ChemComm

Accepted Manuscript



This is an *Accepted Manuscript*, which has been through the Royal Society of Chemistry peer review process and has been accepted for publication.

Accepted Manuscripts are published online shortly after acceptance, before technical editing, formatting and proof reading. Using this free service, authors can make their results available to the community, in citable form, before we publish the edited article. We will replace this Accepted Manuscript with the edited and formatted Advance Article as soon as it is available.

You can find more information about *Accepted Manuscripts* in the **Information for Authors**.

Please note that technical editing may introduce minor changes to the text and/or graphics, which may alter content. The journal's standard <u>Terms & Conditions</u> and the <u>Ethical guidelines</u> still apply. In no event shall the Royal Society of Chemistry be held responsible for any errors or omissions in this *Accepted Manuscript* or any consequences arising from the use of any information it contains.



www.rsc.org/chemcomm

Cite this: DOI: 10.1039/c0xx00000x

www.rsc.org/xxxxx

ARTICLE TYPE

An In-situ Self-developed Graphite as High Capacity Anode of Lithiumion Batteries

Mengyao Gao,^{†a} Naiqiang Liu ,^{†a} Yilei Chen,^a Yuepeng Guan,^a Weikun Wang,^b Hao Zhang,^b Feng Wang, ^{a,*} and Yaqin Huang^{a,*}

s Received (in XXX, XXX) XthXXXXXXX 20XX, Accepted Xth XXXXXXXX 20XX DOI: 10.1039/b000000x

The graphite with a lager inter-planar distance (0.357 nm) was obtained from pig bone. It delivered an improving specific capacity which increased continuously to 538 mAh g-1 at 1 A g-1 after 1000 cycles. With microscopic characterization, it is found that the pig-bone-based graphite was exfoliated to graphene during the charge-discharge.

- ¹⁰ One of the biggest challenges in the modern society is to stabilize a continuous supply that will meet our increasing energy demands. The development of powerful lithium battery with high energy density, high power density, and long cycle life is of great importance for applications such as electric vehicles and electric
- ¹⁵ grid. State-of-art lithium-ion batteries (LIBs) are considered to be one of the most studied, thus the least technological barriers to meet the rapidly growing energy requirements.^[1-3]
- Over the past two decades, various strategies such as the design of organic liquid electrolytes,^[4-7] the modification of the ²⁰ anodes,^[8-11] and the preparation of cathodes^[12-15] have been reported. The great demand for high-energy-density rechargeable LIBs has spurred extensive research on anode materials to improve their performance, including all kinds of carbon-based anode materials such as carbon nanotubes,^[16,17] nanofibers,^[18]
- ²⁵ hollow nanospheres,^[19] graphene,^[20,21] porous carbon^[22] and their hybrids. However, the commercialized Mesocarbon Microbeads (MCMB) anode has the reversible capacity of only about 230 mAh g⁻¹ at 1 C rate,^[23] which is too low for many applications that need higher energy capacity. Graphite appears to be a strong
- ³⁰ candidate anode material to replace MCMB by virtue of the flat and low voltage range, high electronic conductivity, low volume expansion after full lithiation, and low cost.^[24-26] Moreover, it develops through well-identified, reversible stages, corresponding to progressive intercalation within discrete graphene layers, to
- ³⁵ reach the formation of LiC₆ with a maximum theoretical capacity of 372 mAh g⁻¹ (Li+6C \leftrightarrow LiC₆). However, the synthetic graphite production process still involves, as a first step, the selection of suitable carbon materials with easy graphitization.

We choose pig bone to prepare the graphite as the anode 40 materials for its inherent structure and composition advantages: 1)

- layer-by-layer structure of pig bone would be benefit for the formation of the graphite, which will enhance the electrochemical performance of LIBs. 2) The main component of pig bone, collagen, could act as an excellent carbon precursor for its high
- ⁴⁵ carbon content (about 50 wt. %). According to the protein which contained in the pig bone, the yield of the graphite material from pig bone is ~11%. 3) Pig bone, one kind of food industry byproducts, is very cheap and environment benign. In this Article,

we show that the pig-bone-based graphite anode can be self-⁵⁰ developed to graphene with high energy density in battery charge-discharge process. As the cycle number increases, the asprepared graphite anode evolves and its specific capacity increases closely to the theoretical specific capacity of graphene. Our discovery of the in-situ self-improvement of the pig-bone-⁵⁵ based graphite indicates a new promising material for advancing





Figure 1. SEM (a) and HR-TEM (b) images of the as-prepared product, the inset is the Raman spectra.

- The SEM image (Figure1a) shows that the layer-by-layer structure has been preserved after the calcination, which is well consistent with our design expectation. It can be seen that the asprepared material tends to exfoliate. Evidence of the most important features^[27-29] could be obtained by inspection of the 75 Raman spectra using a laser excitation of 514 nm. As shown in the inset of Figure 1a, Raman spectra of microcrystalline graphite shows a tangential mode (G band) at around 1580 cm⁻¹, a weak disorder band (D band) at 1361 cm⁻¹, and 2D band at 2700 cm⁻¹. The D band is related to the presence of sp³ defects whereas the 80 G band is related to the in-plane vibration of sp² carbon atoms.^[30] The I_D/I_G intensity ratio is less than 0.1, which indicates that the concentration of defects in the obtained product was significantly low. Furthermore, the lattice distance that corresponds to the (002)
- low. Furthermore, the lattice distance that corresponds to the (002) plane of the as-prepared material was detected by the HR-TEM. ⁸⁵ The obtained inter-planar distance (0.357 nm) that is relatively larger than that of the common graphite.^[31] The larger spacing between neighboring layers and weak van der Waals forces

between the layers in principal could make the Li⁺ diffuse easier.[21]



Figure 2. Electrochemical characterization of the Cu-supported graphite electrode for lithium-ion batteries. (a) Cycling performance (black dots) and corresponding coulombic efficiency 20 (blue dots) of the cell at a current density of 100 mA g⁻¹.(b) The galvanostatic charge-discharge curves at the 2th, 5th, 20th, 50th and 90th between 3 and 0.005 V (vs Li⁺/Li). (c) Rate capability at various rates between 186 mA g⁻¹ and 3720 mA g⁻¹, (d) Prolonged cycling (black/red dots) and corresponding coulombic $_{25}$ efficiency (blues dots) at a current density of 1 A $g^{-1}.$

The electrochemical performance of the as-prepared pigbone-based graphite was evaluated by galvanostatic discharge/charge cycling at a current density of 100 mA g⁻¹. The $_{\rm 30}$ first discharge and charge capacities are 542 and 248 mAh g $^{-1},$ respectively. After eight discharge/charge cycles, it exhibits a high reversible capacity of ~300 mAh g⁻¹. The coulombic efficiency rapidly rises from 45.6% in the first cycle to 98.4% in the eighth one and then remains above 98% in the following 35 cycles (Figure 2a). The initial capacity loss may result from the

- incomplete conversion reaction and irreversible lithium loss due to the formation of a solid electrolyte interphase (SEI) layer.^[32] Figure 2b shows the discharge/charge profiles of the as-prepared graphite electrode in the 2th, 5th, 20th, 50th and 90th cycle. The
- ⁴⁰ reversible capacity of the as-prepared graphite electrode slightly increases with cycling and reaches 359 mAh g⁻¹ after 90 cycles. It is also seen from Figure 2c that the Cu-supported graphite electrode has a good rate capability, as tested at current densities from 186 mA g⁻¹ to 3720 mA g⁻¹ for 50 cycles each. The as-
- ⁴⁵ prepared anode keeps a reversible capacity of 328 mAh g⁻¹ after the 50th cycle at a current density of 186 mA g^{-1} . The following reversible capacity at other various rates is 320 mAh g⁻¹ for the 100th cycle at 372 mA g⁻¹, 313 mAh g⁻¹ for the 150th cycle at 744 mA g^{-1} , 243 mAh g^{-1} for the 200th cycle at 1860 mA g^{-1} , and
- ⁵⁰ 146 mAh g⁻¹ for the 250th cycle at 3720 mA g⁻¹. Nonetheless, the capacity is recovered after reducing the rate of charge/discharge. The rate returns to 372 mAh g^{-1} at 1860 mA g^{-1} for the 300th cycle, 319 mAh g^{-1} at 744 mA g^{-1} for the 350th cycle, 331 mAh g^{-1} at 372 mA g⁻¹ for the 400th cycle, and recovers to its original
- 55 capacity at 186 mA g⁻¹ (325 mAh g⁻¹). The trend of decreasing capacity with higher rate can be explained by the fact that at high rate, the ionic motion within an electrode and across an electrode/electrolyte interface is not fast enough for charge

distribution to reach equilibrium.[33]

In Figure 3d, the cycling response of the electrode is 60 reported at a discharge/charge current rate of 1 Ag⁻¹ for 1000 cycles. The initial discharge capacity is 719 mAh g⁻¹ while the initial charge capacity is 423 mAh g⁻¹ corresponding to a first cycle coulombic efficiency of 58.9%. Although a slight 65 fluctuation is observed during the following a few cycles (~5), most likely associated with a residual SEI film formation process. With the discharge/charge processing, the specific capacity stabilized and the coulombic efficiency approaching 99%. More interestingly, the specific capacity rises continuously and reaches ⁷⁰ 538 mAh g⁻¹ with the coulombic efficiency of 99.6%. These interesting results intrigued us for further exploration of the detailed mechanism of the increasing cycling performance.



Figure 3. Selected TEM images of flakes prepared at various current density after different cycles. (a) after 30 cycles, (b) after 60 cycles at a current density of 100 mA g^{-1} , and at a current density of 1 A g⁻¹ (c) after 30 cycles, (d) after 60 cycles, (e) after 80 200 cycles, (f) after 500 cycles.

TEM experiments were performed to understand the above phenomenon. Flakes prepared at various current density after different cycles are presented in Figure 3. It can be seen that after 85 30 cycles at 100 mA g⁻¹ (Figure 3a) the as-prepared graphite containing several atomic layers spreads over the inspected area, and the margin (marked with red line) of each layer can be clearly seen. As the cycle number increases, e.g. 60 cycles, the atomic layer becomes thinner as shown in Figure 3b. When the current 90 density is raised to 1 A g⁻¹, the graphite in Figure 3c (after 30 cycles) and Figure 3d (after 60 cycles) are as thin as cicada's wings. With the increasing cycling performance, the TEM images of the flakes prepared after 200 cycles, which corresponds to 18% specific capacity increase, and 500 cycles (454 mAh g^{-1}) are 95 shown in Figure 3e and f. It is exhibited that the pig-bone-based graphite has been exfoliated into 1~3 layers. The obtained structure indicated that the as-prepared pig-bone-based graphite was exfoliated successfully.

Figure 4a depicts the Raman spectra (excited by 514nm laser) to further analyze the as-prepared graphite after 60 dischargecharge cycles at a current density of 1 A g⁻¹. It is clearly seen that

- ⁵ the as-prepared flake exhibits an intense D band at 1350 cm⁻¹, G band at 1580 cm⁻¹, and 2D band at around 2720 cm⁻¹. I_D is proportional to identify the alignment configuration for the layer number ^[34,35]. Compared with the Raman spectra of the pristine graphite exhibited in the inset of Figure 1a, the D band of the
- ¹⁰ resulted graphite after cycling with a sharp increase in Raman intensity (Figure 4a) indicates that the pig-bone-based graphite has been exfoliated to layers. The 2D/G ratio (the integrated peak ratio for 2D over G bands) is about 1.7. Note that the 2D/G ratio has been shown to be related to the degree of recovery for sp²
- ¹⁵ C=C bonds (graphitization) in graphitic structures.^[29] The graphite sample was deposited on an atomic-flat silicon substrate, and the AFM was used to measure the surface morphology and graphite thickness. The selected area seems very clean as seen from the zoomed inset image, and the topography profile in
- ²⁰ Figure 4b suggests that the thickness of the flake is ~0.94 nm, which corresponds to 2-3 graphene layers. To further access the quality of the as-prepared graphene sheet, Figure 4c shows the STM image from the selected area. For most of the area, we can only see a hexagonal arranged carbon atomic structure and some
- ²⁵ are bilayered graphene with A-B stacking that are marked with circles and spots. Therefore, the exfoliation of the pig-bone-based graphite is due to its large interlayer distance (0.357 nm) compared to that of ordinary graphite (0.335 nm), as revealed by the high-resolution TEM in Figure 1b. As the battery is cycled the
- ³⁰ exfoliation results in the formation of more and more graphene layers. This process assists the Li⁺ diffusion and intercalation into the layered structure, which greatly improve the energy density.



Figure 4. (a) Raman spectrum (excited by 514 nm laser) for the ⁵⁰ pig-bone-based graphite obtained after 60 cycles at 1 A g⁻¹, where D, G, and 2D bands are indicated in the Figure. (b) AFM profile of the as-prepared flakes, the inset presents the AFM image of the treated flakes. (c) Corresponding STM image of the obtained material.

In summary, the graphite with layer-by-layer structure has been obtained from pig bone by graphitization, showing a much larger inter-planar distance of 0.357 nm compared to 0.335 nm of normal graphite. When such graphite was used as the anode in lithium-ion batteries, the specific capacity is improved ⁶⁰ continuously until reached the theoretical value of graphene, 538 mAh g⁻¹, during the charge-discharge process. The improvement of energy capacity could be attributed to the in-situ selfdevelopment of graphite to graphene. Our mechanistic studies indicate that this pig-bone-based graphite will be a promising ⁶⁵ material for the anode of advanced LIBs.

Financial support from the National Natural Science Foundation of China (no. 51272017 and 51432003) is gratefully appreciated.

Notes and references

- ⁷⁰ ^aState Key Laboratory of Chemical Resource Engineering, Beijing Laboratory of Biomedical Materials, Beijing University of Chemical Technology, 15 Beisanhuan East Road, Beijing, 100029, China. ^bResearch Institute of Chemical Defense, 35 Huayuan North Road, Beijing, 100191, China
- 75 † These authors contributed equally to this work and should be considered co-first authors *Corresponding author: E-mail: huangyaqin9@gmail.com; E-mail:

*Corresponding author: E-mail: huangyaqin9@gmail.com; E-mail: wangf@mail.buct.edu.cn;

- 80 1. M. Armand, J. M. Tarascon, Nature, 2008, 451, 652-657.
 - K. Kang, Y. S. Meng, J. Bre'ger, C. P. Grey, G. Ceder, *Science*, 2006, 311, 977-980.
 A. S. Arico, P. Bruce, B. Scrosati, J. M. Tarascon, W. V. Schalkwijk,
- *Nat. Mater.* 2005, 4 366. 85 4. D. Guvomard, J. M. Tarascon, *J. Electrochem. Soc.* **1992**, 139, 937.
- D. Guyomard, J. M. Tarascon, J. Electrochem. Soc. 1992, 159, 957.
 J. M. Tarascon, W. R. McKinnon, F. Coowar, T. N. Bowner, G. Amatucci, D. Guyomard, J. Electrochem. Soc. 1994, 141, 1421.
- 6. H. B. Han, S. S. Zhou, D. J. Zhang, S. W. Feng, L. F. Li, K. L. Li, W. F. Feng, J. Nie, H. Li, X. J. Huang, M. Armand, Z. B. Zhou, *J. Power Sources*, **2011**, 196, 3623.
- 7. L. Suo, Y. S. Hu, H. Li, M. Armand, L. Chen, *Nat. Commun.* 2013, 4, 1481.
- 8. Y. Tang, L. Yang, Z. Qiu, J. Huang, J. Mater. Chem. 2009, 19, 5980.
- 9. H. Wu, G. Yu, L. Pan, N. Liu, M. T. McDowell, Z. Bao, Y. Cui, *Nat. Commun.* **2013**, 4.
- 10. Y. Sun, X. Hu, W. Luo, F. Xia, Y. Huang, Adv. Funct. Mater. 2013, 23, 2436-2444.
- 11. Y. W. Cheng, C. K. Lin, Y. C. Chu, A.A bouimrane, Z. Chen, Y. Ren, O. Auciello, *Adv. Mater.* **2014**, 26, 3724-3729.
- 100 12. J. Hassoun, F. Bonaccorso, M. Agostini, M. Angelucci, M. G. Betti, R. Cingolani, B. Scrosati, *Nano lett.* **2014**, 14, 4901-4906.
 - X. Li, J. Liu, M. N. Banis, A. Lushington, R. Li, M. Cai, X. Sun, Energy Environ. Sci. 2014, 7, 768-778.
- 14. F. Lin,I. M. Markus, D. Nordlund,T. C.Weng, M. D.Asta, H. L. Xin, M. M. Doeff, *Nat. Commun.* **2014**, 5.
- M. Gao, N. Liu, Z. Li, W. Wang, C. Li, H. Zhang, Y. Huang, Solid State Ionics, 2014, 258, 8-12.
- 16. E. Yoo, J. Kim, E. Hosono, H. S. Zhou, T. Kudo, I. Honma, *Nano Lett.* **2008**, 8, 2277-2282.
- 110 17. B. J. Landi, M. J. Ganter, C. D. Cress, R. A. DiLeo, R. P. Raffaelle, *Energy Environ. Sci.* **2009**, 2, 638-654.
 - 18. Z. J. Fan, J. Yan, T. Wei, G. Q. Ning, L. J. Zhi, J. C. Liu, D. Cao, F. Wei, ACS nano, 2011, 5, 2787-2794.
 - 19. Z. Wang, L. Zhou, Adv. Mater. 2012, 24, 1903-1911.
- 115 20. G. Wang, X. Shen, J. Yao, J. Park, Carbon, 2009, 47, 2049-2053.
 - R. Chen, T. Zhao, W. Wu, F. Wu, L. Li, J. Qian, X. Rui, H. Wu, H. M. Albishri, A. S. Al-Bogami, D. A. El-Hady, J. Lu, K. Amine, *Nano lett.* 2014, 14, 5899-5904.
- 22. L. Qie, W. M. Chen, Z. H. Wang, Q. G. Shao, X. Li, L. X.Yuan, Y. H.
 Huang, Adv. Mater. 2012, 24, 2047-2050.
 - 23. S. Ahn, Y. Kim, K. J. Kim, T. H. Kim, H. Lee, M. H. Kim, J. Power Sources, 1999, 896, 81-82.
 - 24. Y. W. Cheng, C. K. Lin, Y. C. Chu, A. Abouimrane, Z. Chen, Y. Ren, O. Auciello, *Adv. Mater.* **2014**, 26, 3724-3729.

- 25. W. E. Tenhaeff, O. Rios, K. More, M. A. McGuire, *Adv. Funct. Mater.* **2014**, 24, 86-94.
- 26. J. Jiang, J. Zhu, W. Ai, Z. Fan, X. Shen, C. Zou, J. Liu, H. Zhang, T. Yu, *Energy Environ. Sci.* 2014, 7, 2670-2679.
- 5 27. C. Amrita, K. Bhowmik, G. De, A. Mukherjee, New J. Chem. 2015, 39, 2451-2458.
- 28. Z. Yang, Y. Sun, L. B. Alemany, T. N. Narayanan, W. E. Billups, J. Am. Chem. Soc. 2012, 134, 18689-18694.
- 29. Q. Liu, Z. Wu, Z. Ma, S. Dou, J. Wu, L. Tao, X. Wang, C. Ouyang, 10 A. Shen, S. Wang, *Electrochim. Acta*, **2015**.
- 30. M. J. Allen, V. C. Tung, R. B. Kaner, A. Y. Lu, Y. Xu, F. R. Chen, A. N. Khlobystov, L. J. Li, *Acs Nano*, **2011**, 5, 2332-2339.
- 31. F. S. Li, Y. S. Wu, J. Chou, N. L. Wu, Chem. Commun. 2015.
- 32. K. C. Candace, R. Riccardo, S. H. Seung, Y. Cui, *J. Power Sources*, **2009**, 189, 1132-1140.
- S. R. Gowda, V. Pushparaj, S. Herle, G. Girishkumar, J. G. Gordon, H. Gullapalli, X. B. Zhan, P. M. Ajayan, A. L. Reddy, *Nano Lett.* 2012, 12, 6060-6065.
- 34. A. C. Ferrari, J. C. Meyer, V. Scardaci, C. Casiraghi, M. Lazzeri, F. ²⁰ Mauri, S. Piscanec. *Phys. Rev. Lett.* **2006**, 97, 187401.
- 35. Q. Q. Li, X. Zhang, W. P. Han, Y. Lu, W. Shi, J. B. Wu, P. H. Tan, *Carbon*, **2015**, 85, 221-224.