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A 3D porous honeycomb carbon as Na-ion battery anode material with high capacity, excellent rate performance, and robust stability



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ABSTRACT

Motivated by the synthesis of three-dimensional (3D) honeycomb carbon structures and the subsequent theoretical prediction of an energetically more favorable hexagonal carbon phase composed of 28 carbon atoms in the unit cell (hC28) with ordered pores, excellent mechanical properties, and metallic feature, we explore its potential for a Na-ion battery (NIB) anode material. Using density functional theory based calculations, we find that hC28 is a promising candidate whose specific capacity of 717 mAh/g is almost three times larger than that of hard carbon (~250 mAh/g). In addition, migration barrier of Na ions along the honeycomb channel is only 0.08 eV and the volume change during the charging/discharging process is merely 2.30%, which are much less than those of other carbon-based NIB anode materials. The average voltage is also low (0.36 eV) which can provide high operating voltage when connected to the cathode. These encouraging results would pave the way towards the development of hC28 as NIB anode with high capacity, excellent rate performance, low open-circuit voltage, and long-term cycle life.

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1. Introduction

The depletion of fossil fuels and its adverse effect on the environment have stimulated substantial efforts in developing largescale energy storage systems with high energy and power densities [1,2]. Among various energy storage devices, lithium-ion batteries (LIBs) have played a key role in powering devices from portable electronics to electric vehicles [3–5]. However, given the geographically-constrained lithium reserves NIBs are hotly pursued as an attractive alternative to LIBs in recent years due to the abundant supply, wide distribution, low cost and toxicity of sodium [6,7]. Although the physicochemical properties associated with ion insertion/extraction mechanisms of sodium are similar to those of lithium [8], many Li-ion battery anodes do not work for Na-ion battery due to the larger size of the Na-ion [1,9], which gives rise to sluggish reaction kinetics. In addition, the large volume change during the Na intercalation/deintercalation process leads to low capacity and poor cycling stability [10].

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Up to now, many NIB anode materials have been proposed, including carbon-based materials [1,11], metal alloys/oxides/chalcogenides [12–18], phosphorus [19], intermetallic nanocomposites [1], and organic compounds [20]. Metals or alloy-type anode materials usually deliver high specific capacities, but they are typically accompanied with large volume expansion during the charging/ discharging process. This causes structural degradation of electrode materials, thus leading to fast capacity fading and poor cycle stability [2,7,10,18,21]. Consequently, development of anode materials with high capacity, good rate performance and superior cycling stability for NIBs is urgent and of great importance.

Motivated by the recent synthesis of 3D honeycomb porous carbon [22] and the recently proposed 3D porous hC28 [23] with multiple unconventional emergent fermions, ultra-energetic stability, and excellent mechanical properties, we study its potential as a NIB anode material. Using density functional theory based calculations, we show that hC28 has high capacity, good rate performance, remarkable cycling stability, and low open-circuit voltage.

2. Computational methods

All calculations are performed using the density functional theory (DFT) and Projector Augmented Wave (PAW) potential [22]



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as implemented in the Vienna Ab initio Simulation Package (VASP) [23]. Perdew-Burke-Ernzerhof (PBE) [24] functional within the generalized gradient approximation (GGA) is used to describe exchange and correlation interactions between electrons. The effect of van der Waals (vdW) interaction is considered using the semiempirical long-range dispersion correction by Grimme (DFT-D2 method) [25]. The plane-wave cutoff energy of 520 eV is used for all calculations. Total energies and force components were converged to 0.0001 eV and 0.01 eV/Å, respectively. The reciprocal space of the unit cell and supercell are represented by $(3 \times 3 \times 6)$ and $(1 \times 1 \times 2)$ Monkhorst–Pack k-point meshes, respectively. The phonon spectrum is calculated to check its dynamical stability by using density functional perturbation theory (DFPT) [26] and the corresponding force constants are calculated using Phonopy code [27] based on the dynamical matrix from VASP. The canonical (NVT) ensemble is used for Ab initio molecular dynamics (AIMD) simulations with Nosé thermostat [28]. The diffusion barriers for sodium ions are calculated using the climbing image nudged elastic band (CI-NEB) method embedded in the VASP transition state tools [29,30]. In order to identify the most stable intermediate configurations of hC28 for different Na concentrations, we calculated the electrostatic Ewald energy of all symmetrically distinct structures generated from numerous distinctive structures using the pymatgen package [31,32].

3. Results and discussion

3.1. Single Na atom insertion and diffusion in hC28

The structure of hC28 has a hexagonal primitive cell with a space group D6h-4 (no. 194) and 28 carbon atoms in the unit cell [33]. Its optimized lattice parameters are a = 10.03 Å, b = 10.03 Å, c = 4.88 Å, $\alpha = \beta = 90.00$ and $\gamma = 120.00$ [33]. This structure consists of zigzag graphene nanoribbons with sp^2 bonded carbon and the junction of zigzag graphene nanoribbons with sp^3 bonded carbon forming a honeycomb lattice, as shown in Fig. 1a. We check its dynamical and thermal stability by carrying out phonon spectra calculations and AIMD simulations at 300 K and 1200 K (the results are plotted in Fig. S1), and calculate its band structure (see Fig. S2), which shows that hC28 is metallic. Our results agree with previous work [33]. Because of excellent stability, ordered pores and metallicity, we explore the potential of hC28 as a NIB anode material.

First, we study the insertion of a single Na atom into hC28. We use an $1 \times 1 \times 2$ supercell to prevent the neighboring Na atoms from intercating. Ten possible initial insertion sites are considered based on its symmetry, as shown in Fig. 1b and c. These are: three hollow sites H_1-H_3 (above the center of the carbon rings), three top sites T_1-T_3 (above the carbon atom), and four bridge sites B_1-B_4 (above the midpoint of carbon-carbon bond).

After fully relaxed, all the Na atoms on T and B sites are found to move to their neighboring H sites (see Fig. S3), suggesting that Na adsorption on H site is stable in dilute concentration. The binding energy (E_b) of the Na ions bound to the hC28 substrate is defined as

$$E_{\rm b} = \frac{E_{\rm Na_x"TT5843c571""ADhC28} - E_{\rm hC28} - x\mu_{\rm Na}}{x}$$
(1)

where E_{Na_x-hC28} and E_{hC28} are, respectively, the total energies with and without Na insertion in the pristine hC28 structure. μ_{Na} is the chemical potential of Na. The E_b of Na adsorption on H₁, H₂ and H₃ sites are calculated to be -1.03, -0.74 and -0.87 eV, respectively, which means that H₁ site is energetically the most stable binding site for the Na atom. The calculated E_b at H₁ site is comparable to that of tC4 structure (-1.09 eV) [34], which indicates that Na ions are strongly adsorbed on the hC28 substrate. When the Na ion is adsorbed on the H₁ site at low concentration, the distances between the Na ion and its neighboring C atoms are 2.55 Å and 2.75 Å, respectively.

According to the Bader charge population analysis, as shown in Fig. S4, 0.88|e| electrons move from Na to hC28, i.e. Na atoms donate most of their valence *s* electrons to form Na ions. This leads to an effective Coulomb repulsion between the Na ions, preventing them from clustering. In order to further study the effect of Na atom adsorption on the hC28 substrate, we calculate the charge density difference in this configuration where a single Na atom is adsorbed on the H₁ site. The bonding charge density difference is given in Fig. S5. We can conclude that the hC28 substrate receives electrons transferred from the adsorbed Na atom.

The mobility of Na-ion in the electrode materials is one of the key quantities that is determined by the energy barrier of Na-ion diffusion. From the symmetry of hC28, we find that there are two migration paths of Na ions in the honeycomb channel. These are path S_0-S_1 (path A: along the honeycomb channel) and path S_0-S_2 (path B: crossing the honeycomb channel). We then calculate energy barriers of these two Na ion migration paths (see Fig. 2a and b)



Fig. 1. (a) Perspective view of hC28; (b) Top and (c) the corresponding side view of all possible single Na-ion absorption sites on hC28. (A colour version of this figure can be viewed online.)



Fig. 2. (a) Top and (b) side view of Na migration paths along path A (S₀–S₁) and path B (S₀–S₂), where S₀ represents the start position and S₁ and S₂ represent the end positions. (c) The energy profiles of path A and (d) path B. (A colour version of this figure can be viewed online.)

by using the climbing-image nudged elastic band (CI-NEB) method. Calculated results are showed in Fig. 2c and d, respectively.

For the case of Na diffusion along the honeycomb channel (path A), due to the symmetry of path A, there are two barrier peaks with the same value, namely, 0.08 eV. The energy barrier reaches a climax when the Na atom reaches the top of the C atom. The calculated diffusion barrier is comparable to that of tC_{24} (0.053eV) [34], and smaller than that of black phosphorus (0.18 eV) [35], 2D 2H–MoS₂ (0.68 eV) [36], silicene (0.16 eV) [37] and TiC₃ monolayer (0.18–0.31 eV) [38]. This indicates that Na ions can easily migrate along path A, leading to excellent charging/discharging rate when hC28 is used as an anode for NIBs.

In contrast, when Na ion diffuses through the honeycomb channel (path B), the cooresponding energy barrier is 0.17 eV, which is significantly higher than that along path A, suggesting that Na diffusion along path A is favorable. To further compare the diffusion behavior between path A and path B, temperature-dependent diffusion constant (D) is calculated by the following Arrhenius equation [39]:

$$D \propto exp\left(\frac{-E_a}{K_B T}\right) \tag{2}$$

where E_a and K_B are the diffusion barrier and Boltzmann constant, respectively, and *T* is the temperature. According to the Arrhenius equation, the diffusion mobility of Na along the honeycomb channel is about 33 times faster than that crossing the honeycomb channel at room temperature, indicating that path A is much more favorable for Na-ion diffusion than path B, which is comparable to that in tC₂₄ [34].

3.2. Maximum Na storage capacity and vacancy diffusion

To determine the maximum Na storage capacity of hC28, we have considered the case where Na ions occupy all possible sites.

The resulting configuration of fully Na-intercalated hC28 is shown in Fig. 3. The calculated binding energy E_b is -0.36 eV, suggesting that the binding is stronger than that of Li ions on graphite (-0.11 eV) [40] and VS₂ monolayer (-0.26 eV) [41]. This indicates that Na ions can be stably absorbed in hC28 without causing phase separation, even at such a high Na concentration. In the case of fully Na-loaded configuration, there are 18 Na ions in the supercell of hC28. With 56 carbon atoms in the supercell, the composition of fully Na-loaded hC28 is NaC_{3.1}. This leads to a theoretical specific capacity of 717 mAh/g (see Text. S1 for detail of capacity calculation), which is more than 2.5 times larger than that of hard carbon (~250 mAh/g) [42] as well as that of defective hard carbon (274 mAh/g) [43]. This high capacity is attributed to its unique geometry with large specific surface areas [8,44].

To have a better understanding of Na-ion diffusion, we study the situation in high Na concentration. To this end, we first remove a Na ion from fully loaded hC28 and carry out full structural relaxation. After removing the Na ion, due to electrostatic repulsion, the nearest-neighbor Na ion moves to the S₁ site, leaving a vacancy. The diffusion barriers of single vacancy along path A and path B are calculated to be 0.050 eV and 0.057 eV, respectively (see Fig. 3). The energy barrier for the single vacancy diffusion is less than that of single Na ion diffusion, similar to that of Li ions in bco-C₁₆ [40]. This phenomenon can be explained by the small volume expansion following full Na-intercalation and the strong Coulomb repulsion between Na ions.

3.3. Voltage profile

Open circuit voltage is another important quantity to characterize batteries' performance, which can be obtained by calculating the average voltage of each part in the domain of Na compositions [45,46]. The half-cell reaction vs Na/Na⁺, describing the charging/ discharging processes of hC28, is presented by the following



Fig. 3. (a) Top and (b) side view of vacancy diffusion pathways along path A (S_0 – S_1) and path B (S_0 – S_2), where S_0 represents the start position and S_1 and S_2 represent the end positions. (c)The energy profiles of path A and (d) path B. (A colour version of this figure can be viewed online.)

equation:

$$(x_2 - x_1)Na^+ + (x_2 - x_1)e^- + Na_{x_1} - hC28 \leftrightarrow Na_{x_2} - hC28$$
(3)

By neglecting the effects of volume, pressure, and entropy, the average voltage of Na_x -hC28 within a concentration range of $x_1 < x < x_2$ can be evaluated as [47].

$$V \approx \frac{E_{\mathrm{Na}_{x_1} - \mathrm{hC28}} - E_{\mathrm{Na}_{x_2} - \mathrm{hC28}} + (x_2 - x_1)E_{\mathrm{Na}}}{(x_2 - x_1)e}$$
(4)

where $E_{Na_{x_1}-hC28}$, $E_{Na_{x_2}-hC28}$ and E_{Na} are the total energies of $Na_{x_1}-hC28$, $Na_{x_2}-hC28$, and Na atom in bulk form, respectively. To calculate the average voltage, we search for the most stable occupied Na ion configuration at different intermediate concentrations. We choose five intermediate concentrations (Na_xC_{3.1}: x = 0.11, 0.33, 0.50, 0.67, 0.83). At each intermediate concentration, we enumerate 30 inequivalent adsorption configurations using the *pymatgen* package [31,32] (see Text. S2). Next, we determine the most stable configuration for the above five different concentrations by comparing total energies of different configurations. The corresponding stable configurations are presented in Fig. S6 (see SM).

The calculated binding energies of the most stable structures corresponding to different Na ion adsorption concentrations are found to be all negative. The results are presented in Fig. 4a and indicate that Na ions can be stably adsorbed on the substrate without forming clusters. Additionally, the absolute value of the binding energy decreases with increasing Na ion concentration as the mutual repulsion between sodium ions is enhanced. Based on Bader charge population analysis (see Table S1), we find that the charge transfer from Na to hC28 is reduced as increasing the concentration, thus, the interaction between sodium ions and substrate is weakened.

Next, we use Eq. (3) to calculate the average voltage based on the obtained results. As presented in Fig. 4, in the dilute concentration

limit (x < 0.33), the voltage drops sharply from 0.8 V (0 < x < 0.11) to 0.4 V (0.11 < x < 0.33). As the Na ion concentration increases to 1, the cooresponding voltage drops slowly to 0.2 V. Furthermore, the voltage always remains positive throughout the whole process which indicates that the half-cell reaction can proceed spontaneously to reach the final stage (NaC_{3.1}). As listed in Table 1, the average voltage calculated by the numerical average of the voltage profile is 0.36 V, which is smaller than that of tC₂₄ (0.54 V) [34] and MoS₂ (1.25 V) [36]. The average voltage of hC28 anode is pretty low, indicating that the NIB can provide a higher operating voltage when it is connected to cathode and, thus, can supply a large energy capacity.

3.4. Cycling stability

Cycling stability, which can be estimated from the volume change during the Na charging/discharging process, is another important quantity. By comparing the fully Na-loaded hC28 with the original hC28 structure, we find that there is no bond breaking and the cooresponding volume expansion is merely 2.30%, which is smaller than that of ISN (2.8%) [48] and black phosphorus (317%) [35]. The changes of lattice constants before and after the Na-ion adsorption are listed in Table S2, and labelled in Fig. S8, where the volume expansion is 2.3% being almost isotropic along a, b, c directions, which is much different from that of Li ion in $bct-C_{16}$ where volume change mainly comes from the change in chemical bonding along the z direction [40]. The Young's modulus of hC28 is 218 GPa [33], which is even larger than that of steel and accounts for the small volume expansion of the fully Na-loaded configuration. In addition, we study the total density of states (DOS) before and after hC28 is fully loaded with Na ions. Fig. S9 presents the DOS results, which indicate that the metallic property of hC28 anode can be maintained with good electronic conductivity. Hence, we conclude that hC28 anode not only remains metallic but also is able



Fig. 4. (a) Binding energy and (b) voltage profile of the five stable intermediate configurations for the different Na concentrations. (A colour version of this figure can be viewed online.)

Table 1

Comparison of specific capacity, diffusion barrier, open-circuit voltage (OCV), volume change and electronic property of hC28 with other anode materials for NIBs.

| Materials | Specific capacity, mAh/g | Diffusion barrier, eV | OCV, V | Volume change, % | Conducting feature |
|--------------------------|--------------------------|-----------------------|-----------|---------------------|-------------------------------------|
| | | | | | |
| hC28 | 717 | 0.080 | 0.36 | 2.30 | Metal |
| tC ₂₄ [34] | 232.65 | 0.053 | 0.54 | 0.94 | Topological nodal surface semimetal |
| ISN [48] | 159.5 | 0.005 | 1.35 | 2.80 | Topological nodal line semimetal |
| SiC4–I [49] | 176.3 | 0.410 | 0.55 | 0.57 | Metal |
| 1T-MoS ₂ [36] | 86 | 0.280 | 1.25 | 27.5 | Metal |
| 2H–MoS ₂ [36] | 146 | 0.680 | 0.75 | 27.1 | Semiconductor |
| Si ₂₄ [50] | 159.5 | 0.005 | 0.30 | 2.30 | Metal |
| Black phosphorus [35] | 2596 | 0.180 | - | 317 | Semiconductor |

'-' means data unavailable.

to accommodate Na ions with large concentration during the charging/discharging process, exhibiting a remarkable cycling stability. In addition, compared with the previously proposed carbon honeycomb (C-honeycomb) [51], hC28 possesses a larger pore radius, higher specific capacity, lower diffusion barrier and smaller volume expansion when used as NIB anode.

4. Conclusions

In summary, encouraged by the remarkable electronic and mechanical properties as well as ordered pores of 3D honeycomb carbon (hC28), we have studied its potential for a NIB anode material using density functional theory including vdW corrections. By systematically studying the energetics and kinetics of Na-ion intercalation and diffusion, we have reached the following conclusions: (i) Na ions can be stably intercalated into hC28 without clustering. Na atoms donate almost all their valence electrons to hC28, resulting in a strong ionic bonding with the substrate. (ii) At both low and high Na ion concentrations, the preferred diffusion pathways of sodium proceed along the honeycomb channel with small diffusion barriers of 0.08 and 0.05 eV, respectively. (iii) The maximum Na storage capacity of hC28 is 717 mAh/g, corresponding to the $NaC_{3,1}$ composition, which is much higher than that of most carbon-based NIB anode materials. (iv) The average voltage is 0.36 eV, which is quite low for an anode. Once connected to the cathode, it can supply a large operating voltage. (v) The volume change during the Na-ion intercalation/deintercalation process is 2.30%, which is much smaller than that of carbon-based NIB or even LIB anode materials, suggesting an excellent reversibility. All these extraordinary properties show that hC28 is a promising NIB anode candidate for large-scale energy storage systems.

CRediT authorship contribution statement

Wenyang Zhou: Conceptualization, Methodology, Investigation, Software, Writing - original draft. **Huanhuan Xie:** Data curation. **Shuo Wang:** Visualization, Software. **Qian Wang:** Supervision, Writing - review & editing. **Puru Jena:** Supervision, Writing - review & editing.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.carbon.2020.06.070.

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