Mechanism of Electrochemical Lithiation
of a Metal-Organic Framework Without Redox-Active Nodes

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ABSTRACT

Metal-organic frameworks (MOFs) have many potential uses for separations, storage, and catalysis, but their use as intercalation hosts for batteries has been scarce. In this article, we examine the mechanism of Li insertion in a MOF to provide guidance to future design efforts in this area. As a model system, we choose UiO-66, a MOF with the formula \((\text{Zr}_6\text{O}_4\text{OH})_4(1,4\text{-benzenedicarboxylate})_6\), as an electrode material for lithium-ion batteries. This MOF; this model system is of special interest because the zirconium is not redox active. We report both quantum mechanical characterization of the mechanism and experimental studies in which the material is synthesized as nanoparticles to reduce diffusion lengths for lithium ions and increase the contact area with a conductive carbon phase. The calculated changes in the IR spectra of UiO-66 and lithiated UiO-66 are consistent with the experimental FTIR results. We found experimentally that this MOF can maintain a specific discharge capacity of at least 118 mAh/g for 30 lithiation and delithiation cycles at a rate of C/5, exhibiting good cyclability. Density functional electronic structure calculations show that the charge transfer during lithiation is mainly from Li to node oxygens and carboxylate oxygens, that is, it involves anions rather than cations or aromatic rings, and they provide a mechanistic understanding of the potential for increased Li capacity because the theoretical capacity of UiO-66 with Li at the oxygens in the metal oxide nodes and the carboxylate linkers is more than 400 mAh/g. The lithiation process greatly decreases the band gap of UiO-66, which is expected to increase its electronic conductivity. The electrode material was also characterized by X-ray diffraction and scanning electron microscopy, which were consistent in confirming that smaller particle sizes were obtained in lower-temperature syntheses.

Keywords: metal–organic framework, electrode, lithium-ion battery, UiO-66 nanoparticles, density functional theory
INTRODUCTION

Much research effort is directed at finding new electrode materials for lithium-ion batteries (LIBs) and related alkali-ion or alkaline-earth-ion based batteries to improve their capacity, rate capability, safety, cycle life, and processability and to reduce their cost. One particularly interesting class of potential electrode materials comprises metal-organic frameworks (MOFs).\(^1\) These periodic nanoporous materials, which are a class of coordination polymers, consist of metal or metal-cluster nodes (possibly hydrated), interconnected in multiple dimensions by a network of organic linkers, and they are attractive because of their widely tunable pore architecture and a variety of possibilities for containing redox-active components. With appropriate pore dimensions and geometries, they can permit ready access of Li\(^+\) or other ions and electrolytic solvents to electroactive sites. Several types of MOF have been investigated as cathode or anode materials for LIBs and also as host matrices or precursors for active electrode materials.\(^6,7\) Charge storage mechanisms can involve changes in oxidation state of metal-containing nodes, participation of linkers in redox processes, and conversion reactions that lead to the formation of the fully reduced metal and alloy formation with lithium.

Most MOFs that have been considered for anodes or cathodes contain redox-active transition metals with multiple oxidation states of the ions, including Fe,\(^8\)–\(^12\) Ni,\(^13,14\) V,\(^2,15,16\) Co,\(^13,17\) Mn,\(^18,19\) and Cu.\(^20,21\) One exception involves Zn-based MOFs; an early study of Zn\(_4\)O(1,3,5-benzenetribenzoate) (MOF-177) found this material to be unsuitable as an electrode in LIBs because the MOF framework was irreversibly destroyed during lithiation and delithiation processes.\(^22\) However, when Zn\(_4\)(HCOO)\(_6\) was examined as an anode material, the zinc formate framework reacted reversibly with Li through a conversion reaction involving lithium formate, and a high specific capacity of 560 mAh/g was maintained over 60 cycles at C/10 in the voltage range 0.05–3.0 V.\(^23\) Recently, a Zn-imidazole-based MOF was also shown to have good cyclability over 200 cycles with an increase in specific capacity observed during cycling, while the framework was believed to remain intact during electrochemical cycling.\(^24\) MOFs have also been used as a sulfur impregnation host to impede polysulfide formation in Li–S batteries.\(^25\)

In spite of the attractive features of MOFs, several challenges must be overcome to improve their practicality as electrode materials. Some of these challenges involve the limited ability to achieve full insertion of Li\(^+\) in the MOF framework (e.g., MIL-53(Fe)),\(^8\)–\(^11\) limited cyclability at high energy density because of the poor electronic conductivity of the MOF structure,\(^10\) and
irreversible destruction of the MOF framework during multiple lithiation and delithiation cycles (e.g., MOF-177). Changes in the redox state of the metal centers can result in irreversible structural degradation if the coordination number of the redox center changes, and even if structural variations resulting from lithiation and delithiation are reversible, they can lead to pulverization of the MOF material during cycling. Another disadvantage using MOFs as electrodes where the redox active centers are transition metals is that they would be expected to have low theoretical capacities because the transition metal ions are diluted. For this reason we are interested in understanding the capabilities of MOF electrodes not based on redox-active transition metals. As a first step in this effort we initiated a combined theoretical and experimental study of the use of a MOF electrode with no redox-active metal in a lithium-ion battery. In particular, we study the MOF UiO-66. This MOF consists of Zr$_6$O$_4$(OH)$_4$$^{12+}$ cluster nodes connected by 1,4-benzenedicarboxylate (BDC, terephthalate) linkers to form tetrahedral and octahedral cages with 0.6 nm pores, and it has been demonstrated to exhibit high thermal and chemical stability. UiO-66 has been used as a catalyst support and as a photocatalyst for hydrogen generation, and functionalized UiO-66 materials may be relevant for carbon capture and storage applications. A post-synthetically modified (dehydrated and lithium alkoxide-grafted) version of UiO-66 has been investigated as a solid ionic conductor (room temperature ionic conductivity $1.8 \times 10^{-5}$ S cm$^{-1}$), but because the oxidation state of Zr is not readily variable between the end members Zr(0) and Zr(IV), this MOF has not yet been examined as an electrode material for LIBs. However, the dilithium salt of the linker molecule of UiO-66, dilithium terephthalate, has shown a reversible capacity of 300 mAh/g. Here we show that UiO-66 synthesized as nanoparticles becomes a viable electrode material for LIBs, maintaining a specific discharge capacity of at least 118 mAh/g for 30 lithiation and delithiation cycles at a rate of C/5 and exhibiting good cyclability. In the present work we use this electrode as a cathode, but its low potential would make it more suitable as an anode in practical work. However, we study it not because it is a viable alternative to anode materials in current commercial use (those anodes have better rate and cycling performance), but rather because it is a well characterized model system to elucidate electrochemical Li insertion and removal from a MOF that does not have redox-active transition metals. This is a first step toward defining the optimum design parameters for MOFs as electrode materials. The new experimental results are interpreted and supported by electronic structure calculations, in particular by density functional studies of the possible sites of
lithiation, the voltage and volume change in the lithiation, the density of states, and the charge flow during lithiation.

METHODS

**Materials.** Zirconium chloride (ZrCl$_4$, 99.9%+), terephthalic acid (H$_2$BDC, 98%), and N-methyl-2-pyrrolidone (NMP, 99.5%, anhydrous) were purchased from Sigma-Aldrich. N,N-dimethylformamide (DMF) (sequencing grade) was obtained from Fisher. Timcal Super P carbon black, polyvinylidene fluoride (PVDF), CR2032 coin cell parts, and the battery electrolyte (1 M LiPF$_6$ in a 1:1:1 (volume) mixture of ethylene carbonate, dimethyl carbonate, and diethyl carbonate) were bought from MTI Corporation. Cu foil (99.9%) was obtained from Basic Copper.

**Synthesis of UiO-66 Nanoparticles.** Nanoparticles of UiO-66 of different sizes were synthesized using slight modifications of a previously published method. A mass of 1.2 g (7.2 mmol) of terephthalic acid was dissolved in 40 mL of DMF. Separately, a mass of 1.2 g (5.2 mmol) of ZrCl$_4$ was dissolved in 70 mL of DMF. Each of these mixtures was centrifuged at 3000 rpm for 10 min to remove any insoluble residue, otherwise the insoluble substances can act as nucleation sites for UiO-66, yielding larger particles. The supernatants were then mixed in a 250 mL flask. The mixed solution was heated to 50 °C and stirred at 500 rpm for 10 days. The product was isolated by centrifugation and washed 5 times with DMF. The mother liquor was further heated to 70 °C for 2 days, 90 °C for ~12 h, and 110 °C for ~12 h. After each treatment at a given temperature, solids were isolated by centrifugation as described above and washed 5 times with DMF. The remaining mother liquor was used for the following heating step. All of the products were dried at 150 °C for 2 h in a vacuum oven.

**Structural Characterization.** XRD patterns were collected using a PANalytical X’Pert PRO diffractometer with a Co Kα ($\lambda = 1.789$ Å) source. Crystallite sizes were calculated using the Scherrer equation. For this purpose, the UiO-66 reflection at $\sim$30 °2θ was fitted to obtain its peak width, and a LaB$_6$ standard sample was used to measure the instrumental broadening. The sample morphology was imaged with a JEOL 6500 scanning electron microscope (SEM) after application of a 5-nm-thick Pt coating on each sample. FTIR spectra of the UiO-66 samples in KBr pellets were obtained with a Nicolet Magna IR 760 spectrometer, and ATR-FTIR spectra of
Electrodes were collected with a Nicolet iS50 spectrometer. Thermogravimetric analysis (TGA) was carried out using a Netzsch STA 409 PC Luxx instrument in an air atmosphere with a heating rate of 10 °C/min. A TGA trace for a typical UiO-66 sample is shown in Figure S1 (where figure identifiers beginning with the letter “S” are in supplemental material).

**Electrochemical Characterization.** A typical electrode was prepared as follows: UiO-66 (~30 mg), Super P carbon black, and PVDF were mixed in a mass ratio of 8:1:1. NMP was added dropwise while grinding until the slurry was slightly less viscous than honey. The slurry was applied to 1.27-cm diameter disks of pre-weighed copper foil using a pestle. The electrode was then dried, first under ambient conditions overnight and then in a vacuum oven at 110 °C for 2 h, and weighed after cooling down to room temperature. Electrode masses were between 0.7 and 1.3 mg, giving areal densities between 0.6 and 1.0 mg/cm². CR2032 coin cells were assembled in a helium-filled glovebox with the UiO-66-coated copper foil as the cathode, lithium foil as the anode, a piece of Celgard 3501 membrane, and 1 M LiPF₆ in a 1:1:1 (volume) mixture of ethylene carbonate, dimethyl carbonate, and diethyl carbonate as the electrolyte. These cells were used for galvanostatic charge and discharge tests with an Arbin ABTS 2ADC 4.0 battery tester in the range from 0.01 to 3.0 V vs. Li/Li⁺. After cycling, the coin cells were disassembled, and the electrode was wiped with a Kimwipe tissue and immediately used for ex-situ XRD and ATR-FTIR studies to minimize exposure to air. For these experiments, multiple electrodes were prepared from the same batch of UiO-66 and using the same UiO-66: Super P: PVDF ratio. Each XRD pattern was obtained from a different electrode prepared in this manner. Cyclic voltammetry (CV) experiments were conducted with a three-electrode set-up in a three-necked flask inside the glovebox. In this case, UiO-66-loaded copper foil was used as the working electrode, while lithium foil was used for the counter and reference electrodes, and data were recorded with a Solartron 1287 electrochemical interface.

**Quantum Mechanical Computations.** Density functional theory (DFT) electronic structure calculations were performed in cluster models by using the *Gaussian 09* package and on periodic systems by using the *Vienna Ab Initio Simulation Package* (VASP).

**Periodic Calculations.** A supercell (Figure 1a) that is a 1×1×2 repetition of the primitive cell was used for the periodic calculations; there are two Zr₆O₄(OH)₄ nodes in each supercell. The local PBE (Perdew-Burke-Ernzerhof) generalized gradient approximation (GGA) was used as the exchange-correlation functional in most calculations, except that the hybrid HSE06 (Heyd-
The Perdew-Burke-Ernzerhof exchange-correlation functional was used for calculating the band gap because of its higher accuracy for this kind of calculation. For some PBE calculations, we also added molecular mechanics damped dispersion, yielding the PBE-D2 method (PBE denotes the Perdew-Burke-Ernzerhof exchange-correlation functional, and D2 denotes the addition of Grimme's second-generation damped-dispersion molecular mechanics term). Core electrons were treated by projected augmented wave (PAW) potentials. Full relaxation of the ionic positions with no symmetry constraints was performed on all structures. A cutoff energy of 500 eV was used for all calculations, and the $1 \times 1 \times 1$ $k$-point Monkhorst-Pack mesh was used. The energy criterion for self-consistency was set to less than 0.0001 eV/(unit cell), and the force criterion in the structure relaxation was set to less than 0.01 eV/(unit cell).

The average binding energy for Li atoms adsorbed in UiO-66 is calculated as follows:

$$E_b = \frac{1}{n} \left[ E_{nLi/UiO-66} - nE_{Li} - E_{UiO-66} \right]$$  \hspace{1cm} (1)

where $E_{nLi/UiO-66}$ is the total energy of the optimized Li/UiO-66 system; $E_{Li}$ is the optimized energy of one Li in solid Li; and $E_{UiO-66}$ is the optimized energy of UiO-66.

**Cluster Model Calculations.** A neutral cluster model (Figure 1b) was constructed from periodic unit cells of UiO-66 optimized with PBE functionals. First, the cluster was extracted and dangling bonds were capped with hydrogens (the cluster has one $\text{Zr}_6\text{O}_4(\text{OH})_4$ node and twelve $\text{C}_6\text{H}_5\text{CO}_2$, for a total of 186 atoms per cluster); then the positions of the aromatic H atoms were optimized with all other atoms fixed. Next, the $\text{C}_6\text{H}_5$ units of the phenyl rings were fixed, and the positions of all other atoms were optimized. Both PBE and M06-L exchange-correlation functionals were used in the cluster calculations. The 6-31G(d, p) basis set was used for C, H, O, and Li. The SDD basis set and effective core potential (ECP) were used for Zr. Vibrational analysis was also carried out. The CM5PAC program was used to derive CM5 partial atomic charges from Hirshfeld analysis of the UiO-66 and lithiated UiO-66 calculations.
RESULTS AND DISCUSSION

Control Over Particle Size of UiO-66 via the Synthesis Temperature. The original synthesis of UiO-66 involved heating of a mixture of ZrCl$_4$, 1,4-benzenedicarboxylic acid and $N,N'$-dimethylformamide (DMF) at 120 °C for 24 h. This produced intergrown single crystals with typical edge dimensions of ca. 200 nm. Subsequently, a modification of this synthesis was reported which involved the addition of HCl and overnight heating at 80 °C.

When considering UiO-66 as an electrode material for lithium ion batteries, it is important to minimize particle size to reduce diffusion lengths for lithium ions and increase the contact area with an electronically more conductive phase, such as carbon. To reduce particle sizes, we systematically lowered the synthesis temperature using a prolonged reaction time, as described in the Experimental Section.

Figure 2 shows scanning electron microscopy (SEM) images of the products, and typical dimensions are listed in Table 1. For each synthesis temperature, the particles form agglomerates but are relatively uniformly sized. The average diameter estimated from SEM images decreased from ~115 nm for a synthesis at 110 °C to 38 nm for a synthesis at 50 °C. The X-ray diffraction (XRD) patterns confirmed that the UiO-66 structure was obtained with the altered synthesis conditions (Figure 3). For the sample synthesized at 50 °C, the average crystallite size estimated from X-ray line broadening coincided approximately with the particle sizes observed in the SEM image, suggesting that most of the observed nanoparticles in that sample are single crystals. For samples prepared at higher temperatures, crystallite sizes estimated by the Scherrer equation...
remained consistently lower than the particle sizes observed by SEM, indicating that those particles were polycrystalline.

**Table 1**  Dimensions of UiO-66 particles as a function of synthesis temperature, determined from SEM images and estimated from powder XRD line broadening

<table>
<thead>
<tr>
<th>synthesis temperature (˚C)</th>
<th>average diameter (nm)</th>
<th>standard deviation (nm)</th>
<th>minimum (nm)</th>
<th>maximum (nm)</th>
<th>XRD crystallite size (nm)</th>
</tr>
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<tbody>
<tr>
<td>50</td>
<td>38</td>
<td>6</td>
<td>25</td>
<td>53</td>
<td>34</td>
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<td>115</td>
<td>19</td>
<td>84</td>
<td>147</td>
<td>41</td>
</tr>
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</table>

**Figure 2**  SEM images of UiO-66 particles synthesized at the indicated temperatures.
Figure 3 XRD patterns of UiO-66 powders synthesized at the indicated temperatures. (a) Patterns covering the 5–80 °20 range. See also Figure S2. (b) Patterns focusing on the low-angle peaks. The CIF file provided in the reference by Cavka et al. was used for the simulated pattern.26

**Electrochemical Cycling.** To obtain information about electrochemical events during lithiation and delithiation, cyclic voltammograms (CVs) were obtained for UiO-66 (50 °C) (Figure 4). As shown in Figure 4a, the CV curve exhibits three cathodic and three anodic peaks. During the first lithiation, the CV is featureless until the potential is lower than 1 V, but three peaks are developed in the following cycles at 1.6 V (peak 1), 1.3 V (peak 2) and 0.4 V (peak 3). During delithiation, peaks appear at 1.3 V (peak 4), 1.8 V (peak 5) and 2.7 V (peak 6). The peak positions shift slightly over multiple cycles, and the large overpotential is due to the low electronic conductivity of UiO-66. Figure 4b shows the integrated peak area for each peak; this gives the charge passed through the cell for each peak. Except for the first cycle, the charge is almost identical for peaks 2 and 5, as well as for peaks 1 and 4, starting at the second cycle. The area of peak 3 is larger than that of the others, possibly due to the side reactions such as solid-electrolyte-interface (SEI) formation and decomposition of impurities in the electrolyte. A possible mechanism (shown in Figure 5) is that during lithiation, the terephthalate anion undergoes a two-step reaction, for which one electron is involved in each step, and a free radical is formed as the intermediate; this reaction is reversed during delithiation. Such a two-step electron transfer mechanism has been associated with other organic redox-active materials, for which similar shapes of the CV or the differential capacity vs. potential plot were observed.50,51 However, UiO-66 showed three cathodic and anodic processes, which are not seen in the cyclic
voltammogram of terephthalic acid (Figure S3), implying that the charge storage mechanism may be more complicated. There may be multiple lithium intercalation sites, which will be discussed in detail in the next section.

**Figure 4** (a) Cyclic voltammograms of UiO-66 (50 °C) cycled at 0.5 mV/s using a 3-electrode configuration. Point 0 is the starting point. 1–3 denote peaks associated with lithiation processes, while 4–6 denote peaks associated with delithiation processes. The arrows indicate the scan direction. The dotted lines are the boundaries used for peak integration. (b) Integrated peak areas for the indicated peaks shown in (a). These values were obtained from integrated peak areas of the peaks defined in Figure 4a. Each point corresponds to a single value in a given cycle.

**Figure 5** A possible mechanism of charge storage involving the linkers in UiO-66.

Figure 6a shows the galvanostatic curves for the first two charge and discharge cycles for UiO-66 powders synthesized at the various temperatures. Irreversible behavior is observed during the first cycle, which is quite common for many different types of electrode materials and is often associated with formation of a solid-electrolyte interface (SEI) and other processes.
Involving the electrolyte. For example, ref. 14 associates irreversible capacity in the first cycle with the formation of some amorphous Li$_2$O and an SEI layer. Therefore, we concentrate our interpretation on later cycles.

During lithiation, two steps are observed in Figure 6a, one between 0.2 and 0.8 V and the other between 0.8 and 1.3 V vs. Li/Li$^+$. These lithiation potentials are higher than those for carbon-based anodes and occur in a range that avoids the formation of lithium dendrites, making UiO-66 a potentially safer anode material. The delithiation cycle is characterized by an inflection point at ~1.6 V and a step between 2.0 and 2.6 V vs. Li/Li$^+$. These events correspond to the peaks identified on the CVs. The large irreversible capacity during the first cycle is likely related to SEI formation, with a small fraction possibly due to irreversible capacity associated with the Super P carbon black below 1.0 V vs. Li/Li$^+$. However, any reversible capacity of the Super P carbon is negligible, as determined with a control sample containing silica gel:Super P carbon:PVDF with a mass ratio of 8:1:1 (see Figure S4). Although the materials were dried at 150 °C under vacuum, some remaining water molecules associated with the Zr$_6$O$_4$(OH)$_4$ clusters may also have contributed to this irreversible capacity.

Figure 6b shows specific capacities measured over 30 cycles at varying charge and discharge rates. Whereas during the initial cycles significant capacity fading is observed (which is often associated with structural, textural, or morphological electrode material changes during lithiation and delithiation), the specific capacities stabilize later, and the C/5 capacity discharge capacity after 30 cycles remains relatively high for a MOF, at 118 mAh/g for UiO-66 synthesized at 50 °C and decreasing for materials synthesized at higher temperatures. Cells that had undergone 100 cycles at a rate of C/5 maintained about 65% of their capacity (see Figure S5 for long-term cycling performance), which is good in comparison to MOFs used so far as host materials. These observations indicate that the lithiation and delithiation reactions of UiO-66 were reversible.
Figure 6  Electrochemical lithiation and delithiation data for UiO-66 materials synthesized at the indicated temperatures. (a) Galvanostatic curves of the first and second cycle. (b) The specific capacities of cells measured over 30 cycles at the indicated C-rates. Capacities are shown per gram UiO-66. The rate for 1C was set at 194 mAh/g, based on the hypothesis that lithium uptake involves interactions with the linker with a maximum capacity of 2 Li⁺ per linker molecule.

Possible Charge Storage Mechanisms. The relatively high specific capacity for UiO-66 nanoparticles is surprising because UiO-66 does not contain any redox-active transition metal with easily accessible multiple oxidation states, unlike most of the MOFs tested previously for lithium ion battery electrodes. Therefore, several other possible origins for charge storage were considered for the UiO-66 system. Table 2 lists four possible storage positions of Li in UiO-66, which we next discuss (along with three others) in the order listed. In this discussion recall that the convention established by eq. 1 is that a favorable (exoergic) binding energy is negative.

1. Lithium may be associated with the aromatic ring in the terephthalate linker. Such association of Li with a benzene ring linker was described for a Zn-based MOF. With one Li or two Li per ring (Li are possibly on both sides of each aromatic ring), this would give a theoretical capacity of 97 or 194 mAh/g, respectively. The binding energy calculated for the first Li in this position is 0.08 eV for one Li and 0.20 eV for two Li, but the PBE (Perdew-Burke-Ernzerhof) method is inaccurate for binding energies dominated by dispersion-like interactions.
We therefore used the PBE-D2 functional,\textsuperscript{43} which yields -0.14 eV (i.e., exoergic) for one Li. The PBE-D2 calculations of this kind of adsorption site show Li–C distances ranging from 2.29 to 2.30 Å.

(2) Lithium may be associated with carboxylate groups on linkers.\textsuperscript{52} In Liu’s work, the Li is connected to four carboxylate oxygens. With one Li per carboxylate (two Li per linker), this would result in a theoretical capacity of 194 mAh/g. For a compound that is related to the terephthalate linker, namely lithium terephthalate, it is possible to reversibly add two lithium ions at a potential near 1.0 V vs. Li/Li\textsuperscript{+} to produce tetra-lithium terephthalate.\textsuperscript{34} Both PBE and M06-L\textsuperscript{46} calculations of periodic and cluster models show that the relaxation of an initial structure with Li connected to four carboxylate oxygens yields a structure with Li connected to two carboxylate oxygens. This is different from the structure described by Liu \textit{et al.}\textsuperscript{52} The Li is positioned between two carboxylate oxygens (see Figure S6a).\textsuperscript{53} The Li–O(CO) bond lengths are 1.86 and 1.87 Å, respectively. The C–O distances of the carboxylate bond involving the oxygen close to the Li are increased from 1.28 to 1.32 Å, and the distances of Zr–O(C) near the Li are increased from 2.24, 2.25 to 2.33, 2.34 Å. The binding energy for the first Li is -0.52 eV by the PBE functional. The maximum number of Li that UiO-66 can accommodate at this type of position is 24 per node, which gives a theoretical capacity of 388 mAh/g.

(3) Lithium may be associated with the oxygen in the Zr\textsubscript{6}O\textsubscript{4}(OH)\textsubscript{4} cluster node, which has no proton on it (see Figure S6b).\textsuperscript{53} The Li–O(Zr) bond length is 1.87 Å. In this structure, the Li is also connected to two carboxylate oxygens, and the Li–O(CO) bond lengths are 2.07 and 2.06 Å. The lithiation at this position has only a slight effect on the structure of the Zr\textsubscript{6}O\textsubscript{4}(OH)\textsubscript{4} core of the node, but has larger effects on the distances of C–O and Zr–O(C) near the Li. The distances of C–O on the carboxylate bond involving the oxygen closest to the Li are increased from 1.28 to 1.30 Å, and the distances of Zr–O(C) near the Li are increased from 2.24, 2.25 to 2.32, 2.35 Å. The binding energy for the first Li connected to the node oxygen is -0.62 eV by PBE. The maximum amount of Li by this mode would be four, if we assume the composition Zr\textsubscript{6}O\textsubscript{4}(OH)\textsubscript{4}(C\textsubscript{8}H\textsubscript{4}O\textsubscript{4})\textsubscript{6} in activated UiO-66.

(4) Li may replace the hydrogen in the node and produce hydrogen gas. There are four such hydrogens per node. The reaction energy for the first Li is -0.77 eV by PBE.

(5) The additional negative charge that must be introduced together with Li\textsuperscript{+} insertion may be accommodated on cluster or linker sites as indicated, for example, in Figure 5.
6) Remaining water molecules associated with the cluster hydroxo or oxo sites may react
electrochemically; however, this should not be reversible and the reaction is expected to be
negligible after the first few cycles.

(7) In zinc formate-based MOFs, a conversion reaction has been observed in which Li reacts
reversibly with benzenedicarboxylate linkers, producing metallic zinc and then a lithium-zinc
alloy. However, it is quite unlikely that Zr(IV) will be reduced to metallic Zr under our reaction
conditions, and no X-ray reflections of metallic Zr were observed.

Table 2  The possible positions of Li, the number of Li per node that UiO-66 can accommodate at each
position, the binding energy of the first Li at each position, and the calculated C–O distances\(^a\)

<table>
<thead>
<tr>
<th>position of Li in UiO-66</th>
<th>numbers of Li</th>
<th>energy of binding of first Li (eV)</th>
<th>C–O distance (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(1) aromatic ring</td>
<td>6~12</td>
<td>-0.14</td>
<td>1.29</td>
</tr>
<tr>
<td>(2) carboxylate oxygen</td>
<td>24</td>
<td>-0.52</td>
<td>1.32</td>
</tr>
<tr>
<td>(3) node oxygen</td>
<td>4</td>
<td>-0.62</td>
<td>1.30</td>
</tr>
<tr>
<td>(4) replace node hydrogen</td>
<td>4</td>
<td>-0.77</td>
<td>1.30</td>
</tr>
</tbody>
</table>

\(^a\) based on PBE-D2 for site (1) and PBE for sites (2)–(4).

\(^b\) The C–O distance in the carboxylate bond involving the oxygen close to the Li.

Both PBE and M06-L calculations show that lithiation at a node oxygen is more favorable
than at carboxylate oxygens. The energy of (3) is 0.17 eV lower than that of (2) based on the
M06-L calculations. The binding energies of (2)–(4) are close to the voltage (0.2~0.8 V) of the
lithiation step in the experiments. Table S1 lists the volumes and lattice constants of lithiated
UiO-66, the average lithiation energy for the reaction of UiO-66 + n Li \(\rightarrow\) UiO-66/nLi, and the
lithiation energy for the reaction of UiO-66/(n−1)Li + Li \(\rightarrow\) UiO-66/nLi.\(^53\) In all lithiated UiO-66
in Table S1, unless otherwise noted, all Li are at the same Zr\(_6\)(O)\(_4\)(OH)\(_4\) node even though there
are two nodes in the double primitive cell. The volume of lithiated UiO-66 depends on the
amount of adsorbed Li and the adsorption position of Li. For the same amount of Li in the 1×1×2
supercell, the structures with Li atoms further separated from each other have lower energies and
smaller volumes than the ones with Li closer together (see Figures S7–S10).\(^53\)
The reaction energy of UiO-66/(n-1)Li + Li → UiO-66/nLi depends on the position of the added Li. For some reactions, the reaction energy is more negative than -1.0 eV. The average binding energy for adsorbing 24 Li atoms in the type-(2) sites of the same node in the 1×1×2 primitive cell of UiO-66 is -0.36 eV by PBE, and the change in unit cell volume is very small (it increases 1.5%). For the case of Li in the type-(4) position, the energy barrier may be high due to the additional energy needed for breaking the O-H bond. On the basis of these calculations, the node oxygens and the carboxylate oxygens are the most favorable sites for lithiation. At low Li loadings, the relative probability of these two most probable positions are calculated by

\[
d_{2}/d_{1} \exp \left( \frac{-\left(G_{2} - G_{1}\right)}{RT} \right)
\]

where \(d_{i}\) is the degeneracy of site \(x\), and \(G_{x}\) is the free energy of site \(x\), which we calculated by periodic PBE phonon calculations. In this way we calculated that at 300 K the relative probability of finding Li at a node oxygen is 0.19 times the probability of finding the Li between carboxalate oxygens. For higher loadings, the theoretical capacity of UiO-66 with Li at these two positions is more than 400 mAh/g.

**Electronic Properties.** Table 3 shows the band gaps of UiO-66 before and after lithiation. The calculated band gap for UiO-66 by the PBE and Heyd-Scuseria-Ernzerhof (HSE06)\(^{41}\) functionals is 2.93 and 4.18 eV, respectively. The gap by HSE06 is close to the experimental gap 4.07 eV of hydroxylated UiO-66.\(^{27}\) All the periodic and cluster calculations using PBE, HSE06, and M06-L functionals show that lithiation at the two most likely positions greatly decreases the band gap of UiO-66, which is expected to improve the electronic conductivity of UiO-66. In the Li-insertion process, the additional electrons will go into the conduction bands of UiO-66. Therefore the nature of the electronic states at and near the conduction-band minimum (CBM) is important. Our periodic calculations show that the p orbitals of C and O from the organic linkers dominate the bottom of the conduction band (see Figure S11)\(^{53}\) in agreement with the calculated result of Yang et al.\(^{54}\) After lithiation, the p orbitals of C and O near the Li position dominate the singly occupied molecular orbital (see Figure S12),\(^{53}\) which contributes to the narrow gap.
Table 3 The energy gap (eV) of UiO-66 before and after lithiation

<table>
<thead>
<tr>
<th></th>
<th>PBE</th>
<th>HSE06</th>
<th>M06-L</th>
<th>expt.</th>
</tr>
</thead>
<tbody>
<tr>
<td>UiO-66</td>
<td>2.93</td>
<td>4.18</td>
<td>3.93</td>
<td>4.07</td>
</tr>
<tr>
<td>(i)</td>
<td>0.28</td>
<td>0.36</td>
<td>0.35</td>
<td></td>
</tr>
<tr>
<td>(ii)</td>
<td>0.22</td>
<td></td>
<td>0.24</td>
<td></td>
</tr>
<tr>
<td>(i)+(ii)</td>
<td>0.2–0.3</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(iii)</td>
<td>0.37</td>
<td>0.86</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Note: (i) A Li is between (Zr)O(Zr) and two carboxylate oxygens; (ii) a Li is between two carboxylate oxygens; (i)+(ii): two Li are in present – in the (i) and (ii) positions; (iii) a Li is on top of a phenyl ring. For (i), (ii), and (iii), one Li is added to the double primitive cell. For (i)+(ii), two Li are added to the double primitive cell.

To understand charge redistribution in the lithiation process, we calculated CM5 charges. For UiO-66, oxygen atoms are classified into three types, namely O(C), O(H), and O(N), where O(C) denotes an oxygen of a carboxylate, O(H) denotes a protonated O atom of the node, and O(N) denotes an unprotonated O atom of the node. Before lithiation, the CM5 charge of an O(C) atom is -0.36 (-0.33), that of an O(H) atom is 0.67 (-0.64), and that of an O(N) atom is -0.74 (-0.71) by M06-L (PBE) calculations. During the lithiation process, the charges on Zr, O(H), and H remain almost constant while the charge on Li increases and the charge on the carbon in carboxylate involving the oxygen connected to Li decreases slightly. For the Li bound to both O(C) and O(N), where the Li-O(N) distance is shorter than the Li-O(C) distance, both the O(C) charge and the O(N) charge become less negative, but the change in the O(N) charge is greater.
Table 4 The CM5 charges of O(C), O(H), O(N), Li, and the C of carboxylate groups after Li adsorption at the two most probable positions of UiO-66, based on M06-L cluster calculationsa

<table>
<thead>
<tr>
<th></th>
<th>UiO-66</th>
<th>Li-O(Zr)</th>
<th>Li-O(CO)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Li</td>
<td></td>
<td>0.58</td>
<td>0.62</td>
</tr>
<tr>
<td>O(C)</td>
<td>-0.36</td>
<td>-0.37, -0.38</td>
<td>-0.48</td>
</tr>
<tr>
<td>O(H)</td>
<td>-0.67</td>
<td>-0.66</td>
<td>-0.67</td>
</tr>
<tr>
<td>O(N)</td>
<td>-0.74</td>
<td>-0.83</td>
<td>-0.74</td>
</tr>
<tr>
<td>C(O)</td>
<td>0.31</td>
<td>0.25, 0.25, 0.27</td>
<td>0.26</td>
</tr>
</tbody>
</table>

a O(C) is a carboxylate oxygen; O(H) is a protonated node oxygen; and O(N) is an unprotonated node oxygen. Only the charges of C and O close to the Li are given here. Li-O(CO) represents the lithiated UiO-66 with the Li positioned between two different carboxylate oxygens (which is called case 2 in the text), and Li–O(Zr) denotes the lithiated UiO-66 with the Li mainly connected to the node oxygen (which is called case 3 in the text).

**IR Spectra.** To further help us understand the charge storage mechanism, we carried out ex-situ FTIR and XRD analyses of the electrode materials before and after electrochemical events during multiple lithiation/delithiation cycles. The FTIR spectrum of UiO-66 synthesized at 70 °C (as made, Figure 7) showed the characteristic features of this MOF. The most intense peaks at 1579 and 1399 cm\(^{-1}\) correspond to the in- and out-of-plane stretching modes of the carboxylate groups\(^ {27}\) and other bands at 1511, 1107 and 1022 cm\(^{-1}\) are also present in the spectrum of the terephthalate linker.\(^ {55}\) A series of peaks in the lower-wavenumber region (747, 666, 553, and 485 cm\(^{-1}\)) are mixed modes involving OH and CH bending together with Zr–O modes from the Zr\(_6\)O\(_4\)(OH)\(_4\) nodes.\(^ {27}\) After activation at 150 °C in vacuum for 2 h, intensities of the peak of DMF (which is the solvent sued in the synthesis) at 1660 cm\(^{-1}\) as well as the broad band centered at 3400 cm\(^{-1}\) corresponding to water were greatly reduced.
Several changes in the FTIR spectra (Figure 8) were noted for UiO-66 (50 °C) electrodes that had been lithiated (0.5 cycles), then delithiated (1 cycle), and relithiated (1.5 cycles). Most interestingly, the peak at 1579 cm\(^{-1}\) associated with the asymmetric vibration of the carboxylate groups splits into two peaks (1583 and 1568 cm\(^{-1}\)) upon lithiation, then becomes a single peak again upon delithiation and splits again when lithiated a second time. The PBE phonon calculations with the Vienna Ab Initio Simulation Package (VASP)\(^{38,39}\) show that a peak at 1604 cm\(^{-1}\) splits into two peaks (1601 and 1649 cm\(^{-1}\)) when the Li is bound to two different carboxylate oxygens, which is consistent with the FTIR spectra. In addition, the peak at 1399 cm\(^{-1}\) due to the symmetric carboxylate stretch has a non-resolved shoulder at higher wavenumber in the lithiated UiO-66, which becomes resolved as a separate peak as the original peak shifts to shorter wavenumber (1433 and 1387 cm\(^{-1}\)); after relithiation, the peak returns closer to its original position so that the shoulder is no longer resolved. During all of these changes, the peaks associated with the Zr\(_6\)O\(_4\)(OH)\(_4\) nodes in the low wavenumber range (747, 553 cm\(^{-1}\)) do not change. These observations lead us to the conclusion that lithiation likely occurs at the carboxylate end groups, rather than at cluster sites, resulting in a distortion of the environment near the carboxylate groups and hence in the observed splitting after lithiation. Participation of aromatic rings as Li-sites cannot be excluded from these data, because ring vibrations were not strong enough to permit interpretation. It should be noted that additional peaks in the electrode spectra at 1804, 1773, 1501, 1485, 1076, and 1040 cm\(^{-1}\) are due to the mixed carbonate electrolyte solvent and an intense peak at 840 cm\(^{-1}\) is due to the PF\(_6^-\) ion of the electrolyte.\(^{56}\)
The quantum mechanical IR calculations based on the cluster models of UiO-66 and lithiated UiO-66 (only one Li) support the interpretation of the FTIR spectrum in that after the lithiation the peaks associated with the asymmetric and symmetric stretch vibrations of the carboxylate (around 1600 and 1400 cm$^{-1}$) split (Figure 9). The lithiation has little effects on the peaks in the 400–800 cm$^{-1}$ range, which are associated with the vibration of the Zr$_6$O$_4$(OH)$_4$ nodes. This also agrees with the experimental FTIR spectra.
Figure 9 The calculated IR spectra of the cluster models of UiO-66 and lithiated UiO-66 by M06-L. The C and H atoms in the benzene groups of the linkers are fixed in the frequency calculations, so there are no vibrational peaks for C–C ring and C–H bonds. Li–O(CO) represents the lithiated UiO-66 with the Li positioned between two different carboxylate oxygens, and Li–O(Zr) denotes the lithiated UiO-66 with the Li mainly bound to the node oxygen.

The XRD pattern of UiO-66 remained unchanged during cycling; Figure 10 shows that the UiO-66 structure was preserved during 100 cycles of lithiation and delithiation. (Preservation of the MOF structure after 100 cycles was also observed, e.g., in ref. 14.) This indicates that the electrochemical lithiation and delithiation of UiO-66 occurs by an intercalation rather than a conversion mechanism, and there is no significant volume change during the reaction. This interpretation was checked by density-functional simulations of the XRD spectra; the simulated XRD patterns of lithiated and non-lithiated UiO-66 are also virtually identical (as shown in Figure S13), showing no significant changes in peak positions or intensities, which we interpret as resulting from the low electron density of lithium and the absence of a change in the framework structure or volume during the topotactic lithiation/delithiation processes. Compared with other anode materials, such as Co₃O₄ which goes through a conversion reaction,⁵⁷ or Si or similar alloy-based anodes which undergo large volume expansions during lithiation,⁵⁸ the near zero-volume-change characteristic of UiO-66 is beneficial for long-term cycle performance.
CONCLUDING REMARKS

Nanosized UiO-66 was synthesized by lowering the reaction temperature and tested as an electrode material for lithium-ion batteries. UiO-66 synthesized at lower temperatures had smaller particle sizes, and delivered encouragingly higher specific capacities. Ex-situ FTIR and XRD on electrodes revealed that the electrochemical lithiation of UiO-66 proceeds through an intercalation mechanism with no volume change. Ex-situ FTIR allowed us to observe reversible splitting of peaks that helped identify lithium association with carboxylate groups in the linkers, and theory supported these interpretations of the spectra. The XRD patterns confirmed that the UiO-66 structure was preserved during 100 cycles of lithiation and delithiation and that little volume change occurred during uptake of lithium.

Unlike other MOF lithium batteries that use redox-active metal nodes to store charges, the UiO-66 electrode studied here relies on the anions for the electrode reactions. Density functional electronic structure calculations show that UiO-66 has an excellent Li capacity, and the calculations are consistent with experiment in that the lithiation causes only a very slight volume change. The calculations show that lithiation significantly decreases the band gap of UiO-66, which increases its electronic conductivity. In addition, the calculations identify the most probable sites for lithiation as node oxygens and linker carboxylate oxygens, and during the lithiation of UiO-66, the charge mainly transfers from Li to node oxygens and carboxylate oxygens. This identification of the lithiation sites is supported by the good agreement achieved.
between calculated and measured IR spectra of the lithiated material. Involvement of cluster oxygen atoms in the redox processes can provide the advantage of stabilizing the MOF structure over multiple lithiation and delithiation cycles by maintaining connections between linkers and oxozirconium cluster-based nodes; this contrasts with MOFs that rely on single redox-active metal nodes, which change coordination to the ligands with changing oxidation states.\(^{23}\) Furthermore, such oxozirconium cluster nodes can be modified by attaching redox-active metal atoms,\(^{59}\) which may further enhance the electrode capacity and modify the lithiation/delithiation potentials to enable future use of such MOFs at more cathodic potentials.

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References


53. See supplemental materials at [URL will be inserted by AIP] for structures, cell volumes, lattice constants, lithiation energies, charge densities, molecular orbitals, and partial atomic charges (Figures S1–S7 and Tables S1–S3).


56. H. Yang, G. V. Zhuang and P. N. Ross Jr., Thermal Stability of LiPF₆ Salt and Li-ion Battery Electrolytes Containing LiPF₆, J. Power Sources, 2006, 161, 573.


