The predicted crystal structure of Li$_4$C$_6$O$_6$, an organic cathode material for Li-ion batteries, from first-principles multi-level computational methods†

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In this communication, we use first-principles based multi-level computational methods to predict the crystal structure of Li$_4$C$_6$O$_6$, the key intermediate material that can be oxidized to Li$_2$C$_6$O$_6$ or reduced to Li$_6$C$_6$O$_6$. This predicted structure leads to an X-ray diffraction (XRD) pattern in good agreement with experiment, validating the predicted structure. With this structure in hand one can proceed to determine details for the electrochemical properties of these organic electrodes (chemical potential for Li ion as a function of loading and the mechanism for the lithiation/delithiation process) useful in designing optimum systems.

To achieve the sustainability required for next generation energy storage systems, it is desirable to develop Li rechargeable batteries that involve renewable processes operating at low temperatures with a low CO$_2$ footprint.¹ This led to the proposal that the inorganic electrodes be replaced with abundant organic materials.² Among these systems, lithiated oxocarbon salt (Li$_2$+,C$_6$O$_6$) is considered to be a most promising cathode material due to its high theoretical capacity, 580 mAh g$^{-1}$, for $x = 0$ to $x = 4$, four times the capacity of the conventional cathode material, LiCoO$_2$.²² Fundamental to investigating and optimizing the redox reactions of this organic electrode, is the crystal structure of Li$_{2x}$C$_6$O$_6$. Thus X-ray diffraction (XRD) patterns have been reported by Chen et al. for Li$_2$C$_6$O$_6$ (2009)³ and Li$_6$C$_6$O$_6$ (2009),¹ however, no one yet has been able to solve for the atomic positions within the unit cells of these crystals.

Due to the low electron density of Li, the XRD pattern is dominated by the packing of the C$_6$O$_6$ moieties with modest contributions from the Li atoms. However, intercalation of Li into the C$_6$O$_6$ framework leads to charge transfer complexes that dramatically affect the energy and packing of the C$_6$O$_6$ moieties. Here we combine quantum mechanics (density functional theory, DFT), force-fields (FF) derived from the DFT, and Grand Canonical Monte Carlo (GCMC) to predict the energetics and changes in packing using the following iterative multi-paradigm computational strategy, summarized in Fig. 1:

1. We postulated a variety of hypothetical C$_6$O$_6$ frameworks with various packings of the C$_6$O$_6$ molecules within a large periodic supercell (containing 8 C$_6$O$_6$ units) and used our FF to optimize the geometry (eliminating bad contacts between C$_6$O$_6$ molecules).
2. Keeping each C$_6$O$_6$ moiety fixed, we carried out GCMC simulations using our FF, to locate the optimum positions of Li ions intercalated within each C$_6$O$_6$ framework.
3. We then optimized each of the structures from step 2, using DFT to fully relax the Li$_x$C$_6$O$_6$ structure.
4. The above procedure was iterated several times with various starting points to determine the global minimum crystal structure of Li$_4$C$_6$O$_6$.

Broader context

In recent years, there have been growing demands on organic electrode materials for sustainable Li rechargeable batteries. Li$_{2x}$C$_6$O$_6$ were suggested as promising organic cathode materials due to a high theoretical capacity and the abundance of raw materials. However, the unknown crystal structure of Li$_{2x}$C$_6$O$_6$ is a major hurdle to investigating and optimizing this cathode material. This communication provides the crystal structure of Li$_{2x}$C$_6$O$_6$ predicted with a new multi-level strategy. We show that Li$_x$C$_6$O$_6$ has three different Li sites, two inter-layer sites and one intra-layer site, as well as determining their chemical potentials for lithium extraction. Our findings provide insights about the nature of intermolecular interactions, redox reactions, lithium diffusion, etc., which are useful in designing improved organic cathode materials. This multi-level computational method may also be helpful in predicting the crystal structure of other metal-intercalated molecular crystal structures.
The list of Li$_4$C$_6$O$_6$ structures from step 4 was ranked according to the DFT energies and their predicted XRD patterns were compared with the experimental XRD. Starting with this best structure, we carried out molecular dynamics (MD) simulation at 300 K using forces from the DFT (termed *ab initio* MD or Car–Parrinello MD) to take into account fluctuations due to temperature. Finally the averaged XRD pattern from the 300 K dynamics is compared with the experimental XRD pattern from experiment. This main peak at $\theta = 31.9^\circ$, corresponding to (004) planes of the proposed structure B, is shown in Fig. 3a. Major peaks at $31.9^\circ$ and $14.1^\circ$ show excellent correspondence to the experimental XRD pattern with similar relative intensities. The low intensity peaks at higher angles also match reasonably well with experiments. The slight mismatches remaining between the smaller peaks of the XRD pattern are attributed to the ordering introduced by the small unit cell (8 C$_6$O$_6$) required for the DFT.

To find the most stable stacking pattern, we systematically generated a series of stacking patterns of the C$_6$O$_6$ layers by gradually sliding the layers within the delithiated simulation cell. Then we re-introduced the Li atoms using GCMC simulations with our FF. The structure and the cell parameters were fully relaxed again using DFT. The resulting energies and crystal structure parameters of fifty most stable structures among over 300 tested structures are tabulated in Table S2†.

The most stable structure, denoted as C, is shown in Fig. 2. It has the $C2/m$ space group with lattice parameters of $a = 12.917$ Å, $b = 7.541$ Å, $c = 6.523$ Å, $\alpha = 90^\circ$, $\beta = 119.6^\circ$, and $\gamma = 90^\circ$ (see Table S3 for detailed atomic coordinates†). The computed XRD pattern of the final structure is shown in Fig. 3a. Major peaks at $31.9^\circ$ and $14.1^\circ$ show excellent correspondence to the experimental XRD pattern with similar relative intensities. The low intensity peaks at higher angles also match reasonably well with experiments. The slight mismatches remaining between the smaller peaks of the XRD pattern are attributed to the ordering introduced by the small unit cell (8 C$_6$O$_6$) required for the DFT.
The presence of stacking faults is relatively common in layered materials. The energy cost required for the stacking faults is small, e.g. found that the energy cost required for the stacking faults is small, e.g. with only up to ~300 meV of energy needed to generate 50 different types of stacking faults within four-layer unit cell system. The presence of stacking faults is relatively common in layered materials. In particular, the low temperature synthesis of layered materials often yields to the stacking faults in the structure. Considering the low temperature synthesis (673 K, see supporting information for experimental details†) of the sample, it is expected that structural imperfection such as stacking faults can be easily induced in the experimental sample. The broad nature of experimental XRD peaks is another indirect indication that structural disorder does exist in the experimental sample to some extent. Moreover, we note that the high symmetry imposed in our DFT simulation cell can be broken in the large supercell of the experimental sample due to the defects or thermal fluctuations. We expect that this also can result in mismatches at smaller peaks in the XRD pattern.

We find that every Li atom in the structure is coordinated to four oxygen atoms, which differs from Na2C6O6 and K2C6O6, where Na and K are coordinated with 8 oxygen ions. This is plausible, resulting from the smaller size of Li. Indeed the Li is known to coordinate to four oxygen ions for the LiMn2O4 and Li2NiO2 cathode materials.

We find three types of energetically favorable Li sites in the final Li4C6O6 structure: (see Fig. 2 and 4)

1) Li1 site: coordinated by four oxygen ions of two adjacent C6O6 molecules in same layer,

2) Li2 site: coordinated by four oxygen ions of four C6O6 molecules in neighboring layers, and

3) Li1 site: similar to Li1, but slightly shifted from the C6O6 layers due to electrostatic repulsion of nearby Li ions at Li1 site and Li2 site.

The calculated Li–O distances in Li4C6O6 range from 1.94 to 2.08 Å (see Fig. 4), which are similar to those in typical Li containing cathodes such as LiCoO2 (2.09 Å) and LiFePO4 (2.09 ~ 2.19 Å). The C–C bond lengths range from 1.434 and 1.437 Å, and the C–O bond lengths range from 1.303 and 1.310 Å in our final structure. Such small deviations in bond distances arise because every Li ion coordinates four oxygen atoms within a similar distance, and transfer almost equal charge to each oxygen atom. Therefore, all carbon atoms in the C6O6 molecules should have a similar chemical shift, leading to the single peak observed in 13C MAS NMR spectra reported by H. Chen et al.1 We note that these NMR observations show that the crystal cannot consist of isolated Li4C6O6 molecules, which has 4 C–C bond lengths of 1.303 Å and 2 of 1.409 Å, which two distinct C–O bond lengths of 1.408 and 1.510 Å (see Figure S5†).

To estimate the chemical potential at each Li position, we used DFT to determine the energy cost to extract one Li atom from the 64 Li atoms of the (4a × 2b × 2c) supercell of Li4C6O6 crystal, but keeping the remaining atoms fixed. This “vertical” or snap chemical potential will be too high, but it is useful for determining which Li is easiest to extract. The chemical potentials of Li1, Li2, and Li1' are estimated as −5.38, −5.43 and −5.55 eV, respectively. When we include the relaxation of the systems after the lithium extraction, the chemical potentials of Li1, Li2, and Li1' are estimated as −4.86, −4.99 and −5.07 eV, respectively. This suggests that during the initial delithiation process, Li ions may be extracted mostly from Li1 sites (in-plane sites). Such Li1 vacancies may promote Li diffusion across the layers. Such pathways are not present in LiCoO2 systems because there is no channel across the closed packed cobalt oxide layers.

We then performed ab initio MD at 300 K to validate the thermal stability of our predicted structure and to understand how thermal motions would affect the XRD pattern observed at 300 K. After 30 ps of MD simulation we minimized the structure, and found that the structure remains identical to the original one (cf. Fig. 3a and 3b). This confirms the stability of our predicted structure. The averaged
diffraction pattern over 300 different configurations from the MD, collected every 100 steps (Fig. 3c) leads to thermally averaged peak intensities that match much more closely to the experimental XRD peaks.

No crystal structure of Li$_2$C$_6$O$_6$, Li$_4$C$_6$O$_6$, or Li$_6$C$_6$O$_6$ have previously been reported; however speculations have considered the Li$_{2+}$C$_6$O$_6$ to have each Li coordinated within a single molecule of Li$_{2+}$C$_6$O$_6$. This is in stark contrast to our predictions in which each Li is coordinated to four oxygen ions of two or four neighboring C$_6$O$_6$ units.

We further investigated other possible C$_6$O$_6$ packing arrangements to confirm that our procedure has provided a global minimum structure. We used the Polymorph module of Materials Studio to randomly generate C$_6$O$_6$ frameworks in 14 space groups (P$\overline{1}$, P$\overline{2}_1$, C$2$, C$c$, P$\overline{2}_1$m, P$\overline{2}_2$m, C$2$1m, P$\overline{2}$1c, P$\overline{2}$1c, C$c$21, P$\overline{2}$121, P$m$n$a$, P$\overline{2}$1n, P$n$a$c$, and P$n$a$n$a$c$). To efficiently examine the large search domain, we used a Monte Carlo simulated annealing process (MC-SA), and then fully minimized the resulting structures using our FF. These structures were clustered by crystal similarity measure to generate 113 possible C$_6$O$_6$ frameworks. Then, we performed our multi-level computational method used here was validated by confirming that our procedure has provided a global minimum structure. We used the Perdew–Burke–Ernzerhof (PBE) exchange–correlation functional [16] to treat the van der Waals interaction among the molecules correctly, we added low-gradient (lg) pair-wise dispersion potential to the conventional Kohn–Sham DFT Hamiltonian. This is in stark contrast to our predictions in which each Li is coordinated within a single molecule of Li$_{2+}$C$_6$O$_6$. We used the Perdew–Burke–Ernzerhof (PBE) exchange–correlation functional [16] to treat the van der Waals interaction among the molecules correctly.

The multi-level computational method used here was validated by showing that the XRD pattern generated from the structure with the lowest DFT energy is in good agreement with the experimental pattern. This allows us to determine the character of the lithium binding sites. We find both inter-layer and intra-layer Li positions showing that the XRD pattern generated from the structure with the lowest DFT energy is in good agreement with the experimental XRD. This multi-level strategy may also be helpful in predicting the crystal structure of other metal-intercalated materials for Li rechargeable battery applications. This multi-level strategy may also be helpful in predicting the crystal structure of other metal-intercalated molecular crystal structures.

Computational details

We used the Perdew–Burke–Ernzerhof (PBE) exchange–correlation parameterization (spin-polarized Generalized Gradient Approximation) of DFT [18] as implemented in the Vienna Ab initio Simulation Package (VASP) program[19]. To treat the van der Waals interaction among the molecules correctly, we added low-gradient (lg) pair-wise dispersion potential to the conventional Kohn–Sham DFT Hamiltonian. Ab initio MD calculations were performed at 300 K using the canonical (NVT) ensemble for 30 ps using the VASP software[18]. The DFT calculations considered 8 Li$_2$C$_6$O$_6$ formula units. A plane-wave basis with a kinetic energy cut-off of 500 eV was used and reciprocal-space $k$-point meshes of $2 \times 2 \times 3$ were used to ensure that the total energies are converged within 5 meV per formula unit. The GCMC simulations were performed at 600 K with the Sorption module within the Cerius 2 software[20] using 8 Li$_2$C$_6$O$_6$ formula units. The GCMC simulations used the DREIDING force-field parameters[21], after optimization of the Li–O and Li–C parameters based on the quantum mechanical binding energies obtained from DFT calculation (GAUSSIAN 03 program[22] using Becke-Lee–Yang–Parr (B3LYP) hybrid exchange-correlation functional[23]).

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