

Communication

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A Metal-Organic Framework of Organic Vertices and Polyoxometalate Linkers as a Solid-State Electrolyte

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Supporting Information Placeholder

ABSTRACT: A new three-dimensional metal-organic framework (MOF) was synthesized by linking ditopic amino functionalized polyoxometalate $[N(C_4H_9)_4]_3[MnMo_6O_{18}\{(OCH_2)_3CNH_2\}_2]$ with 4-connected tetrahedral tetrakis(4-formylphenyl)methane building units through imine condensation. The structure of this MOF, termed MOF-688, was solved by single crystal X-ray diffraction and found to be triply interpenetrated diamond-based **dia** topology. Tetrabutylammonium cations fill the pores and balance the charge of the anionic framework. They can be exchanged with lithium ions to give high ionic conductivity ($3.4 \times 10^{-4} S cm^{-1}$ at 20 °C), high lithium ion transference number ($t_{Li^+} = 0.87$), and low interfacial resistance (353 Ω) against metallic lithium — properties that make it ideally suited as a solid-state electrolyte. Indeed, a prototype lithium metal battery constructed using MOF-688 as the solid electrolyte can be cycled at room temperature with a practical current density of $\sim 0.2 C$.

Lithium metal has the highest theoretical energy density of all anode materials in lithium batteries.¹ In practice, the uneven electrodeposition of lithium causes formation of dendrites² that penetrate the batteries' separator and lead to short circuits. This is a safety concern as the organic electrolyte in lithium batteries can catch fire and cause explosions. As such, solid-state electrolytes that act as a physical barrier to prevent the penetration of lithium dendrites are highly sought after, making the design of materials combining high chemical and mechanical stability with sufficient lithium ion conductivity an important synthetic goal.³ To date, sulfide- and oxide-type inorganic lithium ion conductors display high conductivity but suffer from chemical instability against lithium metal.⁴ In contrast, electrolytes based on lithium salts in polymer matrices are limited by both low ionic conductivity and low lithium ion transference number. The latter is caused by the mobility of electrochemically inactive anions which results in high polarization.⁵ While covalent anchoring of anions onto the polymer matrix has proved effective in increasing the lithium ion transference number, the low ionic conductivity of polymer electrolytes still prevents battery application at room temperature.⁶ Toward this end, it was found that addition of organic solvents into the polymer matrix improves ionic conductivity to a practical level. This does however inevitably lead to the solvation of the polymer and the formation of a gel which no longer precludes dendrite penetration.⁷

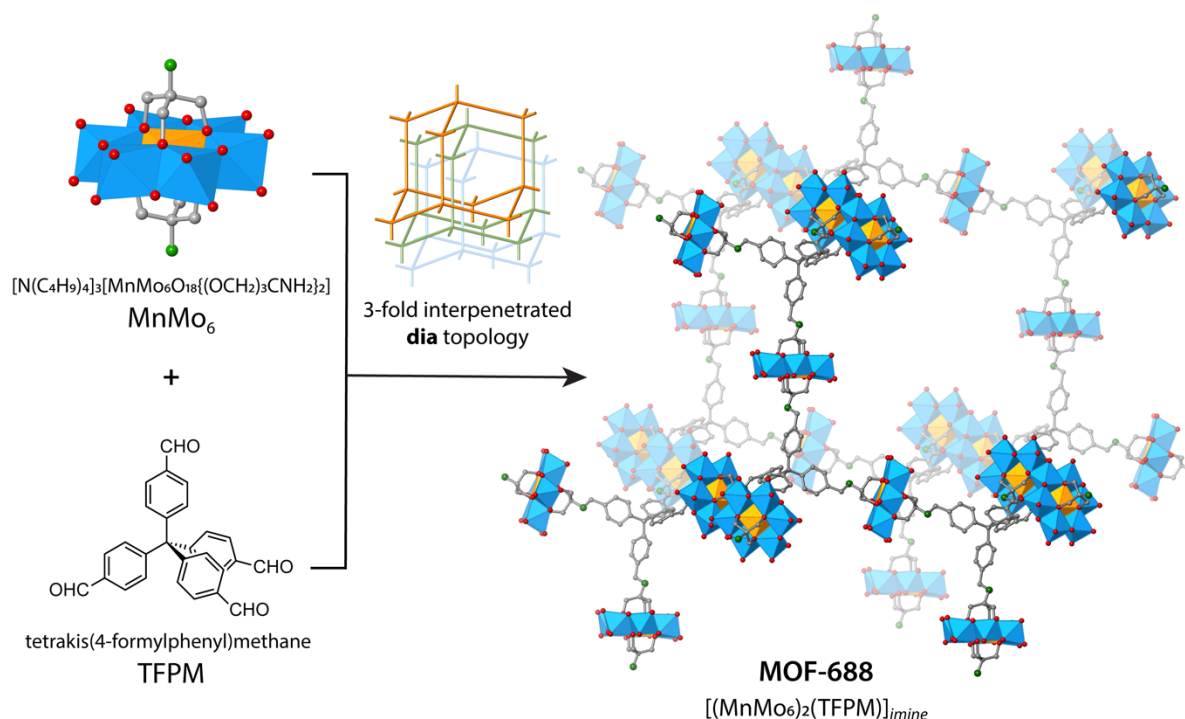
Taking stock of these findings, metal-organic frameworks (MOFs) and covalent organic frameworks (COFs) hold high promise in

addressing the shortcomings of polymer electrolytes.⁸⁻¹³ The combination of a three dimensional pore system with a highly connected crystalline structure built from strong bonds allows these frameworks to accommodate organic electrolyte without turning into a gel. The molecular building units of MOFs and COFs can be chosen such that they accommodate a high density of immobilized anions (since they are the reticulated units in the framework), leaving lithium ion as the only mobile species.

Two strategies have been devised to immobilize anions in framework materials: (i) Binding of anions to coordinatively unsaturated metal sites in charge neutral frameworks and (ii) directly linking negatively charged constituents.¹⁷⁻²⁰ The inevitable competition between anions and solvent molecules for unsaturated metal sites in charge neutral frameworks leads to partial dissociation of anions and thus to the contribution of anion mobility to the measured ionic conductivity. In intrinsically anionic frameworks the lithium ion conductivity depends on the overall charge, as well as chemical identity of the charged species. Conventional building units of MOFs and COFs carry no more than one charge, thus limiting the charge density of the framework.^{12,13} Here, we report an intrinsically anionic framework, termed MOF-688, constructed from highly charged Anderson type polyoxometalates. MOF-688 shows high ionic conductivity ($3.4 \times 10^{-4} S cm^{-1}$ at 20 °C), high lithium ion transference number ($t_{Li^+} = 0.87$), and low interfacial resistance (353 Ω) against metallic lithium. A prototype lithium metal battery constructed using MOF-688 as the solid electrolyte can be cycled at room temperature with a practical current density of $\sim 0.2 C$.

MOF-688 was synthesized by linking ditopic amino functionalized Anderson type polyoxometalate $[N(C_4H_9)_4]_3[MnMo_6O_{18}\{(OCH_2)_3CNH_2\}_2]$ ($MnMo_6$) with 4-connected tetrahedral tetrakis(4-formylphenyl)methane (TFPM) building units through imine condensation (Scheme 1, Supporting Information (SI) Section S2). Imine bond formation was confirmed by Fourier-transform infrared spectroscopy (FT-IR); the aldehyde C=O stretch of TFPM at 1688 cm^{-1} was strongly attenuated, while a characteristic C=N imine stretch at 1636 cm^{-1} emerged (Figure S3). MOF-688 forms rod-shaped single crystals suitable for analysis by single crystal X-ray diffraction (SXRD). The framework crystallizes in the tetragonal space group $I4_1/a$ with an underlying **dia** topology. The **dia** net is self-dual and as such prone to interpenetration. Specifically, the accessible void space of MOF-688 affords a 3-fold interpenetrated structure (**dia-c3**, Scheme 1). Each $MnMo_6$ carries 3 negative charges which are balanced by three

Scheme 1. Synthetic Strategy and Structure Illustration of MOF-688.



tetrabutylammonium (TBA⁺) cations that occupy the 8.6 Å wide 1D channels running along the crystallographic *c* direction (Figure S2). The phase purity of the MOF was confirmed by powder X-ray diffraction patterns of the bulk sample (PXRD, Figure S5).

Exchange of TBA⁺ with Li⁺ was carried out by immersing crystals of MOF-688 in an acetonitrile solution of lithium bis(trifluoromethanesulfonyl)imide (LiTFSI) at room temperature. The process was monitored by digestion ¹H NMR, where peaks assigned to TBA⁺ disappeared upon cation exchange (SI Section S7 and Figure S9). Inductively coupled plasma atomic emission spectroscopy (ICP-AES) confirmed the expected 3:1 ratio for Li⁺ and MnMo₆ building units. Upon Li⁺ exchange, only a slight shift in the C=N imine stretch from 1636 cm⁻¹ (as-synthesized) to 1628 cm⁻¹ (Li⁺ exchanged) was observed by FT-IR, indicating that the connectivity of the framework was retained. This is corroborated by the fact that upon treatment of the material with an excess of TBA⁺, a reverse shift back to 1633 cm⁻¹ was observed (Figure S4). The retention of the Mo–O–Mo stretch at 650 cm⁻¹ further supports the fact that the backbone of the framework remained unaffected by the ion exchange. Scanning electron microscopy (SEM) images of crystals before and after cation exchange confirm that the rod-shaped morphology of the MOF is retained (Figure S7). The PXRD pattern after Li⁺ exchange showed a loss of crystallinity, but the original pattern was recovered when TBA⁺ was reintroduced into the framework (Figure S6). COFs built from TFPM building units are prone to structural variability, which is commonly assigned to the high degree of flexibility of TFPM.¹⁴

Residual acetonitrile in Li⁺ exchanged MOF-688 was replaced with anhydrous propylene carbonate to enhance the dissociation of Li⁺ from the polyoxometalate backbone.¹⁵ The amount of propylene carbonate in the MOF was determined by thermogravimetric analysis (TGA) where a weight loss of 55% was attributed to the loss of solvent (Figure S9).

The obtained Li⁺ exchanged MOF was then pressed into a cylindrical die and sandwiched between two stainless steel blocking electrodes in an Ar filled glovebox. Ionic conductivity measurements for Li⁺ exchanged MOF-688 were carried out by electrochemical impedance spectroscopy (EIS) at temperatures between -40 °C and 60 °C. The

Nyquist plots of the MOF measured at temperatures between -40 °C and 0 °C show a semicircle in the high frequency region (representing the resistance at grain boundaries) and a linear tail in the low frequency

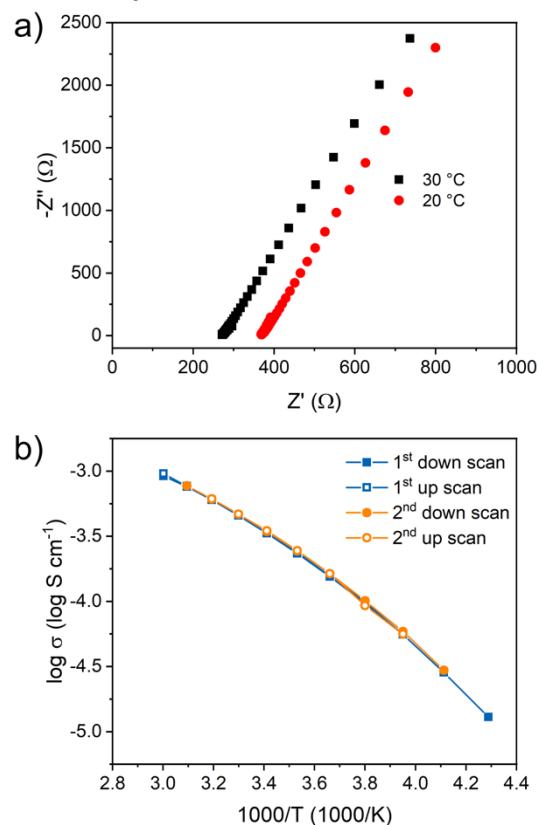


Figure 1. (a) Nyquist plots of MOF-688 at 20 °C and 30 °C. (b) Ionic conductivity as a function of temperature from -40 °C to 60 °C at 10 °C intervals.

region (Figure S10). The high frequency semicircle becomes unobservable when the temperature is raised to 10 °C or above, suggesting a low resistance at grain boundaries (Figure 1a and Figure S11).¹⁶ The ionic conductivity of MOF-688 was measured from -40 °C to 60 °C at 10 °C intervals for multiple cycles (Figure 1b). At each temperature, the measurements were found to be reproducible as the up and down scan traces overlay. The ionic conductivity was calculated to be $3.4 \times 10^{-4} \text{ S cm}^{-1}$ and $4.6 \times 10^{-4} \text{ S cm}^{-1}$ at 20 °C and 30 °C, respectively. These values are an order of magnitude higher than those of reported frameworks without external lithium electrolyte (e.g. $\text{Mg}_2(\text{DOT})\cdot 0.06\text{LiO}^i\text{Pr}$, $\sigma = 1.2 \times 10^{-5} \text{ S cm}^{-1}$; LiO^iBu -functionalized UiO-66 , $\sigma = 1.8 \times 10^{-5} \text{ S cm}^{-1}$; MIT-20-LiCl , $\sigma = 1.3 \times 10^{-5} \text{ S cm}^{-1}$; ICOF-2 , $\sigma = 3.05 \times 10^{-5} \text{ S cm}^{-1}$) and comparable to frameworks where lithium electrolyte has been added.¹⁷⁻²¹ At the risk of sounding critical, we wish to note here that adding external lithium salts into the framework has become common practice to increase the ionic conductivity of the framework. However, this is an undesirable practice since it makes the measurement of such systems intrinsically flawed due to the difficulties in convoluting the contribution of the solid electrolyte and that of external electrolyte between crystal particles. Furthermore, since the ionic conductivity measured from EIS is the sum of conductivities of both Li^+ and counter anions, and possible contaminating ions, referring to the measured ionic conductivity as “ Li^+ conductivity” is inaccurate and overstated. This is especially true when the value for the Li^+ transference number has not been measured.

The Li^+ transference number of MOF-688 was determined through a potentiostatic polarization method.²² The MOF was mixed with polyvinylidene fluoride (PVDF) in a 3:1 weight ratio and subsequently cast onto a macroporous cellulose support to form a membrane separator. The ion exchanged membrane was solvated with anhydrous propylene

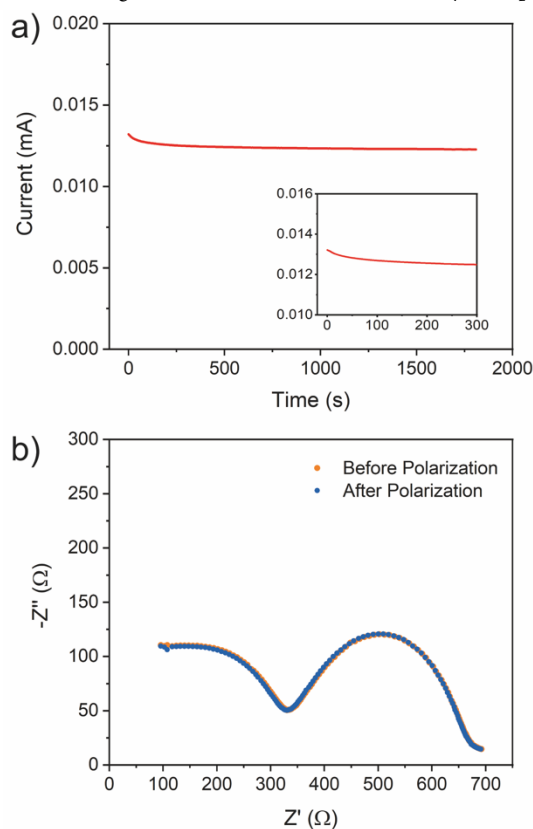


Figure 2. (a) Polarization of the Li|MOF-688|Li cell at an applied voltage of 10 mV. (b) Nyquist plots of the Li|MOF-688|Li cell before and after polarization.

carbonate and sandwiched between two lithium metal chips in a 2032 battery cell under Ar atmosphere. A 10 mV voltage was applied to the cell and the current response dropped from $I_0=0.0132 \text{ mA}$ to its steady state $I_s=0.0123 \text{ mA}$ (Figure 2a). EIS measurements showed a negligible change before and after potentiostatic polarization, suggesting a stable interface between the MOF and lithium metal. The interfacial resistance was found to be $R_0=353.2 \Omega$ and $R_s=353.3 \Omega$ before and after the measurement, respectively (Figure 2b). These values are markedly lower than those of other framework-based solid electrolytes (e.g. MIT-20-LiCl , 5.5 k Ω ; ICOF-2 , 4 k Ω)^{19,20} and comparable to examples where additional electrolyte was added for better interfacial properties.²¹ Stability of interfaces between lithium metal and framework materials is often overlooked but it is important to consider. In some literature reports, the extremely high interfacial resistance suggests electrochemical instability against lithium metal and thus precludes practical use.²³ The transference number of MOF-688 was found to equal $t_{\text{Li}^+} = 0.87$ (SI Section S10). This value is significantly higher than that of liquid lithium-ion electrolytes, which typically display transference numbers between $t_{\text{Li}^+} = 0.2-0.4$.²⁴ The fact that the transference number is close to 1 indicates that most of the charges in the MOF are carried by Li^+ , with the polyoxometalate anions being immobilized on the framework's backbone. The observed transference number is higher than that of most other framework electrolytes and comparable to single-ionic polymer electrolytes.^{9,25}

To investigate the compatibility of MOF-688 with cathode materials, a coin cell battery based on a lithium metal anode and a LiFePO_4 cathode was assembled. In order to measure the intrinsic performance of the MOF solid electrolyte, no additional lithium salt was added. At ambient temperature the battery was cycled between 3 V and 3.8 V

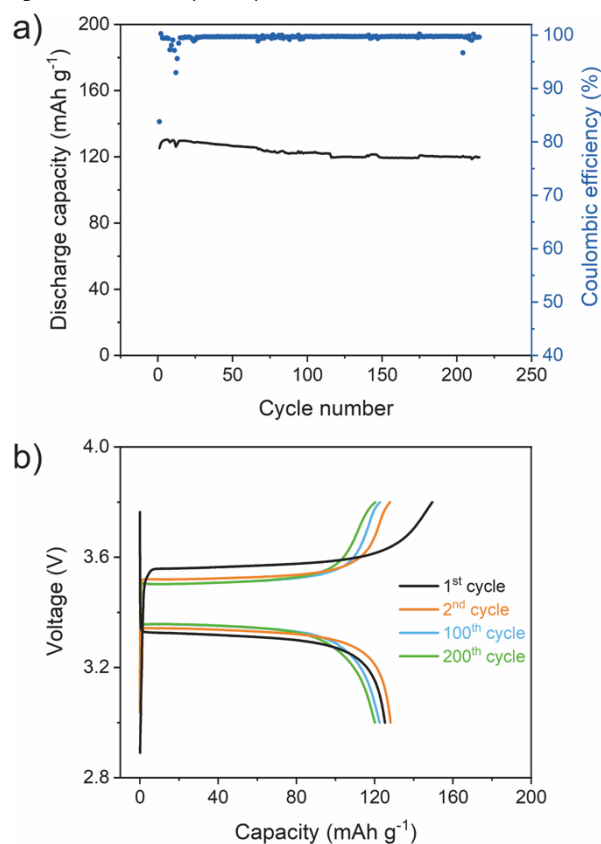


Figure 3. (a) Discharge capacity and Coulombic efficiency of the Li|MOF-688|LiFePO₄ cell. (b) Charge and discharge profile of the Li|MOF-688|LiFePO₄ cell for the 1st, 2nd, 100th, and 200th cycle.

with a current density of 30 mA g⁻¹ (Figure 3a). The initial charge capacity was found to be 149 mAh g⁻¹, 88% of the theoretical capacity of the cathode material (170 mAh g⁻¹ for LiFePO₄). The initial discharge capacity was found to be 125 mAh g⁻¹, indicating that not all the cathode material was utilized. Over the first 10 cycles, the discharge capacity of the cell increased slightly to 130 mAh g⁻¹ and kept relatively stable thereafter. The discharge capacity slightly declined to 120 mAh g⁻¹ after 200 cycles, representing 96% of the initial capacity and 92% of the capacity of the 10th cycle. An initial voltage gap between the charge and discharge profiles of 0.26 V was measured for the first cycle and decreased to 0.18 V from the second cycle (Figure 3b). Over the course of 200 cycles the charge and discharge voltage remained stable. The average Coulombic efficiency was found to be 99.6% (excluding the first cycle), indicating limited side reactions on both the cathode and the anode. This high Coulombic efficiency, the stable voltage, and the limited capacity decay suggest high electrochemical stability of MOF-688 against both lithium metal and LiFePO₄.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website.
General experimental methods, supplementary spectra, and analysis details (PDF)
Crystallographic data for MOF-688 (CIF)

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Notes

The authors declare no competing financial interests.

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