

Composites, Methods of Fabrication and Uses in Battery Applications

Technical Field

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The present invention relates, in general terms, to a composite and methods of fabrication thereof. The present invention also relates to the use of the composite in battery applications.

Background

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Due to the abundant resources of sodium in the earth, sodium-ion batteries (SIBs) have been considered as an efficient supplement to lithium-ion batteries (LIBs). Despite of the advances in the development of electrolytes and cathode materials, comprehensively high-performance anode materials are also in urgent need, which play a great role in the further improvement of energy density in SIBs. However, the commercially available graphite anode in LIBs is not suitable for SIBs because the formation energy of Na-graphite intercalation compounds (Na-GIC) is positive. Compared with alloy- and conversion-based anode materials with high plateau voltage and poor cycling stability, hard carbon are still considered as one of the most promising candidate for the anode materials of SIBs due to its lower plateau voltage and acceptable capacity ($\sim 300 \text{ mAh g}^{-1}$).

Low-voltage plateau capacity of anode can enable a higher energy density in full-cell batteries. According to the typical “intercalation/pore-filling” model for sodium-ion storage mechanism, the sloping section results from the intercalation of Na^+ inside the graphitic nanodomains, while the low-voltage plateau section is attributed to the pore-filling process of the bare Na^+ into the closed pores blocked by the graphitic nanodomains. Therefore, several strategies have been proposed to increase the plateau capacity via creating more closed pores. For example, a pore-forming agent or adopted pre-oxidation/high-temperature carbonization was used in prior work to tune the closed pore structure of the hard carbon and hence to realize a large reversible plateau capacity. Some workers obtained hard carbon

fibers with high population of closed pores by heating waste silk fabrics even at an ultrahigh temperature of 2000 °C. Despite of the aforementioned advances in synthesis of hard carbon with enhanced reversible plateau capacity, a high carbonization temperature (much higher than 1300°C) is not safe and environmentally unfriendly. In addition, a poor rate capability
5 always accompanies with the high plateau capacity. Therefore, ongoing efforts are still required to design a targeted structure of hard carbon under a mild temperature, realizing a large plateau capacity and satisfying rate capability.

It would be desirable to overcome or ameliorate at least one of the above-described
10 problems.

Summary

In this work, a strategy is proposed to increase ultra-micropores inside the carbon materials
15 through molten diffusion of aromatic hydrocarbons into the microporous carbon followed by further carbonization. As a result, the rationally designed carbon anode displays a low-voltage plateau at ~ 0.1 V in the discharge/charge curves, along with a high capacity of 346 and 125 mAh g⁻¹ at 30 and 2000 mA g⁻¹, respectively. Moreover, the high-loading electrode (~ 19mg cm⁻²) also exhibits a high areal capacity of 6.14 mAh cm⁻² at 25°C and 5.32 mAh
20 cm⁻² at -20 °C, allowing a good temperature endurance. Furthermore, the coin-type full battery enables a high capacity of ~ 97.1 mAh g⁻¹. The proposed molten diffusion-carbonization strategy is facile and energy-efficient to prepare high-performance carbon anode materials with great practical potential for SIBs. An electrode formed from the composite disclosed herein can be used for enhancing capacity and rate capability in
25 room/low-temperature sodium-ion storage.

The present invention discloses a method of fabricating a modified porous carbon composite, comprising

- a) mixing porous carbon with a rylene dye in order to form a mixture;
 - 30 b) heating the mixture from about 300 °C to about 600 °C under an inert atmosphere;
- and

c) carbonising the mixture at a temperature of about 700 °C to about 1300 °C.

Advantageously, the heating step under an inert atmosphere allows the rylene dye to become molten, and accordingly, coats the porous carbon and diffuse into the pores of porous carbon.

5 The pores blocked by rylene dye is then carbonised within the porous carbon to convert the open pores to closed pores. This method alters the pore size of the porous carbon, does not completely block the pores and is also less energy intensive compared to high temperature annealing. The aperture size is also reduced but not blocked, thus allowing naked Na^+ to form within the pores. Anode formed using this method for sodium-ion storage exhibits
10 increased plateau capacity, improved cycling stability, satisfying rate capability and high areal capacity.

In some embodiments, the composite comprises ultra-micropores, the ultra-micropores having a pore diameter (based on CO_2 adsorption) of about 0.2 nm to about 0.8 nm; and
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In some embodiments, the composite has a BET (CO_2) specific surface area of about $10 \text{ m}^2 \text{ g}^{-1}$ to about $220 \text{ m}^2 \text{ g}^{-1}$.

In some embodiments, a mass ratio of porous carbon to rylene dye is about 1:1 to about 1:4.
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In some embodiments, the porous carbon is selected from activated carbon, mesoporous carbon, carbonised sugar, high specific surface area carbon and low specific surface area carbon.

25 In some embodiments, the rylene dye is selected from perylenetetracarboxylic dianhydride (PTCDA), perylenediimide, terrylendiimide, terrylen, perylen, quaterrylen and naphthalin.

In some embodiments, the mixture is mechanically blended.

30 In some embodiments, the inert atmosphere is argon.

In some embodiments, the heating step is performed for about 2 h to about 10 h.

In some embodiments, the carbonisation step is performed for at least 3 h.

- 5 In some embodiments, the carbonisation step is performed under a rate of about 3 °C/min to about 10 °C/min.

The present invention also discloses a modified porous carbon composite comprising:

- a) a porous carbon structure; and
10 b) a carbonised rylene dye;
wherein the carbonised rylene dye coats at least inner pores of the porous carbon structure.

In some embodiments, the composite comprises ultra-micropores, the ultra-micropores having a pore diameter (based on CO₂ adsorption) of about 0.2 nm to about 0.8 nm.

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In some embodiments, the composite has a BET (N₂) specific surface area of about 5 m² g⁻¹ to about 80 m² g⁻¹.

- In some embodiments, the composite has a BET (CO₂) specific surface area of about 10 m² g⁻¹ to about 220 m² g⁻¹.
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In some embodiments, a mass ratio of porous carbon structure to at least partially carbonised rylene dye is about 1:1 to about 1:4.

- 25 In some embodiments, the composite has a BET (CO₂) specific surface area to BET (N₂) specific surface area ratio of about 0.1 to about 50.

- In some embodiments, the composite has an XRD pattern which indicates the presence of a (002) peak of a carbon derived from the carbonised rylene dye and a (002) peak of the porous
30 carbon structure.

In some embodiments, the (002) peak of a carbon derived from the carbonised rylene dye is about 25.2°.

In some embodiments, the (002) peak of the porous carbon structure is about 21.2°.

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In some embodiments, the composite has a total volume (based on N₂ adsorption) of about 0.01 cm³ g⁻¹ to about 0.13 cm³ g⁻¹.

10 In some embodiments, the composite has a total volume (based on CO₂ adsorption) of about 0.08 cm³ g⁻¹ to about 0.4 cm³ g⁻¹.

In some embodiments, the composite has a **R** value of about 2 to about 5.

15 In some embodiments, the composite has a skeletal density of about 1.8 g cm⁻³ to about 2.5 g cm⁻³.

The present invention also discloses a method of fabricating an electrode, comprising:

- a) mixing a composite as disclosed herein with a binder solution to form a slurry;
- b) applying the slurry on a surface of an electrical conductor; and
- 20 c) drying the slurry.

In some embodiments, a weight ratio of composite to binder solution is about 80:20 to about 95:5.

25 In some embodiments, the binder solution has a concentration of about 10 mg/mL to about 20 mg/mL.

In some embodiments, the binder solution comprises a binder selected from sodium carboxymethyl cellulose and/or polyvinylidene fluoride (PVDF).
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In some embodiments, the drying step is performed at about 40 °C to about 80 °C.

In some embodiments, the drying step is performed for about 2 h to about 6 h.

5 In some embodiments, the drying step further comprises vacuum drying the slurry at about 100 °C to about 140 °C for at least 8 h.

The present invention also discloses an electrode, comprising:

- a) a composite as disclosed herein;
 - b) a binder; and
 - 10 c) an electrical conductor;
- wherein the composite and the binder are homogenously combined; and
wherein the composite and the binder coats at least a surface of the electrical conductor.

15 In some embodiments, a weight ratio of composite to binder is about 80:20 to about 95:5.

In some embodiments, the electrode has a capacity of more than 100 mAh g⁻¹ at a current density of about 2000 mA g⁻¹ or a capacity of more than 300 mAh g⁻¹ at a current density of about 30 mA g⁻¹.

20 In some embodiments, the electrode has a retention of at least 80% of its initial capacity after 200 cycles.

25 In some embodiments, a mass loading of the composite and binder on the electrical conductor is at least 15 mg cm⁻².

In some embodiments, the electrode has an areal capacity of about 6 mAh cm⁻² at a current density of about 0.1 mA cm⁻² or an areal capacity of about 3 mAh cm⁻² at a current density of about 0.5 mA cm⁻².

30 In some embodiments, at least 80% of an area capacity is retained at about -20 °C.

The present invention also discloses a battery, comprising:

- a) an organic cathode;
- b) an anode, the anode comprising the composite as disclosed herein; and
- c) sodium metal, the sodium metal applied on at least a surface of the anode.

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In some embodiments, the organic cathode comprises a rylene dye.

In some embodiments, a mass loading ratio of the organic cathode to the anode is about 1:2 to about 1:3.

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In some embodiments, a N/P ratio (the areal capacity ratio of negative to positive electrode) is about 1.1:1 to about 1.2:1.

15 In some embodiments, during a charging and/or discharge of the battery, the battery is characterised by a peak at 4.44 ppm in *ex-situ* ^{23}Na MAS NMR.

In some embodiments, when the battery is fully discharged, the battery is characterised by a peak at 4.44 ppm and a peak from about -20 ppm to about -30 ppm in *ex-situ* ^{23}Na MAS NMR.

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Brief description of the drawings

Embodiments of the present invention will now be described, by way of non-limiting example, with reference to the drawings in which:

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Figure 1. Characterizations of the AC, GC and ACGC900: (A) Scheme of the molten diffusion-carbonization strategy (T represents the carbonization temperature). SEM image of the micrometer-sized (B) AC, and (C) ACGC900. (D) TEM image of the thin edge area of a typical ACGC900 particle and corresponding selected area electron diffraction (SAED) pattern (inset). (E) N_2 adsorption/desorption isotherm, (F) pore size distribution from N_2

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adsorption/desorption measurement and (G) peak fitting of the (002) peaks in the XRD patterns;

Figure 2. Electrochemical performance of the AC, GC and ACGC900 electrode in SIBs: (A) Galvanostatic discharge-charge curves at 50 mA g⁻¹. (B) CVs in a voltage range of 0.001-3.0 V versus Na/Na⁺ at a scan rate of 0.1 mV s⁻¹. (C) Cycling performance at 50 mA g⁻¹;

Figure 3. Effects of carbonization temperature and pore volume on the electrochemical performance: (A) Galvanostatic discharge-charge curves of ACGCx at 50 mA g⁻¹, and (B) the relationship between the sloping capacity contribution and the calculated **R** value from XRD. (C) Galvanostatic discharge-charge curves of ACGC, HCGC, LCGC electrodes at 50 mA g⁻¹. (D) The relationship between the plateau capacity and the mass ratio of the filler/host. (E) rate performance and (F) the comparison of the rate capability of LCGC anode with that of other hard carbon anodes recently reported in SIBs;

Figure 4. Analysis of sodium-ion storage mechanism: (A) CV curves at varied scan rates from 0.1 to 1.0 mV s⁻¹, (B) plots of log(*i*) versus log(*v*) and the corresponding linear fitting and (C) *D*_{Na⁺} values calculated from GITT measurement during discharge-charge process. (D-E) The *in-situ* XRD mapping with the capacity-potential curve under voltage windows of 0.001-3 V. (F) The *ex-situ* solid-state NMR spectra of ²³Na at different potentials;

Figure 5. Thick electrode and full-cell test. (A) Cycling performance, and (B) rate capability of the thick electrode with a mass loading of 19 mg cm⁻². (C) galvanostatic discharge/charge curves at 0.2 mA cm⁻² in the temperature range from -20 to 40 °C and (D) the capacity retentions of thick electrode. (E) Galvanostatic discharge/charge curves at 10 mA g⁻¹ and (F) rate capability of full cell in the voltage range of 0.5-3.0 V;

Figure 6. (A) CO₂ adsorption isotherms and (B) the corresponding pore size distribution of ACGC900;

Figure 7. Schematic representation of the definition of the parameter **R** used to empirically determine the degree of graphitization of the carbon samples. **R** value ($R = B/A$) can determine the graphitization degree of the samples. A lower **R** value suggests a lower degree of graphitization or less stacked graphene layers. **R**, is measured as the ratio of the (002) Bragg peak intensity to the background;

Figure 8. Raman spectra of AC, GC and ACGC900;

Figure 9. Rate performance at various current densities of the AC, GC and ACGC900 electrodes;

Figure 10. (A1-E1) Low-resolution and (A2-E2) high-resolution SEM images of AC, ACGC750, ACGC900, ACGC1050, and ACGC1200, respectively. (Scale bar: 10 μm for A1-E1, 1 μm for A2-E2);

Figure 11. N_2 adsorption/desorption isotherm and the corresponding pore size distribution of ACGCx. The hysteresis between the adsorption and desorption branches of the isotherm indicates the existence of restricted pore;

Figure 12. CO_2 adsorption isotherm and the corresponding pore size distribution of ACGCx;

Figure 13. XRD patterns of ACGCx;

Figure 14. (A) Specific capacity and (B) contribution of ACGCx contributed from the slope and plateau regions;

Figure 15. First five galvanostatic discharge-charge curves of (A) AC, (B) GC, (C) ACGC750, (D) ACGC900, (E) ACGC1050, (F) ACGC1200, (G) HCGC, and (H) LCGC at 50 mA g^{-1} ;

Figure 16. Relationship between the ICE value and the BET specific surface area obtained from N_2 adsorption/desorption test;

Figure 17. (A) rate performance and (B) cycling performance of ACGCx at 50 mA g^{-1} . The ACGC1050 electrode displays the best rate performance and cycling stability. Specifically, the ACGC1050 electrode can reach $\sim 118 \text{ mAh g}^{-1}$ even at 2000 mA g^{-1} . Moreover, $\sim 97.3\%$ of the initial capacity can be maintained after 200 cycles at 50 mA g^{-1} ;

Figure 18. (A, B) N_2 adsorption/desorption isotherm and (C, D) the corresponding pore size distribution of AC, CMK8, HC, LC, ACGC, CMK8GC, HCGC, and LCGC. The hysteresis between the adsorption and desorption branches of the isotherm indicates the existence of restricted pores;

Figure 19. The pore size distribution of CMK8 and CMK8GC;

Figure 20. The TEM images of (A) CMK-8 and (B) CMK8GC. (Scale bar: 50 nm) As shown in Figure 21, CMK8GC electrode derived from mesopore-dominated carbon host (CMK-8) displays no plateau capacity during discharge-charge process. That could be because the mesopore inside CMK-8 (cubic Ia3d , rod-type) is interconnected and large enough to host the quasi-graphitic nanodomains derived from the filling PTCDA (Figure 19-20). As a result,

nanodomains with layered graphitic structure instead of nanocavity was introduced into the CMK8GC and then no plateau occurs;

Figure 21. (A) Galvanostatic discharge-charge curves at 50 mA g⁻¹, (B) cycling performance, and (C) Rate performance of CMK8GC electrodes;

- 5 **Figure 22.** (A) Rate performance and (B) cycling performance of ACGC, HCGC, LCGC electrodes at 50 mA g⁻¹;

Figure 23. Current step diagram at 0.304 V vs. Na/Na⁺ of third sodiation process of ACGC electrode for sodium ion batteries;

Figure 24. GITT potential profiles of ACGC;

- 10 **Figure 25.** Linear behaviour of the potential vs. $\tau^{1/2}$ in GITT at (A) 0.304 V vs. Na/Na⁺ of ACGC during the third sodiation process;

Figure 26. Schematic illustration of the proposed sodium-ion storage mechanism;

Figure 27. Discharge-charge profiles of the LCGC thick electrode at different current densities; and

- 15 **Figure 28.** D_{Na^+} values calculated from GITT tests during the discharge-charge process of the thick LCGC electrode at various temperatures.

Detailed description

- 20 Disordered porous carbon, such as biomass-derived carbon and porous coordination polymer-derived carbon, can be readily synthesized under a mild temperature lower than 1000°C. These porous carbon materials deliver improved diffusion kinetics and a satisfying rate capability in SIBs, which benefits from the existence of developed porosity. However, their discharge/charge profiles are sloping curves, due to the capacitive ion
- 25 adsorption/desorption only on the surface sites of the micropores, where bare Na⁺ and solvated Na⁺ co-exist. Indeed, the existing electrolyte has a significant influence on the ionic interaction inside the pore. It is postulated that if the electrolyte can be obstructed outside the micropores, a different storage mechanism from capacitive adsorption could be introduced. It is believed that the aperture size of carbon materials displays an ionic-sieving
- 30 effect on the solvated Na⁺ and the pore size has a great influence on the electron distribution inside the pore. Specifically, the desolvation will happen around the aperture when the

- aperture size is smaller than the solvated Na^+ . In addition, according to calculation and simulation results, the Na^+ concentration inside the pore increases with the decreasing pore width. Moreover, the electrons tend to be spread out over all neighboring Na^+ instead of a single Na^+ inside the pore with the decreasing pore width. The tendency of Na^+ clustering inside the pores thereby becomes notable. Given that the micropores ($> 1 \text{ nm}$) in porous carbon can be modulated to be ultra-micropores with smaller aperture size and pore width, pore-filling and clustering of bare Na^+ can be introduced and the fast diffusion of Na^+ can still be ensured during sodiation/desodiation process. Therefore, tuning the aperture size and pore width of porous carbon could be an efficient strategy to boost the plateau capacity without sacrificing rate capability. Due to the smaller molecular size ($3.3 \text{ \AA}$ for CO_2 vs $3.64 \text{ \AA}$ for N_2) and the higher working temperature (273 K for CO_2 vs 77 K for N_2), CO_2 adsorption measurement is highly efficient to detect the existence of ultra-micropores ($< 0.8 \text{ nm}$).
- The present invention discloses a method of fabricating a modified porous carbon composite, comprising
- mixing porous carbon with a rylene dye in order to form a mixture;
 - heating the mixture from about 300°C to about 600°C under an inert atmosphere; and
 - at least partially carbonising the mixture at a temperature of about 700°C to about 1300°C .

In some embodiments, the method of fabricating a modified porous carbon composite comprises:

- mixing porous carbon with a rylene dye in order to form a mixture;
 - heating the mixture from about 300°C to about 600°C under an inert atmosphere; and
 - carbonising the mixture at a temperature of about 700°C to about 1300°C .
- The inventors have found that the aperture size and pore size (or width) of porous carbon can be tuned by the above method. In this regard, the rylene dye entered the pores of the

porous carbon, and when at least partially carbonised, the rylene dye narrows the pore width and aperture size of the pores. This can be further controlled by varying the temperature. The present invention provides the advantages of a high plateau capacity, high specific capacity and high average voltage in full-cell battery by blocking the open pores of porous carbon into the closed ones and then turn the capacitive sodium storage process to pore-filling mechanism. As the synthesis process is easy, there is also scalability for industrialisation processes. The low synthesis temperature compared to conventional (1500 °C and higher) also provides energy conservation benefits. The formed electrode can have a high mass loading and low- temperature endurance while a full-cell battery can have good electrochemical performance, indicating reasonable practical applications.

As used herein, a rylene dye is a dye based on the rylene framework of naphthalene units linked in peri-positions. In homologues additional naphthalene units are added, forming compounds - or poly(peri-naphthalene)s - such as perylene, terrylene and quarterrylene. The rylene dyes can be functionalised with polar and/or hydrophilic moieties such as carboxylate, amide, amine, anhydride and diacetamide groups.

In some embodiments, the rylene dye is selected from perylenetetracarboxylic dianhydride (PTCDA; melting point 350 °C; MW 392 g/mol), perylenediimide, terrylendiimide, terrylen, perylen, quaterrylen and naphthalin. Other rylene dyes displaying similar properties (e.g., molten point, molecular size, etc.) can also be used. In some embodiments, the rylene dye is perylenetetracarboxylic dianhydride (PTCDA). PTCDA consists of a perylene core to which two anhydride groups have been attached, one at either side. It occurs in two crystalline forms, α and β . Both have the $P2_1/c$ monoclinic symmetry and a density of ca. 1.7 g/cm³. Functionalised PTCDA and derivatives thereof are also included within this scope.

The porous carbon is carbon which is characterized by their highly developed micro- and meso-pore structures. The pores are able to absorb fluids (liquid and/or gas) or allow fluids to pass through. The major properties of porous carbon are huge surface area and hierarchical porosity. Pores can be categorized into three classes such as macropores, mesopores, and micropores. Macroporous materials have pore diameter larger than 50 nm, mesoporous

materials have pore diameter smaller than 50 nm and higher than 2 nm, and microporous materials have pore diameter smaller than 2 nm and higher than 0.8 nm. Ultra-microporous materials have pore diameter smaller than 0.8 nm. Further, the pores can be interconnected to each other.

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In some embodiments, the porous carbon is selected from activated carbon, mesoporous carbon, carbonised sugar, high specific surface area carbon and low specific surface area carbon. In other embodiments, the porous carbon is mesoporous carbon and/or microporous carbon. The activated carbon can be a microporous carbon. In other embodiments, the porous carbon is microporous carbon, carbonised sugar, high specific surface area carbon and low specific surface area carbon.

In some embodiments, the porous carbon is mesoporous carbon. The mesoporous carbon can have a pore diameter of about 2 nm to about 50 nm. In other embodiments, the pore diameter is about 2 nm to about 45 nm, about 2 nm to about 40 nm, about 2 nm to about 35 nm, about 2 nm to about 30 nm, about 2 nm to about 25 nm, about 2 nm to about 20 nm, about 2 nm to about 15 nm, about 2 nm to about 10 nm, or about 2 nm to about 5 nm.

In other embodiments, the porous carbon is microporous carbon. The microporous carbon can have a pore diameter of more than 0.7 nm to about 2 nm. In other embodiments, the pore diameter is more than 0.7 nm to about 1.5 nm, more than 0.7 nm to about 1.2 nm, more than 0.8 nm to about 2 nm, more than 0.8 nm to about 1.5 nm, or more than 0.8 nm to about 1.2 nm.

In some embodiments, a mass ratio of porous carbon to rylene dye is about 1:1 to about 1:4. The mass ratio of the porous carbon and rylene dye can be calculated according to the pore volume of porous carbon and the density of the rylene dye. For example, for $1.391 \text{ cm}^3\text{g}^{-1}$ pore volume of AC, the mass ratio of the AC (host) to PTCDA (filler) is about 1:2.36. In other embodiments, the mass ratio is about 1:1 to about 1.3, about 1:1 to about 1.25, about 1:15 to about 1.25, or about 1:2. The mass ratio of rylene dye to porous carbon can alternatively be referred to a filler/host ratio.

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In some embodiments, the mixture is mechanically blended. This can be done by stirring the mixture or by subjecting the mixture to a shearing force. In other embodiments, the mixture is homogenously blended.

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In a subsequent step, the mixture is heated. Advantageously, the heating step under an inert atmosphere allows the rylene dye to become molten, and accordingly, diffuse into the pores of porous carbon. The heating step alters the physical and optionally the chemical properties of a rylene dye such that it is more workable. Towards this end, the heating step involves
10 heating the rylene dye above its recrystallization temperature, maintaining a suitable temperature for an appropriate amount of time and then optionally cooling. The heating step can also be an annealing step.

In some embodiments, the mixture is heated from about 300 °C to about 600 °C. In other
15 embodiments, the mixture is heated from about 300 °C to about 550 °C, about 300 °C to about 500 °C, about 300 °C to about 450 °C, or about 300 °C to about 400 °C. In other embodiments, the mixture is heated to about 450 °C.

In some embodiments, the inert atmosphere is argon. The inert atmosphere is devoid of
20 oxygen.

In some embodiments, the heating step is performed for about 2 h to about 10 h. In other embodiments, the heating step is performed for about 2 h to about 9 h, about 2 h to about 8 h, about 2 h to about 7 h, about 2 h to about 6 h, about 2 h to about 5 h, about 2 h to about 4
25 h, or about 2 h to about 3 h.

The method subsequently involves at least partially carbonising the mixture at a temperature of about 700 °C to about 1300 °C. As the rylene dye has a thermal decomposition temperature of about 550-600 °C under TGA, depending on the holding temperature and the holding
30 period, the amount of carbonisation of rylene dye can be controlled. In other embodiments, the temperature is about 750 °C to about 1300 °C, about 800 °C to about 1300 °C, about 850

°C to about 1300 °C, about 900 °C to about 1300 °C, about 1000 °C to about 1300 °C, about 1100 °C to about 1300 °C, about 700 °C to about 1200 °C, about 750 °C to about 1200 °C, about 800 °C to about 1200 °C, about 850 °C to about 1200 °C, about 900 °C to about 1200 °C, about 1000 °C to about 1200 °C, or about 1100 °C to about 1200 °C.

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Carbonization is the conversion of organic matters into carbon through destructive distillation. Destructive distillation is a chemical process in which decomposition of organic matter is achieved by heating it to a high temperature; the term generally applies to processing of organic material in the absence of air or in the presence of limited amounts of oxygen or other reagents, catalysts, or solvents, such as steam or phenols. Carbonization is a pyrolytic reaction, therefore, is considered a complex process in which many reactions take place concurrently such as dehydrogenation, condensation, hydrogen transfer and isomerization. The amount of heat applied controls the degree of carbonization and the residual content of foreign elements. In particular, 1 g of PTCDA when carbonised can provide about 0.4 g of carbon.

Advantageously, the pores blocked by rylene dye is then carbonised within the porous carbon to convert the open pores to closed pores. This method alters the pore size of the porous carbon, does not completely block the pores and is also less energy intensive compared to high temperature annealing. Anode formed using this method for sodium-ion storage exhibits increased plateau capacity, improved cycling stability, satisfying rate capability and high areal capacity.

In some embodiments, the carbonisation step is performed for at least 3 h. In other embodiments, the step is performed for at least 4 h, 5 h, 6 h, 8 h, 10 h or 12 h.

In some embodiments, the carbonisation step is performed under a rate of about 3 °C/min to about 10 °C/min. In other embodiments, the step is performed under a rate of about 3 °C/min to about 9 °C/min, about 3 °C/min to about 8 °C/min about 3 °C/min to about 7 °C/min about 3 °C/min to about 6 °C/min, or about 4 °C/min to about 6 °C/min.

In some embodiments, at least 40% of the rylene dye is retained in and/or on the porous carbon and partially carbonised. In this regard, at least 40% of the rylene dye is partially carbonised while the remainder is removed via evaporation. The remainder rylene dye can be expelled via a flow of inert gas in the inert atmosphere. In other embodiments, the rylene dye is carbonised by at least 50%, at least 60%, at least 70%, at least 80%, at least 90%, or at least 95%.

In some embodiments, the carbonisation step is performed under an inert atmosphere. In other embodiments, the inert atmosphere is argon. The inert atmosphere is devoid of oxygen.

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By taking at least these steps, the aperture size of the pores and the pore width or diameter of the porous carbon can be modulated such that it is suitable for use as an electrode material and in a battery. Further, depending on the type of porous carbon used, the skeletal density can be altered, thus changing the density of the pores present in the carbon.

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In some embodiments, the method of fabricating a modified porous carbon composite comprises:

a) mixing porous carbon with a rylene dye in order to form a mixture;
b) heating the mixture from about 300 °C to about 600 °C under an inert atmosphere;
20 and

c) carbonising the mixture at a temperature of about 700 °C to about 1300 °C in order to form ultra-micropores within the porous carbon;

wherein the ultra-micropores have a pore diameter (based on CO₂ adsorption) of about 0.2 nm to about 0.8 nm, and

25 wherein the composite has a BET (CO₂) specific surface area of about 10 m² g⁻¹ to about 220 m² g⁻¹.

In some embodiments, the method of fabricating a modified porous carbon composite comprises:

30 a) mixing porous carbon with a rylene dye in order to form a mixture;

- b) heating the mixture from about 300 °C to about 600 °C under an inert atmosphere; and
 - c) carbonising the mixture at a temperature of about 700 °C to about 1300 °C in order to form ultra-micropores within the porous carbon;
- 5 wherein the ultra-micropores have a pore diameter (based on CO₂ adsorption) of about 0.2 nm to about 0.8 nm,
- wherein the composite has a BET (N₂) specific surface area of about 5 m² g⁻¹ to about 80 m² g⁻¹, and
- wherein the composite has a BET (CO₂) specific surface area of about 10 m² g⁻¹ to about 220
- 10 m² g⁻¹.

In some embodiments, the method of fabricating a modified porous carbon composite comprises:

- a) mixing porous carbon with a rylene dye in order to form a mixture;
 - 15 b) heating the mixture from about 300 °C to about 600 °C under an inert atmosphere; and
 - c) carbonising the mixture at a temperature of about 700 °C to about 1300 °C in order to form ultra-micropores within the porous carbon;
- wherein the ultra-micropores have a pore diameter (based on CO₂ adsorption) of about 0.2
- 20 nm to about 0.8 nm,
- wherein the composite has a BET (N₂) specific surface area of about 5 m² g⁻¹ to about 80 m² g⁻¹,
- wherein the composite has a BET (CO₂) specific surface area of about 10 m² g⁻¹ to about 220 m² g⁻¹; and
- 25 wherein the composite has a BET (CO₂) specific surface area to BET (N₂) specific surface area ratio of about 0.1 to about 50.

In some embodiments, the method of fabricating a modified porous carbon composite comprises:

- 30 a) mixing porous carbon with PTCDA in order to form a mixture;

- b) heating the mixture from about 300 °C to about 600 °C under an inert atmosphere; and
- c) carbonising the mixture at a temperature of about 700 °C to about 1300 °C in order to form ultra-micropores within the porous carbon.

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In some embodiments, the method of fabricating a composite comprises:

- a) mixing porous carbon with PTCDA in order to form a mixture;
 - b) heating the mixture from about 300 °C to about 600 °C under an inert atmosphere; and
 - 10 c) carbonising the mixture at a temperature of about 700 °C to about 1300 °C in order to form ultra-micropores within the porous carbon;
- wherein the ultra-micropores have a pore diameter (based on CO₂ adsorption) of about 0.2 nm to about 0.8 nm, and
- wherein the composite has a BET (CO₂) specific surface area of about 10 m² g⁻¹ to about 220
- 15 m² g⁻¹.

In some embodiments, the method of fabricating a modified porous carbon composite comprises:

- a) mixing porous carbon with PTCDA in order to form a mixture;
 - 20 b) heating the mixture from about 300 °C to about 600 °C under an inert atmosphere; and
 - c) carbonising the mixture at a temperature of about 700 °C to about 1300 °C in order to form ultra-micropores within the porous carbon;
- wherein the ultra-micropores have a pore diameter (based on CO₂ adsorption) of about 0.2
- 25 nm to about 0.8 nm,
- wherein the composite has a BET (N₂) specific surface area of about 5 m² g⁻¹ to about 80 m² g⁻¹, and
- wherein the composite has a BET (CO₂) specific surface area of about 10 m² g⁻¹ to about 220
- m² g⁻¹.

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In some embodiments, the method of fabricating a modified porous carbon composite comprises:

- a) mixing porous carbon with PTCDA in order to form a mixture;
 - b) heating the mixture from about 300 °C to about 600 °C under an inert atmosphere;
 - 5 and
 - c) carbonising the mixture at a temperature of about 700 °C to about 1300 °C in order to form ultra-micropores within the porous carbon;
- wherein the ultra-micropores have a pore diameter (based on CO₂ adsorption) of about 0.2 nm to about 0.8 nm,
- 10 wherein the composite has a BET (N₂) specific surface area of about 5 m² g⁻¹ to about 80 m² g⁻¹,
- wherein the composite has a BET (CO₂) specific surface area of about 10 m² g⁻¹ to about 220 m² g⁻¹; and
- wherein the composite has a BET (CO₂) specific surface area to BET (N₂) specific surface
- 15 area ratio of about 0.1 to about 50.

The present invention also discloses a modified porous carbon composite comprising:

- a) a porous carbon; and
- b) an at least partially carbonised rylene dye;
- 20 wherein the at least partially carbonised rylene dye coats a pore and an external surface of the porous carbon.

The present invention also discloses a modified porous carbon composite comprising:

- a) a porous carbon structure; and
 - 25 b) a carbonised rylene dye;
- wherein the carbonised rylene dye coats at least inner pores of the porous carbon structure.

In some embodiments, the modified porous carbon composite comprises:

- a) a porous carbon structure; and
 - 30 b) a carbonised rylene dye;
- wherein the carbonised rylene dye coats at least inner pores of the porous carbon structure.

The term “porous carbon structure” is used to represent the skeletal carbon structure of the composite. This is distinct from “porous carbon”, which refers to the porous carbon used as a raw material for making the composite. Accordingly, the “porous carbon” when processed,
5 forms a composite with a “porous carbon structure”.

The carbonised rylene dye coats at least inner pores of the porous carbon structure, and can coat inner pores and external surface of the porous carbon structure. The coating of the carbonised rylene dye at least in inner pores reduces the pore size and the aperture size.
10 When coated on the external surface, a negligible increase in composite particle size can be observed.

In some embodiments, a mass ratio of porous carbon structure to at least partially carbonised rylene dye is about 1:1 to about 1:4. In other embodiments, the mass ratio is about 1:1 to
15 about 1:3.5, about 1:1 to about 1:3, about 1:1 to about 1:2.5, about 1:1 to about 1:2, or about 1:1 to about 1:1.5.

In some embodiments, the at least partially carbonised rylene dye is at least 40% carbonised. In this regard, at least 40% of the rylene dye in/on the porous carbon is thermally
20 decomposed into carbon. As the rylene dye has a thermal decomposition temperature of about 550-600 °C under TGA, depending on the holding temperature and the holding period, the amount of carbonisation of rylene dye can be controlled. In other embodiments, the carbonisation is at least 50%, at least 60%, at least 70%, at least 80%, at least 90%, or at least 95%. In some embodiments, the rylene dye is completely carbonised.

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The coating of the at least partially carbonised rylene dye on a pore of the porous carbon structure reduces its pore size (pore diameter). In this regard, a mesoporous carbon when coated with a at least partially carbonised rylene dye is formed as a microporous carbon. Similarly, a microporous carbon when coated with a carbonised rylene dye is formed as a
30 ultra-microporous carbon.

The coating of the carbonised rylene dye on a pore of the porous carbon structure reduces its aperture size. This is a result of the coating of the rylene dye at the aperture of the pores, which after carbonisation, forms a carbonised layer at the aperture and in turn narrows the aperture size.

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In some embodiments, the composite has an XRD pattern which indicates the presence of a (002) peak of a carbon derived from the carbonised rylene dye and a (002) peak of the porous carbon. In some embodiments, the (002) peak of the carbon derived from the carbonised rylene dye is about 25.2°. In some embodiments, the (002) peak of the porous carbon is about 21.2°.

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In some embodiments, the composite has a BET (N₂) specific surface area of about 5 m² g⁻¹ to about 80 m² g⁻¹. In other embodiments, the BET (N₂) specific surface area is about 5 m² g⁻¹ to about 75 m² g⁻¹, about 5 m² g⁻¹ to about 70 m² g⁻¹, about 5 m² g⁻¹ to about 65 m² g⁻¹, about 5 m² g⁻¹ to about 60 m² g⁻¹, about 5 m² g⁻¹ to about 55 m² g⁻¹, about 5 m² g⁻¹ to about 50 m² g⁻¹, about 5 m² g⁻¹ to about 45 m² g⁻¹, about 5 m² g⁻¹ to about 40 m² g⁻¹, about 10 m² g⁻¹ to about 40 m² g⁻¹, or about 20 m² g⁻¹ to about 40 m² g⁻¹.

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In some embodiments, the composite has a micropore (N₂) specific surface area of about 5 m² g⁻¹ to about 80 m² g⁻¹. In other embodiments, the micropore (N₂) specific surface area is about 5 m² g⁻¹ to about 75 m² g⁻¹, about 5 m² g⁻¹ to about 70 m² g⁻¹, about 5 m² g⁻¹ to about 65 m² g⁻¹, about 5 m² g⁻¹ to about 60 m² g⁻¹, about 5 m² g⁻¹ to about 55 m² g⁻¹, about 5 m² g⁻¹ to about 50 m² g⁻¹, about 5 m² g⁻¹ to about 45 m² g⁻¹, about 5 m² g⁻¹ to about 40 m² g⁻¹, about 10 m² g⁻¹ to about 40 m² g⁻¹, or about 20 m² g⁻¹ to about 40 m² g⁻¹.

25

In some embodiments, the composite has an external (N₂) specific surface area of about 0.5 m² g⁻¹ to about 30 m² g⁻¹. In other embodiments, the external (N₂) specific surface area is about 1 m² g⁻¹ to about 30 m² g⁻¹, about 5 m² g⁻¹ to about 30 m² g⁻¹, about 10 m² g⁻¹ to about 30 m² g⁻¹, about 15 m² g⁻¹ to about 30 m² g⁻¹, about 15 m² g⁻¹ to about 25 m² g⁻¹, or about 15 m² g⁻¹ to about 20 m² g⁻¹.

30

In some embodiments, the composite has a micropore volume (based on N₂ adsorption) of about 0.002 cm³ g⁻¹ to about 0.030 cm³ g⁻¹. In other embodiments, the micropore volume is about 0.002 cm³ g⁻¹ to about 0.025 cm³ g⁻¹, about 0.002 cm³ g⁻¹ to about 0.020 cm³ g⁻¹, about 0.002 cm³ g⁻¹ to about 0.015 cm³ g⁻¹, or about 0.010 cm³ g⁻¹ to about 0.015 cm³ g⁻¹.

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In some embodiments, the composite has an external volume (based on N₂ adsorption) of about 0.005 cm³ g⁻¹ to about 0.1 cm³ g⁻¹. In other embodiments, the external volume is about 0.005 cm³ g⁻¹ to about 0.090 cm³ g⁻¹, about 0.005 cm³ g⁻¹ to about 0.080 cm³ g⁻¹, about 0.005 cm³ g⁻¹ to about 0.070 cm³ g⁻¹, about 0.005 cm³ g⁻¹ to about 0.060 cm³ g⁻¹, about 0.010 cm³ g⁻¹ to about 0.060 cm³ g⁻¹, about 0.020 cm³ g⁻¹ to about 0.060 cm³ g⁻¹, about 0.030 cm³ g⁻¹ to about 0.060 cm³ g⁻¹, or about 0.040 cm³ g⁻¹ to about 0.060 cm³ g⁻¹.

In some embodiments, the composite has a total volume (based on N₂ adsorption) of about 0.01 cm³ g⁻¹ to about 0.13 cm³ g⁻¹. In other embodiments, the total volume is about 0.01 cm³ g⁻¹ to about 0.12 cm³ g⁻¹, about 0.01 cm³ g⁻¹ to about 0.11 cm³ g⁻¹, about 0.01 cm³ g⁻¹ to about 0.10 cm³ g⁻¹, about 0.01 cm³ g⁻¹ to about 0.09 cm³ g⁻¹, about 0.01 cm³ g⁻¹ to about 0.08 cm³ g⁻¹, about 0.01 cm³ g⁻¹ to about 0.07 cm³ g⁻¹, about 0.02 cm³ g⁻¹ to about 0.07 cm³ g⁻¹, about 0.03 cm³ g⁻¹ to about 0.07 cm³ g⁻¹, about 0.04 cm³ g⁻¹ to about 0.07 cm³ g⁻¹, or about 0.05 cm³ g⁻¹ to about 0.07 cm³ g⁻¹.

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In some embodiments, the composite has a BET (CO₂) specific surface area of about 10 m² g⁻¹ to about 220 m² g⁻¹. In other embodiments, the BET (CO₂) specific surface area of about 20 m² g⁻¹ to about 220 m² g⁻¹, about 30 m² g⁻¹ to about 220 m² g⁻¹, about 40 m² g⁻¹ to about 220 m² g⁻¹, about 50 m² g⁻¹ to about 220 m² g⁻¹, about 60 m² g⁻¹ to about 220 m² g⁻¹, about 70 m² g⁻¹ to about 220 m² g⁻¹, about 80 m² g⁻¹ to about 220 m² g⁻¹, about 90 m² g⁻¹ to about 220 m² g⁻¹, about 90 m² g⁻¹ to about 210 m² g⁻¹, about 90 m² g⁻¹ to about 200 m² g⁻¹, about 90 m² g⁻¹ to about 190 m² g⁻¹, about 90 m² g⁻¹ to about 180 m² g⁻¹, about 90 m² g⁻¹ to about 170 m² g⁻¹, or about 90 m² g⁻¹ to about 160 m² g⁻¹.

30 In some embodiments, the composite has a total volume (based on CO₂ adsorption) of about 0.08 cm³ g⁻¹ to about 0.4 cm³ g⁻¹. In other embodiments, the total volume is about 0.08 cm³

g^{-1} to about $0.39 \text{ cm}^3 \text{ g}^{-1}$, about $0.08 \text{ cm}^3 \text{ g}^{-1}$ to about $0.38 \text{ cm}^3 \text{ g}^{-1}$, about $0.08 \text{ cm}^3 \text{ g}^{-1}$ to about $0.37 \text{ cm}^3 \text{ g}^{-1}$, about $0.08 \text{ cm}^3 \text{ g}^{-1}$ to about $0.36 \text{ cm}^3 \text{ g}^{-1}$, about $0.08 \text{ cm}^3 \text{ g}^{-1}$ to about $0.35 \text{ cm}^3 \text{ g}^{-1}$, about $0.08 \text{ cm}^3 \text{ g}^{-1}$ to about $0.3 \text{ cm}^3 \text{ g}^{-1}$, about $0.08 \text{ cm}^3 \text{ g}^{-1}$ to about $0.25 \text{ cm}^3 \text{ g}^{-1}$, about $0.08 \text{ cm}^3 \text{ g}^{-1}$ to about $0.2 \text{ cm}^3 \text{ g}^{-1}$, or about $0.08 \text{ cm}^3 \text{ g}^{-1}$ to about $0.15 \text{ cm}^3 \text{ g}^{-1}$.

5

In some embodiments, the composite has a BET (CO_2) specific surface area to BET (N_2) specific surface area ratio of about 0.1 to about 50. As N_2 and CO_2 has different molecular sizes, the ratio can quantify the ratio of aperture size less than 0.5 nm to aperture size more than 0.5 nm of the pores within the porous carbon. In other embodiments, the ratio is about 10 0.2 to about 50, about 0.5 to about 50, about 1 to about 50, about 5 to about 50, about 10 to about 50, about 15 to about 50, about 20 to about 50, or about 30 to about 50.

In some embodiments, the composite comprises ultra-micropores, the ultra-micropores having a pore diameter (based on CO_2 adsorption) of about 0.2 nm to about 0.8 nm. In other 15 embodiments, the pore diameter is about 0.2 nm to about 0.7 nm, about 0.2 nm to about 0.6 nm, about 0.2 nm to about 0.5 nm, or about 0.3 nm to about 0.5 nm.

Graphitization is the process of heating amorphous carbon for a prolonged period of time, so as to rearrange the atomic structure to achieve an ordered crystalline structure. During 20 graphitization, carbon atoms are rearranged to fill atom vacancies and improve atom layout. The graphitization degree depends on the structure of the carbon material (graphitability) and the applied graphitization temperature. It can be determined by x-ray measurements. In some embodiments, the composite has a **R** value of about 2 to about 5. In other embodiments, the R value is about 2.5 to about 5, about 3 to about 5, about 3.5 to about 5, or about 4 to 25 about 5.

Skeletal or true density of the composite is a determination of the density of the composite per se, excluding any voids or spaces between the carbon particles, or on their surfaces. In some embodiments, the composite has a skeletal density of about 1.8 g cm^{-3} to about 2.5 g cm^{-3} . In other embodiments, the skeletal density is about 1.8 g cm^{-3} to about 2.4 g cm^{-3} , about 30 cm^{-3} .

1.8 g cm⁻³ to about 2.3 g cm⁻³, about 1.8 g cm⁻³ to about 2.2 g cm⁻³, about 1.9 g cm⁻³ to about 2.2 g cm⁻³, about 2.0 g cm⁻³ to about 2.2 g cm⁻³, or about 2.1 g cm⁻³ to about 2.2 g cm⁻³.

In some embodiments, the thickness of the carbonised rylene dye is about 0.2 nm to about 1.2 nm. In other embodiments, the thickness is about 0.2 nm to about 1.0 nm, about 0.2 nm to about 0.9 nm, about 0.2 nm to about 0.8 nm, about 0.2 nm to about 0.7 nm, about 0.2 nm to about 0.6 nm, about 0.2 nm to about 0.5 nm, or about 0.2 nm to about 0.4 nm. This can be quantified by measuring the pore size before and after carbonisation, or from BET results.

10 In some embodiments, the modified porous carbon composite comprises:

- a) a porous carbon structure; and
- b) a carbonised rylene dye;

wherein the carbonised rylene dye at least coats inner pores of the porous carbon structure; wherein the composite comprises ultra-micropores, the ultra-micropores having a pore diameter (based on CO₂ adsorption) of about 0.2 nm to about 0.8 nm; and
15 wherein the composite has a BET (CO₂) specific surface area of about 10 m² g⁻¹ to about 220 m² g⁻¹.

In some embodiments, the modified porous carbon composite comprises:

- 20
- a) a porous carbon structure; and
 - b) a carbonised rylene dye;

wherein the carbonised rylene dye at least coats inner pores of the porous carbon structure; wherein the composite comprises ultra-micropores, the ultra-micropores having a pore diameter (based on CO₂ adsorption) of about 0.2 nm to about 0.8 nm;
25 wherein the composite has a BET (N₂) specific surface area of about 5 m² g⁻¹ to about 80 m² g⁻¹; and
wherein the composite has a BET (CO₂) specific surface area of about 10 m² g⁻¹ to about 220 m² g⁻¹.

30 In some embodiments, the modified porous carbon composite comprises:

- a) a porous carbon structure; and

- b) a carbonised PTCDA;
wherein the carbonised PTCDA at least coats inner pores of the porous carbon structure;
wherein the composite comprises ultra-micropores, the ultra-micropores having a pore diameter (based on CO₂ adsorption) of about 0.2 nm to about 0.8 nm; and
5 wherein the composite has a BET (CO₂) specific surface area of about 10 m² g⁻¹ to about 220 m² g⁻¹.

In some embodiments, the modified porous carbon composite comprises:

- a) a porous carbon structure; and
10 b) a carbonised PTCDA;
wherein the carbonised PTCDA at least coats inner pores of the porous carbon structure;
wherein the composite comprises ultra-micropores, the ultra-micropores having a pore diameter (based on CO₂ adsorption) of about 0.2 nm to about 0.8 nm;
wherein the composite has a BET (N₂) specific surface area of about 5 m² g⁻¹ to about 80 m² g⁻¹; and
15 wherein the composite has a BET (CO₂) specific surface area of about 10 m² g⁻¹ to about 220 m² g⁻¹.

- In some embodiments, the composite comprises a porous carbon structure having ultra-
20 micropores, wherein the ultra-micropores have a pore diameter (based on CO₂ adsorption) of about 0.2 nm to about 0.8 nm, wherein the composite has a BET (N₂) specific surface area of about 5 m² g⁻¹ to about 80 m² g⁻¹, and wherein the composite has a BET (CO₂) specific surface area of about 10 m² g⁻¹ to about 220 m² g⁻¹. In some embodiments, the composite comprises a porous carbon structure having ultra-micropores, wherein the ultra-micropores
25 have a pore diameter (based on CO₂ adsorption) of about 0.2 nm to about 0.8 nm, wherein the composite has a BET (N₂) specific surface area of about 5 m² g⁻¹ to about 80 m² g⁻¹, and wherein the composite has a BET (CO₂) specific surface area of about 10 m² g⁻¹ to about 220 m² g⁻¹, wherein the composite has a skeletal density of about 1.8 g cm⁻³ to about 2.5 g cm⁻³.
30 In some embodiments, the composite comprises a porous carbon structure having ultra-micropores, wherein the ultra-micropores have a pore diameter (based on CO₂ adsorption)

of about 0.2 nm to about 0.8 nm, wherein the composite has a BET (CO₂) specific surface area to BET (N₂) specific surface area ratio of about 0.1 to about 50. In some embodiments, the composite comprises a porous carbon structure having ultra-micropores, wherein the ultra-micropores have a pore diameter (based on CO₂ adsorption) of about 0.2 nm to about 0.8 nm, wherein the composite has a BET (CO₂) specific surface area to BET (N₂) specific surface area ratio of about 0.1 to about 50, wherein the composite has a skeletal density of about 1.8 g cm⁻³ to about 2.5 g cm⁻³.

The present invention also discloses a method of fabricating an electrode, comprising:

- a) mixing a composite as disclosed herein with a binder solution to form a slurry;
- b) applying the slurry on a surface of an electrical conductor; and
- c) drying the slurry.

In some embodiments, a weight ratio of composite to binder solution is about 80:20 to about 95:5. In other embodiments, the weight ratio is about 85:15 to about 95:5, or about 90:10 to about 95:5.

In some embodiments, the binder solution has a concentration of about 10 mg/mL to about 20 mg/mL. In some embodiments, the concentration is about 10 mg/mL to about 18 mg/mL, about 10 mg/mL to about 16 mg/mL, about 10 mg/mL to about 14 mg/mL, or about 12 mg/mL to about 14 mg/mL.

In some embodiments, the binder solution comprises a binder selected from sodium carboxymethyl cellulose and/or polyvinylidene fluoride (PVDF).

In some embodiments, the drying step is performed at about 40 °C to about 80 °C. In other embodiments, the temperature is about 50 °C to about 80 °C, about 60 °C to about 80 °C, or about 70 °C to about 80 °C.

In some embodiments, the drying step is performed for about 2 h to about 6 h. In other embodiments, the time is about 3 h to about 6 h, about 4 h to about 6 h, or about 5 h to about 6 h.

- 5 In some embodiments, the drying step further comprises vacuum drying the slurry at about 100 °C to about 140 °C for at least 8 h. In other embodiments, the temperature is about 110 °C to about 140 °C, about 120 °C to about 140 °C, or about 130 °C to about 140 °C.

- The electrical conductor can be a current collector. A current collector carry charges that is
10 formable at the interface and within the pores of the composite to an electrical component configured to receive the electrical charges.

In some embodiments, the method of fabricating an electrode comprises:

- a) mixing a composite as disclosed herein with a binder solution to form a slurry;
15 b) applying the slurry on a surface of a current collector; and
c) drying the slurry.

The present invention also discloses an electrode, comprising:

- a) a composite as disclosed herein;
20 b) a binder; and
c) an electrical conductor;

wherein the composite and the binder are homogenously combined; and

wherein the composite and the binder coats at least a surface of the electrical conductor.

- 25 In some embodiments, the electrode comprises:

- a) a composite as disclosed herein;
b) a binder; and
c) a current collector;

wherein the composite and the binder are homogenously combined; and

- 30 wherein the composite and the binder coats at least a surface of the current collector.

In some embodiments, the composite and the binder coats at least two surfaces of the electrical conductor. In other embodiments, the composite and the binder fully coats the electrical conductor.

- 5 In some embodiments, a weight ratio of composite to binder is about 80:20 to about 95:5. In other embodiments, the weight ratio is about 85:15 to about 95:5, or about 90:10 to about 95:5.

- 10 In some embodiments, a mass loading of the composite and binder on the electrical conductor is at least 15 mg cm^{-2} . In other embodiments, mass loading of composite and binder on the electrical conductor is at least 16 mg cm^{-2} , at least 17 mg cm^{-2} , at least 18 mg cm^{-2} , at least 19 mg cm^{-2} , or at least 20 mg cm^{-2} .

- 15 In some embodiments, the electrode has a capacity of more than 100 mAh g^{-1} at a current density of about 2000 mA g^{-1} . This capacity can be reversible. In other embodiments, the capacity is more than 110 mAh g^{-1} , more than 120 mAh g^{-1} , more than 130 mAh g^{-1} , more than 140 mAh g^{-1} , or more than 150 mAh g^{-1} . In other embodiments, the electrode has a capacity of about 100 mAh g^{-1} to about 200 mAh g^{-1} at a current density of about 2000 mA g^{-1} .

- 20 In some embodiments, the electrode has a capacity of more than 300 mAh g^{-1} at a current density of about 30 mA g^{-1} . This capacity can be reversible. In other embodiments, the capacity is more than 310 mAh g^{-1} , more than 320 mAh g^{-1} , more than 330 mAh g^{-1} , more than 340 mAh g^{-1} , or more than 350 mAh g^{-1} . In other embodiments, the electrode has a capacity of about 300 mAh g^{-1} to about 400 mAh g^{-1} at a current density of about 30 mA g^{-1} .

- 30 In some embodiments, the electrode has a retention of at least 80% of its initial capacity after 200 cycles. The cyclability can be tested at about 50 mAh g^{-1} . In other embodiments, the electrode has a retention of at least 85%, at least 90% or at least 95% of its initial capacity after 200 cycles.

In some embodiments, the electrode has an areal capacity of about 6 mAh cm⁻² to about 8 mAh cm⁻² at a current density of about 0.1 mA cm⁻². In other embodiments, the areal capacity is about 6 mAh cm⁻² to about 7.5 mAh cm⁻², or about 6 mAh cm⁻² to about 7 mAh cm⁻².

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In some embodiments, the electrode has an areal capacity of about 3 mAh cm⁻² to about 5 mAh cm⁻² at a current density of about 0.5 mA cm⁻². In other embodiments, the areal capacity is about 3 mAh cm⁻² to about 4.5 mAh cm⁻², or about 3 mAh cm⁻² to about 3 mAh cm⁻².

- 10 In some embodiments, at least 80% of an areal capacity is retained at about -20 °C to about 40 °C. In other embodiments, the areal capacity is retained at least 85%, at least 90%, or at least 95%.

- 15 In some embodiments, the electrode has an areal capacity of about 5.3 mAh cm⁻² at about -20 °C.

- 20 In some embodiments, when in the presence of an electrolyte during a discharge and/or charge process, the electrode is able to undergo a capacitive adsorption process and a diffusion-controlled process. In some embodiments, the cations of the electrolyte can be adsorbed onto a surface of the electrode. In other embodiments, the cations of the electrolyte can be inserted into an ultra-micropore of the electrode. In other embodiments, the cations of the electrolyte is not intercalated with the ultra-micropore. Intercalation expands the van der Waals gap between sheets, which requires energy. Usually this energy is supplied by charge transfer between the guest and the host solid. In this regard, there is no charge transfer
- 25 between the cations and the ultra-micropores, but the cations cluster together for increased stability. In some embodiments, an XRD (002) peak is not shifted after incorporation of cations within the ultra-micropore.

The present invention also discloses a battery, comprising:

- 30 a) an organic cathode;
b) an anode, the anode comprising the composite as disclosed herein; and

c) sodium metal, the sodium metal applied on at least a surface of the anode.

In some embodiments, the anode comprises the electrode as disclosed herein.

- 5 In some embodiments, the battery is capable of demonstrating a low voltage plateau region and a high voltage sloping region under varying capacity.

In some embodiments, the organic cathode comprises a rylene dye.

- 10 In some embodiments, a mass loading ratio of the organic cathode to the anode is about 1:2 to about 1:3.

In some embodiments, a N/P ratio (the areal capacity ratio of negative to positive electrode) is about 1.1:1 to about 1.2:1.

15

Coulombic efficiency is the ratio of the total charge extracted from the battery to the total charge put into the battery over a full cycle. High initial coulombic efficiency is desirable because it implies effective interface construction and few electrolyte consumption, indicating enhanced batteries' life and power output. In some embodiments, the battery has an initial coulombic efficiency of about 70% to about 90%. In other embodiments, the initial coulombic efficiency is about 75% to about 90%, about 80% to about 90%, about 85% to about 90%, or about 90% to about 90%. Initial coulombic efficiency (ICE) can be calculated as following formula:

20

$$ICE = \frac{\text{desodiation capacity of 1st cycle}}{\text{sodiation capacity of 1st cycle}}$$

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In some embodiments, during a charging and/or discharge of the battery, the battery is characterised by a peak at 4.44 ppm in *ex-situ* ^{23}Na MAS NMR which indicates adsorption of Na^+ on the surface sites of the composite.

- 30 In some embodiments, when the battery is fully discharged, the battery is characterised by a

peak from about -20 ppm to about -30 ppm in *ex-situ* ^{23}Na MAS NMR which indicates the presence of Na^+ in the ultra-micropore of the composite. In other embodiments, when the battery fully discharged, the battery is characterised by a peak at 4.44 ppm in *ex-situ* ^{23}Na MAS NMR which indicates the adsorption of Na^+ on the surface sites of the composite.

5

As is disclosed herein, a high-performance hard carbon anode in sodium-ion batteries (SIBs) can be synthesized using a facile, cost-efficient, and massive process by using the ultra-micropores (< 0.5 nm) dominated hard carbon composite formed via a molten diffusion-carbonization strategy (**Figure 1A**). For example, microporous carbon and perylenetetracarboxylic dianhydride (PTCDA) can be first mechanically blended with a specific mass ratio and then annealed at 400 °C in argon for 3 h. Above the melting point (~ 350 °C) of PTCDA, the molten PTCDA diffused into the microporous carbon and subsequently adsorbed on the inner surface of micropores. During the further carbonization process, the PTCDA inside the micropores was carbonized while the residual PTCDA was evaporated and expelled along with the argon flow. For consistency of measurements and to showcase the invention, commercial activated carbon (AC) was first selected as a model host due to its developed porosity.

Scanning electron microscopy (SEM) images display that the morphology of the micron-sized AC particles is maintained well without obvious residual of PTCDA-derived carbon after the molten diffusion-carbonization process (**Figure 1B, 1C**). Transmission electron microscopy (TEM) image of an exemplary composite, ACGC900 (using activated carbon and PTCDA as starting material and carbonated at 900 °C; the related abbreviations can be seen in the **Experimental Section**), reveals a disordered structure without obvious porosity, which is different from the microporous structure of AC (**Figure 1D**). The selected area electron diffraction (SAED) pattern of ACGC900 particle indicates a certain degree of graphitization with an obvious reflection ring corresponding to the (110) planes of graphitic structure, which can be attributed to the introduction of PTCDA-derived carbon inside the micropores (inset in **Figure 1D**). In addition, the Brunauer–Emmett–Teller (BET) specific surface area (S_{BET}) is greatly reduced from 1429 $\text{m}^2 \text{g}^{-1}$ for AC to 48.4 $\text{m}^2 \text{g}^{-1}$ for the designed ACGC900. Compared with AC, the micropores with a size of ~ 1.5 nm cannot be detected

in ACGC900 (**Figure 1F**), suggesting that most of the micropores are modulated to be inaccessible by N₂. Notably, as shown in **Figure 1E** and **Figure 11**, there exists an obvious hysteresis between the N₂ adsorption/desorption isotherms of ACGC900, indicating the existence of restricted pores or ultra-micropores. Due to the smaller molecular size (3.3 Å for CO₂ vs 3.64 Å for N₂) and the higher working temperature (273 K for CO₂ vs 77K for N₂), CO₂ adsorption measurement is highly efficient to detect the potential existence of ultra-micropores (<0.5 nm). As can be seen in **Figure 6** and **Table 2**, the S_{BET} of ACGC900 calculated from CO₂ adsorption measurement is ~ 196.6 m² g⁻¹, much higher than that calculated from N₂ adsorption/desorption. Moreover, the pore size (or pore diameter) of ACGC900 is mainly distributed at 0.3-0.5 nm, along with a pore volume of ~ 0.365 cm³ g⁻¹. The aforementioned results demonstrate the existence of numerous ultra-micropores in ACGC900, which can reduce the interfacial contact between the inner surface of carbon and electrolyte and thus minimize side reactions.

Table 1. Specific surface area and volume of ACGCx calculated from N₂ adsorption/desorption tests.

Sample	S _{BET} [m ² g ⁻¹]	S _{micropore} [m ² g ⁻¹] ^[a]	S _{external} [m ² g ⁻¹] ^[b]	V _{micropore} [cm ³ g ⁻¹] ^[c]	V _{external} [cm ³ g ⁻¹] ^[d]	V _{total} [cm ³ g ⁻¹] ^[e]
AC	1429	1364	65	0.691	0.700	1.391
AC-PTCDA	29.6	5.2	24.4	0.012	0.034	0.046
ACGC750	66.2	42.6	23.6	0.028	0.090	0.118
ACGC900	48.4	32.8	15.6	0.019	0.065	0.084
ACGC1050	36.1	20.6	15.6	0.015	0.054	0.069
ACGC1200	9.7	8.1	1.6	0.004	0.007	0.011

[a] Micropore specific surface area determined by the t-method by N₂ adsorption branch at 77 K.

[b] External specific surface area determined by the t-method external surface area

[c] Micropore volume determined by the HK method by N₂ adsorption branch at 77 K

[d] External volume determined by the summation of mesopore volume from the DFT method and macropore volume calculated from adsorption curve by BJH method

[e] Total volume determined by the summation of the micropore, the external volume

Notes: The specific surface area of ACGCx calculated from N₂ adsorption/desorption test decreases with the increasing carbonization temperature.

5 **Table 2.** Specific surface area for ACGCx calculated from CO₂ and N₂ adsorption/desorption tests.

Sample	$S_{\text{BET}}^{\text{N}_2}$ [m ² g ⁻¹]	$S_{\text{BET}}^{\text{CO}_2}$ [m ² g ⁻¹]	$V_{\text{total}}^{\text{N}_2}$ [cm ³ g ⁻¹] ^[e]	$V_{\text{total}}^{\text{CO}_2}$ [cm ³ g ⁻¹] ^[e]	Skeletal density [g cm ⁻³]
ACGC750	66.2	201.4	0.118	0.369	1.89
ACGC900	48.4	196.6	0.084	0.365	1.98
ACGC1050	36.1	99.9	0.069	0.185	2.08
ACGC1200	9.7	18.6	0.011	0.096	2.14

Notes: skeletal (true) density data were recorded on an AccuPyc II 1340 analyzer using Helium as analysis gas.

10 The microstructure of the rationally designed carbon was further investigated via X-ray diffraction (XRD) measurements (**Figure 1G**). Compared with that of AC, the (002) peak of ACGC900 becomes broader and shifts to a higher degree. By applying the profile-fitting method, the broad peak of ACGC900 can be divided into two parts. Specifically, the fitted peak located at around 25.21° and 21.21° can match well with the (002) peak of the GC and AC, respectively (inset table in **Figure 1G**). The coexistence of two different carbon phases
15 further demonstrates the successful encapsulation, consistent with the SEM results (**Figure 1B and 1C**). The *R* value, an indicator of graphitization degree in carbon materials, is also calculated from XRD patterns (**Figure 7**). As shown in the inset table of **Figure 1G**, the *R* value of ACGC900 is higher than that of AC, indicating a higher graphitization degree for ACGC900, which is in good accordance with the Raman results (**Figure 8**). The improved
20 graphitization can enable a good electroconductivity, which promotes a fast discharge/charge capability.

The electrochemical properties of AC, GC, and ACGC900 electrodes were explored through galvanostatic discharge/charge measurements. From **Figure 2A**, the discharge/charge profiles of AC and GC electrodes are all sloping curves, which mainly result from the capacitive storage of Na^+ on surface sites. For ACGC900 electrode, a plateau appears at ~ 0.1 V in addition to the sloping region above 0.1 V. Accordingly, a couple of redox peaks at ~ 0.1 V are also present in the cyclic voltammetry (CV) curves (**Figure 2B**). Note that the sloping capacity of ACGC900 electrode is nearly equal to that of AC electrode, the increased capacity originating from the plateau region can be attributed to the extra storage sites from the ultra-micropores. Furthermore, the cycling performance and rate capability of these three electrodes were compared in **Figure 2C** and **Figure 9**. When AC electrode was cycled at 50 mA g^{-1} , sharp drop of capacity can be observed from the tenth cycles and nearly no capacity can be obtained after 200 cycles. The rapid failure of AC electrode could be ascribed to the high accessible surface area and low electroconductivity, which may lead to increased solid electrolyte interface (SEI) layers. While for ACGC900 electrode, ~ 90% initial capacity can be reserved after 200 cycles. The improved cycling stability could be attributed to the unique structure after the encapsulation, including the reduced interfacial contact between the electrode and electrolyte and the increased degree of graphitization. Besides, more than 100 mAh g^{-1} can be obtained for the ACGC900 electrode at 2000 mA g^{-1} while nearly no capacity for the AC electrode, further demonstrating the advantage of the unique structure after the molten diffusion-carbonization.

To further explore the relationship between the microstructure and sodium-ion storage performance, ACGCx ($x=750, 900, 1050$, and 1200) samples were prepared under various carbonization temperatures. The morphology of ACGCx can be found in **Figure 10**. Besides, CO_2 and N_2 adsorption/desorption measurements were conducted to explore the evolution of pore structure in ACGCx (**Figure 11-12**). As shown in **Table 1** and **Table 2**, the S_{BET} of ACGCx decreases with the increasing temperature. Moreover, the skeletal (true) density monotonically increases from 1.89 g cm^{-3} (ACGC750) to 2.14 g cm^{-3} (ACGC1200) as the temperature elevated, which is obtained from helium pycnometry test. These temperature-dependent properties suggest more ultra-micropores in ACGCx with the increasing temperature. **Figure 3A** displays the discharge/charge curves of ACGCx electrodes at 50

mA g⁻¹ with a voltage range of 0.001-3 V. The increasing plateau capacity with the increasing temperature indicates increased Na⁺ storage sites generated from the ultra-micropores, which is consistent with the results from helium pycnometry test and CO₂ adsorption measurement. The sloping capacity contribution decreases linearly with the increasing **R** value of the ACGCx (**Figure 3B, Figure 7, 13-15 and Table 3**), where a lower **R** value suggests a lower degree of graphitization or more defect sites. The decreasing sloping capacity with increasing temperature could be attributed to the reduced graphitic interlayer spacing or defect sites. Moreover, the initial coulombic efficiency (ICE) value increases linearly with the decreasing S_{BET} from N₂ adsorption/desorption measurement (**Figure 16 and Table 4**), indicating reduced parasitic reactions towards electrolyte. On the whole, the ACGC1050 electrode displays the highest plateau capacity and whole capacity among all ACGCx electrodes, along with the best rate performance and cycling stability (**Figure 17**). Therefore, the optimized temperature is determined to be 1050 °C.

Table 3. The calculated **R** value of various samples

Sample	R value
ACGC750	2.93
ACGC900	3.54
ACGC1050	4.09
ACGC1200	4.23
GC	5.77
AC	1.61

Table 4. The initial coulombic efficiency (ICE) value of various samples

Sample	ICE (%)
ACGC750	73.0
ACGC900	75.7
ACGC1050	79.5
ACGC1200	87.9
HCGC	75.3
LCGC	80.6
GC	73.3
AC	68.1

Furthermore, the relationship between the pore structure of the porous carbon raw material (porous carbon host) relative to the final composite product and the electrochemical performance was also studied at the optimized temperature (**Figure 18-20**, and **Table 5**). Mesoporous and microporous carbon materials with different S_{BET} were selected as host for comparison. As can be seen in **Figure 3C** and **Figure 21**, the LCGC electrode delivers the highest capacity among these carbon electrodes and a stable cycling performance (**Figure 22**). A quantitative relationship was built between the plateau capacity and the mass ratio of the filler/host, that is, a lower filler/host ratio can ensure a larger plateau capacity (**Figure 3D**). Therefore, porous carbon host with micropore-dominated structure can enable more plateau capacity at the optimized temperature of 1050 °C. Apart from a high reversible capacity of 346 mAh g⁻¹ at 30 mA g⁻¹, the LCGC electrode also demonstrates satisfying rate capability. As shown in **Figure 3E**, a high reversible capacity of 125 mAh g⁻¹ can still be delivered at 2000 mA g⁻¹, which proves a superior performance to that of the previously reported hard carbon anode (**Figure 3F** and **Table 6**).

Table 5. Specific surface area and volume calculated from N₂ adsorption/desorption tests.

Sample	S_{BET} [m ² g ⁻¹]	$S_{\text{micropore}}$ [m ² g ⁻¹] ^[a]	S_{external} [m ² g ⁻¹] ^[b]	$V_{\text{micropore}}$ [cm ³ g ⁻¹] ^[c]	V_{external} [cm ³ g ⁻¹] ^[d]	V_{total} [cm ³ g ⁻¹] ^[e]
CMK8	668	0	668	0.274	1.749	2.023
LC	224	199	25	0.097	0.170	0.267
AC	1429	1364	65	0.691	0.700	1.391
HC	2939	2455	484	1.197	1.723	2.920
CMK8GC	55.6	32.6	23	0.024	0.074	0.098
LCGC	19.4	4.3	15.1	0.005	0.06	0.065
ACGC	36.1	20.6	15.6	0.015	0.054	0.069
HCGC	29	11	18	0.012	0.053	0.065

[a] Micropore specific surface area determined by the t-method by N₂ adsorption branch at 77 K.

- [b] External specific surface area determined by the t-method external surface area
- [c] Micropore volume determined by the HK method by N₂ adsorption branch at 77 K
- [d] External volume determined by the summation of mesopore volume from the DFT method and macropore volume calculated from adsorption curve by BJH method
- 5 [e] Total volume determined by the summation of the micropore, the external volume

From the aforementioned electrochemical results, it can be concluded that it is indeed the introduction of ultra-micropores that leads to the plateau capacity. To demonstrate the sodium-ion storage mechanism, scan-rate-dependent CV from 0.1 to 1.0 mV s⁻¹ and the

10 galvanostatic intermittent titration technique (GITT) measurements were further conducted (**Figure 4A-4C** and **Figure 23-25**). During the discharge/charge process, both surface capacitive adsorption and diffusion-controlled process exist for sodium-ion storage. The contribution ratio of the two mechanisms can be quantitatively determined by the power-law formula: $i=av^b$. As shown in **Figure 4B**, the b -values of the high-voltage sloping region in

15 ACGC electrode are ~ 1.0 , corresponding to a fast adsorption/desorption of Na⁺ at the surface-active sites. However, the b -values of the low-voltage plateau region in the ACGC electrode are ~ 0.5 , suggesting a diffusion-controlled process. Meanwhile, the profiles of the Na⁺ diffusion coefficient (D_{Na^+}) as a function of potential reveal a U-turn point at ~ 0.05 V during the discharge/charge process (**Figure 4C**). The rapid drop of D_{Na^+} at ~ 0.05 V could

20 be ascribed to the large diffusion barrier for Na⁺ insertion into the ultra-micropores, consistent with the low b -values of the low-voltage plateau region (**Figure 4B**). The reversely increasing D_{Na^+} near the cut-off voltage corresponds to the adsorption and clustering of the Na⁺ inside the ultra-micropores. In other words, the adsorption of Na⁺ on the surface sites is deemed as a capacitive behavior whereas the insertion of Na⁺ into the

25 ultra-micropores is a diffusion process.

In-situ XRD measurement is an efficient and real-time technique to detect the possible variation of interlayer spacing during the discharge/charge process. Hence, the *in-situ* XRD pattern of the second discharge/charge cycle at 0.15 mA cm⁻² were collected for analysis. As

30 shown in **Figure 4D**, the band located at 25.6° represents the (002) peak, suggesting a d-spacing of ~ 3.5 Å. If intercalation exists, (002) peak detected from XRD pattern will suffer from peak shifting during discharge/charge process. However, from **Figure 4D** and **4E**, no peak shift of the (002) peak or new peak can be observed during the whole process, proving

no intercalation/deintercalation into/from the graphene interlayers in both sloping region and plateau region. Along with the relationship between the sloping capacity and R value (**Figure 3B**), *in-situ* XRD results further demonstrate that the sloping capacity results from the adsorption/desorption of Na^+ to/from the surface sites, which is also in accordance with the high b -values of the sloping region.

To further explore the sodium-ion storage mechanism in the plateau region, *ex-situ* ^{23}Na MAS NMR measurements were conducted. As can be seen in **Figure 4F**, two resonances at -6.87 ppm and 4.44 ppm can be observed in the spectra obtained from the electrode discharged to 0.5 V and 0.2 V. Note that there is no washing process for the electrode, the peak at -6.87 ppm can be ascribed to the sodium salt in the electrolyte. Along with discharging, the appearance of the peak at 4.44 ppm indicates the adsorption of Na^+ on the surface sites. When the electrode was fully discharged to 0.001 V, a broad peak located in the region from -20 to -30 ppm appears, indicating the existence of Na^+ with a more restricted mobility, e.g., in ultra-micropores. When the electrode is recharged to 3 V, only the peak at -6.87 ppm retains and other peaks disappear accordingly, suggesting the reversible storage of Na^+ on the surface and inside the ultra-micropores. When the electrode is recharged to 0.1 V, the peak nearly returns to the peak location of the electrode discharged to 0.1 V, demonstrating the high reversibility of the pore-filling process. Therefore, it is indeed the pore-filling of Na^+ into the ultra-micropores and then the clustering of Na^+ that contribute to the low-voltage plateau at ~ 0.1 V. Therefore, an “adsorption/pore-filling” mechanism in a sodiation process can be demonstrated (Figure 26).

For the practical applications, advanced sodium-ion storage performance under room/low-temperature in thick electrode is also significant. Hence, a thick electrode of LCGC with a mass loading of $\sim 19 \text{ mg cm}^{-2}$ was further fabricated. As shown in **Figure 5A**, a high areal capacity of 6.14 mAh cm^{-2} can be achieved at 0.1 mA cm^{-2} . After 41 cycles (~ 7.5 months cycling), nearly no capacity degradation can be observed, indicating an excellent cycling stability of this electrode even at a high loading. Compared with the high reversible capacity at a small current density (0.1 mA cm^{-2}), $\sim 53.1\%$ of capacity (3.26 mAh cm^{-2}) can still be maintained at a much higher current density (0.5 mA cm^{-2}), indicating the superior rate

capability of the fabricated thick electrode (**Figure 5B** and **Figure 27**). As shown in **Figure 5C**, the low-temperature performance of the thick LCGC electrode was further explored from -20 to 40 °C. Specifically, the capacity retentions of the thick electrode are around 87%, 90%, 95%, 100%, and 100% compared to the capacity obtained at 25 °C (**Figure 5D**).

5 Moreover, similar diffusion kinetics of Na⁺ inside the thick electrode at various temperatures can be observed from the potential-dependant D_{Na^+} profiles in **Figure 28**, suggesting a satisfying low-temperature performance. Furthermore, the electrochemical performance was evaluated for a coin-type full battery. The sodiated LCGC anode and an organic cathode (PTCDA) were assembled into the full battery with a N/P ratio (the areal capacity ratio of

10 negative to positive electrode) of 1.15:1. **Figure 5E** displays the initial five discharge/charge cycles of the full cell at 10 mA g⁻¹ with a voltage range of 0.5–3.0 V. A high reversible capacity of ~ 97.1 mAh g⁻¹ can be obtained. It should be noted that the current density and the capacity are calculated from the total mass of the active materials. When the current density is increased to 90 mA g⁻¹, a reversible capacity of 63.6 mAh g⁻¹ can be reversed with

15 a high capacity retention ratio of 65.5 % (**Figure 5F**), indicating an excellent rate capability of the full-cell battery. Briefly, the superior performance of the thick electrode and the full-cell battery reveals the great potential of this carbon anode for commercial applications in SIBs.

20 In summary, a molten diffusion-carbonization strategy was developed to block the micropores of porous carbon into ultra-micropores (0.3-0.5 nm). The ultra-micropores can only be accessible by bare Na⁺ without electrolyte, which can effectively minimize the decomposition of electrolytes and then induce a high ICE value of ~ 87.9%. Besides, the optimized anode exhibits a comprehensively outstanding electrochemical performance (i.e.

25 high reversible capacity, superior cycling stability, and satisfying rate capability). With the help of a series of scan-rate-dependent CV, GITT, *in-situ* XRD, and *ex-situ* solid-state NMR, an “adsorption/pore-filling” sodium-ion storage mechanism can be reliably demonstrated. It is noteworthy that the thick electrode with a high areal capacity of 6.14 mAh cm⁻² displays an ultrahigh cycling stability with a running time over 7.5 months, a satisfying rate capability

30 and an outstanding low-temperature performance. Moreover, the coin-type full battery based on the PTCDA cathode and the sodiated anode demonstrates a high reversible capacity and

superior rate performance. These findings disclose a promising strategy to design practical carbon anode materials for SIBs with high energy density, high rate capability and excellent low-temperature performance.

5 **Table 6.** A survey of hard carbon anode for SIBs

Anode material	Reversible capacity (mAh g ⁻¹ @ mA g ⁻¹)	Cyclability (capacity retention rate (%) @ mA g ⁻¹ @ cycle number)	Rate capacity (mAh g ⁻¹ @ mA g ⁻¹)	Carbonization Temperature (°C) @ ICE (%)
Hollow carbon nanowires	251@50	82@50@400	149@500	1150@50.5
G-HC	281@20	97@20@195	~20@1000	1100@78
P-doped hard carbon	359@20	96@20@60	~50@1000	1100@73
Hard carbon with low defects/surface area	338@20	93@20@100	NA	1300@78.9
Hard carbon paper	338@20	84@200@1000	170@2000	1300@91.2
Waste cork-derived hard carbon	358@30	87@30@200	~175@600	1600@81
Phenolformaldehyde resin-derived hard carbon	410@30	93@30@40	~25@600	1550@83
P-doped hard carbon	310@20	92@20@100	NA	1300@85
Hard carbon	254@30	89@20@150	162@300	1400@82
Hard carbon	284@30	94@30@100	90@600	1400@88
Pre-oxidation hard carbon	300@30	93@30@200	~50@1200	1400@88
This work	346@30	97@50@200	125@2000	<u>1050@79.5</u> 1200@87.9

Experiment Section

Chemicals and materials: Activated carbon (AC, XFP06) and cubic structure of mesoporous carbon (CMK-8, XFP02) were purchased from Jiangsu XFNANO Materials Tech Co.,Ltd. Perylene-3,4,9,10-tetracarboxylic dianhydride (PTCDA) and potassium

hydroxide (KOH, AR, pellets, $\geq 85\%$) were obtained from SIGMA-ALDRICH PTE LTD. All the chemicals used throughout this work were used as received without any further purification.

- 5 **Synthesis of GC:** The dried PTCDA was heated to 900°C in argon at a rate of $5^{\circ}\text{C}/\text{min}$ and then maintained for 5 hours. After then, the furnace was cooled to room temperature at a rate of $5^{\circ}\text{C}/\text{min}$. The obtained product was denoted as GC.

- 10 **Synthesis of ACGCx:** The AC and PTCDA were vacuum dried overnight at 110°C before usage. Firstly, the dried AC and PTCDA were mechanically mixed. The mass ratio of the AC and PTCDA is calculated according to the pore volume of AC and the density of PTCDA (e.g. for $1.391\text{ cm}^3/\text{g}$ pore volume of AC, the mass ratio of the AC and PTCDA is about 1:2.36). After then, the PTCDA was encapsulated into the AC via molten diffusion-carbonization method in argon at 400°C for 3 h, followed by further carbonization at a
15 specific temperature for another 5 h with a rate of $5^{\circ}\text{C}/\text{min}$. Subsequently, the furnace was cooled to room temperature at a rate of $5^{\circ}\text{C}/\text{min}$. The obtained products carbonized at different temperature (i.e. 750°C , 900°C , 1050°C , 1200°C) were denoted as ACGCx ($x=750$, 900, 1050, 1200).

- 20 **Synthesis of ACGC, CMK8GC, HCGC, and LCGC:** For hydrothermal reactions, a solution (40 mL) with 6.4 g sugar was filled into an autoclave (50 mL) and then heated at 180°C for 8 hours to get black powder. After drying, the obtained black powder (denoted as BP) was carbonized in Ar at 900°C for 5 h at a rate of $3^{\circ}\text{C}/\text{min}$, which was denoted LC (Low-specific-surface-area Carbon). For synthesis of HC (High-specific-surface-area
25 Carbon), the dried BP was firstly carbonized in Ar at 500°C for 2 h at a rate of $5^{\circ}\text{C}/\text{min}$. Then the obtained product was physically mixed with KOH with a mass ratio of 1:4. The mixture was activated at 800°C for 2 h at a rate of $5^{\circ}\text{C}/\text{min}$. The synthesis of ACGC, CMK8GC HCGC, and LCGC are similar with that of ACGC1050.

- 30 **Characterization:** The morphology and structure of the electrode material were investigated by SEM (JSM6700F) and TEM (JEOL-2010). XRD analysis was performed on

a Bruker D8 Advance X-ray diffractometer equipped with Cu K α radiation ($\lambda = 1.5418 \text{ \AA}$). The Raman spectra were collected on a Horiba Jobin Yvon Modular Raman Spectrometer at 514nm (Green). The specific surface area, pore diameter distribution and cumulative pore volume were measured on a NOVA 2200e, calculated from the N₂ adsorption-desorption isotherms. The CO₂ adsorption test was conducted on an Autosorb-iQ. ²³Na Magic Angle Spinning Nuclear Magnetic Resonance (MAS NMR) experiments was recorded on a Bruker Advance III 400 NMR spectrometer equipped with an 89 mm wide-bore 9.4 T superconducting magnet and a 1.3 mm HX probe at Larmor frequencies of 105.8 MHz. Single pulses were applied in acquiring ²³Na NMR data at a spinning speed of 80 kHz. ²³Na chemical shifts was referenced to 1M NaCl solution. True density was measured via an AccuPyc II 1340 analyzer with Helium as analysis gas.

Electrochemical measurements: CMCNa binder was first dissolved into DI water to form a uniform binder solution with a concentration of 12.5mg/mL. After then, the vacuum-dried active material was subsequently added into the binder solution with a weight ratio of 90:10 for active material and binder. The slurry was stirred overnight and then pasted onto copper foil, followed by drying at 50°C for 4 h. Circular electrodes were obtained via a punch machine and then vacuum-dried at 120°C overnight. The average mass loading of each electrode was about 1.5-2.0 mg cm⁻². The coin-type cells (2032) were assembled in an argon-filled glove box, where the concentrations of moisture and oxygen were maintained below 0.2 ppm. Sodium metal was applied as the anode. A Whatman GF/B glass fiber was used as the separator, and the electrolyte was a 1 M sodium triflate (NaOTf) solution dissolved in diethylene glycol dimethyl ether (DEGDME). Galvanostatic charge/discharge cycling was performed using a LAND-CT2001A multichannel galvanostat (Wuhan, China) in a voltage range of 0.001–3.0 V (vs. Na/Na⁺) at room temperature. CV profiles were obtained in a voltage window of 0.001–3.0 V at a scan rate of 0.1 mV s⁻¹ on an AUTOLAB electrochemical workstation. The full cells were assembled using a sodiated LCGC anode and PTCDA cathode with a weight ratio of 1:2.54. The full cell was cycled in the voltage window of 0.5–3.0 V.

If the cell voltage is linearly proportional to $\tau^{1/2}$, the diffusion coefficient can be calculated from the GITT potential profiles by Fick's second law with the following equation:

$$D = \frac{4}{\pi\tau} \left(\frac{m_B V_M}{M_B S} \right)^2 \left(\frac{\Delta E_s}{\Delta E_\tau} \right)^2$$

The density of carbon was calculated according to the following equation:

$$\rho = \frac{1}{V_{\text{total}} + \frac{1}{\rho_{\text{carbon}}}}$$

where ρ (g cm⁻³) is the density of carbon, V_{total} (cm³ g⁻¹) is the total pore volume measured from the N₂ isotherm, ρ_{carbon} is the true density of carbon (2 g cm⁻³).

For the GITT tests, the cell was discharged/charged at C/10 with a current pulse duration of 0.5 h and an interval of 1 h.

10

It will be appreciated that many further modifications and permutations of various aspects of the described embodiments are possible. Accordingly, the described aspects are intended to embrace all such alterations, modifications, and variations that fall within the spirit and scope of the appended claims.

15

Throughout this specification and the claims which follow, unless the context requires otherwise, the word "comprise", and variations such as "comprises" and "comprising", will be understood to imply the inclusion of a stated integer or step or group of integers or steps but not the exclusion of any other integer or step or group of integers or steps.

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The reference in this specification to any prior publication (or information derived from it), or to any matter which is known, is not, and should not be taken as an acknowledgment or admission or any form of suggestion that that prior publication (or information derived from it) or known matter forms part of the common general knowledge in the field of endeavour

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to which this specification relates.

Claims

1. A method of fabricating a composite, comprising
 - a) mixing porous carbon with a rylene dye in order to form a mixture;
 - b) heating the mixture from 300 °C to 600 °C under an inert atmosphere; and
 - c) carbonising the mixture at a temperature of 700 °C to 1300 °C;wherein the heating step is performed for 2 h to 10 h.
2. The method according to claim 1, wherein a mass ratio of porous carbon to rylene dye is 1:1 to 1:4.
3. The method according to claim 1 or 2, wherein the porous carbon is selected from activated carbon, mesoporous carbon, carbonised sugar, low specific surface area carbon and low specific surface area carbon.
4. The method according to any one of claims 1 to 3, wherein the rylene dye is selected from perylenetetracarboxylic dianhydride (PTCDA), perylenediimide, terrylendiimide, terrylen, perylen, and quaterrylen.
5. The method according to any one of claims 1 to 4, wherein the inert atmosphere is argon.
6. The method according to any one of claims 1 to 5, wherein the carbonisation step is performed for at least 3 h under a rate of 3 °C/min to 10 °C/min.
7. A modified porous carbon composite comprising:
 - a) a porous carbon structure; and
 - b) a carbonised rylene dye;wherein the carbonised rylene dye coats at least inner pores of the porous carbon structure; wherein the composite has a BET (CO₂) specific surface area of 10 m² g⁻¹ to 220 m² g⁻¹ and/or a BET (N₂) specific surface area of 5 m² g⁻¹ to 80 m² g⁻¹.

8. The composite according to claim 7, wherein the composite comprises ultra-micropores, the ultra-micropores having a pore diameter (based on CO₂ adsorption) of 0.2 nm to 0.8 nm.
9. The composite according to claim 7 or 8, wherein a mass ratio of porous carbon structure to at least partially carbonised rylene dye is about 1:1 to about 1:4.
10. The composite according to any one of claims 7 to 9, wherein the composite has a BET (CO₂) specific surface area to BET (N₂) specific surface area ratio of about 0.1 to about 50.
11. The composite according to any one of claims 7 to 10, the composite having an XRD pattern which indicates the presence of a (002) peak of a carbon derived from the carbonised rylene dye and a (002) peak of the porous carbon structure;
wherein the (002) peak of a carbon derived from the carbonised rylene dye is about 25.2°, and/or wherein the (002) peak of the porous carbon is about 21.2°.
12. The composite according to any one of claims 7 to 11, the composite having a total volume (based on N₂ adsorption) of about 0.01 cm³ g⁻¹ to about 0.13 cm³ g⁻¹ and/or a total volume (based on CO₂ adsorption) of about 0.08 cm³ g⁻¹ to about 0.4 cm³ g⁻¹.
13. The composite according to any one of claims 7 to 12, the composite having a R value of about 2 to about 5.
14. The composite according to any one of claims 7 to 13, the composite having a skeletal density of about 1.8 g cm⁻³ to about 2.5 g cm⁻³.
15. A method of fabricating an electrode, comprising:
 - a) mixing a composite according to any one of claims 7 to 14 with a binder solution to form a slurry;

- b) applying the slurry on a surface of an electrical conductor; and
- c) drying the slurry.

16. The method according to claim 15, wherein a weight ratio of composite to binder solution is about 80:20 to about 95:5.

17. The method according to claim 15 or 16, wherein the binder solution comprises a binder selected from sodium carboxymethyl cellulose and/or polyvinylidene fluoride (PVDF); and

wherein the binder solution has a concentration of about 10 mg/mL to about 20 mg/mL.

18. The method according to any one of claims 15 to 17, wherein the drying step is performed at 40 °C to 80 °C for 2 h to 6 h; and

wherein the drying step further comprises vacuum drying the slurry at 100 °C to 140 °C for at least 8 h.

19. An electrode, comprising:

- a) a composite according to any one of claims 7 to 14;
- b) a binder; and
- c) an electrical conductor;

wherein the composite and the binder are homogeneously combined; and

wherein the composite and the binder coats at least a surface of the electrical conductor;

wherein a mass loading of the composite and binder on the electrical conductor is at least 15 mg cm⁻².

20. A battery, comprising:

- a) an organic cathode; and
- b) an anode, the anode comprising the composite according to any one of claims 7 to 14;

wherein a mass loading ratio of the organic cathode to the anode is about 1:2 to about 1:3.