

A Solid Lithium Electrolyte via Addition of Lithium Isopropoxide to a Metal–Organic Framework with Open Metal Sites

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S Supporting Information

ABSTRACT: The uptake of LiO^iPr in $\text{Mg}_2(\text{dobdc})$ ($\text{dobdc}^{4-} = 1,4\text{-dioxido-2,5-benzenedicarboxylate}$) followed by soaking in a typical electrolyte solution leads to the new solid lithium electrolyte $\text{Mg}_2(\text{dobdc}) \cdot 0.35\text{LiO}^i\text{Pr} \cdot 0.25\text{LiBF}_4 \cdot \text{EC} \cdot \text{DEC}$ (EC = ethylene carbonate; DEC = diethyl carbonate). Two-point ac impedance data show a pressed pellet of this material to have a conductivity of $3.1 \times 10^{-4} \text{ S/cm}$ at 300 K. In addition, the results from variable-temperature measurements reveal an activation energy of just 0.15 eV, while single-particle data suggest that intraparticle transport dominates conduction.

Because of their high energy density and operating potential, lithium ion batteries have been widely adopted in portable electronics. However, to enable their implementation in traction applications, such as for electric vehicles, considerable improvements must still be made in terms of cost, energy and power density, manufacture, and safety.¹ Advances in electrode chemistries as well as the separator are needed to meet those challenges. Currently, macroporous polymer membranes swelled with lithium salts dissolved in organic carbonates are utilized as the separator in lithium ion batteries.² The use of a liquid electrolyte restricts battery shape and processing while also posing numerous safety problems due to the potential leakage of corrosive liquids and the volatility and flammability of the electrolyte solvent.³ Furthermore, the lack of rigidity for current battery separators precludes the use of solid lithium as an anode, as repeated cycling leads to lithium dendrites that can pierce the separator and cause cell failure.⁴ In contrast, a rigid, solid separator could inhibit lithium dendrite growth and allow the use of metallic lithium as an anode.⁵ In view of the high theoretical capacity of lithium metal (3860 A h/kg) and its very negative reduction potential (-3.04 V vs SHE), such an advance would enable tremendous gains in energy capacity. Since the 1970s, salts dissolved in solid polyethers have been investigated as solid electrolyte materials.⁶ However, the low conductivities of such materials at room temperature (10^{-6} S/cm) currently prevent their use in battery applications. Other solid lithium electrolytes either display total conductivities that are also too low or are poorly compatible with the battery electrodes.⁷

Metal–organic frameworks (MOFs) are a broad class of microporous solids that have been investigated primarily for

their gas adsorption properties⁸ as well as for possible applications in sensing,⁹ drug delivery,¹⁰ catalysis,¹¹ and optoelectronics.¹² Recently, studies of electronic¹³ and proton conductivity¹⁴ have also been reported. While the intercalation of lithium ions into such materials has been observed¹⁵ and porous zeolites have been investigated as fillers in solid polymer lithium electrolyte systems¹⁶ as well as stand-alone solid electrolytes operating at high temperatures ($>300 \text{ }^\circ\text{C}$),¹⁷ there have been no reports to date of the use of MOFs as lithium electrolytes for possible battery separator applications. Here we show that the incorporation of lithium isopropoxide into a MOF with open metal cation sites can produce a solid with an ionic conductivity of greater than 10^{-4} S/cm at 300 K.

In our initial evaluation of MOFs as possible lithium electrolyte materials, we tested the ionic conductivity attained upon uptake of a common electrolyte solution within MOF-177,¹⁸ Cu-BTTri,¹⁹ and $\text{Mg}_2(\text{dobdc})$.²⁰ Each compound was soaked in a 1 M solution of LiBF_4 in a 1:1 mixture of ethylene carbonate (EC) and diethyl carbonate (DEC), and the resulting materials were dried and pressed into pellets. The pellets were then placed in a thermostatted press, and their conductivities were measured via two-point alternating current (ac) impedance spectroscopy. A Solartron 1260 frequency response analyzer connected to a Solartron 1296 dielectric interface and blocking stainless steel electrodes were employed for this process. The conductivity of each material was obtained by measuring the real impedance of the semicircles of the Nyquist plots, taking the geometry of the pellets into account. The impregnated frameworks showed conductivities on the order of 10^{-9} to 10^{-6} S/cm (see Figure S1 in the Supporting Information). The most promising material was $\text{Mg}_2(\text{dobdc})$, which upon uptake of the electrolyte solution afforded a room-temperature conductivity of $1.8 \times 10^{-6} \text{ S/cm}$. Although $\text{Mg}_2(\text{dobdc})$ was the most conductive of the materials we measured, its conductivity was still 3 orders of magnitude below what is desired for a battery electrolyte (10^{-3} S/cm at ambient temperature)⁴ and 2 orders of magnitude below what is considered the technological limit for a functional battery electrolyte (10^{-4} S/cm).⁷

Researchers have previously effected postsynthetic modifications of MOFs via covalent modification of organic ligands^{11c,21} as well as through grafting of neutral ligands onto open metal centers.¹⁹ The structure of $\text{Mg}_2(\text{dobdc})$ consists of

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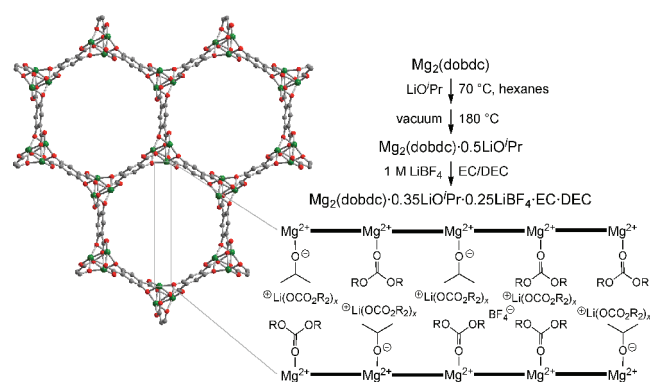


Figure 1. Structure of $\text{Mg}_2(\text{dobdc})$ and the scheme for its modification to form the solid electrolyte. A representation of a cross-sectional view along a channel of the solid is shown at the lower right [$R = -\text{CH}_2-\text{CH}_2-$ (EC) or $-\text{CH}_2\text{CH}_3$ (DEC)].

one-dimensional hexagonal channels with diameters of $\sim 14 \text{ \AA}$ that are lined with coordinatively unsaturated Mg^{2+} cation sites (see Figure 1). We hypothesized that the presence of these sites could facilitate the uptake of a lithium alkoxide, leading to a higher ionic conductivity. Here the alkoxide anions might preferentially bind the Mg^{2+} ions of the framework, pinning them in place while leaving the Li^+ cations relatively free to move along the channels. Moreover, variation of the alkyl group might allow screening of the negative charge of the oxygen atom and modification of the pore content. Indeed, preliminary measurements showed grafting of Li^iOPr to give higher conductivities than grafting of either LiOMe or LiOEt .

To perform the grafting, $\text{Mg}_2(\text{dobdc})$ was activated by heating under vacuum to remove all solvent followed by soaking for two weeks with a hot solution of Li^iOPr in hexanes (see Figure 1). The solids were then washed with hexanes and dried under reduced pressure. IR spectra of the resulting materials revealed the emergence of aliphatic C–H stretches at 3200 cm^{-1} , a new C–O stretch at 1080 cm^{-1} , and a broadening of what we assigned as a Mg–O stretch at 450 cm^{-1} (see Figure S2).²² The results from elemental analyses are consistent with the formula $\text{Mg}_2(\text{dobdc}) \cdot 0.5\text{Li}^i\text{OPr}$. Subsequent soaking of the material in a 1 M solution of LiBF_4 in 1:1 EC/DEC resulted in uptake of 0.25 equiv of LiBF_4 and 2 equiv of carbonate solvent (either EC or DEC) to give a compound having the formula $\text{Mg}_2(\text{dobdc}) \cdot 0.35\text{Li}^i\text{OPr} \cdot 0.25\text{LiBF}_4 \cdot \text{EC} \cdot \text{DEC}$. The decrease in Li^iOPr content may be due to leaching of unbound lithium alkoxide and/or exchange with LiBF_4 . It should be noted that in concentrated solutions, Li^+ cations can be solvated by as few as two carbonate molecules.²³ Powder X-ray diffraction data for this material indicated that the framework structure was preserved throughout the impregnation process (see Figure S3). Thus, within the pores of the framework, we anticipate a high density of charge carriers in close proximity to each other, allowing Li^+ cations to hop from site to site while remaining solvated by the carbonate molecules. The final sample was obtained as a dry, free-flowing powder that could be readily pressed into pellets.

Measurements performed on pellets of this material from multiple preparations afforded room-temperature conductivities falling in the range $(0.9\text{--}4.4) \times 10^{-4} \text{ S/cm}$ (see Figure 2). These values are 2 orders of magnitude greater than the value of $1.8 \times 10^{-6} \text{ S/cm}$ measured for a pellet of $\text{Mg}_2(\text{dobdc}) \cdot 0.05\text{LiBF}_4 \cdot x\text{EC/DEC}$

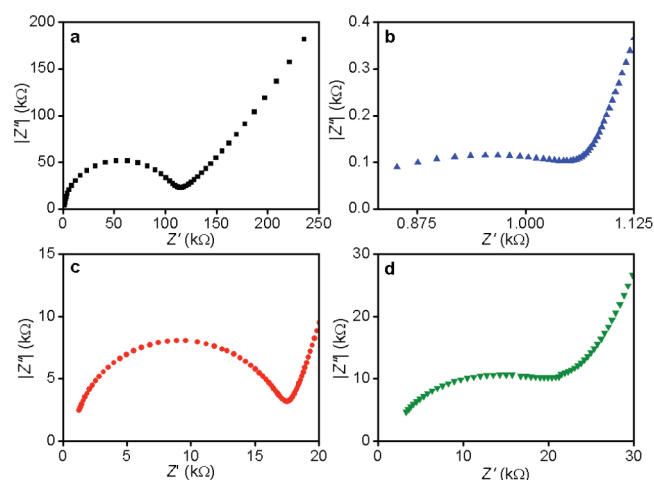


Figure 2. Nyquist plots of the ac impedance data obtained for (a–c) pellets of (a) $\text{Mg}_2(\text{dobdc}) \cdot 0.05\text{LiBF}_4 \cdot x\text{EC/DC}$ (black \blacksquare), (b) $\text{Mg}_2(\text{dobdc}) \cdot 0.35\text{Li}^i\text{OPr} \cdot 0.25\text{LiBF}_4 \cdot \text{EC} \cdot \text{DEC}$ (blue \blacktriangle), and (c) $\text{Mg}_2(\text{dobdc}) \cdot 0.06\text{Li}^i\text{OPr} \cdot x\text{EC/DC}$ (red \bullet) and for (d) thin films of $\text{Mg}_2(\text{dobdc}) \cdot 0.35\text{Li}^i\text{OPr} \cdot 0.25\text{LiBF}_4 \cdot \text{EC} \cdot \text{DEC}$ (green \blacktriangledown).

Table 1. Conductivities, Molar Li^+ Concentrations, Molar Conductivities, and Activation Energies for Pellets of $\text{Mg}_2(\text{dobdc})$ with Various Electrolyte Loadings

electrolyte loading	σ (S/cm)	c_{Li^+} (M)	Λ_{M} ($\text{S} \cdot \text{cm}^{-1} \text{ M}^{-1}$)	E_a (eV)
0.05LiBF ₄	1.8×10^{-6}	0.19	9.6×10^{-6}	0.31
0.06Li ⁱ Pr	1.2×10^{-5}	0.23	5.2×10^{-5}	0.14
0.35Li ⁱ Pr + 0.25LiBF ₄	3.1×10^{-4}	1.3	2.4×10^{-4}	0.15

obtained simply by soaking $\text{Mg}_2(\text{dobdc})$ in a LiBF_4 electrolyte solution. Evaluation of the molar conductivities for these two materials showed that in addition to increasing the lithium electrolyte content by a factor of 6.8, the grafting increased the molar conductivity by a factor of 25, leading to the 170-fold increase in conductivity (see Table 1). It should be noted that grain versus grain boundary conduction within a pellet could not be resolved by examination of the Nyquist plots because only one semicircle was observed in each data set. However, the data did not form complete, regular semicircles, indicating the presence of inhomogeneities in the conduction pathway and therefore possible multiple conduction mechanisms, albeit with similar time constants.²⁴

Varying the temperature of the pellets during the measurements revealed Arrhenius-type activated behavior (see Figure 3). The data indicated a low activation barrier of 0.15 eV for conduction in the grafted material. In contrast, a much higher activation energy of 0.31 eV was observed for the material incorporating just LiBF_4 , suggesting a fundamental difference in the conduction mechanism. As a solid electrolyte with 10^{-4} S/cm conductivity and an activation energy of less than 0.4 eV, the new isopropoxide-grafted material can be classified as a superionic conductor.²⁵

To probe the role of LiBF_4 in the conductivity of the new electrolyte, we prepared pellets of a sample of $\text{Mg}_2(\text{dobdc})$ incorporating Li^iOPr and the EC/DEC solvent but no LiBF_4 . Variation of the grafting conditions enabled the preparation of $\text{Mg}_2(\text{dobdc}) \cdot 0.06\text{Li}^i\text{OPr} \cdot x\text{EC/DC}$, for which the Li^+ concentration was approximately the same as in $\text{Mg}_2(\text{dobdc}) \cdot 0.05\text{LiBF}_4 \cdot x\text{EC/DEC}$.

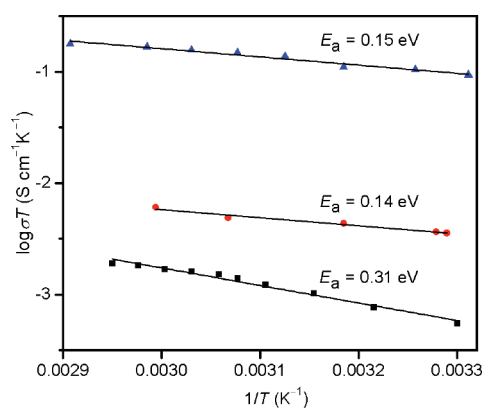


Figure 3. Arrhenius plots of ionic conductivity data obtained for $\text{Mg}_2(\text{dobdc}) \cdot 0.05\text{LiBF}_4 \cdot x\text{EC}/\text{DC}$ (black \blacksquare), $\text{Mg}_2(\text{dobdc}) \cdot 0.35\text{LiO}^+\text{Pr}^- \cdot 0.25\text{LiBF}_4 \cdot \text{EC} \cdot \text{DEC}$ (blue \blacktriangle), and $\text{Mg}_2(\text{dobdc}) \cdot 0.06\text{LiO}^+\text{Pr}^- \cdot x\text{EC}/\text{DC}$ (red \bullet).

For pellets of the new isopropoxide-grafted sample, a typical conductivity of 1.2×10^{-5} S/cm was obtained (Figure 2c); however, considerable variation was observed here, with results sometimes being as low as 10^{-7} S/cm. We speculate that without the presence of additional LiBF_4 on the surfaces of the MOF crystallites, it may be difficult to obtain good interparticle conductivity as well as reproducible interfacial contacts between the pressed pellet and the electrodes. This observation is consistent with other reports on the measurement of conductivities of solid electrolytes.²⁶ Importantly, despite the lower conductivity values, the activation energy of 0.14 eV for this sample was similar to that obtained for $\text{Mg}_2(\text{dobdc}) \cdot 0.35\text{LiO}^+\text{Pr}^- \cdot 0.25\text{LiBF}_4 \cdot \text{EC} \cdot \text{DEC}$.

While the impedance measurements were unable to distinguish intra- versus interparticle conduction, a peculiarity of $\text{Mg}_2(\text{dobdc})$ crystallite growth provided a means of probing the intraparticle conductivity. The compound can be formed as polycrystalline solid thin films in which the channel axes, along which ionic transport would be expected, are oriented normal to the film.²⁷ Indeed, scanning electron microscopy imaging showed our preparations to afford material mainly of this form (see Figure S4), as grown on the surface of the borosilicate glass vials. A free-standing sheet of one of these films with the dimensions $1 \text{ mm} \times 2 \text{ mm} \times 0.4 \text{ mm}$ was isolated and subjected to the same grafting and lithium electrolyte soaking treatment as used in the preparation of the bulk solid electrolyte, and ac impedance measurements performed directly on the film revealed a conductivity of 5.5×10^{-5} S/cm (see Figure 2d), which is on the same order of magnitude as obtained for pressed pellets of the bulk material. This result suggests that intraparticle processes rather than boundary processes dominate the conduction. It is possible that alignment of the conduction channels in the polycrystalline particles may even help to increase conductivity, since studies of lithium conductivity in polymers with anisotropic domains have revealed strong alignment and orientation effects.²⁸ The attainability of thin, oriented films could perhaps facilitate the development of methods for processing the new solid electrolyte and integrating it within devices.

The foregoing results demonstrate a promising new approach for creating solid lithium electrolyte materials. Incorporation of a lithium alkoxide within a porous metal–organic framework with open metal centers, such as $\text{Mg}_2(\text{dobdc})$, can lead to pinning of

the counteranions and high ionic conductivities at ambient temperatures. The resulting conductivity values of 10^{-4} S/cm are highly reproducible and at the technological limit for battery separator applications. Efforts are underway to elucidate the mechanisms of ionic conduction within the new electrolyte material and obtain Li^+ ion mobilities and transference numbers via direct current polarization transference measurements and ^7Li NMR diffusion measurements.^{25a} In addition, the performance of this material upon cycling within a lithium battery cell will be evaluated.

■ ASSOCIATED CONTENT

S Supporting Information. Synthetic methods, PXRD patterns, IR spectra, SEM micrographs, thermogravimetric analysis data, elemental analysis results, conductivity data, and complete ref 12a. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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■ REFERENCES

- (1) (a) *Lithium Batteries: Science and Technology*; Nazri, G.-A., Pistoia, G., Eds.; Kluwer Academic: Boston, 2004. (b) Whittingham, M. S. *Chem. Rev.* **2004**, *104*, 4271.
- (2) Arora, P.; Zhang, Z. *Chem. Rev.* **2004**, *104*, 4419.
- (3) Tarascon, J.-M.; Armand, M. *Nature* **2001**, *414*, 359.
- (4) Xu, K. *Chem. Rev.* **2004**, *104*, 4303.
- (5) Monroe, C.; Newman, J. *J. Electrochem. Soc.* **2005**, *152*, A396.
- (6) (a) Wright, P. V. *J. Polym. Sci., Phys. Ed.* **1976**, *14*, 955. (b) Armand, M. B.; Chabango, J. M.; Duclot, M. J. In *Fast Ion Transport in Solids*; Duclot, M. J., Vashishta, P., Mundy, J. N., Shenoy, G. K., Eds.; North Holland: Amsterdam, 1979. (c) Ratner, M. A.; Shriver, D. F. *Chem. Rev.* **1988**, *88*, 109 and references therein. (d) Gadjourova, Z.; Andreev, Y.; Tunstall, D. P.; Bruce, P. G. *Nature* **2001**, *412*, 520.
- (7) (a) Nagata, K.; Nanno, T. *J. Power Sources* **2007**, *174*, 832. (b) Goodenough, J. B.; Kim, Y. *Chem. Mater.* **2010**, *22*, 587.
- (8) (a) Eddaoudi, M.; Kim, J.; Rosi, N.; Vodak, D.; Wachter, J.; O'Keefe, M.; Yaghi, O. M. *Science* **2002**, *295*, 469. (b) Matsuda, R.; Kitaura, R.; Kitagawa, S.; Kubota, Y.; Belosludov, R. V.; Kobayashi, T. C.; Sakamoto, H.; Chiba, T.; Takata, M.; Kawazoe, Y.; Mita, Y. *Nature* **2005**, *436*, 238. (c) Dincă, M.; Dailly, A.; Liu, Y.; Brown, C. M.; Neumann, D. A.; Long, J. R. *J. Am. Chem. Soc.* **2006**, *128*, 16876. (d) Sun, D.; Ma, S.; Ke, Y.; Collins, D. J.; Zhou, H.-C. *J. Am. Chem. Soc.* **2006**, *128*, 3896. (e) Kaye, S. S.; Dailly, A.; Yaghi, O. M.; Long, J. R. *J. Am. Chem. Soc.* **2007**, *129*, 14176.
- (9) (a) Allendorf, M. D.; Houk, R. J. T.; Andruszkiewicz, L.; Talin, A. A.; Pikarsky, J.; Choudhury, A.; Gall, K. A.; Hesketh, P. J. *J. Am. Chem. Soc.* **2008**, *130*, 14404. (b) Lan, A.; Li, K.; Wu, H.; Olson, D. H.; Emge, T. J.; Ki, W.; Hong, M.; Li, J. *Angew. Chem., Int. Ed.* **2009**, *48*, 2334. (c) Lu, G.; Hupp, J. T. *J. Am. Chem. Soc.* **2010**, *132*, 7832.
- (10) (a) Horcajada, P.; Serre, C.; Maurin, G.; Ramsahye, N. A.; Balas, F.; Vallet-Regí, M.; Sebban, M.; Taulelle, F.; Férey, G. *J. Am. Chem.*

Soc. **2008**, *130*, 6774. (b) Rieter, W. J.; Pott, K. M.; Taylor, K. M. L.; Lin, W. *J. Am. Chem. Soc.* **2008**, *130*, 11584.

(11) (a) Seo, J. S.; Whang, D.; Le, H.; Jun, S. I.; Oh, J.; Jeon, Y. J.; Kim, K. *Nature* **2000**, *404*, 982. (b) Wu, C.-D.; Hu, A.; Zhang, L.; Lin, W. *J. Am. Chem. Soc.* **2005**, *127*, 8940. (c) Cho, S.-H.; Ma, B.-Q.; Nguyen, S. T.; Hupp, J. T.; Albrecht-Schmitt, T. E. *Chem. Commun.* **2006**, 2563. (d) Horike, S.; Dincă, M.; Tamaki, K.; Long, J. R. *J. Am. Chem. Soc.* **2008**, *130*, 5854. (e) Garibay, S.; Cohen, S. M. *Inorg. Chem.* **2010**, *49*, 8086.

(12) (a) Park, Y. K.; et al. *Angew. Chem., Int. Ed.* **2007**, *46*, 8230. (b) White, K. A.; Chengelis, D. A.; Gogick, K. A.; Stehman, J.; Rosi, N. L.; Petoud, S. *J. Am. Chem. Soc.* **2009**, *131*, 18096.

(13) (a) Takaishi, S.; Hosoda, M.; Kajiwara, T.; Miyasaka, H.; Yamashita, M.; Nakanishi, Y.; Kitagawa, Y.; Yamaguchi, K.; Kobayashi, A.; Kitagawa, H. *Inorg. Chem.* **2008**, *48*, 9048. (b) Kobayashi, Y.; Jacobs, B.; Allendorf, M. D.; Long, J. R. *Chem. Mater.* **2010**, *22*, 4120. (c) Okubo, T.; Tanaka, N.; Kim, H. K.; Anma, H.; Seki, S.; Saeki, A.; Maekawa, M.; Kuroda-Sowa, T. *Dalton Trans.* **2011**, *40*, 2218.

(14) (a) Bureekaew, S.; Horike, S.; Higuchi, M.; Mizuno, M.; Kawamura, T.; Tanka, D.; Yanai, N.; Kitagawa, S. *Nat. Mater.* **2009**, *8*, 831. (b) Hurd, J. A.; Vaidhyanathan, R.; Thangadurai, V.; Ratcliffe, C. I.; Moudrakovski, I. L.; Shimizu, G. K. H. *Nat. Chem.* **2009**, *1*, 705. (c) Shigematsu, A.; Yamada, T.; Kitagawa, H. *J. Am. Chem. Soc.* **2011**, *133*, 2034. (d) Sadakiyo, M.; Yamada, T.; Kitagawa, H. *J. Am. Chem. Soc.* **2009**, *131*, 9906.

(15) (a) Férey, G.; Millange, F.; Morcette, M.; Serre, C.; Doublet, M.-L.; Grenèche, J.-M.; Tarascon, J.-M. *Angew. Chem., Int. Ed.* **2007**, *46*, 3259. (b) de Combarieu, G.; Morcette, M.; Millange, F.; Guillou, N.; Cabana, J.; Grey, C. P.; Margiolaki, I.; Férey, G.; Tarascon, J.-M. *Chem. Mater.* **2009**, *21*, 1602. (c) Mulfort, K. L.; Wilson, T. M.; Wasielewski, M. R.; Hupp, J. T. *Langmuir* **2009**, *25*, 503.

(16) (a) Vitadello, M.; Suarez, S.; Chung, S. H.; Fujimoto, K.; Di Noto, V.; Greenbaum, S. G.; Furukawa, T. *Electrochim. Acta* **2003**, *48*, 2227. (b) Xi, J.; Bai, Y.; Qiu, X.; Zhu, W.; Chen, L.; Tang, X. *New J. Chem.* **2005**, *29*, 454.

(17) (a) Krogh Andersen, E.; Krogh Andersen, I. G.; Metcalf-Johansen, J.; Simonsen, K. E.; Skou, E. *Solid State Ionics* **1988**, *28*, 249. (b) Ben Saad, K.; Hamzaouhi, H.; Mohamed, M. M. *Mater. Sci Eng, B* **2007**, *139*, 226.

(18) Chae, H. K.; Siberio-Pérez, D. Y.; Kim, J.; Go, Y.; Eddaoudi, M.; Matzger, A.; O'Keefe, M.; Yaghi, O. M. *Nature* **2004**, *427*, 523.

(19) Demessence, A.; D'Alessandro, D. M.; Foo, M. L.; Long, J. R. *J. Am. Chem. Soc.* **2009**, *131*, 8784.

(20) Caskey, S. R.; Wong-Foy, A. G.; Matzger, A. J. *J. Am. Chem. Soc.* **2008**, *130*, 10870.

(21) (a) Morris, W.; Doonan, C. J.; Furukawa, H.; Banerjee, R.; Yaghi, O. M. *J. Am. Chem. Soc.* **2008**, *130*, 12626. (b) Wang, Z.; Tanabe, K. K.; Cohen, S. M. *Inorg. Chem.* **2009**, *48*, 296. (c) Gadzikwa, T.; Farha, O. K.; Malliakas, C. D.; Kanatzidis, M. G.; Hupp, J. T.; Nguyen, S. T. *J. Am. Chem. Soc.* **2009**, *131*, 13613.

(22) Jung, H. S.; Lee, J.-K.; Kim, J.-Y.; Hong, K. S. *J. Colloid Interface Sci.* **2003**, *259*, 127.

(23) (a) Cazzanelli, E.; Croce, F.; Appetecchi, G. B.; Benevelli, F.; Mustarelli, P. *J. Chem. Phys.* **1997**, *107*, 5740. (b) Soetens, J.-C.; Millot, C.; Maigret, B. *J. Phys. Chem. A* **1998**, *102*, 1055.

(24) Hasbach, A.; Retter, U.; Siegler, K.; Kautek, W. *J. Electronal. Chem.* **2004**, *561*, 29.

(25) (a) Chandra, S. *Superionic Solids*; North-Holland: Amsterdam, 1981. (b) Colomban, P.; Novak, A. *J. Mol. Struct.* **1988**, *177*, 277.

(26) Barpanda, P.; Chotard, J.-N.; Delacourt, C.; Reynaud, M.; Filinchuk, Y.; Armand, M.; Deschamps, M.; Tarascon, J.-M. *Angew. Chem., Int. Ed.* **2011**, *50*, 2526.

(27) Bétard, A.; Zacher, D.; Fischer, R. A. *CrystEngComm* **2010**, *12*, 3768.

(28) Singh, M.; Odusanya, O.; Wilmes, G. M.; Eitouni, H. B.; Gomez, E. D.; Patel, A. J.; Chen, V. L.; Park, M. J.; Fragou, P.; Iatrou, H.; Hadjichristidis, N.; Cookson, D.; Balsara, N. P. *Macromolecules* **2007**, *40*, 4578.