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Small graphite nanoflakes as an advanced cathode material for aluminum ion batteries†

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Here, we prepared small graphite nanoflakes (SGN) by a new strategy of pulverization as the cathode of aluminum ion batteries (AIBs). Electrochemical measurements show that SGN has a very high discharge capacity, excellent rate performance and good cycling stability mainly due to its enlarged edge plane, reduced thickness and high crystallinity. This work provides a new route for preparing high performance graphite-based materials for AIBs.

Due to the heavy use of fossil fuels, environmental problems are becoming more and more serious, which forces society to reduce its dependence on fossil energy and develop new types of clean energy, such as hydroelectric, geothermal and solar energy. However, these new energy resources are intermittent and unstable, and the energy needs to be stored by electrochemical energy storage systems (EESS) before being fed into the power grid. Therefore, there is a need for an EESS with high energy density, high efficiency, good cycling performance and low cost to store these energies.1

As an efficient EESS, lithium-ion batteries have been widely used since the 1990s, but unfortunately, lithium reserves and safety issues have limited their future development. Compared with lithium, aluminum metal has higher volumetric capacity (8050 mAh L⁻¹ vs. 2080 mAh L⁻¹ of lithium) and comparable gravimetric capacity (2980 mAh g⁻¹ vs. 3860 mAh g⁻¹ of lithium). Moreover, aluminum is rich in reserves and non-flammable. This endows aluminum-ion batteries (AIBs) with characteristics of low cost, high safety, and potentially high specific energy. So, AIBs are considered to be a good candidate for stationary energy storage.2

Early aluminum-based batteries used aqueous electrolytes to form battery systems such as Al//MnO₂,3 Al//AgO₄,4 Al//H₂O₂,4,5 Al//S,6,7 Al//ferricyanide,8 and Al//NiOOH.9 However, the Al negative electrode forms an oxide layer in the aqueous electrolyte, which causes serious polarization. The aluminum oxide layer can be dissolved in an alkaline electrolyte, which, however, causes severe corrosion and shortens battery life,10 so it is necessary to select non-aqueous electrolytes.

With the development of AIBs, imidazolium-based aluminum chloride room-temperature ionic liquid electrolyte was found to have stable electrochemical behavior11–15 and has been widely used in today's AIBs. However, AIBs still cannot perform satisfactorily due to the limitations of the cathode materials.16 At present, the cathode materials used in AIBs can be mainly divided into two categories, that is, metal chalcogenides and carbon-based materials. The metal chalcogenides investigated thus far include metal oxides,11,12,17–19 metal sulfides,20–22 and metal selenides.1,23 However, these materials encountered problems such as poor cycle life, low conductivity, and low coulombic efficiency.

In contrast, carbon-based materials have the advantages of high electrical conductivity, good cycling stability, and low cost. Among them, graphite-based materials have shown good commercial prospects. Gifford and Palmisano24 reported the first graphite-based cathode in 1988 and its discharge capacity can reach 35–40 mAh g⁻¹ at current densities of 1–10 mA g⁻¹. Jiao's research team19 used commercial graphite paper as the cathode, which achieved a discharge capacity of 84.55 mAh g⁻¹ at a current density of 50 mA g⁻¹. But the discharge capacity dropped markedly to 70 mAh g⁻¹ at a current density of 100 mA g⁻¹. Dai et al.25 made a breakthrough in AIBs using a graphite foam cathode that showed a discharge capacity of 70 mAh g⁻¹ and excellent cycling stability. Subsequently, Dai's team reported a natural graphite sheet cathode26 with a discharge capacity of 60 mAh g⁻¹ at a current density of 660 mA g⁻¹. Although these reported graphite-based materials have achieved stable electrochemical performance, conventional graphite materials are...
limited in capacity and rate performance. So, it is imperative to develop graphite-based materials with promoted capacity and rate performance.

In this work, a new strategy was proposed to prepare small graphite nanoflakes (SGN) from natural graphite using an electrochemically assisted pulverization technique. In this strategy, natural graphite was lithiated firstly, followed by a violent reaction with an aqueous solution to pulverize the natural graphite to SGN. The as-prepared SGN shows a much higher discharge capacity and much better rate performance than pristine natural graphite and is also superior to other graphite-based materials recently reported. The SGN material and its synthetic strategy are significant to the further development of graphite-based materials for AIB cathodes.

The synthesis process of SGN is shown in Fig. 1a. Natural graphite (NG) was first lithiated electrochemically, resulting in its color change from black to golden yellow (Fig. S1, ESI†). After coming in contact with an aqueous solution of hexadecyl trimethyl ammonium bromide (CTAB), the lithiated graphite reacted intensely with water to produce LiOH and hydrogen. The in situ generated H2 bubbles resulted in the pulverization of the natural graphite. The presence of CTAB helps to protect the pulverized graphite nanoflakes from re-aggregation. Furthermore, a detailed analysis (Fig. S2 and S3, ESI†) proved that almost no Li remained in the SGN. The morphology of NG and SGN was observed by SEM (Fig. 1b and c). The NG particles are mainly large aggregates with a size larger than 10 µm. In contrast, much smaller graphite nanoflakes with a uniform size of about 2–3 µm were observed in the SGN sample. This results in an enlarged edge plane of SGN. It is expected that the enlarged edge plane will provide more active sites for [AlCl4]− intercalation/de-intercalation and facilitate the rate performance of SGN. Besides, the layer thickness of SGN is about 45 nm (about 125 layers), while that of NG is about 90 nm (about 250 layers) (Fig. S4, ESI†). The smaller thickness may also influence the electrochemical performance of SGN.

TEM observation further revealed the structure of SGN (Fig. S5, ESI†). SGN with a very low contrast was observed, indicating that the obtained SGN is thin graphite nanoflakes. Its selected area electron diffraction (SAED) pattern (the inset of Fig. S5, ESI†) demonstrates the single crystal property of SGN. Its XRD pattern exhibited well-resolved diffraction peaks of graphite, indicating its high crystallinity (Fig. S6a, ESI†). Of special interest is the fact that the (002) crystal plane has a distinct preferred orientation, so that the relative intensity of (101) and (004) is much weaker than those in the powder diffraction file (PDF) card [03-065-6212]. This preferred orientation should be due to the lamellar morphology of the NG and SGN particles. The XRD spectra of SGN in a semilog plot can prove that no additional crystalline or amorphous phase formed due to the lithiation/delithiation processing (Fig. S6b, ESI†); the wide peak at 20–25 degrees comes from the glass sample holder (Fig. S6c, ESI†). It can be observed through the XRD data refined by Rietveld that there is no change in the cell parameters, which further proves that no lithium remains in the SGN (Fig. S7a, b and Table S1, ESI†). Moreover, the (002) reflection peak of SGN shows significant broadening because of the reduction in the number of graphite layers (Fig. S8, ESI†). The thickness of graphite can also be estimated by the Scherrer formula, after deducting the widening influence of the instrument itself. The FWHM (Full Width at Half Maximum) of the (002) reflections are 0.165 (10) and 0.125 (10) degree for SGN and NG, respectively. Accordingly, the L-values for SGN and NG are calculated to be 490 Å (about 145 layers) and 650 Å (about 200 layers), respectively. This is basically consistent with the SEM observations (Fig. S4, ESI†).

Raman spectroscopy was employed to further characterize the structure of the carbon skeleton in the SGN (Fig. S9, ESI†). Both NG and SGN exhibit a typical 2D band of bulk graphite, indicating the large number of graphene layers in these two samples.\(^{27-29}\) The relative intensity of the D peak (defect-related) and the G peak (doubly degenerate zone center E\(_{2g}\) mode) is often used to check the crystalline quality of graphite.\(^{30}\) The D peak to G peak intensity ratio \(I_D/I_G\) of SGN is 0.07 (vs. 0.07 of NG), which is substantially lower than that of the sample derived from oxidative exfoliation \(I_D/I_G \approx 0.5–0.2\).\(^{31,32}\) The \(I_D/I_G\) intensity ratio of \(<0.1\) indicates that the concentration of defects in SGN is significantly low, proving that the SGN produced in this work does not contain many defects. The low defect concentration and high crystallinity of SGN would be favorable to its electrochemical performance in AIBs.\(^{26}\)

In order to evaluate the electrochemical performance of SGN in AIBs, we used SGN as a cathode and Al foil as an anode to assemble a custom Swagelok cell (Fig. S10, ESI†). Its cyclic voltammetry curves show a series of redox peaks (Fig. 2a), indicating that the intercalation of [AlCl\(_4\)]\(^-\) into SGN occurs in multiple steps. Among these redox peaks, two very distinct oxidation peaks around 1.8 V and 2.25 V, corresponding to two reduction peaks at around 1.7 V and 1.85 V can be observed. With the rise in scan rate, the intensity of these peaks increases. The relation between the peak current and scan rate can be expressed as:\(^{33}\)

\[
i = a \nu^b
\]

(1)

\[
\log(i) = \log(a) + b \log(\nu)
\]

(2)

where \(i\) is the response current (mA) and \(\nu\) is the scan rate (mV s\(^{-1}\)), and \(a\) and \(b\) are adjustable values. From Fig. 2b, it is found that the \(b\)-values for all lines are 0.72, 0.84, 0.69, and 0.85, respectively, indicating that the electrode kinetics is controlled by both diffusion and surface processes. Here, surface processes...
The discharge capacity of the SGN can reach up to 115 mA h g\(^{-1}\) with a current density of 500 mA g\(^{-1}\). The energy storage performance of the SGN cathode can be expressed as follows (eqn (3)): \[ C_n + [\text{AlCl}_4^-] \leftrightarrow C_n[\text{AlCl}_4] + e^- \] (3)

where \(n\) is the number of carbon atoms coordinated per intercalated anion.

In order to confirm the difference in capacity between SGN and NG, TGA was conducted to evaluate how many [AlCl\(_4\)]\(^-\) are intercalated into the samples. It is shown that pure PVDF (the binder used in the electrode), NG and SGN have been totally burned off at about 570, 720 and 770 °C, respectively, and the kink in the SGN TGA curve comes from the decomposition of PVDF (Fig. S14a, ESIF). But there are different amounts of residue left (mainly Al\(_2\)O\(_3\)) for the NG and SGN samples at different charging states (Fig. S14b and c, ESIF), indicating that more and more [AlCl\(_4\)]\(^-\) are intercalated into graphite with the rise in charging voltage. At the fully charged state (2.45 V), the percentages of residue mass are 17.0 and 11.9% for SGN and NG, respectively, indicating that more [AlCl\(_4\)]\(^-\) are intercalated into the SGN sample (Fig. S14d, ESIF). As for the amount of [AlCl\(_4\)]\(^-\) inserted, the ratio of SGN to NG is about 1.43, which is basically consistent with the ratio (1.60) of the specific capacity determined at 500 mA g\(^{-1}\) for SGN to NG (Fig. 2c and d).

Through the Electrochemical Impedance Spectroscopy (EIS) measurements (Fig. 3a), it is found that the ohmic resistance (the intercept of EIS curve with the X axis) and the charge transfer resistance (the diameter of the semicircle at a high frequency region) of SGN are apparently smaller than those of NG. This may explain the better rate performance of SGN than NG. Moreover, a galvanostatic intermittent titration technique (GITT) test\(^{15,16}\) was performed to evaluate the diffusion coefficient of various scan rates from 1 to 20 mV s\(^{-1}\). The cycling performance and the coulombic efficiency of SGN at a current density of 1000 mA g\(^{-1}\) are almost overlapped, suggesting excellent electrochemical reversibility of the material (Fig. S11, ESIF). Through the rate performance test (Fig. 2d), we found that NG cannot easily withstand large current densities.\(^{34}\) As the current density rises from 500 to 5000 mA g\(^{-1}\), the discharge capacity of NG decreases drastically from ∼72 to ∼35 mA h g\(^{-1}\), but that of SGN only decreases moderately from ∼110 to 90 mA h g\(^{-1}\). It is worth noting that the specific capacity of SGN at a current density of 5000 mA g\(^{-1}\) (∼90 mA h g\(^{-1}\)) can exceed the NG at a current density of 500 mA g\(^{-1}\) (∼72 mA h g\(^{-1}\)), which means that the current density of SGN can be enlarged tenfold to achieve a better performance. In addition, the capacity retention ratio of SGN is above 97% after 1000 cycles at a current density of 500 and 1000 mA g\(^{-1}\) (Fig. 2e and Fig. S12, ESIF), exhibiting excellent cycling stability. Compared to the reported graphite materials (Table S2, ESIF), the discharge capacity and rate performance of SGN are among those of the best graphite materials reported for AIBs.

In Fig. 2c, obviously, there are two long and shiny platforms in the process of charging and discharging, which could be related to the intercalation/deintercalation of [AlCl\(_4\)]\(^-\). The discharge capacity of the SGN can reach up to 115 mA h g\(^{-1}\), which is much higher than that of NG (72 mA h g\(^{-1}\)) at a current density of 500 mA g\(^{-1}\). This capacity increment can be mainly ascribed to the small size and thickness of SGN that allows more [AlCl\(_4\)]\(^-\) intercalation/deintercalation. Besides, the charge and discharge curves of the 100th, 300th and 500th cycles are almost overlapped, suggesting excellent electrochemical reversibility of the material (Fig. S11, ESIF). Through the rate performance test (Fig. 2d), we found that NG cannot easily withstand large current densities.\(^{34}\) As the current density rises from 500 to 5000 mA g\(^{-1}\), the discharge capacity of NG decreases drastically from ∼72 to ∼35 mA h g\(^{-1}\), but that of SGN only decreases moderately from ∼110 to 90 mA h g\(^{-1}\). It is worth noting that the specific capacity of SGN at a current density of 5000 mA g\(^{-1}\) (∼90 mA h g\(^{-1}\)) can exceed the NG at a current density of 500 mA g\(^{-1}\) (∼72 mA h g\(^{-1}\)), which means that the current density of SGN can be enlarged tenfold to achieve a better performance. In addition, the capacity retention ratio of SGN is above 97% after 1000 cycles at a current density of 500 and 1000 mA g\(^{-1}\) (Fig. 2e and Fig. S12, ESIF), exhibiting excellent cycling stability. Compared to the reported graphite materials (Table S2, ESIF), the discharge capacity and rate performance of SGN are among those of the best graphite materials reported for AIBs.

Elemental mapping and EDS analysis (Fig. S13a and b, ESIF) proved that the intercalated ion is [AlCl\(_4\)]\(^-\). The energy storage mechanism of the SGN cathode can be expressed as follows (eqn (3)): \[ C_n + [\text{AlCl}_4^-] \leftrightarrow C_n[\text{AlCl}_4] + e^- \] (3)

where \(n\) is the number of carbon atoms coordinated per intercalated anion.

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[AlCl₄]⁻ in SGN and NG. The change of voltage with time is recorded in Fig. 3b, and the voltage profile for a few titration steps at around 2.4 V is shown in Fig. 3c with schematic labelling of different parameters. The equation used to calculate the diffusion coefficient can be written as follows:

\[
D_{\text{AlCl}_4} = \frac{4}{\pi t} \left( \frac{n_m V_m}{S} \right)^2 \left( \frac{\Delta E}{\Delta E_0} \right)^2
\]

where \( t \) is the relaxation time; \( n_m \) is the number of moles of active materials; \( V_m \) is the molar volume of the active materials; \( \Delta E \) is the voltage change caused by the pulse and \( \Delta E_0 \) is the voltage change of the constant current charge. Based on eqn (4), the ion diffusion coefficients in the voltage range of 1.9–2.45 V were calculated (Fig. 3d and Fig. S15, ES1†). The diffusion coefficient of NG is in the range from \( \sim10^{-11} \) to \( \sim10^{-15} \) cm² s⁻¹ and that of SGN is in the range from \( \sim10^{-10} \) to \( \sim10^{-12} \) cm² s⁻¹. It is apparent that SGN has a much higher diffusion coefficient than NG. This also explains why SGN has better rate performance than NG.

From the above systematic investigations, the excellent electrochemical performance of SGN can be attributed to the following reasons: (1) the small size and thickness of SGN makes [AlCl₄]⁻ intercalation/deintercalation easier, resulting in more efficient utilization of the material and larger capacity. (2) SGN with a large edge plane provides a number of active sites for [AlCl₄]⁻ intercalation/deintercalation, in favor of rate performance; (3) the small particle size of SGN makes the ion diffusion distance much shorter and improves the rate performance; (4) high crystallinity and low defect concentration contribute to its good cycling stability.

In summary, SGN was successfully prepared by lithiation followed by a violent reaction with aqueous solution. Compared with NG, the as-prepared SGN sample is much smaller, thinner and uniformly dispersed. When used as a cathode material in AIBs, SGN exhibits large discharge capacity, excellent rate performance (115 mA h g⁻¹ at 500 mA g⁻¹ and 90 mA h g⁻¹ under 5000 mA g⁻¹) and good cycling stability (capacity retention > 97% after 1000 cycles). This performance is one of the best for graphite-based materials reported to date. Considering that lithiated graphite can be obtained from spent lithium ion batteries, SGN also has commercialization prospects. Moreover, the strategy used to prepare SGN and new understanding of its electrochemical performance would be significant for further development of graphite-based cathode materials for AIBs.

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**Conflicts of interest**

There are no conflicts to declare.

**Notes and references**