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To Study the Effect of Particle Size of Sand and Magnesium Powder on conversion of Sand to Nano-silicon

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Abstract : Silicon is an interesting candidate to be used as an anode material for the next generation Li-ion battery. Silicon due to its high specific capacity (mAh/g) among the known anode materials for Li-ion battery is expected to fulfill the existing demands of the market. It is also abundant and cheap. Unfortunately, significant breaking impact during lithiation procedure of lithium in continuous charge-release process that causes structural degradation, in this way losing specific capacity and contact amongst electrolyte and cathode. To overcome the results noteworthy achievements have been made in creating silicon nanosheets. Thermic reduction of SiO_2 can be done by few known methods that includes carbothermal, magnesiothermic, aluminothermic, and calciothermic lessening. In this work, we have synthesized silicon nanosheets by using magnesiothermic reduction. Magneisothermic reduction of sand by furnace heating was found successful to produce silicon nanosheets at 600°C. According to results, we have observed that the silicon nanosheets have a leaf-like sheet morphology ranging from a few ten to hundred nanometer.
Keywords: Magnesiothermic Reduction; Sand; Silicon Sheets; Leaching; Porous Silicon

1. Introduction

The revolutionary change in the field of batteries has played a pivotal role in advancing their application in hybrid electric vehicles (HEVs), back-up electricity storage units, and lightweight and portable electric devices.[1]This has made Lithium-ion batteries the centre of research in energy storage field.[3] Silicon has gained significant interest as a promising anode material for lithium-ion batteries because of its high energy density and high specific and volume capacity[1][2].Although, due to lithiation, silicon-based electrodes undergo a large volume change which results into pulverization and loss of electrical connectivity affecting the performance of the battery. To overcome this limitation, fabrication of Si nanostructures comprising of nanoparticles, nanosheets, nanowires, nanohollows and nano-core-shells is carried out. [3]Among these nanostructures, Nanosheets has the highest theoretical capacity (i.e. 4300 $mAhg^{-1}$) and coulombic efficiency (i.e. 84%).[2][4] The synthesis of Silicon Nanosheets can be carried out by methods like, electrochemical etching, metal assisted chemical etching, chemical vapour deposition, carbothermal reduction, metallothermic reduction (Ca, Al, Mg). However, magnesiothermic (metallothermic) reduction of sand allows straightforward and low-cost synthesis of Silicon Nanosheets at low temperature range which results in the formation of uniform nanosheets.[5][6][7]. In this work, experiment has been performed for the fabrication of Silicon Nanosheets from SiO_2 by magnesiothermic reduction process. Low cost Sand sourcehas been considered for the fabrication as it is environmentally benign and highly abundant in nature. [1]

2. Experimental Procedure

In this study the focus is on preparation of Nanosheets from sand (SiO_2) by magnesiothermic reduction process.

2.1. Material Used

Sigma Aldrich Sand (i.e.commercial sand), sand from the construction site, Sigma Aldrich Magnesium, HCl and HF and deionized water were used in this work.

2.2. Procedure

In magnesiothermic reduction, silicon dioxide is reduced to silica using magnesium as reducing agent. Initially, natural sand was collected from the construction site was purified with deionized water several times in order to remove any trace of alkali or acid present in the sand. The washed sand was dried in an oven at 100ºC. Along with that, Sigma Aldrich Sand was also heated to remove the impurities present. After the purification process, both the sands were pulverized and sieved to obtain different particle sizes i.e. <25 , 25-45 , 45-53 , 53-63 , 63-75 , 75-90, 90-106. Same particle size of pulverized Magnesium was also sieved. The weighed samples of purified sand and magnesium were taken in desired ratio of 1:0.9, thoroughly mixed and were then used for magnesiothermic reduction.
Several experiments were conducted with different mixtures of construction sand and magnesium as well as Sigma Aldrich sand and magnesium to study the effect of particle size of sand and magnesium. All the prepared samples were then heated at 600ºC in a muffle furnace for different time intervals (1h, 2h, 3h). The heated samples were than leached with 5M HCl at 100 ºC with continuous stirring for 1 hr for the removal of MgO and Mg_2Si. with continuous stirring at 100ºC. The HCl leached sample was then washed with 5 wt/wt% HF for 5min or 20 min at room temperature for the removal of unreacted SiO_2 and to get pure Silicon.

2.3. Characterization

Characterization of synthesized Si nanosheets from sand was done using various sophisticated techniques like X-Ray Diffractometer (XRD), Scanning Electron Microscope (SEM) and Transmission Electron Microscope (TEM). The surface morphology of silicon nanosheets was examined using SEM and TEM and the phase evolution was investigated using a XRD technique.

3. Results and Discussion

The Silicon samples were synthesized for both, construction sand and Sigma Aldrich sand using magnesiothermic reduction and were analyzed for their morphology and phase formation.

3.1. Physical Appearance

The physical appearance of the heattreated samples of mixture of different particle sizes of constructional sand and sigma sand with Mg powder is shown in Fig: 1(A). The physical appearance of the heated product obtained from constructional sand and sigma aldrich sand showed a very similar pattern. The particle sizes of sand chosen were<25, 25-45, 45-53 and 53-63 representing the same in the Fig: 1(A) from (a) to (d). The intensity of the color of the sand gradually decreases from (a) to (d), which suggests that, with the decrease in the particle size of sand the reaction proceeds to completion resulting in the formation of silicon with other byproducts. In fig: 1(B) the heated mixture containing magnesium powder of different particle size, <45μ, 45 – 63μ, 63 – 105μ, 105 – 150μ, 150 – 200μ and 200 – 250μ from (a) to (d) is shown. The color of the samples has changed with the increase in the size of magnesium particles in the mixture, which depicts completion of the reaction.

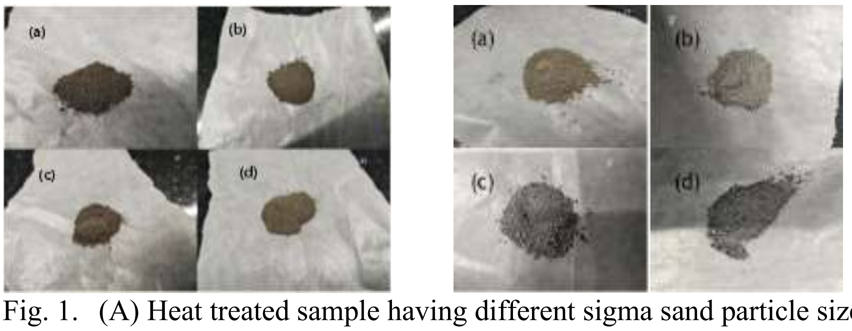

Fig. 1. (A) Heat treated sample having different sigma sand particle size ;
(B) Heat treated sample having different Mg particle size.

3.2. XRD Analysis

X-Ray diffraction is used to investigate phase development during magnesiothermic reduction and acid

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leaching and the pattern for pulverized sand magnesium mixture, heat-treated and HCl etched and heat –treated and HCl and HF etched samples are shown in Fig: 2. Here, SxMgy(HT,HCl,HF) is used where, x and y are the particles size of sand and magnesium and HT, HCl and HF depicts the time for heat treatment (in hr), leaching with HCl (in hr) and leaching with HF (in minutes). The XRD pattern reveals that the mixture of sand and magnesium before heat treatment contains SiO_2 and Mg. It also shows that the reduced samples comprises of silicon and the peak of MgO, which is formed during reduction reaction diminishes as it is completely dissolved in the HCl solution. But unreacted SiO_2 is still present, which is removed by leaching of the heat treated and HCl leached sample with HF solution which resulted in the increase in the amount Si formed. In fig: 3. The product from commercial sand and construction sand are compared. The phase analysis using XRD reveals that the intensity of the Si peak formed is more in case of commercial sand. In order to get better results and maintain the homogeneity in the sand quality it was decided to use sigma aldrich sand for further experiments.

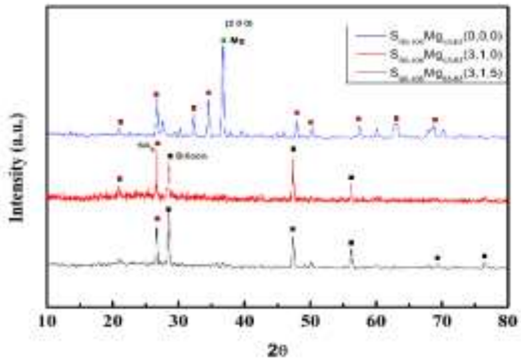


Fig. 2. XRD of the whole process

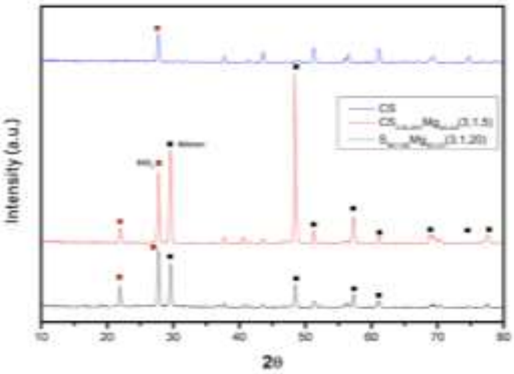
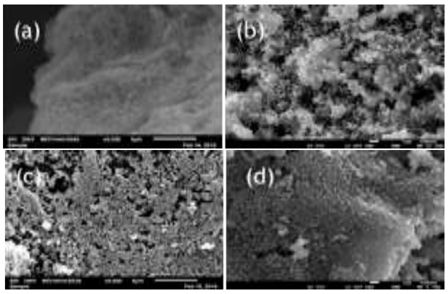


Fig. 3. XRD of different types of Sand

3.3 SEM Analysis

SEM analysis of different product samples has been carried out and the observed changes in the morphology were analysed. In Fig.4, the images can be distinguished on the basis of different structures formed from different particle size feed and it can be said thatparticle size plays a vital role on the formation of Si nanosheets. In fig.4(a), all the particles are coagulated forming a sheet like structure. With the decrease in the particle size of magnesium in fig.4(b), the surface morphology changes and small flower type structures are observed. By decreasing the particle size of sand in fig.4(c) the image depicts the formation of nanoparticles and by increasing the particle size of sand, bigger flower like structure can be seen. Hence, any modifications in the particle size of sand and magnesium in the feed will lead to variations in the size of nanosheets formed. In fig.5, four phases of the sample during the process are compared. In fig.5(a) shows large cell like structure portraying simple mixture of sand and magnesium particles before heating. Fig.5(b) represents the heat treated sample of the mixture and due to reduction reaction a change in the structure of the mixture can be observed. When the heat-treated sample is leached with HCl the particle size of the product increases, as shown in fig.5(c) and after leaching this product with HF, agglomeration of the particles takes place for the formation of huge sheet like structure possessing small flower like structure as witnessed in fig.5(d).



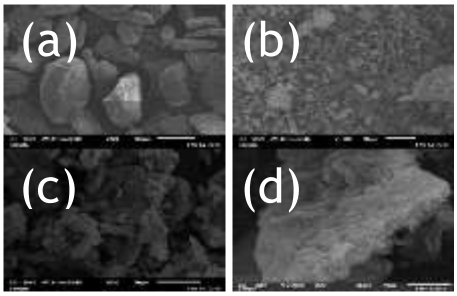


Fig.4

1.4. TEM Analysis

Fig.5

(a) SEM image of $S_{90-106}Mg_{53-63}(3,1,5)$
(b) SEM image of $S_{90-106}Mg_{45-53}(3,1,5)$
(c) SEM image of $S_{75-90}Mg_{25-45}(3,1,5)$
(d) SEM image of $S_{210-297}Mg_{25-45}(3,1,5)$.

(a) SEM image of $S_{90-106}Mg_{53-63}(0,0,0)$
(b) SEM image of $S_{90-106}Mg_{53-63}(3,0,0)$
(c) SEM image of $S_{90-106}Mg_{53-63}(3,1,0)$
(d) SEM image of $S_{90-106}Mg_{53-63}(3,1,5)$.

Morphology of the product of silicon formed as observed in TEM is shown in fig.6. TEM images indicate that Si sheets are composed of several nanosheets. Fig. 6. (a-b) indicates the formation of nanosheet as we can observe agglomeration of particles. On focusing on the edge of the solid structure in Fig.6. (c-d), we can observe a transparent sheet like structure which indicates the formation of nanosheet. Fig. 6. (e) shows the electron diffraction pattern which reveals the presence of white dots denoting the crystalline nature of Silicon.

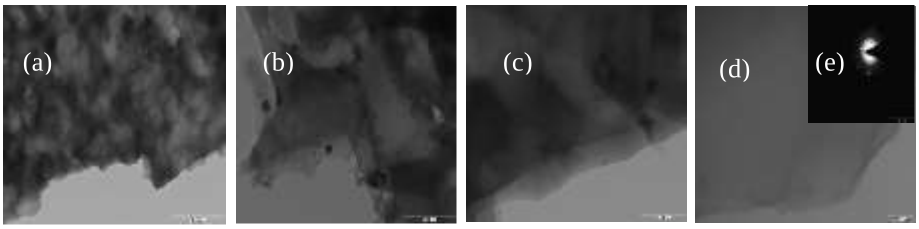


Fig. 6. (a-b) Low magnified TEM image of $S_{90-106}Mg_{45-53}$ (3,1,5),
(c-d) High magnified TEM image of $S_{90-106}Mg_{45-53}(3,1,5)$,
(e) Electron diffraction of $S_{90-106}Mg_{45-53}$ (3,1,5).

4. Conclusion

In this work, Si nanosheets were successfully synthesized from sand by magnesiothermic reduction followed by two-stage leaching using HCl and HF solutions for the removal of excess metal and metal oxides formed during reduction reaction. The change in the color of mixture of sand and magnesium having different sizes indicated the effect of particle size on the reaction. SEM analysis also revealed the effect of particle size on fabrication of Si nanosheets as well as how the structure of the mixture of sand and magnesium transformed from one stage to another. A comparison was also carried out of both the sands, commercial and natural in XRD analysis, which lead to the conclusion that commercial sand should be preferred to enhance the results. The sheet like structure of nanosheets and the presence of silicon was determined with the help of TEM analysis and electron diffraction pattern.

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SEM and TEM at Biological & Life Sciences, School of Arts and Sciences, Ahmedabad University XRD at chemical department of Pandit Deendayal Petroleum University during this research work.

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