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RESEARCH ARTICLE



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RECOVERY OF ENERGY-INTENSIVE SI PARTICLES FROM RICE HUSK FOR LI-ION BATTERIES

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ABSTRACT

Silicon existed naturally in the form of nanoparticles in rice husk about 20 per cent of its dry weight. Silicon could be produced from Rice husk using a simple, energy-efficient and easily scalable method. The silicon that was recovered maintained the unique nanostructure of silica as it existed in the husk, which made for many applications like very good battery performance, fertilizer additives, stockbreeding rugs, fuels, land filling or paving materials etc.,. In this paper we show that pure Si nanoparticles (SiNPs) can be produced from rice husks. Using Rice husk as the raw material source, overall energy-efficient, green and large scale synthesis of low-cost and functional Si nanomaterials is possible. According to research recently published in Scientific Reports, Nano-size silicon particles could be produced from rice husk, an abundant agricultural waste for the next-generation Lithium-ion batteries. Nanostructured silicon materials, because of their unique properties and small size, have promising applications in a range of new technologies, such as nano electronics, photonics biotechnology, energy harvesting, and energy storage.

Keywords : Energy-intensive Si nano particles, Rice husk, next-generation Lithium-ion Batteries

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INTRODUCTION

Ricehusk is the outer covering of a rice kernel and protects the inner ingredients from external attack by insects and bacteria. To perform this function rice plants have developed unique nano porous silica layers in their husks through years of natural evolution taking advantage of this interconnected nanoporous structure existing in rise husk it can be converted to silicon which is capable of exhibiting excellent electrochemical performance [1] as a lithium battery anode. As silicon(Si) is relatively inexpensive and highly conductive its use as an alternative anode material for Li-ion battery (LIB) has been found. But silicon undergoes much larger volume changes(~300%) during lithiation and delithiation steps [2] and silicon surfaces may be relatively more reactive with the electrolyte. But the 3-D nanoporous structure of Si from rice husk prevent this from happening by permitting the Li-ion to move in a channel like structure. The above mentioned quality of rice husk yields a valuable component for modern high capacity Li-batteries [3]. So for rice husk has been recycled only for low value agricultural items. An effort is made to recycle rise husk for high value applications [4].

Li-ion batteries are common in consumer electronics [5]. They are one of the most popular types of rechargeable batteries for portable electronics, with one of the best energy densities, no memory effect and only a slow loss of charge when not in use. LIB's are also growing in popularity for military, electric vehicle and aerospace applications they are becoming a common replacement for the lead acid batteries that have been historically for golf carts and utility vehicles [6]. Instead of heavy lead plates and acid electrolytes the trend is to use light weight lithium electrodes, which can provide the same voltage as lead acid batteries LIB's based on lithium cobalt oxide, can offer high energy density but pose a safety hazard when damaged. Other LIB's offer comparatively low energy density and inherent safety [7]. Depending on material choices the characteristics of LIB's vary dramatically. To overcome this pitfall in LIB's. An alternate anode source is needed. A good choice would be nanoporous Si from rice husk. Rice husk accounts for 20% of the paddy in weight [8] it has high average calorific value and silica content and recognized as a potential source for Si.

Materials and Methods

3 grams of Rice husk was refluxed with 45 ml of 10% HCl for 2 hours to remove the metal ions inside. The leached Rice husk was filtered, washed with the large amount of deionized water and dried at 100°C.and heated in air at 700°C for 2 hours. A white nanosilicon remnant will be formed and weigh about 0.5 gm. The obtained nanosilicon was thouroughly ground along with equal amount of Mg powder and kept in a muffle furnace at 400°C (1) for 10 min and further exposed to 650°C (2) for 2 h. After this process, the resulting powder was soaked in 1M HCl solution for 6 h to remove MgO and Mg₂Si. Furtehr HF etching was carried out for 10 min. The end products were dried under vacuum at room temperature. This yields nanoSi powders which weighs about 2mg.

 $2Mg(g) + SiO_2(s) \rightarrow 2MgO(s) + Si(s), \Delta H = -546.42 \text{ kJ mol}^{-1}$ -- (1) $2Mg(s) + SiO_2(s) \rightarrow 2MgO(s) + Si(s), \Delta H = -291.62 \text{ kJ mol}^{-1}$ - (2) Unlike other long cycle life and high capacity nano structured Si anodes the nanoSi here is derived without any use of energy intensive processes such as SiLAN-CVD or Laser ablation. Our approach uses abundant and sustainable source i.e. Rice Husks. The Mg metal reducing reagent can be regenerated through electrolysis and thus the whole process is green. Moreover the method here has superior scalability to other nanoSi fabrication processes.

Electrochemical behavior of nanoSi from Rice husk

Unlike bulk Si, the recovered nanoSi has high functionality due to the small size and porous nature. It exhibits excellent electrochemical behavior without any further coating or modification [9]. Upon rigorous galvanostatic cycling between 0.01 and 1 V, the discharge capacity reaches 2790 mAhg⁻¹. For the first cycle at C/50 it stabilizes around 1750 mAhg⁻¹. For later cycles at C/2 these values are 7 and 5 times the theoretical capacity of graphite (372 mAhg⁻¹). The cycling stability is excellent as well. No capacity decay was observed over the 150 cycles after the initial lower current cycles, and the capacity retention values after 200 and 300 cycles are 95 % and 86 % respectively [10]. The similarity of the profiles over 300 cycles indicates highly reversible Li insertion and extraction.

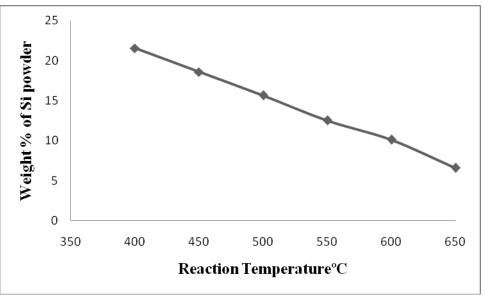
Battery Fabrication

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 were assembled. The entire assembling was done in Glove box in Argon atmosphere. The arrangement was sealed up by crimp sealing method. The performance of a cell type battery was analyzed by battery cycler.

RESULTS AND DISCUSSION

Effect of Temperature on yield of Si

Reaction Temperature is an important parameter to get the optimum yield of nanoSi particles. The reaction between Si and Mg was carried out between 650 to 400°C. From figure 1 it is clear that as the temperature decreases the yield of Si particles is high. Our intention is to produce nao Si it is mandatory to verify the size of the Si powder. Temperature not only decides the yield but also the size of Si particles. If the yield is more it is not accepted that the size of the Si particles would be the same for any temperature within the given range.





Effect of Temperature on size of Si particles

From the yield obtained for different reaction temperatures, the collected samples were tested for its size and surface morphology. The results are provided in Figures 2 and 3. It is evident that the size reduces as the temperature increases. It is confirmed

that reaction temperature is directly proportional to the yield but inversely proportional to the size. The smaller the size of the Si particles the stability of the particle would be comparatively high for energy intensive performance.

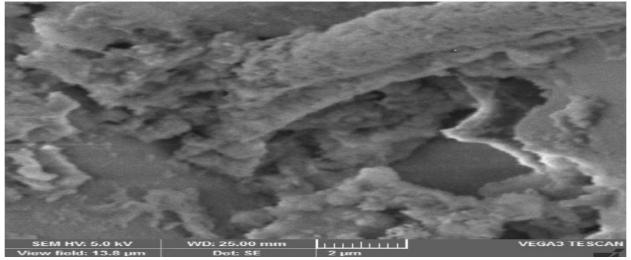


Figure 2 SEM result of nanoSi for 650°C

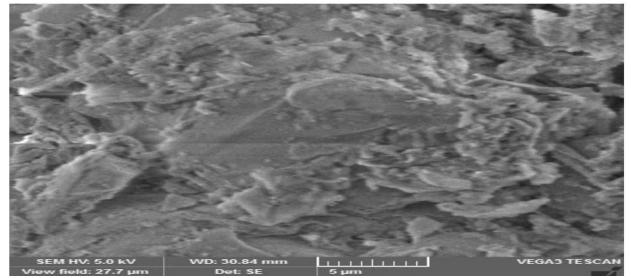
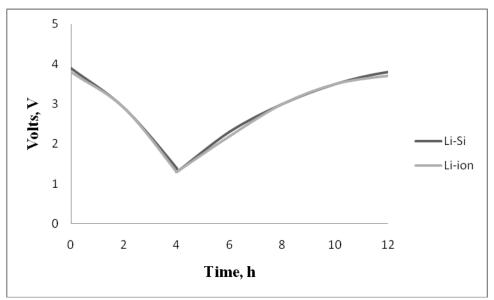
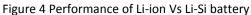


Figure 3 SEM result of nanoSi for 550°C

Performance of conventional Li-ion battery with carbo anode Vs Li-ion battery with Si anode

Li -ion battery with Si anode was fabricated by crimp sealing method and performance analysis was checked which was shown in figure 4.





Conclusion

Recovery of nanoSi from rice husks was done and utilized as a source for anode material in Li- ion batteries. The uniquely small size and porous nature of the obtained nanoSi gives on par performance with commercial Li-ion batteries. The simplicity, cost effective and scalability of the fabrication process makes rice husk derived nanoSi anode as a promising one for next generation. More accuracy is needed in maintaining the reaction temperature to get precised results. The important factor is the size of the Si particle which will enhance the performance of Liion battery with Si anode.

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