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Can T-carbon serve as Li storage material and Li battery anode?

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Abstract – Carbon can form a wide variety of bulk structures. The possibility of carbon-based materials to be utilized in future energy applications has attracted extensive attention. T-carbon is a newly discovered diamond-like phase with acetylene-bond supported hollow structure. This feature inspires us to consider its possibility of serving as high-capacity Li storage material and Li battery anode. Density functional theory calculations are performed to investigate the structure evolution, energy spectrum, stability, and electrode potential of Li-loaded T-carbon. The adsorption of T-carbon to Li atoms originates from the valence electrons of Li filling into the antibonding π* orbitals of acetylene bonds. The maximum theoretical Li capacity is three times that of graphite (1116 mAh/g). At low Li density, too strong adsorption is disadvantageous to the release of Li and the discharge of anode. At high Li density, Li atoms push against each other and fight against the adsorption of T-carbon. Such advantageous issue leads to a decrease in anode potential. The significant difference of Li adsorption between low and high density makes a “dead zone” that only a half of Li capacity could be useful for the discharge of anode.

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I. Introduction

As a fundamental element on the earth, carbon possesses a unique ability to form a variety of complex structures. With $sp^3$, $sp^2$, and $sp$ hybridization, carbon-based structures exhibit chemical and biological diversity. Besides graphite and diamond in nature, people have synthesized many new carbon allotropes including fullerenes, carbon nanotubes, and graphene. With the development of synthesis technology, a large number of carbon allotropes with $sp$ bonds or $sp$-$sp^2$ and $sp$-$sp^3$ combinations have been obtained. Beyond that, theoretical predictions on new carbon crystalline phases, e.g. M-carbon, bct C$_4$ carbon, penta-graphene, BC14 penta-diamond, BCO-C$_{16}$, and the graphyne family have been proposed. For a long time, carbon materials have been widely utilized in energy technology. Carbon matrices (amorphous carbon and many other forms) and carbides are always used for catalyst supports. The utilization of newly discovered carbon allotropes (e.g. graphdiyne) and carbides on emerging energy applications such as catalysis, Li-ion batteries, solar cells and hydrogen storage have been paid much attention.

In 2011, T-carbon, a new diamond-like carbon allotrope (space group Fd$ar{3}$m), was theoretically proposed. The structure of T-carbon is constituted by substituting each atom in diamond by a carbon tetrahedron which connects with each other by acetylene bond. The calculated results show that T-carbon possesses a much lower density of 1.50 g/cm$^3$ and a Vickers hardness of 61.1 GPa (smaller than diamond (93.7 GPa) but comparable with the cubic boron nitride). Recently, T-carbon has been successfully prepared by picosecond laser irradiation on carbon nanotubes and plasma-enhanced chemical vapor deposition. The potential applications of T-carbon in photocatalysis,
solar cells, adsorption, energy storage, supercapacitors, aerospace materials, electronic devices are widely concerned\textsuperscript{28, 29}. With a hollow structure, T-carbon is expected to be a promising material for Li storage. Its excellent carrier mobility\textsuperscript{29} and mechanical ductility\textsuperscript{30} ensure favorable properties for use as the electrode of Li-ion battery.

In this paper, density functional theory (DFT) calculations are employed to investigate the possibility of T-carbon serving as the material of Li storage and Li battery anode. We carry out DFT-based Monte Carlo simulations to build the structure and energy spectrum of Li-loaded T-carbon. Molecular dynamics (MD) simulations are performed to confirm the structural stability. The convex hull of the energy spectrum is built to predict the structure evolution in the Li loading process. C-Li bonding and the mechanism of the change of Li adsorption strength in the loading process are analyzed. The anode potential exhibits a significant difference between the case of low and high Li density, which makes a “dead zone” that only a half of Li capacity could be useful for the discharge of anode. This work provides basic guidance to future studies on the possibility of other carbon allotropes utilizing in emerging energy applications.

II. Computational methods

DFT calculations are performed with the projector augmented wave (PAW) method\textsuperscript{31, 32} as implemented in the Vienna \textit{ab initio} simulation package (VASP)\textsuperscript{33-36}. The electron exchange and correlation are described at the level of Perdew-Burke-Ernzerhof (PBE) functional\textsuperscript{37}. The correction of van der Waals interactions is treated by the DFT-D3 method with Becke–Jonson damping\textsuperscript{38, 39}. A plane-wave basis set is used with a kinetic energy cutoff of 500 eV. The Brillouin-zone integration for 1×1×1 (2×2×2) T-carbon supercell is performed with 8×8×8 (4×4×4) \textGamma-centered Monkhorst-Pack grid. For electronic structure calculations, 25×25×25 \textGamma-centered Monkhorst-Pack grid is used. The convergence of total energy is considered to be achieved until the total energy difference of two iterated steps is less than 10\textsuperscript{-5} eV. Geometry relaxations are performed until all the atomic forces are below 0.001 eV/Å. The climbing image nudged elastic band method\textsuperscript{40-42} was used to find the minimum energy paths and
barriers of Li migrations in T-carbon.

To verify the DFT parameters, we perform computation on graphite as the anode of Li battery. The main phases of Li-loaded graphite are C_{12}Li (Supplementary Fig. S1(a), called as stage II in Ref. 43) and C_{6}Li (Fig. S1(b), called as stage I in Ref. 43). For the two phases, the calculated Li adsorption energy (Eq. (1), Fig. S1(c)) and the anode potential of graphite (see Sec. 3.3, Fig. S1(d)) are close to the results in Ref. 43.

For a certain number of Li atoms loading on T-carbon supercell, the structure evolution is carried out using Metropolis Monte Carlo method for the sampling of the energy spectrum. In every random move, each Li atom is moved with a displacement less than 1.5 Å, and then the structure is fully relaxed. Every relaxed configuration is accepted according to a Gibbs distribution on the DFT total energy within an effective temperature of 4000 K. The structural stability is then verified by molecular dynamics (MD) simulations with the Nose-Hoover thermostat.

III. Results and discussion

3.1 Preliminary understanding

The structure of T-carbon is shown in Supplementary Fig. S2(a) (8 C atoms in one unit cell). T-carbon possesses a diamond-like architecture with acetylene bonds connecting neighboring C tetrahedrons. The energy bands and density of state (DOS) are shown in Supplementary Fig. S2(b) and (c). It is known that the PBE functional always underestimate the bandgap. Thus, we further calculate electronic structures by the hybrid Heyd-Scuseria-Ernzerhof (HSE06) functional44, 45. T-carbon presents a semiconducting feature with a calculated band gap of T-carbon is 2.23 (3.18) eV at the level of PBE (HSE06). Its hollow cage structure allows Li atoms to be stored in it.

To obtain a simple view of basic information, we first investigate Li adsorption in 1×1×1 T-carbon cell. To measure the strength of Li adsorption in T-carbon, we employ the Li adsorption energy

\[ E_{\text{ad}} = \frac{[E(\text{T-carbon-Li}_n) - E(\text{T-carbon}) - nE(\text{Li})]}{n} \]  

(1)

relative to Li bulk. Here, \( E(\text{T-carbon}) \) is the total energy of the T-carbon cell, \( E(\text{Li}) \) is
the energy per Li atom in the bulk bcc phase, and $E(\text{T-carbon-Li}_n)$ is the total energy of the T-carbon cell with $n$ Li atoms. For single Li atom, the preferred position of Li is located in the C-cage (Fig. 1(a)). The structure of T-carbon-Li$_4$ (C:Li = 2:1) is shown in Fig. 1(b), in which the Li-Li distance (2.4 ~ 3.3 Å) is shorter or close than that of Li bulk (3.0 Å). More Li atoms inserted into T-carbon may enlarge and destroy the C skeleton. So, this is considered as the state of maximum Li density. If T-carbon is used as Li-ion battery anode (with discharge process Li → Li$^+$ + e), the maximum Li capacity is three times that of graphite (1116 mAh/g). The structural stability of 1×1×1-T-carbon-Li$_4$ is confirmed by an MD simulation at 300 K (Supplementary Movie 1). The evolution of temperature and total energy (Fig. 1(d)) fluctuating near the average values exhibits the stability of the system. We utilize Monte Carlo simulations to search the structure and energy spectrum of Li$_n$ with $n = 1$~4 (Fig. 1(c), each line denotes the Li adsorption energy $E_{ad}$ of an individual structure). It can be seen that the $E_{ad}$ of the most stable structure gradually increases with Li number $n$, showing a gradually saturated carrying of T-carbon to Li atoms. In 1×1×1-T-carbon-Li$_4$, C-Li binding causes structure distortion making the lattice become low-symmetry system and leading to a relaxation of the structure with extra energy decrease. Therefore, the most stable structure of Li$_4$ possesses lower energy than the most stable structure of Li$_3$. The Li-rich T-carbon is then stabilized by the distortion effect.
Fig. 1 (a) The most stable structure of 1×1×1 T-carbon cell with Li1. (b) The most stable structure of 1×1×1 T-carbon cell with Li4. (c) The energy spectrum of 1×1×1 T-carbon cell with Liₙ. Some parts of Li₁ and Li₂ are enlarged. (d) The evolution of temperature and total energy in the MD simulation of 1×1×1 T-carbon cell with Li₄ at 300 K.

3.2 Li distribution and the convex hull of the energy spectrum

To realize more realistic spectrum of Li distribution in T-carbon, we turn to the structure search in a larger 2×2×2 T-carbon cell. The most stable structure of Li₄ in 2×2×2 T-carbon (Fig. 2(a)) exhibits partial segregation with more Li atoms aggregate together. Aggregated Li atoms may obtain lower energy. But for more Li atoms (Fig. 2(b) for Li₈ and Fig. 2(c) for Li₁₆), it is closer to well distribution because the energy would be high if too many Li atoms aggregate in a small corner. The lattice of 2×2×2-T-carbon-Li₁₆ shows structure distortion with tilted unit cell. The extra structure relaxation leads to the lowest energy and the T-carbon-Li system is then stabilized. This distortion can be known as structural phase transition. For 2×2×2-T-carbon-Liₙ with \( n \geq 16 \), Li atoms are filled into this new phase. But the repulsion of denser Li causes an increase in Li adsorption energy. As we infer before that 1×1×1-Li₄ is the state of maximum Li storage, for a 2×2×2 T-carbon cell the maximum is Li₃₂ (Fig. 2(d)). MD simulation confirms the structural stability of 2×2×2-Li₃₂ (Supplementary Movie 2), with the evolution of temperature and total energy always fluctuate near the average values (Fig. 2(e)). A full energy spectrum for Liₙ with \( n = 1 \sim 32 \) is obtained by Monte Carlo simulations (Fig. 2(f)). It can be seen that the most stable structure of Li₁₆ has the
lowest energy, while the most stable energies of both sides Li_{1} and Li_{32} are high. In a complex energy spectrum, we mainly concern about the lowest energy structure of every Li_{n}. The phases of Li_{n1} (with an energy $E(n_1)$) and Li_{n2} (with an energy $E(n_2)$) may mix with ratios $f$ and $1-f$, and the average energy per formula is

$$E = fE(n_1) + (1 - f)E(n_2).$$

In comparison with the structure of Li number $n = fn_1 + (1 - f)n_2$, if $E(n)$ is lower than $E$, the structure of Li_{n} would be the actually formed phase in the evolution of the T-carbon anode. However, in Fig. 2(f) the structures between Li_{1} and Li_{16} all have high energy than $E$ (see the red line). So, we infer that in the realistic charging process, the anode would be composed of the mixture of Li_{1} and Li_{16}. Similarly, the structures between Li_{16} and Li_{32} all have high energy than the average energy of Li_{16} and Li_{32} ($f': 1 - f$). So in the subsequent charging process, the anode would be composed of the mixture of Li_{16} and Li_{32}.

### 3.3 Anode potential of Li-loaded T-carbon

In this section, we will estimate the electrode potential of T-carbon serving as the anode of Li battery. Generally, the ideal maximum electrode potential can be estimated by the change of Gibbs free energy in the process. In the last section, we infer that in the charge or discharge process, the phases 2×2×2-Li_{1} and 2×2×2-Li_{16} (or 2×2×2-Li_{16} and 2×2×2-Li_{32}) could coexist. For a phase 2×2×2-Li_{n2} changing into 2×2×2-Li_{n1} during discharge, the reaction on the side of the T-carbon anode is

$$2×2×2-Li_{n2} \rightarrow 2×2×2-Li_{n1} + (n_2 - n_1) \text{Li}^+ + (n_2 - n_1) \text{e}.$$  

Generally, the electrode potential is measured relative to Li bulk. If Li bulk is taken as the cathode, the reaction is

$$\text{Li}^+ + \text{e} \rightarrow \text{Li} \text{ (bulk)}.$$  

The change of Gibbs free energy in the whole process $2×2×2-Li_{n2} \rightarrow 2×2×2-Li_{n1} + (n_2 - n_1) \text{Li (bulk)}$ is then

$$\Delta G = G(2×2×2-Li_{n1}) + (n_2 - n_1) G(\text{Li bulk}) - G(2×2×2-Li_{n2}).$$
then reads \( V = \Delta G/e \) (\( e \) is the elementary charge).

![Images of structural models and graphs](image-url)

**Fig. 2** The most stable structure of 2×2×2 T-carbon cell with (a) Li\(_1\), (b) Li\(_8\), (c) Li\(_{16}\), and (d) Li\(_{32}\). (e) The evolution of temperature and total energy in the MD simulation of 2×2×2 T-carbon cell with Li\(_{32}\) at 300 K. (f) The energy spectrum and convex hull of 2×2×2 T-carbon cell with Li\(_n\). (g) The anode voltage of T-carbon as the anode of Li battery.

The discharge of T-carbon anode can be generally divided into three stages,

\[
2\times2\times2-\text{Li}_{32} \rightarrow 2\times2\times2-\text{Li}_{16} + 16\text{Li}^+ + 16e, \tag{6}
\]

\[
2\times2\times2-\text{Li}_{16} \rightarrow 2\times2\times2-\text{Li}_{1} + 15\text{Li}^+ + 15e, \tag{7}
\]

and

\[
2\times2\times2-\text{Li}_{1} \rightarrow \text{T-carbon} + \text{Li}^+ + e. \tag{8}
\]

In the calculation result (Fig. 2(g), \( x(\text{Li}) = 0 \sim 0.5 \) is the ratio of Li:C), we can see that the anode voltages of these three stages are very different. Since the Li adsorption
energy $E_{ad}$ in $2\times2\times2$-Li$_{16}$ is much lower than the $E_{ad}$ in $2\times2\times2$-Li$_{32}$, the process (6) is easy to proceed with because the energy goes down. This leads to a lower anode voltage. When the discharge reaches a certain degree, process (7) occurs thereupon. Since the $E_{ad}$ in $2\times2\times2$-Li$_{1}$ is much higher than the $E_{ad}$ in $2\times2\times2$-Li$_{16}$, the process (7) is difficult to proceed and then the anode voltage increases. The anode voltage of the first stage (6) is close to the anode voltage of graphite anode (about 0 V). But the voltage of the second stage (7) is too high. Therefore, we infer that (7) is disadvantageous to Li battery. The exploitable part is (6), in which the Li load is $x(Li) = 0.25 \sim 0.50$. Only a half of Li storage in T-carbon could be usable for battery discharge. Regarding $2\times2\times2$-Li$_{16}$ as substrate, the maximum load (16 more Li within) corresponds to a Li capacity of 487 mAh/g, which is about 1.3 times the capacity of graphite.

3.4 Electronic structure and the conductivity

To use T-carbon as the anode of Li battery, the electronic conductivity should be paid attention to. The widely used graphite is conductive, but pure T-carbon is a semiconductor with weaker conductivity. Li loading may enhance the conductivity of T-carbon. To investigate the effect of Li, we calculate the projected density of states (PDOS). In $2\times2\times2$-Li$_{1}$, Li bonds with C atoms and a part of Li electrons fill into C 2$p$ orbitals (Fig. 3(a)). This leads to an energy level broadening near the Fermi level, and make some contribution to conductivity. A doping level locates at about 1 eV above the Fermi level. With more Li atoms filling into T-carbon, more electrons of Li fill into C 2$p$ orbitals. At the maximum of Li loading, i.e. $2\times2\times2$-Li$_{32}$, the extra electrons just fill a whole band, and a new small bandgap appears at the Fermi level (Fig. 3(b)). There should gradually exhibit a change between the case of Li$_{1}$ and Li$_{32}$, which is discussed in the following text.
The electronic conductivity of bulk materials depends on electron-phonon relaxation and the electronic distribution in the bands. The conductivity tensor reads

\[
\sigma = \frac{e^2}{4\pi^2} \tau \int \langle \hat{V} \hat{V} \rangle \nabla \hat{V} \cdot \hat{v} \, dE_k, \tag{9}
\]

where \( E \) is the electron energy, \( \tau \) is the electron-phonon relaxation time, \( \hat{V} = \partial E / \hbar \partial \hat{k} \) is the electron velocity, and \( f = 1 / (1 + \exp[(E-E_F)/k_B T]) \) is the Fermi-Dirac distribution. We know that \( \partial f / \partial E \) is a delta-like function that is sharp near the Fermi energy \( E_F \).

In Fig. 4, we plot the density of states (DOS) in \( 2\times2\times2-\text{Li}_n \) along with the outline of function \( \partial f / \partial E \) at \( T = 300 \) K. For \( 2\times2\times2-\text{Li}_1 \) and \( 2\times2\times2-\text{Li}_8 \) (Fig. 4(a) and (b)), the contribution of DOS in the peak of \( \partial f / \partial E \) is small, and the conductivity would be low. For \( 2\times2\times2-\text{Li}_{16} \) and \( 2\times2\times2-\text{Li}_{24} \) (Fig. 4(c) and (d)), DOS in the peak of \( \partial f / \partial E \) is much larger and the conductivity would be higher. For \( 2\times2\times2-\text{Li}_{32} \), since the electrons of Li fill a whole hand, a gap forms near the Fermi energy and the electronic structure is semiconducting (a bandgap of 0.30 eV). The electron and hole density in the intrinsic semiconductor are

\[
n = \int_{\text{conduction band}} f \cdot \text{DOS}(E) dE \tag{10}
\]

and

\[
p = \int_{\text{valence band}} (1-f) \cdot \text{DOS}(E) dE, \tag{11}
\]
respectively. The calculated full carrier density $n+p$ in $2\times2\times2$-$\text{Li}_{32}$ is $2.2\times10^{17}$ cm$^{-3}$. Such a high carrier density ensures $2\times2\times2$-$\text{Li}_{32}$ to be conductive. Overall, we infer that Li-rich T-carbon has enough carriers for the anode of the Li battery to be conductive.

\[ \text{Fig. 4} \] DOS of $2\times2\times2$ T-carbon cell with (a) Li$_{1}$, (b) Li$_{8}$, (c) Li$_{16}$, (d) Li$_{24}$, (e) Li$_{32}$. Some parts are enlarged in (f). The red curves outline the function $-\partial f / \partial E$ ($f$ is the Fermi-Dirac distribution function at 300 K).

To investigate the ionic conductivity, the migration barriers of Li in T-carbon are investigated. In the initial charging process, low-concentration Li atoms form the $2\times2\times2$-$\text{Li}_{1}$ phase, in which Li atoms can wander in the free space of T-carbon. Fig. 5(a) exhibits the migration process of Li atom from one adsorption site to the neighboring site. The migration barrier $E_b$ (Li$_{1}$) = 0.13 eV is smaller than the Li diffusion barrier on pristine graphene (about 0.3 eV)$^{46, 47}$, graphene with a point defect (about 0.4 ~ 0.5 eV)$^{46}$ and graphite (about 0.5 eV)$^{48}$. This promises a faster Li diffusion in T-carbon.

In the final charging process, the system is saturated with Li (the $2\times2\times2$-$\text{Li}_{32}$ phase). Thus, we consider the Li migration in the state of $2\times2\times2$-$\text{Li}_{31}$ which is close to the saturation. Since $2\times2\times2$-$\text{Li}_{31}$ is less filled than $2\times2\times2$-$\text{Li}_{32}$, in $2\times2\times2$-$\text{Li}_{31}$ a Li atom can migrate to a nearing vacancy. Such processes successively proceed, and then the Li atoms migrate. In $2\times2\times2$-$\text{Li}_{31}$, a Li atom is affected by other Li in all directions, and the chemical environment is more isotropic. So, the Li migration barrier in $2\times2\times2$-$\text{Li}_{31}$ $E_b$ (Li$_{31}$) = 0.02 eV (Fig. 5(b)) is much lower than in T-carbon with low-concentration Li.
In Li-filled T-carbon, the easier migration is beneficial to charging and discharging at high Li density. As the anode of Li ion battery, T-carbon is better than graphite with faster Li ion migration.

![Image]( LIC123.png)

**Fig. 5** The migration barrier of Li atom in 2×2×2 T-carbon cell with (a) Li$_1$ and (b) Li$_{31}$. The migratory Li atom is shown in yellow.

**IV. Conclusion**

The combination of T-carbon and Li is systematically studied by DFT calculations and Monte Carlo simulations. T-carbon could serve as Li storage and Li ion battery anode. Possible energy-favorable phases are C$_{64}$Li, C$_{64}$Li$_{16}$ and C$_{64}$Li$_{32}$. The maximum Li capacity is 1116 mAh/g. The T-carbon-Li system prefers to form the mixture of these stable phases rather than other unstable phases. In the discharge process of the T-carbon anode, the transition C$_{64}$Li$_{32}$ → C$_{64}$Li$_{16}$ → C$_{64}$Li causes a significant change in anode potential due to the difference of Li adsorption energy on these phases. The anode potential of the first stage C$_{64}$Li$_{32}$ → C$_{64}$Li$_{16}$ + 16Li$^+$ + 16e is close to the anode potential of graphite anode, while the anode potential of the second stage C$_{64}$Li$_{16}$ → C$_{64}$Li + 15Li$^+$ + 15e is high and disadvantageous to Li battery. This leads to a “dead zone” that only half of Li capacity could be usable (with an effective capacity of 487 mAh/g). Li storage in T-carbon contributes extra electrons into C $\pi_{2p}$ orbitals and ensures its conductivity serving as an anode. Out work may provide guidance to future study on the electrodes of Li, Na or K ion battery in emerging energy applications.
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Conflict of Interest

The authors declare that they have no conflict of interest.

Data Availability

The raw/processed data required to reproduce these findings cannot be shared at this time as the data also forms part of an ongoing study.

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