential window of 4.5 V, potentially suitable for battery applications.34 MOF-LiBr features a slightly narrower potential window of 3.5 V, likely due to partial oxidation of Br⁻ (Figure S7). Both MOF-LiCl and MOF-LiBr possess potential windows wider than those of many nonaqueous liquid electrolytes, which are commonly limited to ~3 V.35

**Mg²⁺ transport studies.** Although the high volumetric capacity and reversible redox activity intrinsic to lithium identifies Li and Li-ion batteries as attractive energy sources, safety, performance, and abundance (consequently, cost) obstacles that cannot be overcome with cell optimization has encouraged exploration of other metals for battery applications. Mg²⁺, although less reducing than Li⁺, has almost double the volumetric capacity of Li⁺, due to its divalent charge and still relatively small ionic radius.2 Additionally, Mg is not plagued by the dendrite formation issues faced by Li, and is 5 orders of magnitude more abundant than Li.2 As such, we sought to explore the potential of Cu₄(tpm)₂·0.6CuCl₂ as a solid electrolyte for Mg²⁺. EIS of MOF-MgCl₂ and MOF-MgBr₂ collected at 25 °C revealed the same modular trend as observed in the Li⁺ analogues, in that the bromide salts lead to higher conductivity than chloride (Figure 3, Table 3). Most importantly, MOF-MgBr₂ exhibits an ionic conductivity of 1.3·10⁻⁴ S·cm⁻¹, and thus shares the spotlight as the most conductive Mg²⁺-ion solid electrolyte to date.36 Activation energies calculated from the temperature-dependent EIS data fit to Arrhenius plots were in-line with the trend observed for Li⁺ salts: the values were

<table>
<thead>
<tr>
<th>Electrolyte</th>
<th>σ (S·cm⁻¹)</th>
<th>Eₐ (eV)</th>
<th>Li⁺ transference #</th>
</tr>
</thead>
<tbody>
<tr>
<td>MOF-LiCl</td>
<td>2.4·10⁻⁵</td>
<td>0.34</td>
<td>0.69</td>
</tr>
<tr>
<td>MOF-LiBr</td>
<td>3.2·10⁻⁵</td>
<td>0.30</td>
<td>0.42</td>
</tr>
<tr>
<td>MOF-LiI</td>
<td>1.1·10⁻⁴</td>
<td>0.24</td>
<td>0.34</td>
</tr>
</tbody>
</table>

![Figure 3](image-url)
point to a potential connection between pore size, pore polarity, and mobile ion identity that combine better for promoting Mg\textsuperscript{2+}-ion transport in Cu\textsubscript{4}(ttpm)\textsubscript{2}.0.6CuCl\textsubscript{2} than in other materials. Indeed, there may be an ideal pore size and pore polarity that will minimize activation energy for these higher valence ions. Owing to their compositional and structural tunability, MOFs are attractive targets for exploring this possibility.

**ASSOCIATED CONTENT**

Supporting Information. Materials and Methods. Weight percentages of M\textsuperscript{m+} ions in the electrolytes. 'H NMR spectra of MOF-MX\textsubscript{2}/PC. [110] reflection of Cu[(CuCl)(ttpm)]\textsubscript{2}.CuCl\textsubscript{2}. Electrolyte potential windows of MOF-LiX- SEM-EDS. 1-V curve of Cu\textsubscript{4}(ttpm)\textsubscript{2}.0.6CuCl\textsubscript{2}. Variable temperature EIS spectra of MOF-MX\textsubscript{2}. Li\textsuperscript{+} transference number data of MOF-LiX. Li redox CVs with MOF-LiX. Arrhenius data of MOF-AlCl\textsubscript{3}.

The Supporting Information is available free of charge on the ACS Publications website.

**AUTHOR INFORMATION**

**Corresponding Author**
mdinca@mit.edu

**Notes**
The authors declare no competing financial interests.

**ACKNOWLEDGMENT**

This work was supported by the U.S. Department of Energy, Office of Science, Office of Basic Energy Sciences (DE-SC0008235). E.M.M. gratefully acknowledges the National Science Foundation for partial support through a Graduate Research Fellowship under Grant No. 1122374.

**REFERENCES**

(1) Kurzweil, P. Gaston Planté and his invention of the lead–acid battery—the genesis of the first practical rechargeable battery. *J. Power Sources* 2010, 195, 4424–4434.

(2) Bucur, C. B. Challenges of a Rechargeable Magnesium Battery; SpringerBriefs in Energy; Springer International Publishing: Cham, 2018.


(7) Li, S.; Zhu, J.; Wang, Y.; Howard, J. W.; Lü, X.; Li, Y.; Kumar, R. S.; Wang, L.; Daemen, L. L.; Zhao, Y. Reaction mechanism studies towards effective fabrication of lithium-rich anti-perovskites Li\textsubscript{X}O\textsubscript{X} (X = Cl, Br). *Solid State Ionics* 2016, 284, 14–19.

approaches towards enhanced sodium ionic conductivity in Na-rich antiperovskites. *J. Power Sources* 2015, 293, 735-740.


(32) Diederichsen, K. M.; McShane, E. J.; McCloskey, B. D. Promising routes to a high Li⁺ transference number electrolyte for lithium ion batteries. *ACS Energy Lett.* 2017, 2, 2563–2575.


