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Research Article

Rice Husks as a Sustainable Source of Nanostructured Silica for High Performance Lithium-Ion Battery Anodes

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Abstract

As India is a hub of agricultural waste, annually 12 million tons of rice husk is produced. So far rice husk has been recycled only for low-value agricultural items. In an effort to recycle rice husk for high-value applications, we convert the silica to silicon and use it for high-capacity lithium battery anodes. The rice husk is the outer covering of a rice kernel and it protects the inner ingredients from external attack by insects and bacteria. To perform this function of ventilating air and moisture, rice plants have a unique nanoporous silica layers in their husk. Also, rice husk contains 67% of silica and rice husk ash contains 80-90% of silica. Taking these advantages, the converted silicon exhibits excellent electrochemical performance as a lithium battery anode, with high reversible capacity (2,790 mA h/g , seven times greater than graphite anodes) and long cycle life (86% capacity retention over 300 cycles) suggesting that rice husk be a massive resource to use in high-capacity lithium battery negative electrodes. In the present work, we extract silica from rice husk by means of simple chemical processes such as acid and alkali treatments of rice husk rice and husk ash. To extract silica from rice husk, acid wash is done and high-temperature heating is needed to get Si remnant. Then it is grounded with MgO and allowed to react in a furnace. Then acid wash is done to remove oxides. The obtained silica was utilised to fabricate Li anode having Cu as a current collector using an appropriate binder. Thus the performance of Li-ion batteries is being enhanced.

Keywords: Rice husk; Nanoporous silica; Lithium battery; Anode.

Introduction

Rice husk is the by-product of the rice industry and in India the amount of waste generated in the form of rice husk is enormous. Annually 12 million tons of rice husk is produced in India [1]. Rice husk contains 67% of silica and rice husk ash contains 80-90% of silica. Also, rice plants have developed unique nanoporous silica layers in their husks through years of natural evolution. Thus An effective method to recycle rice husk is enumerated in this work as silica present in the rice husk is converted to silicon and used it for high-capacity lithium battery anodes as the converted silicon exhibits excellent electrochemical performance [2].

Lithium-ion batteries are widely used modern batteries. As silicon is relatively inexpensive and highly conductive, its use as an alternative anode material of Li-ion battery can be explored [3]. Anodes made of layered silicon plates swell and shrink during the charge/discharge process and silicon undergoes much larger volume changes (~300%) during lithiation and delithiation steps, thus silicon surfaces may be relatively more reactive with the electrolyte [4-6]. But the 3D nanoporous structure of Si nanoparticles from rice husk prevents this from happening by permitting the Li ions to move in a channel like arrangement. Also Si monoxide and its suboxides (SiOx) are promising anode materials for lithium-ion batteries for future [7].

Lithium-ion batteries are comprised of cells that employ lithium intercalation compounds as positive and negative materials. When a battery is cycled, lithium ions exchange between the positive and negative electrodes. They are also referred as rocking chair batteries, as lithium ions "rock" back and forth below the

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positive and negative electrodes as the cell is charged and discharged. The positive electrode material is typically a metal oxide such as layered structure $LiCoO_2$ and $LiMn_2O_4$ on a current collector of aluminum foil [8]. The negative electrode material is typically graphitic carbon. A lithium-ion battery is a rechargeable battery. In Li-ion battery lithium ions move from the negative electrode to the positive electrode during discharge and back when it is charged. Li-ion batteries use an intercalated lithium compound as the electrode material, whereas the metallic lithium used in non-rechargeable lithium battery.

The negative electrode of a typical lithium-ion cell is made of carbon [9,10]. The positive electrode is the metal oxide and the electrolyte is lithium salt in an organic solvent. Depending on the direction of current flow through the cell, the electrochemical roles of the electrodes reverse between anode and cathode. The most commercial negative electrode is graphite. The positive electrode is one the of three materials: a layered oxide (such as lithium cobalt oxide), a poly anion (such as lithium iron phosphate) or a spinel(such as lithium manganese oxide) [11].

The electrolyte is generally a mixture of organic carbonates such as ethylene carbonate or diethyl carbonate containing complexes of lithium ions. These non-aqueous electrolytes mostly use non-coordinating anion salts such as lithium hexa fluorophosphate (LiPF hexafluoroarsenate monohydrate ($LiAsF_6$) lithium perchlorate ($LiClO_4$). Depending on materials choices made, the voltage, energy density, life and safety of a lithium-ion battery can change dramatically [12,13].

As pure lithium is highly reactive, it reacts vigorously with water to form lithium hydroxide and hydrogen gas. Thus, a non-aqueous electrolyte is used, and a sealed container rigidly excludes moisture from the battery pack. Advantages of Li-ion battery include long shelf life, Low self-discharge rate, rapid charge capability, high columbic and energy efficiency and high specific energy and energy density.

Materials and methods

Rice husk

Rice husks are the hard protecting cover of grains of rice. Rice hulls are the coating for the grains of the rice plant. To protect the seed during the growing season, the hull forms from hard materials, including opaline silica and lignin. During the milling processes, the hulls are removed from the raw grain to reveal whole rice.

Properties of rice husk

Rice husk accounts for 20% of the paddy in weight. It has resistance to moisture penetration and fungal decomposition. Its average calorific value is high and it has high silica content above 90% [14,15]. Rice husk contains a high amount of organic volatiles and hence rice husk is recognized as a potential source of energy. Typical composition of rice husk is tabulated below in table 1.

Table 1. Composition of rice husk

Composition	Percentage
Cellulose	31.12
Hemi cellulose	22.48
Lignin	22.34
Mineral ash	13.87
Water	7.86
Extractives	2.33

Recovery of nano-Si from rice husk

The extraction process of Si from RH is elucidated from the literature [16]. With the same process yield gets increased with proper temperature control. The sample taken here is 5g of RH. 5 g of RH is first refluxed with 75 ml of 10% HCl for 2 h to remove the metal ions inside. The leached RH is collected by filtration then washed with a large amount of deionized water. It is then dried up at 100°C and heated in air at 700°C for 2 h. A white nano-SiO_2 remnant formed with a yield of about 0.896 g. The obtained nano-SiO_2 was thoroughly ground along with equal amount of Mg powder and kept it in a muffle furnace at 400°C over 10 min, then it is heated to 650°C and held for 2 h. The reactions are as follows:

$$2Mg\ (g) + SiO_2\ (s) \rightarrow 2MgO\ (s) + Si\ (s),\ \Delta H = -546.42\ kJ/mol \qquad (1)$$

$$2Mg\ (s) + SiO_2\ (s) \rightarrow 2MgO\ (s) + Si\ (s),\ \Delta H = -291.62\ kJ/mol \qquad (2)$$

After this process, The obtained powder is soaked in 1 M HCl solution (molar ratio of HCl :H_2O:EtOH = 0.66:4.72 :8.88) for 6 h to remove MgO and Mg_2Si and then it is soaked in 5% hydrofluoric acid for 10 min to ensure that any unreacted or newly formed SiO_2 is removed.

After drying under vacuum at room temperature, the nano-Si powder is obtained with a yield of about 0.355 g.

Battery fabrication

To fabricate a battery stainless steel sealing, wave springs, gaskets, $LiCoO_2$ cathode , $LiPf_6$ 1 mol in Ethylene Carbonate Diethylene Carbonate electrolyte and Si anode are assembled [17]. The entire assembling is done in glove box in Argon atmosphere. Then this arrangement is sealed up by crimp sealing method. The performance of a cell type battery was analysed by battery cycler. The fabricated Li-ion battery is shown in fig. 1.

Fig. 1. Fabricated Li-ion coin battery

Results and discussion

Reaction of SiO_2 and Mg at various reaction temperatures

The reaction between Mg and Si is carried out at different temperatures of 650℃, 600℃. 550°**C** and 500℃. Fig. 2 represents the graphical representation of the influence of temperature on weight % if Si produced. As temperature decreases the weight loss also decreases. Thus at lower temperature yield % is increased. But beyond 550°C temperature does not have a significant influence on weight % of Si produced.

SEM analysis results

The Si powder produced is analysed with the Scanning Electron Microscope [18-25]. The SEM analysis represents that the size of the produced Si is 2µm. SEM analysis result corresponds to the reaction temperatures of 650℃ and 550℃ is shown in fig. 3 and fig. 4 respectively. As reaction temperature decreases to 550°C, the size of the Si particles gets increased to 5µm. Thus the size of the Si particles is influenced by the reaction temperature. By stringent temperature control, the nanostructure could be attained.

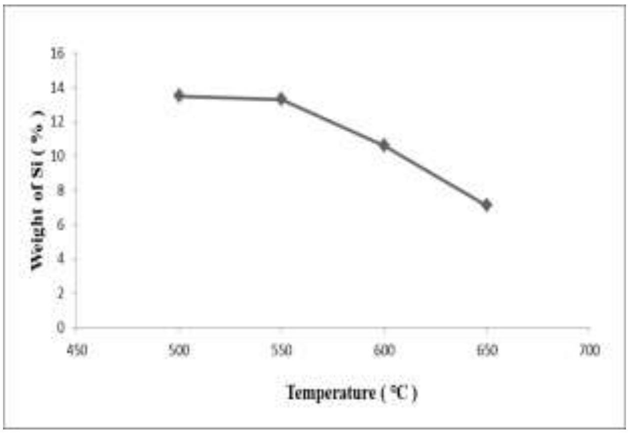

Fig. 2. Weight % of Si Vs Reaction temperature

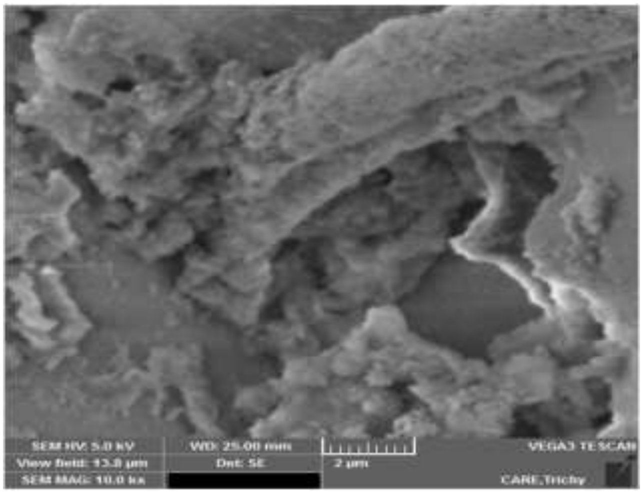

Fig. 3. SEM results for 650℃ of reaction temperature

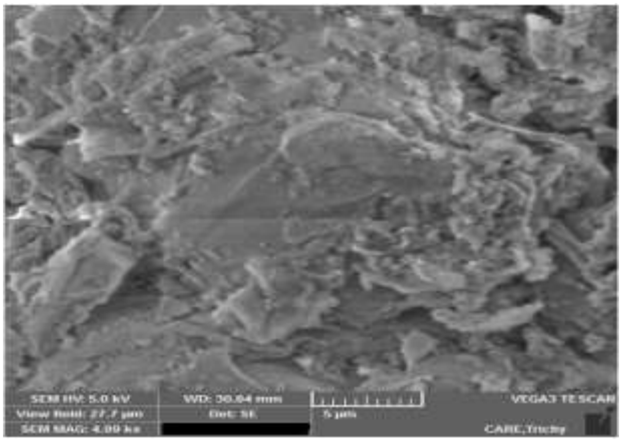

Fig. 4. SEM results for 550℃ of reaction temperature

Performance of the Li-ion battery

After SEM analysis the produced Si powder is sent to CECRI for performance analysis. In CECRI Li-ion coin battery is produced using the crimp sealing method. The produced battery performance is checked in battery cycler. The performance graphs are obtained. Fig. 5 represents the graph which explains the time taken by the fabricated Li-ion battery to get discharged. Fig. 6 represents the comparison between the conventional Li-ion battery with graphite anode and fabricated Li-ion battery with Si anode material. The performance of the fabricated Li-ion battery is considerably lesser than the graphite anode Li-ion battery and this is because of the produced Si particles' size is larger. To get enhanced performance, the size of the Si particles has to be in nano range. Fig. 7 and fig. 8 represents the discharge of Li-ion battery with Si anode material and with different cathode materials at 20°C.

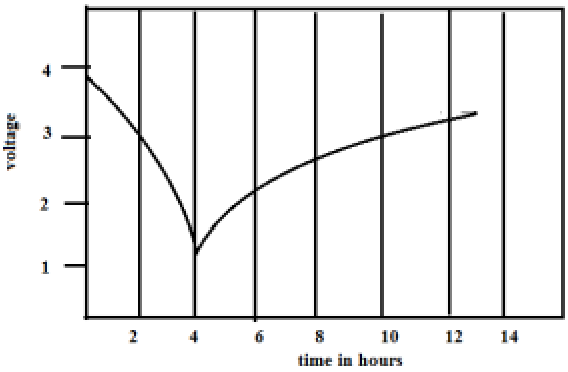

Fig. 5. Performance of fabricated Li-ion battery

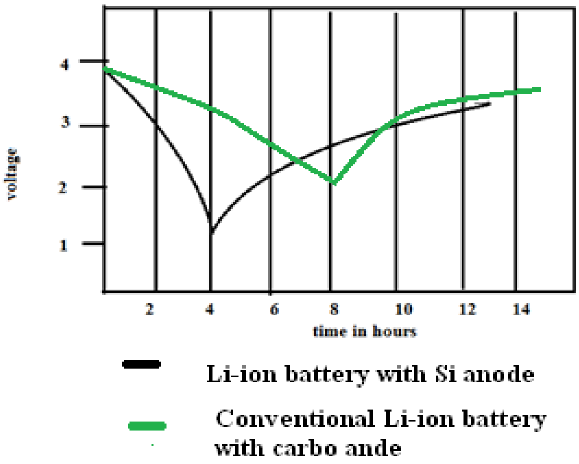

Fig. 6. Comparison of fabricated battery with a conventional battery

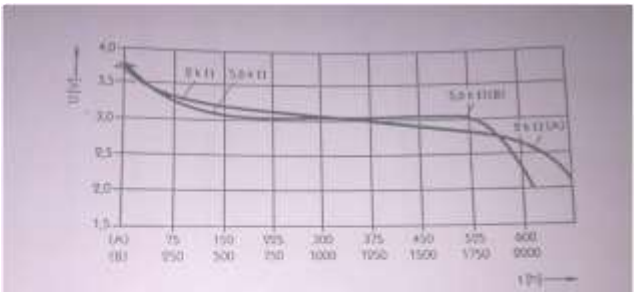

Fig. 7. Discharge of a 1 Ah cell lithium-chromium oxide at 20°C

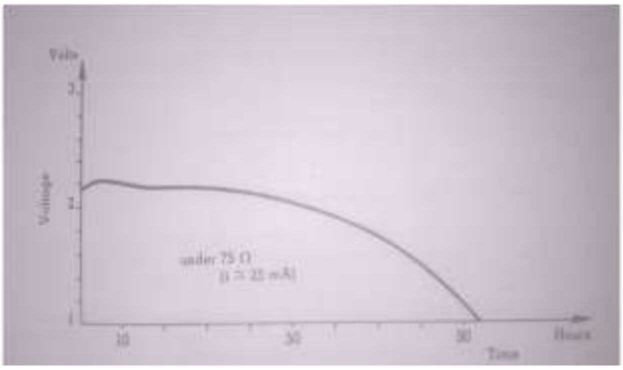

Fig. 8. 2.3 Ah round cell of the system Li-$Cu_4O(PO_4)_2$ at 20°C

Conclusions

Silicon nano materials have found potential application in a number of areas, but green, cost-effective, and scalable synthesis of them from sustainable sources is still remained challenging. This work conquers this barrier by recovering nano-Si directly from rice husks, an agricultural waste, in which silicon naturally exists in the form of silica nano particles. By coping with the strongly exothermic reactions, it is possible to preserve the nanostructure of silicon. Moreover, the uniquely small size and porous nature of the obtained nano-Si gives superior performance as Li-ion battery anode. And the simplicity, cost-effectiveness, and scalability of the fabrication process make our RH-derived nano-Si anode promising for next-generation Li-ion batteries. In addition to Li-ion batteries, potential large-scale application of nanostructured Si renders tremendous opportunities for this kind of agricultural byproduct derived nanomaterial.

Conflicts of interest

The authors declare no conflict of interest.

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