Cluster-Inspired Design of High-Capacity Anode for Li-Ion Batteries

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Supporting Information

ABSTRACT: One of the greatest challenges in next-generation Li-ion batteries (LIB) is to develop high charge capacity anodes with long cycle life. Inspired by the experimental observation of a magic Ti13C22 cluster and its layer-by-layer growth, we have constructed one-dimensional nanowires using Ti6C13 clusters as well as those based on planar-tetracoordinate carbon-containing (ptC) Ti8C12 metcar and TiC clusters with bulk cubic crystal structure. Using density functional theory and molecular dynamics we studied their energetic and thermal stability as well as their potential for LIB anode. The Ti6C13 nanowire is found to be stable up to 2500 K and has a charge capacity five times larger than that of the graphite anode being used today. Furthermore, unlike silicon nanotube anode materials, the Ti6C13 nanowire does not suffer from volume expansion/contraction during lithiation/delithiation processes.

Rechargeable batteries are an indispensable part of modern society. Because of their several attractive properties, Li-ion batteries (LIB) have been the preferred choice for portable electronics, transportation, and energy storage devices. However, to meet future demand, considerable material challenges must be overcome to produce the next-generation LIB.1-3 Among these is the development of anodes with increased capacity, power density, cycle life, and safety. Because of stability and low cost,4 graphite-based materials are widely used for anode material,4 but their low specific capacity (372 mAh g−1) and poor cycle life limit further applications.5,6 Recent developments of one-dimensional (1D) materials such as 1D carbon and silicon nanotubes provide promising choices. For example, silicon nanotubes offer a high theoretical charge capacity of 4200 mAh g−1, which is 11 times higher than that of the graphite anodes. Unfortunately, silicon expands volumetrically by up to 400% on full lithiation and contracts significantly with delithiation,1 creating stability issues. In addition, unstable solid electrolyte interphase limits the cycle life of silicon anodes to a few hundred cycles. Recently, Cui and co-workers7 designed a silicon nanotube anode coated with an ion-permeable silicon oxide shell that substantially improves cycle life while retaining more than 85% of its initial capacity. The coating layer also prevents the silicon nanotube from expanding outward. However, it will be ideal if one can develop high-capacity anode material, without a coating layer, that does not suffer from expansion and contraction during lithiation—delithiation processes.8

In the past, most 1D LIB anodes such as single-walled carbon, silicon, and germanium nanotubes were known to grow along the nanotube direction,9 and no 1D carbon-based structures that grow with a layer-by-layer process are known. In this Letter we discuss the design of such an anode composed of Ti and C. We drew inspiration from an early experiment by Wang and Cheng10 who observed an intense peak of the Ti8C12−x metcar and TiC clusters with bulk cubic crystal structure. Clusters with such pronounced stability are referred to as magic clusters and have been considered as building blocks of a new class of cluster assembled materials.11,12 A classic example of such materials is C60 fullerene.13 We wondered if it is possible to create a nanowire based on the Ti13C22 cluster motif. We recall that Ti6C13 clusters date back to the early 1990s when Castleman and co-workers14 observed an intense peak corresponding to Ti6C13 in the mass spectra of TiC metcar clusters.14 They termed this magic cluster “metcar” and proposed that it can be used as building blocks of cluster-assembled materials, just as fullerenes are created by assembling C60 fullerences. Successive experiments on other transition metal carbide clusters have observed the magic peak corresponding to Ti6C13 in the mass spectra of TiC metcar clusters.15 However, materials with Ti8C12 as building blocks have not yet been realized, and later studies showed that metcars are reactive and tend to coalesce.16 The
structure of metcars has been a topic of debate in the literature. Observation of very stable Ti$_{11}$C$_{13}$ magic clusters$^{19,20}$ suggested the existence of a cubic structure reminiscent of the cubic structure of TiC crystal. Wang and Cheng$^{10}$ addressed this issue of cagelike or cubiclike structure of transition-metal carbide clusters using photoelectron spectroscopy when they observed a bimodal distribution of Ti$_x$C$_y$ anion clusters with a pronounced peak in the spectrum at Ti$_{13}$C$_{22}^-$. Using density functional theory (DFT), they calculated the geometry of this cluster to be an ABA layered structure (see Figure 1a) where the A layer (Ti$_4$C$_9$) is formed with C$_2$ dimers at the cube corners, Ti atoms at the edge centers, and a lone C atom at the face-center. The B layer is composed of Ti$_8$C$_{12}$ with four Ti atoms occupying cube corner sites and the fifth Ti at the face-center site while the four C atoms occupy edge centers. The validity of this structure was confirmed by comparing the calculated photoelectron spectra with their experimental result. The authors further showed that such a layer-by-layer growth involving C$_2$ dimers can explain all the magic numbers in a TiC crystal. This feature may be important for further device application because it has advantage over other 1D LIB anodes composed of carbon and silicon nanotubes which need to be attached covalently to base sheets to form seamless structures.$^{22}$ The Ti$_9$C$_{13}$ nanowire has no such requirement because it can grow on the TiC surface. We have calculated the cohesive energy of 1D Ti$_9$C$_{13}$ nanowire and compared it with other Ti and C binary compounds, such as 1D Ti$_8$C$_{12}$ nanowire, Ti$_{13}$C$_{22}$ cluster, Ti$_{12}$C$_{12}$ cluster, and TiC bulk. We found 1D Ti$_9$C$_{13}$ nanowire to be energetically favorable over Ti$_{12}$C$_{12}$ cluster which has been observed in experiment (see Figure 1b). Details of our results are given in section I of the Supporting Information.

The phonon bands and density of states (DOS) given in Figure S1a confirm that the Ti$_9$C$_{13}$ nanowire is dynamically stable. We also carried out molecular dynamics (MD) simulations to further study the stability of Ti$_9$C$_{13}$ nanowire at elevated temperatures and found it to be stable at 2500 K. The results are given in section III, Figure S1b of the Supporting Information. On the basis of the phonon spectrum, we found that 1D Ti$_9$C$_{13}$ nanowire exhibits large heat capacity and possesses a high Debye temperature; details are given in section IV, Figure S2 of the Supporting Information.

We next studied the electronic properties of Ti$_9$C$_{13}$ nanowire by calculating its electronic band structure. To get an accurate description of the band gap we used the HSE06 functional.$^{23,24}$ The results are plotted in Figure 2a. Note that the Ti$_9$C$_{13}$ nanowire is metallic, which is further confirmed by orbital analysis. Energy bands near the Fermi level are dominated by Ti-3d states, while the C-2s and 2p make only a small contribution to the observed metallic behavior. For more details, we project the DOS onto the atomic orbitals of the Ti and C atoms. The electronic states near the Fermi level are

Figure 1. (a) Geometry of Ti$_9$C$_{13}$ with its perspective view. Layers A and B represent different layers; C$_1$, C$_2$, C$_3$, Ti$_1$, Ti$_2$, and Ti$_3$ represent different nonequivalent atoms sites. (b) Cohesive energy of binary compounds with composition Ti$_x$C$_{1-x}$. The solid line links the cohesive energies of graphene (x = 0) and bulk Ti (x = 1). Formation energy, $\delta F$, is positive (negative) above (below) the solid line.
mainly contributed by Ti 3d orbitals, while the hybridized C 2p and Ti 3d states are mainly distributed in the energy range from −1.5 to −2.5 eV, below the Fermi level. The electronic structure was further studied by calculating the electron localization function (ELF) of Ti9C13 nanowire. Slices parallel to the y-axis crossing Ti atoms and those along the z direction crossing C atoms and Ti atoms in Figure 1 are plotted in panels c and d of Figure 2, respectively. ELFs in the regions near Ti1, Ti2, C1, and C2 atoms are delocalized, while those on Ti3 and C3 atoms are localized.

Having illustrated the origin of metallic behavior in the Ti9C13 nanowire, we extended this study by removing both C3 and Ti3 atoms in the unit cell to examine the stability and metallic behavior of Ti8C12 in the 1D phase. The corresponding structure of Ti8C12 nanowire is shown in Figure 3f; there are 8 titanium and 12 carbon atoms in the primitive cell. Analogous to the metcar (Ti8C12) cluster,2 Ti8C12 nanowire shows chemical stability, and the binding energy of Ti8C12 nanowire is 5.21 eV per formula unit (0.261 eV per atom) lower than the that of Ti8C12 cluster (Td) shown in Figure 1b. Phonon spectra in Figure 3a confirm that 1D Ti8C12 nanowire is also dynamically stable. The high-frequency mode of Ti8C12 due to C3 atoms is at 1700 cm−1 lower than that in Ti9C13. A parallel study of the electronic structure reveals that the Ti8C12 is also metallic, as seen in Figure 3b, and the bands near the Fermi Level are mainly contributed by Ti 3d orbitals. Ti 3dxy and 3dx2−y2 orbitals mainly contribute to the metallic bands near the Fermi level. The ELF analyses shown in Figure 3c–e confirm that the delocalized charges come from Ti1, Ti2, C1, and C2 atoms. Because there are no Ti3 atoms, all the C1 atoms become planar-tetracoordinated carbon, a concept put forth by Hoffmann et al. in 1970.25 Subsequent bonding rules proposed by Boldyrev and co-workers in 199126 and further developed by

**Figure 2.** (a) Band structure and partial density of states (PDOS) of the Ti9C13 structure, with size of circles denoting the contribution from Ti and C, respectively. The high-symmetry k point path is Γ(0,0) → X(1,0). (b) Slices of ELF of the Ti9C13 panels are viewed from the y direction; (c, d) two different layers from the z direction.

**Figure 3.** (a) Phonon dispersion and DOS of the Ti8C12 structure, (b) band structure and PDOS of the Ti8C12 nanowire, with size of circles denoting the contribution from Ti and C, respectively. The high-symmetry k point path is Γ(0,0) → X(1,0). (c) Slices of ELF of the Ti8C12 panels are viewed from the y direction; (d, e) two different layers from the z direction. (f) Geometry of Ti8C12 nanowire.
Figure 4. (a) Three optimized configurations of the Li-adsorbed Ti$_9$C$_{13}$ nanowire (Ti$_{18}$C$_{26}$Li) and their relative energies with respect to the lowest-energy configuration Li$_i$. (b) Considered migration paths of Li diffusion on the Ti$_9$C$_{13}$ nanowire and (c) the corresponding diffusion energy barrier profiles.

Boldyrev and Wang in 2001$^{27}$ contributed greatly to the theoretical design of ptC molecules. Extended ptC systems have attracted much attention recently; however, nearly all of the predictions correspond to 2D materials, such as B$_2$C graphene$^{28}$ and its analogue Al$_2$C.$^{29,30}$ No 1D nanowire built from ptC-network has yet been studied. Bader charge analysis of our predicted 1D Ti$_9$C$_{13}$ nanowire shows that the charges on C$_1$, C$_2$, Ti$_1$, and Ti$_3$ are 5.27, 4.75, 2.81, and 2.51$e$, respectively, and the charge on C$_2$ is less than that of imperfect ptC atom (5.60) in 2D TiC sheet. Thus, Ti$_9$C$_{13}$ may be suitable as a LIB anode. While 2D metcars have been studied both theoretically$^{37}$ and experimentally$^{38}$ as candidates for LIB anode materials,$^{39-42}$ the potential of 1D metcars as LIB anodes remains to be demonstrated.$^{41}$

Considering that Ti$_9$C$_{13}$ nanowires are stable and possess a higher concentration of light atoms, we can expect it to have a large Li storage capacity. In the following, we systematically explore the potential of the Ti$_9$C$_{13}$ nanowire as a Li ion battery anode material by studying the Li adsorption and diffusion behavior as well as their relative electrochemical properties.

To determine the preferable adsorption site of Li on Ti$_9$C$_{13}$ nanowire, we created a supercell by doubling its size and depositing one Li atom on different adsorption sites. This corresponds to a supercell with chemical stoichiometry of Ti$_{18}$C$_{26}$Li. Three typical adsorption configurations (labeled as Li$_i$, Li$_{ii}$, and Li$_{iii}$) with high structural symmetry are considered, as shown in Figure 4a. We relaxed these configurations and calculated their total energies. Here, Li$_i$ is the hollow site formed by three neighboring carbon atoms, Li$_{ii}$ the hollow site formed by two neighboring carbon atoms, and Li$_{iii}$ the bridge site of the C$_2$ dimer. Full geometry optimizations and total energy calculations are performed to identify their relative stability. Li$_i$ is found to be the lowest-energy configuration which lies 0.316 and 0.093 eV lower than those of Li$_{ii}$ and Li$_{iii}$ sites, respectively. This suggests that Li atom prefers to occupy the Li$_i$ configuration. Each adsorbed Li atom transfers 0.88 electrons to the neighboring C atoms, according to Bader charge analysis. The energy of the structure where Li is intercalated inside the Ti$_9$C$_{13}$ nanowire is 0.738, 0.422, and 0.645 eV higher than that of the Li$_i$, Li$_{ii}$, and Li$_{iii}$ configuration in Figure 4a, respectively, making it unlikely that Li can reside in the interior of the nanowire.

To evaluate the potential application of the Ti$_{18}$C$_{26}$Li as an anode material for LIB, we investigate the possible diffusion paths of Li atom on its surface and their corresponding energy barriers. We considered four trial diffusion paths that connect the two neighboring most preferable Li adsorption sites with high structural symmetry, as indicated in Figure 4b. Pathway IV, which depicts a spiral diffusion route, is found to have the lowest diffusion barrier of 0.35 eV (Figure 4c). The magnitude of the energy barrier is less than half of those in carbon nanotubes and silicon nanotubes.

After investigating the adsorption site and the migration path, we studied the adsorption of Li with high concentration. For application, the storage capacity of electrode materials is the key indicator of battery performance. Hence, the average adsorption energies are calculated to investigate the storage capacity of Li on nanowires. We first increased the concentration of Li by depositing a single layer of Li atoms on the surface of the nanowire, leading to a stoichiometry of Ti$_9$C$_{13}$Li$_{20}$. The average adsorption energy for each Li ion in this situation is 0.98 eV. We then introduced a second layer of Li on the surface of the Ti$_9$C$_{13}$Li$_{20}$. The average adsorption energy corresponding to a chemical composition of Ti$_{18}$C$_{26}$Li$_{36}$ was found to be 0.86 eV for each Li ion. This value is the same as that in the 2D Li ion battery.$^{38,39}$ Here, we see that the Ti$_9$C$_{13}$ nanowire has high Li storage capacity yet does not suffer volume expansion during lithiation (details are given in section V in the Supporting Information). This is different from silicon nanotube anodes where 400% volume expansion was noted after full lithiation.$^7$

We next calculated the average open-circuit voltage (OCV) as a function of Li coverage and the theoretical Li specific capacity, which are important electrochemical properties for an electrode material. Details of these calculations are given in section VI in the Supporting Information. For single-layer...
adsorption, the estimated OCV is 0.980 V and theoretical capacity is calculated to be 525 mAh·g⁻¹. When second-layer adsorption is considered, the OCV and the theoretical specific capacity of Ti₉C₁₃Li₅₆ are 0.858 V and 1542 mAh·g⁻¹ (in Table 1), respectively. The later value is five times larger than that of the graphite anode currently used in LIB.

Table 1. Comparison of Specific Capacity, Diffusion Barrier, OCV, and Volume Expansion of Candidate Anode Materials for Li Ion Battery

<table>
<thead>
<tr>
<th>Material</th>
<th>Specific Capacity (mAh/g)</th>
<th>Diffusion Barrier (eV)</th>
<th>OCV (V)</th>
<th>Volume Expansion</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ti₉C₁₃</td>
<td>1542</td>
<td>0.35</td>
<td>0.86</td>
<td>no</td>
</tr>
<tr>
<td>TiC nanowire</td>
<td>1019</td>
<td>1.13</td>
<td></td>
<td>no</td>
</tr>
<tr>
<td>C nanotube</td>
<td>515.4</td>
<td>450.4</td>
<td>10.12</td>
<td>yes</td>
</tr>
<tr>
<td>Si nanotube</td>
<td>1961.5</td>
<td>3247.35</td>
<td>1.41</td>
<td>yes</td>
</tr>
<tr>
<td>Ge nanotube</td>
<td>1384.50</td>
<td>963.54</td>
<td>1.70</td>
<td>yes</td>
</tr>
<tr>
<td>TiO₂ wire</td>
<td>275.52</td>
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</tr>
<tr>
<td>Ti₃C₂ metcar</td>
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<td>410.41</td>
<td>0.07</td>
<td>no</td>
</tr>
<tr>
<td>graphite</td>
<td>372.44</td>
<td>372</td>
<td>0.2</td>
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</tr>
</tbody>
</table>

We also calculated the structure, stability, and properties of 1D TiC nanowire using a cluster motif that mimics its bulk cubic structure. Note that recently PbS clusters were found to grow with the geometry reminiscent of its bulk structure. The cubic TiC nanowire is energetically nearly degenerate with that based on the Ti₉C₁₃ motif discussed before. The details of our results on cubic TiC nanowire are given in sections V and VI of the Supporting Information. The calculated LIB specific capacity of the cubic TiC nanowire is 1019 mAh·g⁻¹, which is smaller than that in the Ti₉C₁₃ nanowire.

In conclusion, inspired by the experimental observation of layered growth of Ti₉C₁₃ clusters, we carried out systematic studies of the equilibrium geometry and stability of 1D nanowires based on Ti₉C₁₃, Ti₈C₁₂, and cubic TiC cluster motifs. We also examined the potential of the Ti₉C₁₃ nanowire as an effective anode material for Li-ion batteries. The following are the major conclusions of our Letter: (1) While all the above nanowires were found to be dynamically stable, not only was Ti₉C₁₃ nanowire found to be more stable than its cluster analogues as well as that constructed from a Ti₈C₁₂ metcar motif, but also it is thermally stable up to 2500 K. (2) Ti₉C₁₃ exhibits metallic properties and high heat capacity. (3) To the best of our knowledge, Ti₉C₁₃ nanowire is the first planar-tetracoordinated carbon (ptC)-containing 1D nanowire with metallic properties. (4) Compared to other carbon and silicon nanotube-based anodes for Li ion batteries, not only does the Ti₉C₁₃ nanowire offer great advantage, but also, due to lattice matching, it can grow seamlessly on TiC surface. (5) Unlike carbon and silicon nanotube anodes, there is no thermal expansion/contraction following lithiation/delithiation. In addition, the specific capacity of Ti₉C₁₃ nanowire-based LIB is five times bigger than that of graphite anodes, thus making TiC a promising material for anode design in Li-ion batteries. (6) Although 1D TiC cubic nanowire is energetically nearly degenerate with the Ti₉C₁₃ nanowire, its specific capacity as a LIB anode is not as large as that of the Ti₉C₁₃ nanowire. We hope that these results will motivate experimentalists to synthesize these nanowires and examine their potential for next-generation LIB anodes.

**COMPUTATIONAL METHODS**

Atomic structures and electronic properties are calculated using density-functional theory as implemented in Vienna ab initio simulation package (VASP). The projector augmented wave (PAW) method and Perdew–Burke–Emzerhof (PBE) exchange correlation functional within the generalized gradient approximation (GGA) are used. The 2s¹, 2s²2p⁵ and 3d⁴4s⁴ atomic orbitals are treated as valence states for Li, C, and Ti, respectively. A plane-wave cutoff of 500 eV is used for all the calculations. The convergence criteria for total energy and Hellmann–Feynman force are set to 10⁻⁴ eV and 10⁻⁵ eV/Å, respectively. A vacuum space of 20 Å in the radial directions (x and y) is kept to avoid mirror interactions. In all calculations, the k-point grid is sampled by a 1 × 1 × 9 mesh using the Monkhorst–Pack scheme. To check the dynamic stability, Phonopy code is used to calculate the vibrational spectra. Ab initio molecular dynamics (AIMD) simulations are performed to assess the thermal stability of the nanowire. Canonical ensemble (NVT) is adopted using the Nosé heat bath method. Bader charge analysis is carried out to study charge transfer. By using the nudged elastic band (NEB) method, we calculate the diffusion energy barrier and the minimum energy pathways for Li diffusion on the nanowire.

**ASSOCIATED CONTENT**

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsenergylett.6b00120.

Stability relative to other Ti–C compounds, dynamic stability, thermal stability, thermodynamic properties, volume expansion/contraction during lithiation/delithiation process, open-circuit voltage, and specific capacity (PDF)

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Notes

The authors declare no competing financial interest.

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