

RSC Advances



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. This *Accepted Manuscript* will be replaced by the edited, formatted and paginated article as soon as this 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 [Terms & Conditions](#) and the [Ethical guidelines](#) 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.

Rice Husk Derived Carbon-silica Composites as Anodes for Lithium Ion Batteries

Cite this: DOI: 10.1039/x0xx00000x

Received 00th January 2012,
Accepted 00th January 2012

DOI: 10.1039/x0xx00000x

www.rsc.org/

Liping Wang,^{a*} Jing Xue,^a Bin Gao,^a Peng Gao,^b Chengxu Mou,^a Jingze Li^a

Carbon-silica composites were obtained via simply heating rice husk at 900 °C under N₂ atmosphere. This composite exhibits a high capacity and superior cycling performance as anodes for lithium ion batteries.

Energy consumption is concomitantly growing with the economic growth and the world's population expansion. Due to limited fossil sources, developments of clean, alternative, and sustainable energy technologies are imperative¹. In parallel, the intermittent renewable energies (e.g. wind, solar, hydro/geothermal) need the implementation of high efficient energy storage devices. As of today, lithium ion batteries (LIBs) are the contenders for these power source systems, which have been widely used in the portable electronics and present a promising future in the electric vehicles and hybrid electric vehicles².

Electrode materials with sustainable and low cost features are the primary choices for the next-generation high performance LIBs. In this respect, natural-born biomass related materials with zero CO₂ emissions are the best candidates. According to the-state-of-the-art, carbon derived from biomass (e. g. banana fibers, charcoal, peanut shell) has been investigated for high capacities and good capacity retentions anodes for LIBs³⁻⁷. Among them, rice husk with a global production of 600 million tons per year is one of the most common agriculture wastes. The main components of rice husk are hydrocarbon compounds (cellulose, lignin, and hemicelluloses) and silica⁸. In our pervious study⁹, we used hydrothermal carbonization method to fabricate carbon fibers from rice husk with removal of silica as anodes for lithium ion batteries, which showed superior capacity retentions and rate capabilities. Recently, Liu *et al.* took the advantages of SiO₂ in rice husk to produce Si by Mg reduction^{10,11}. The as-obtained Si with nanosize and porous characteristic delivered high reversible capacity (2790 mAh.g⁻¹) and long cycling life with retention of 86 % after 300 cycles as anodes for LIBs¹⁰.

The study of C/SiO₂ composites from biomass as electrode materials has not been performed yet since the silica is generally considered to be electrochemically inactive. In fact, it has been reported that nanosize or porous SiO₂ towards electrochemical activity¹²⁻¹⁵. Sun *et al.* firstly reported that SiO₂ thin film obtained by radio frequency sputtering demonstrated reversible capacity of more than 400 mAh.g⁻¹ in a SiO₂/Li half cell¹³. As for rice husk,

SiO₂ naturally exists in nanosize form and accumulates around cellulose components^{10, 16}. Watari *et al.* fabricated porous C/SiO₂ composites pellets with a surface area of 450 m².g⁻¹ and pore size distribution of about 2 nm through a simply calcination of rice husk¹⁷. Inspired by these concepts, we directly combust the rice husk under inert atmosphere to obtain porous C/SiO₂ composites and their electrochemical performance as anodes for lithium ion batteries is evaluated. To our best knowledge, it is the first time to report C/SiO₂ composites from biomass as anodes for lithium ion batteries.

The elemental analysis of RH and RH-900 is provided in **Table 1**. As is known to us, the major components of lignocellulose biomass materials are cellulose, lignin, hemicelluloses, and silica. In our cases, the carbon takes up 33.56 wt % of the pristine RH. Except C, N, S, and H elements, the other elements those could not be detected are mainly attributed to oxygen and silicon. From our TG analysis⁹, 29 wt% of SiO₂ was detected via combustion of the pristine RH in O₂ atmosphere. After calcinations at 900 °C in inert atmosphere, the carbon takes up 41.08 wt% in the total weight and others (mainly SiO₂, other constituents of rice husk ash, such as Fe₂O₃, K₂O, Al₂O₃, CaO, MgO, Na₂O, are less than 1%¹⁸) take up of 57.18 wt%.

Table 1 Elemental analysis of RH and RH-900.

Sample	N%	C%	H%	S%	Others
RH	0.40	33.56	4.78	0.98	60.29
RH-900	0.68	41.08	1.06	1.00	57.18

Fig. 1 shows the typical TEM characterizations of RH-900. Its SEM images and corresponding EDX images of elemental C and Si are show in Figure S1. The surface of the pristine RH from SEM images was smooth in low magnification. Actually, during the heat treatment in inert atmosphere, organic compounds decompose and partially change to H₂O, CO, CO₂, and volatile compounds¹⁸. It can lead a porous structure, which is seen in the high angle annular dark

field STEM (Z-contrast) image of Fig. 1a. Under this condition, heavier SiO_2 has a brighter contrast than carbon. The size of SiO_2 ranges from 10 nm to 50 nm, which is consistent with the study of Jung *et al.*¹¹ Meanwhile, the carbon and SiO_2 were homogeneously distributed in the RH-900 (Fig. 1b and Figure S1 c-d), which means that the C/ SiO_2 is a natural born composite. This composite (Fig. 1d) shows almost amorphous features with weak diffraction rings corresponding to (002) and (100) planes of pyrolytic carbon¹⁹, complying with our XRD results (Figure S2). Its corresponding Raman spectroscopy and nitrogen sorption isotherms (BET surface area $270 \text{ m}^2 \cdot \text{g}^{-1}$ and pore volume $0.15 \text{ cm}^3 \cdot \text{g}^{-1}$) are provided in Figure S3 and S4, respectively.

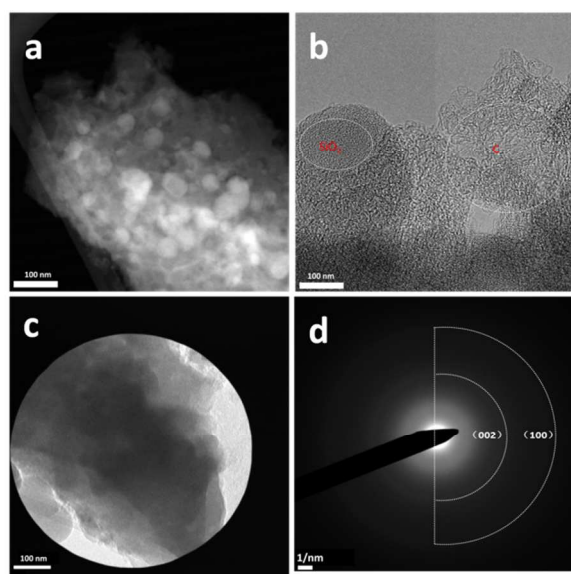


Figure 1 (a) A Z-contrast (high angle annular dark field) STEM image of RH-900, (b) High magnification TEM image of RH-900 showing amorphous SiO_2 and weak crystalline nature of carbon, (c) Bright-field TEM images and (d) corresponding selected area electron diffraction patterns of RH-900.

The electrochemical properties of a RH-900/ Li cell are displayed in **Fig 2**. The first three cyclic voltammograms for the as-prepared RH-900 electrode between 0 V and 3.0 V measured at a scan rate of $0.02 \text{ mV} \cdot \text{s}^{-1}$ are shown in Fig. 2a. As for the electrochemical reaction of SiO_2 with Li, several mechanisms were proposed¹²⁻¹⁵. Whereas it is still difficult to draw a conclusion owing to the difficulty in identifying the almost amorphous crystal structure of the silicates and various valence states of Si in the Li-Si alloys. In our case, the SiO_2 was electrochemically reduced to produce $\text{Li}_2\text{Si}_2\text{O}_5$ or Li_4SiO_4 and Si first ($\sim 0.79 \text{ V}$), then for the formation of Li-Si alloy (below 0.25 V) in the initial discharge process, which is consistent with the results of Guo *et al.*¹⁴. During the charge process, the anodic peaks were not well resolved, which coincides with the typical report of the C and SiO_2 materials^{15,20}. It is worthy to note that the anodic and cathodic current intensities increased with the cycles (from the second cycle) indicating that the charge-discharge capacity increases in their following cycles. The corresponding galvanostatic charge-discharge curves are shown in Fig. 2b. These voltage profile signatures are in good agreement with the cyclic voltammograms measurements. It is known that pyrolytical carbon with disordered structure often demonstrates lithium storage capacity of more than the theoretical capacity $372 \text{ mAh} \cdot \text{g}^{-1}$ of graphite. For a comparison, we also tested the electrochemical properties of individual carbon and silica in the mixture (Figure S5) under the same current rate of

$74 \text{ mA} \cdot \text{g}^{-1}$. The carbon derived from RH-900 after removal of silica via NH_4HF_2 showed an average reversible capacity of about $300 \text{ mAh} \cdot \text{g}^{-1}$. The silica derived from the RH-900 after calcination at 500°C under O_2 atmosphere demonstrated an average reversible capacity of $40 \text{ mAh} \cdot \text{g}^{-1}$. Here, C/ SiO_2 (RH-900) demonstrated an initial discharge capacity of $325 \text{ mAh} \cdot \text{g}^{-1}$. Note that this capacity is obtained by using the active weights of C/ SiO_2 (41.08 wt%: 58.92 wt%) composites. If we simply calculate the carbon as an active material and consider the SiO_2 as an inert component, it can be inferred that the discharge capacity is $791 \text{ mAh} \cdot \text{g}^{-1}$, which is much higher than carbon materials, indicating that silica in our mixture has electrochemical activity. Since the theoretical capacity of SiO_2 are more than $749 \text{ mAh} \cdot \text{g}^{-1}$ based on different mechanisms¹⁵. It means that our SiO_2 in the RH-900 has comparatively low electrochemical activity. We believe that the SiO_2 with size of 10-50 nm is not small enough to achieve full electrochemical capacity. It is interesting to note that the capacity is continuous increase with the increase of cycling number (Fig. 2c). The initial discharge capacity of $325 \text{ mAh} \cdot \text{g}^{-1}$ increased to $485 \text{ mAh} \cdot \text{g}^{-1}$ after 84 cycles, suggesting that an electrochemical activation of C/ SiO_2 is responsible for the increased capacity. Since our SiO_2 has the size distribution from 10-50 nm, we presume that the surface part of SiO_2 is electrochemically active. The inner part of SiO_2 are inactive but be activated in the later cycles. It is notly that the SiO_2 not only contributes to the electrochemical activity but also acts as “*in-situ*” hard template framework to keep the structure stable thus to improve its electrochemical capacity retention behavior. The discharge and charge capacity of the first cycle are $611 \text{ mAh} \cdot \text{g}^{-1}$ and $325 \text{ mAh} \cdot \text{g}^{-1}$, respectively, with a low initial coulombic efficiency of 53% (Fig. 2d), which is quite low probably due to the related structure of composite C/ SiO_2 itself as well as the parasitic reaction of electrolyte reduction to the formation of solid electrolyte interphase (SEI). The coulombic efficiency recovered to $\sim 97\%$ after several cycles, presumably due to the structure activation and incomplete stabilization of SEI. In all, compared with the most successful commercial anode materials of graphite, which is normally obtained at high temperature $> 2000^\circ \text{C}$ and has a theoretical capacity of $372 \text{ mAh} \cdot \text{g}^{-1}$ ²¹, our C/ SiO_2 composites obtained via a *chimie-douce* and sustainable way display higher capacity as well as better capacity retention behavior.

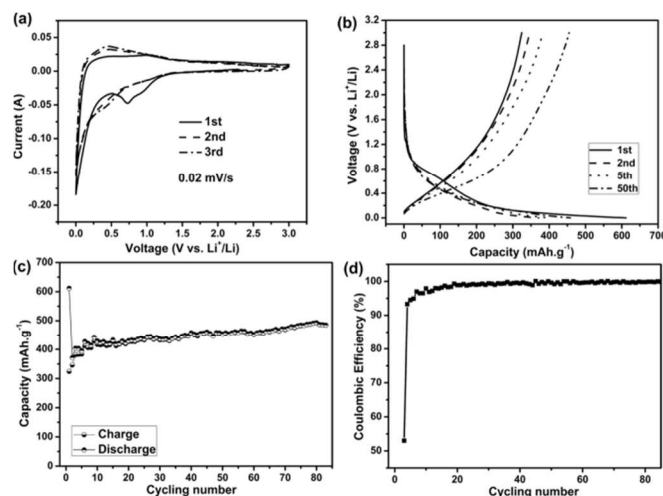


Figure 2 Electrochemical performance of RH-900 as an anode for LIBs. (a) Cyclic voltammetry of RH-900 at a scan rate of $0.02 \text{ mV} \cdot \text{s}^{-1}$, (b) Charge-discharge profiles of RH-900 at 1st, 2nd, 5th and 50th cycle in the voltage range of 0-3.0 V. (c) Cycling performance of RH-900, (d) Coulombic efficiency of RH-900.

In summary, C/SiO₂ composites synthesized via one-step fire process of rice husk were applied as anode electrodes for lithium ion batteries for the first time. It showed an initial discharge capacity of 325 mAh.g⁻¹ and increased to 485 mAh.g⁻¹ after 84 cycles. The presence of SiO₂ with nanosize 10 -50 nm in this composite not only has electrochemical activity but also plays a role in stabilizing the structure of the electrode. This low cost, facile, and sustainable strategy brings new perspectives in the utilization of biomass waste as electrodes for energy storage devices.

Acknowledgments

Thank Dr. Maria-Magdalena Titirici from Queen Mary University of London for fruitful discussions. Dr. Yanhong Wang from Chinese Academy of Sciences is acknowledged for nitrogen sorption isotherms measurements. This work was supported in part by NSFC (Nos. 21073029, 51033006, 51211140045, 51102039, 21473022), the Fundamental Research Funds for the Central Universities (Nos. ZYGX2012Z003).

Notes and references

^a State Key Laboratory of Electronic Thin Films and Integrated Devices, University of Electronic Science and Technology of China, Chengdu 610054, China

^b Institute of Engineering Innovation, The University of Tokyo, 2-11-16 Yayoi, Bunkyo, Tokyo 113-8656, Japan

† Electronic Supplementary Information (ESI) available: [details of any supplementary information available should be included here]. See DOI: 10.1039/c000000x/

References

1. H. Chen, M. Armand, G. Demailly, F. Dolhem, P. Poizot and J. M. Tarascon, *Chemsuschem*, 2008, **1**, 348-355.
2. J. B. Goodenough and Y. Kim, *Chem Mater*, 2010, **22**, 587-603.
3. G. T. K. Fey, Y. D. Cho, C. L. Chen, Y. Y. Lin, T. P. Kumar and S. H. Chan, *Pure Appl Chem*, 2010, **82**, 2157-2165.
4. T. Liu, R. Y. Luo, W. M. Qiao, S. H. Yoon and I. Mochida, *Electrochim Acta*, 2010, **55**, 1696-1700.
5. F. Zhang, K. X. Wang, G. D. Li and J. S. Chen, *Electrochem Commun*, 2009, **11**, 130-133.
6. A. Caballero, L. Hernan and J. Morales, *Chemsuschem*, 2011, **4**, 658-663.
7. A. M. Stephan, T. P. Kumar, R. Ramesh, S. Thomas, S. K. Jeong, K. S. Nahm, *Materials Science and Engineering A*, 2006, **430**, 132-137.
8. W. Arayaprane, N. Na-Ranong and G. L. Rempel, *J Appl Polym Sci*, 2005, **98**, 34-41.
9. L. P. Wang, Z. Schnepf and M. M. Titirici, *J Mater Chem A*, 2013, **1**, 5269-5273.
10. N. A. Liu, K. F. Huo, M. T. McDowell, J. Zhao and Y. Cui, *Sci Rep-Uk*, 2013, **3**.
11. D. S. Jung, M. H. Ryou, Y. J. Sung, S. B. Park and J. W. Choi, *P Natl Acad Sci USA*, 2013, **110**, 12229-12234.
12. W.S. Chang, C.M. Park, J. H. Kim, Y.U. Kim, G. Jeong, H.J. Sohn, *Energy Environ Sci*, 2012, **5**, 6895-6899.
13. Q. Sun, B. Zhang and Z. W. Fu, *Appl Surf Sci*, 2008, **254**, 3774-3779.
14. B. K. Guo, J. Shu, Z. X. Wang, H. Yang, L. H. Shi, Y. N. Liu and L. Q. Chen, *Electrochem Commun*, 2008, **10**, 1876-1878.
15. N. Yan, F. Wang, H. Zhong, Y. Li, Y. Wang, L. Hu and Q. W. Chen, *Sci Rep-Uk*, 2013, **3**.
16. A. I. Hochbaum, R. K. Chen, R. D. Delgado, W. J. Liang, E. C. Garnett, M. Najarian, A. Majumdar and P. D. Yang, *Nature*, 2008, **451**, 163-165.
17. T. Watari, A. Nakata, Y. Kiba, T. Torikai and M. Yada, *J Eur Ceram Soc*, 2006, **26**, 797-801.

18. S. Kumagai and J. Sasaki, *Bioresource Technol*, 2009, **100**, 3308-3315.
19. L. P. Wang, C. Schutz, G. Salazar-Alvarez and M. M. Titirici, *Rsc Adv*, 2014, **4**, 17549-17554.
20. L. Qie, W. M. Chen, Z. H. Wang, Q. G. Shao, X. Li, L. X. Yuan, X. L. Hu, W. X. Zhang and Y. H. Huang, *Adv Mater*, 2012, **24**, 2047-2050.
21. J. R. Dahn, T. Zheng, Y. H. Liu and J. S. Xue, *Science*, 1995, **270**, 590-593.

Table of Contents

Rice husk derived carbon-silica composites were applied as anodes for lithium ion batteries for the first time.

