Supporting Information for

Tetragonal C$_{24}$: A Topological Nodal-surface Semimetal with Potential as an Anode Material for Sodium Ion Batteries

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Table S1. Lattice parameters ($a$, and $c$, in Å) and relative energies with respect to graphite ($\Delta E$, in eV/atom) for tC$_{24}$, diamond, and graphite calculated using different exchange-correction functionals.

<table>
<thead>
<tr>
<th>Methods</th>
<th>tC$_{24}$</th>
<th>Diamond</th>
<th>Graphite</th>
</tr>
</thead>
<tbody>
<tr>
<td>$a$</td>
<td>11.30</td>
<td>2.53</td>
<td>2.47</td>
</tr>
<tr>
<td>PBE</td>
<td>$c$</td>
<td>2.47</td>
<td>2.53</td>
</tr>
<tr>
<td>$\Delta E$</td>
<td>0.22</td>
<td>0.13</td>
<td>0.00</td>
</tr>
<tr>
<td>$a$</td>
<td>11.29</td>
<td>2.52</td>
<td>2.46</td>
</tr>
<tr>
<td>PBE-D2</td>
<td>$c$</td>
<td>2.47</td>
<td>2.52</td>
</tr>
<tr>
<td>$\Delta E$</td>
<td>0.24</td>
<td>0.03</td>
<td>0.00</td>
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</table>
Figure S1. Total energy as a function of volume per atom for tC\textsubscript{24} in comparison with graphite, diamond, IGN-C\textsubscript{6}, bct-C\textsubscript{40}, bct-C\textsubscript{16}, T-carbon and tC\textsubscript{8}.

Figure S2. (a) Phonon dispersion of tC\textsubscript{24}. (b) Total energy fluctuation during the AIMD simulation at 300 K.

Table S2. Independent elastic constants (C\textsubscript{ij}), Young’s moduli (E\textsubscript{x,y,z}), bulk moduli (B), shear modulus (G) and total Young’s moduli (E) of tC\textsubscript{24}, tC\textsubscript{8} and diamond. (Unit: GPa)

<table>
<thead>
<tr>
<th></th>
<th>tC\textsubscript{24}</th>
<th>tC\textsubscript{8}</th>
<th>Diamond</th>
</tr>
</thead>
<tbody>
<tr>
<td>C\textsubscript{11}</td>
<td>192.81</td>
<td>566.07</td>
<td>1048.14</td>
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<tr>
<td></td>
<td>$C_{33}$</td>
<td>$C_{44}$</td>
<td>$C_{66}$</td>
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<td>---------</td>
<td>---------</td>
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<tr>
<td></td>
<td>678.33</td>
<td>142.20</td>
<td>14.20</td>
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<tr>
<td></td>
<td>894.34</td>
<td>224.84</td>
<td>16.12</td>
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<td></td>
<td></td>
<td></td>
<td>560.53</td>
</tr>
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Because of its 1D channel structure along the $c$ direction, the mechanical properties of tC$_{24}$ are highly anisotropic. We plot the polar diagrams of Young’s modulus ($E(\theta)$) along $ab$ and $ac$ plane in Figure S3(a) and (b). The Young’s modulus of tC$_{24}$ along $a$ direction is equal to that along the $b$ direction due to its tetragonal symmetry. Besides, the smallest value exactly appears in $a$ and $b$ direction, while the largest Young’s modulus of tC$_{24}$ occurs in the $c$ direction, which is much larger than those along the $a$ and $b$ directions. On account of the identical tetragonal crystal symmetry and 1D channel framework between tC$_8$ and tC$_{24}$, the Young’s modulus of the tC$_8$ structure along the $a$ direction is also equal to that along the $b$ direction, and the largest Young’s modulus of tC$_8$ occurs in the $c$ direction, which is same as that in tC$_{24}$. The smallest value of tC$_8$ appears in the angular bisectors of $a$ and $b$ direction, which is different from tC$_{24}$. In addition, according to Voigt-Reuss-Hill approximation [1], the average bulk modulus ($B$), shear modulus ($G$) and Young’s modulus ($E$) of tC$_{24}$ are calculated to be 149.27, 70.65 and 72.62 GPa, respectively. These values are significantly smaller than those of diamond and also less than those of tC$_8$ (see Table
S2), which can be attributed to the more porous structure of tC$_{24}$ than that of tC$_8$. According to the criterion proposed by Pugh, the ratio of shear to bulk modulus ($G/B$) can be used to evaluate the brittle character of the material, if the value is less than 0.57 [2]. In this respect, $G/B$ value of tC$_{24}$ is 0.47, indicating it is ductile and external strain can be applied to it easily.

Figure S3. The projections of Young’s modulus $E(\theta)$ for tC$_{24}$ (a) along the $ab$ plane, (b) along the $ac$ plane. And $E(\theta)$ for tC$_8$ (c) along the $ab$ plane, (d) along the $ac$ plane.
Figure S4. Band structure and PDOS of tC₈.

Figure S5. Electronic band structure of the tC₂₄ optimized using the (a) PBE and (b) PBE-D2 methods, respectively. The band structures are calculated by using the HSE06 functional.
Figure S6. Band structure of tC$_{24}$ when considering SOC. Right panel: the amplified band structure.

Estimate the maximum capacity

During the charging process of the anode, sodium would be continuously absorbed in the tC$_{24}$ structure until the chemical potential of Na on the anode ($\mu_{Na-tC_{24}}$) equals to that of Na metal ($\mu_{Na}$), which requires:

$$\mu_{Na-tC_{24}} \leq \mu_{Na} \quad (1)$$

The chemical potential of Na on tC$_{24}$ equals to:

$$\mu_{Na-tC_{24}} = \left( \frac{\partial G}{\partial N_{Na}} \right)_{T,P,N_e} \quad (2)$$

where $G = E + PV - T$. If we ignore PV and TS, it can be written as:

$$\mu_{Na-tC_{24}} = \left( \frac{\partial E_{Na-tC_{24}}}{\partial N_{Na}} \right)_{T,P,N_e} \quad (3)$$

Combing the above equations, the sodium charging process requires:

$$\left( \frac{\partial E_{Na-tC_{24}}}{\partial N_{Na}} \right)_{T,P,N_e} < \mu_{Na}$$
Here, we define formation energy \( (E_f) \) as the following:

\[
E_f = E_{\text{Na}_x \text{tC}_{24}} - E_{\text{tC}_{24}} - x\mu_{\text{Na}} \quad (5)
\]

Finally, Eq.4 and Eq.5 gives:

\[
\left( \frac{\partial E_f}{\partial N_{\text{Na}}} \right)_{T,P,N_t} < 0 \quad (6)
\]

Therefore, the sodium loading process requires the slope of the formation energy curve to be negative. The maximum amount of adsorbed Na corresponds to the concentration at which the slope of the formation energy curve becomes positive. Given that H2, H3, H5 are the stable adsorption sites for Na atom with negative binding energies of -0.47, -0.89 and -1.09 eV, respectively, and among which H5 site is energetically the most favorable binding site, sodium atoms would first occupy the most stable adsorption site H5, then the second stable adsorption site H3 and finally the least stable site H2. We can then determine the maximum Na intercalation capacity. We note that after Na atom are absorbed on H2 site, the slope of formation energy curve becomes positive, as shown in Figure S7, suggesting the stoichiometric formula of maximum Na-intercalated tC_{24} is Na_5C_{48}. This corresponds to the specific capacity of 232.65 mAh/g and the geometry of maximum Na-intercalated tC_{24} is displayed in Figure S8.

![Figure S7. Formation energy of sodiated tC_{24}.](image)
Figure S8. (a) Top and (b) side views of the fully Na-intercalated geometries of tC$_{24}$.

Figure S9. (a) The considered migration path that interpenetrating through the carbon hexagon ring and (b) the corresponding diffusion energy barrier profile of Na diffusion in tC$_{24}$. The yellow and brown spheres represent sodium and carbon atoms, respectively.
Figure S10. Geometries of the four stable intermediate Na$_{5x}$C$_{48}$ phases (x=0.1, 0.3, 0.4, 0.5).

Figure S11. Total DOS of Na$_{5x}$C$_{48}$ at different Na concentration.
Figure S11 gives the total density of states (TDOS) of fully Na-inserted tC24 and intermediate Na5xC48 phases (x= 0.1, 0.3, 0.4 and 0.5), which shows that the metallicity of the anode is maintained and a good electrical conductivity is ensured during the sodiation/desodiation process.

Figure S12. (a) Phonon dispersion of tC24 with vdW corrections. (b) Total energy fluctuation during the AIMD simulation at 300 K calculated with vdW corrections.

Table S3. Independent elastic constants $C_{ij}$ of tC24 with vdW corrections.

<table>
<thead>
<tr>
<th></th>
<th>$C_{11}$</th>
<th>$C_{33}$</th>
<th>$C_{44}$</th>
<th>$C_{66}$</th>
<th>$C_{12}$</th>
<th>$C_{13}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Value</td>
<td>193.99</td>
<td>682.87</td>
<td>143.07</td>
<td>10.35</td>
<td>172.27</td>
<td>46.24</td>
</tr>
</tbody>
</table>

Unit: GPa