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COMMUNICATION

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

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 imperative. 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 vehicles.

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 LIBs. 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 silica. In our previous study, 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. The as-obtained Si with nanosize and porous characteristic delivered high reversible capacity (2790 mAh.g1) and long cycling life with retention of 86% after 300 cycles as anodes for LIBs.

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 activity. Sun et al. firstly reported that SiO2 thin film obtained by radio frequency sputtering demonstrated reversible capacity of more than 400 mAh.g1 in a SiO2/Li half cell. As for rice husk, 

SiO2 naturally exists in nanosize form and accumulates around cellulose components. Watari et al. fabricated porous C/SiO2 composites pellets with a surface area of ~ 450 m2.g1 and pore size distribution of about 2 nm through a simply calcination of rice husk. Inspired by these concepts, we directly comb 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 ligninollose 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 analysis, 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% take up of 57.18 wt%).

Table 1 Elemental analysis of RH and RH-900.

<table>
<thead>
<tr>
<th>Sample</th>
<th>N%</th>
<th>C%</th>
<th>H%</th>
<th>S%</th>
<th>Others</th>
</tr>
</thead>
<tbody>
<tr>
<td>RH</td>
<td>0.40</td>
<td>33.56</td>
<td>4.78</td>
<td>0.98</td>
<td>60.29</td>
</tr>
<tr>
<td>RH-900</td>
<td>0.68</td>
<td>41.08</td>
<td>1.06</td>
<td>1.00</td>
<td>57.18</td>
</tr>
</tbody>
</table>

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 compounds. It can lead a porous structure, which is seen in the high angle annular dark
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shows almost amorphous features with weak diffraction rings corresponding to (002) and (100) planes of pyrolytic carbon and various valence states of Si in the Li-Si alloys. In our case, it’s still difficult to draw a conclusion owing to the difficulty in Raman spectroscopy and nitrogen sorption isotherms (BET surface area 270 m²/g and pore volume 0.15 cm³/g) are provided in Figure S3 and S4, respectively.

C and SiO₂ were not well resolved, which coincides with the typical report of the discharge curves are shown in Fig. 2b. These voltage profile second cycle) indicating that the charge-discharge capacity increases the theoretical capacity 372 mAh.g⁻¹. It means that our SiO₂ in the RH-900 has comparatively low electrochemical activity. We believe that the SiO₂ 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 mAh g⁻¹ increased to 485 mAh g⁻¹ after 84 cycles, suggesting that an electrochemical activation of C/SiO₂ is responsible for the increased capacity. Since our SiO₂ has the size distribution from 10-50 nm, we presume that the surface part of SiO₂ is electrochemically active. The inner part of SiO₂ is inactive but be activated in the later cycles. It is notly that the SiO₂ 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 mAh g⁻¹ and 325 mAh 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/SiO₂ itself as well as the parasitic reaction of electrolyte reduction to the formation of solid electrolyte interphase (SEI). The coulombic efficiency recovered to ~ 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 °C and has a theoretical capacity of 372 mAh.g⁻¹, our C/SiO₂ composites obtained via a chimie-douce and sustainable way display higher capacity as well as better capacity retention behavior.

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 mV.s⁻¹ are shown in Fig. 2a. As for the electrochemical reaction of SiO₂ with Li, several mechanisms were proposed. 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 SiO₂ was electrochemically reduced to produce Li₅Si₄O₁₂ or Li₃SiO₂ and Si first (~ 0.79 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.. During the charge process, the anodic peaks were not well resolved, which coincides with the typical report of the C and SiO₂ materials. 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 mAh.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 40 mAh.g⁻¹ to 2000 mAh.g⁻¹. The carbon derived from RH-900 after removal of silica via NH₄HF₂ showed an average reversible capacity of about 300 mAh.g⁻¹. The silica derived from the RH-900 after calcination at 500 °C under O₂ atmosphere demonstrated an average reversible capacity of 40 mAh.g⁻¹. Here, C/SiO₂ (RH-900) demonstrated an initial discharge capacity of 325 mAh.g⁻¹. Note that this capacity is obtained by using the active weights of C/SiO₂ (41.08 wt%, 58.92 wt%) composites. If we simply calculate the carbon as an active material and consider the SiO₂ as an inert component, it can be inferred that the discharge capacity is 791 mAh.g⁻¹, which is much higher than carbon materials, indicating that silica in our mixture has electrochemical activity. Since the theoretical capacity of SiO₂ are more than 749 mAh.g⁻¹ based on different mechanisms. It means that our SiO₂ in the RH-900 is a natural born composite. This composite (Fig. 1d) is a natural born composite. This composite (Fig. 1d) shows good electrochemical properties compared to pure silica or graphite. The inner part of SiO₂ has comparatively low electrochemical capacity, which is normally obtained at high temperature > 2000 °C and has a theoretical capacity of 372 mAh.g⁻¹, our C/SiO₂ composites obtained via a chimie-douce and sustainable way display higher capacity as well as better capacity retention behavior.

![Figure 1](image1.png)

**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 SiO₂ and weak crystalline nature of carbon, (c) Bright-field TEM images and (d) corresponding selected area electron diffraction patterns of RH-900.

![Figure 2](image2.png)

**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 mV.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/SiO$_2$ 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 SiO$_2$ 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.

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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/

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