Silicon Conversion From Bamboo Leaf Silica By Magnesiothermic Reduction for Development of Li-ion Baterry Anode

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Abstract. Silicon (Si) is a promising alternative material for the anode Lithium ion Battery (LIB). Si has a large theoretical capacity about 3579 mA hg -1, ten times greater than the commercial graphite anode (372 mA hg -1). Bamboo is a source of organic silica (bio-silica). Most part biogenetic content of SiO_2 is obtained in bamboo leaves. This paper aims to investigate the synthesis nano Si from bamboo leaves through magnesiothermic reduction after silica extraction using sol–gel method and to observe nano Si of bamboo leaf as mixed material for lithium ion baterry. Silica and silicon content was determined using XRF. Silica product has 96,3 wt. % yield of extraction from bamboo leaf, while silicon yield was obtained 61.2 wt. %. The XRD pattern revealed that silica and silicon product were amourphous. The extracted silica and silicon from bambo leaf has spherical shape and agglomerated form. As anoda material for LIB, silicon product achieved 0,002 mAh capacity for 22 cycle.
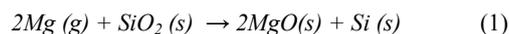
1 Introduction

Silicon, the second most common element in the earth's crust have attracted so many attention in the energy storage application because of their high potential capacity. Silicon has been considering most promosing candidate to replace graphite anode. They have large theoretical capacity about 3579 mAh g^{-1}, almost 10 times higher theoretical specific capacity than graphite anode(372 mAhg^{-1}) [1]. Silicon usually has obtained from mineral in rock and sand, however, silicon also can be obtained in organic material such as risk husk, bamboo leaf, wheat husk and another agricultural waste.

Bamboo is a source of organic silica (bio-silica). The bamboo absorbs silicic acid from the water and then convert it into SiO_2 hydrate in the root branches and leaves [2].Most part biogenetic content of SiO_2 is obtained in bamboo leaves. Bamboo leaves have a silica content of 17 -23% by weight, higher than the silica content in rice husk (9.3-13.5% by weight)[3]. Bamboo leaf ash has a large SiO_2 content of 75.90-82.86 wt% [4] [5].

The sol gel technique mainly used for extracting silica from agricultural material like rice husk [6], sugar cane bagasse [7-8], wheat husk [9], corn cob [10], and wheat staw [11]. The sol-gel process is widely used to produce pure silica particles due to its ability to control the particle size, size distribution and morphology through systematic monitoring of reaction parameters [12].
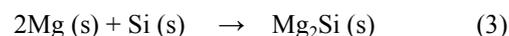
Silica can be reduced to silicon by using several method: carbothermic reduction, aluminothermic reduction, calciothermic reduction, and magnesiothermic reduction [13]. Conventional carbothermic reduction was usually used by industrial apllication to reducing silica into silicon. Oxygen is removed by reaction sequences of heterogeneous-homogeneous at a temperature of about 3000 ^{o}C [14]. In the present work, magnesium as a reducing agent, was introduced to reduce the reaction temperature until 650°C [15]. Silica can be reduced by magnesium (magnesiothermic reduction) to produce silicon through following reaction:

$$2Mg\ (g) + SiO_2\ (s) \rightarrow 2MgO(s) + Si\ (s) \qquad (1)$$

or

$$2Mg\ (s) + SiO_2\ (s) \rightarrow 2MgO(s) + Si\ (s) \qquad (2)$$

If Mg excess,

$$2Mg\ (s) + Si\ (s) \rightarrow Mg_2Si\ (s) \qquad (3)$$

The formation of Mg_2Si is affected by the excess Mg and reduction temperature. Decreasing magnesium amount resulted in decreasing Mg_2Si and with increasing temperatures at fixed ratio of Mg to SiO_2, the formation of Mg_2Si increased [16].

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2 Experimental Method

2.1. Silica Extraction

Bamboo leaves was collected from Sragen, Central Java To remove alkali impurities, the bamboo leaf were crushed and leached by 1M HCl for 2 hours, after washing in water and drying the bambo leaves were calcined at 650°C for 2 hours in muffle furnace to remove organic impurities.

Silica was extracted from Bamboo Leaf Ash, (BLA) using sol-gel Method to produce silica xerogel [7]. In this method, 60 ml NaOH 2M were added to 10g BLA and boiled for 1 h with constant stirring to extract the silica and produce sodium silicate solution. The solution were filtered trough whatman No.41. The filtrate solution was sodium silicate, cooled to room temperature and the pH solution was reduced with 1N HCl to 7.0 under constant stirring to produce silica gels. When the solution gel was formed ,it was aged for 18 h. After aging, the soft gel gently broken by adding 100 ml destilled water and centifuged at 3000 rpm to make a slurry. The slurry was filtered and washed. The supernatant was discarded and the gel was dried at 80 at 12 h to produce white powder silica (xero-gel).

2.2 Silica Reduction

Synthesis of silicon from the as-produced silica was conducted by a magnesiothermic reduction process. Silica (xero gel) mixed with magnesium powder with the SiO$_2$:Mg ratio of 1:0,4. The powder was heated in a furnace under Ar gas flow and held at 650°C for 2 hours. After the reaction the powders were immersed in 1M HCl solution for 6 hour to remove MgO, MgSi and unreacted Mg [15].

3 Result And Discussion

3.1. Silica Extraction Composition

The silicas's purity can be determined using XRF method. It shown in table 1, sol–gel method can produced silica with purity of 96.3% wt.%. The remaining elements include metallic impurities such K, Ca, Fe, Ni, Cu, In, Yb. This high yield of silica indicated that during sol-gel extraction, only anmorphous silica was synthesized. Silica dissolved from BLA in sodium hydroxide and produce sodium silicate. The reaction as follows:

$$x\ SiO_2 + 2\ NaOH \rightarrow Na_2O. \times SiO_2 + H_2O \qquad (4)$$

The sodium silicate solution reacts with hydrochloric acid to produce silica gel. The reaction is:

$$Na_2O.\times SiO_2 + HCl \rightarrow \times SiO_2\ (gel) + NaCl + H_2O \qquad (5)$$

The presence of ion Na+ have important rule in this reaction. Interaction between Na$^+$ and negatively silicate would speed up the reaction. Ion Na + promoted the gel

formation by screening the surface charge of particles that favors their agregation. [7].

Table 1. Silica product from sol gel method.

Compound	Si	K	Ca	Fe	Ni	Cu	In	Yb
Concentration Unit	96.3	0.2	1.8	0.42	0.52	0.16	0.4	0.1

The SEM image of silica xerogel BLA was shown in Fig.1. The extracted silica was spherical an agglomerated form. The particle has various size in nano scale.
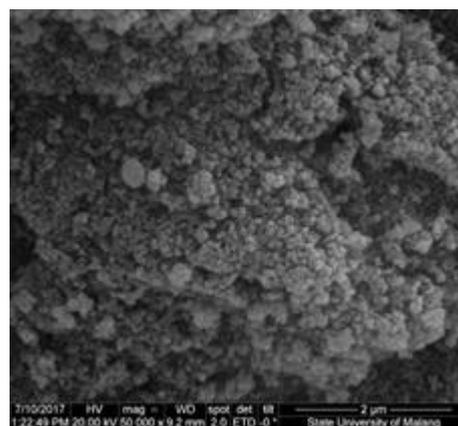

Fig.1. The scanning electron micrograph (SEM) image of silica xerogels from BLA

An XRD pattern of prepared silca gel from bamboo leaf is shown in Fig.2. The diffused peak at 2θ=22,6 indicated that silica gel were solid amorphous [3][6]. It was confirmed by the absence of any ordered crystalline structure. This XRD pattern also proved that sol-gel process completely eliminates most of crystalline structured impurities in BLA, ie K$_2$O, Fe$_2$O$_3$, CaO [17].
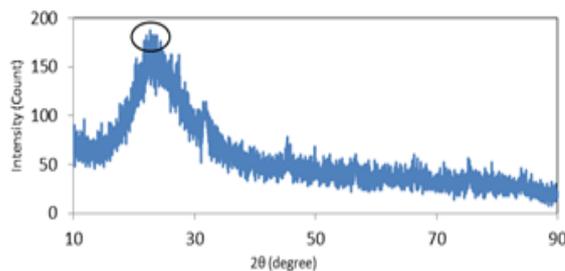

Fig. 2. XRD diagram of Silica BLA

The amorphous, nano scaled silica have many advantages, it can be easily dissolved , have high porosity and high surface area that provide higher activities reaction [18].

3.2. Silicon Reduction

The component of silicon from magnesiothermic reduction were characterized using XRF. The main component was silicon (61.2 %.wt) and Magnesium (31 %.wt). It was also confirmed from XRD Diffractorams (**Fig 3**). There is an another strong peak beside of silica that indicate the presence of magnesium.
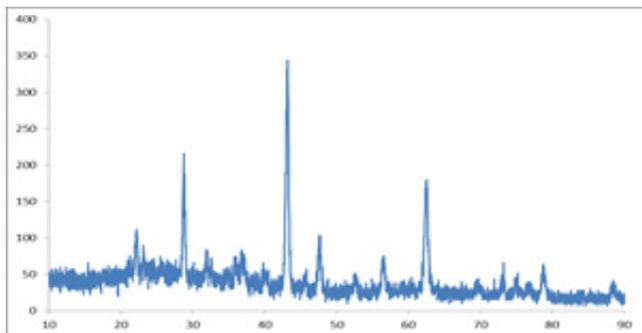

Fig.3. X-ray diffraction pattern of silicon produced from magnesio-thermic reduction.

It is suspected that in this experiment, there was magnesium excess in reaction, and as a result, following Equation 3, the silicon product was reduced [19]. Leaching process method taking big role to obtain high purity silicon. It is need to optimize the condition and variable of leaching process due the low purity silicon product.

From the morphology characterization by using SEM, it was shown in Fig.4., that nano silicon has spherical particle shape and agglomerated. Hence there is no significant difference between silica and silicon product in a term of morphology.
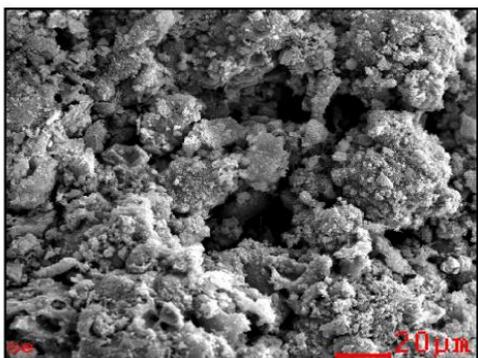

Fig.4. The scanning electron micrograph (SEM) image of silicon product from magnesiothermic reduction

3.3. Silicon as anoda material for LIB

Lithum ion batteries performance. with silicon BLA as anoda material was tested by the galvanostatic cycling method. As the result (Fig.6.) the maximum capacity of electroda was 0.002 mAh at 22 cycles.
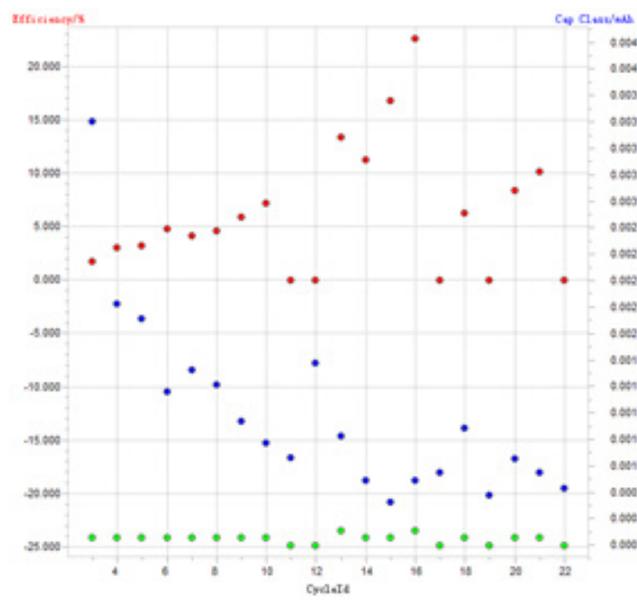

Fig.6. Galvanostatic cycles

The present of MgO has significant effect for the low electroda capacity. MgO is insulator material because of its wide band gap (~7.8 e), that may decrease the elctroda capacity [20].

Conclusion

Nano silica has suscesfully extracted from bamboo leaves by sol gel technique and then reducted into silicon using magnesiothermic reduction. Silica from bamboo leaves has 93.6 % %.wt purity while silicon was 61.2 % .wt. From XRD and SEM analysis reveals that silica and silicon BLA were amorphous with spherical shape and agglomerated form. Silica performance as LIB anoda material was tested using eight channel baterry. The electroda's capacity was 0.002 mAh for 22 cycle.

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