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Development of Fe-doped amorphous nanosilica from Philippine waste rice hull as anode material for lithium battery

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ABSTRACT

Silica or silicon dioxide (SiO_2) is an indispensable material in many industrial applications. The increasing use of silicon-based material in the development of anode electrodes for batteries is owed to the high theoretical capacity of silicon. The problem of silicon's large volume change upon lithiation can be circumvented by obtaining an amorphous structure in its oxide form and reducing the particle size to nano-size particles. On the other hand, the silicon oxide electronic conductivity can be improved by doping or incorporating an electronically conductive material like iron. Furthermore, the development of cheap anode material for lithium (Li) batteries using silica from waste rice hull (RH) is sustainable and a promising approach. In the present study, the microstructure of the iron-doped amorphous nanosilica (Fe-doped AnS) synthesized from Philippine waste RH (PWRH) and its initial electrochemical performance as an anode material for Li battery were investigated. Properties of the Fe-doped AnS material were characterized using Scanning Electron Microscope with Energy Dispersive Spectroscopy (SEM-EDS), X-ray Diffraction (XRD), and Fourier Transform Infrared (FTIR). Results of the SEM-EDS and XRD analyses of the Fe-doped AnS revealed the presence of amorphous silica (SiO_2), amorphous carbon (C), and maghemite (γ-Fe_2O_3) structure with a homogeneous distribution of the elements as suggested by EDS. FTIR spectra revealed the occurrence of the different absorption bands of the synthesized material while the galvanostatic discharge-charge performance of the Fe-doped AnS working electrode revealed a specific capacity of 1,232 mAh/g upon lithiation and 8 mAh/g upon delithiation. The resulting lithiation capacity of the prepared battery cell is almost four times more as compared to the commercial graphite anode material. These results suggest that AnS synthesized from cheap and abundant PWRH can be promising anode material for Li batteries.

Keywords: agricultural waste, anode material, lithium battery, nanosilica, rice hull

1. Introduction

The issue of energy mobility and support for the intermittency of renewable energy are some of the reasons for the improvement and development of lithium-ion batteries (LIB) [1]. The development of silicon-based anode material for LIB is rapidly increasing; this is because of the inherent theoretical specific capacity of silicon which is around 4,000 – 4,200 mAh/g [1-3]. Nevertheless, silicon usually suffers capacity fading due to large volume changes during the charge and discharge cycling process; however, such issue can be improved when the particles are reduced to nanoscale sizes [1, 2, 4]. In addition, bulk silica is known to have low electronic conductivity and is an electrochemically inactive material for LIB [3]. In order to improve electronic conductivity, silica can be doped with electronically conductive materials like Fe [5]. Along with the increasing demand for the use of these energy storage for portable gadgets and renewable energy support, more alternative materials are likewise needed to sustain its production and to make it at an even cheaper cost.

RH is known as very rich in silica and is considered among the top agricultural waste in the Philippines [6, 7]. The volume of waste RH is continuously increasing elsewhere because of its limited direct uses and applications. Farmers and millers often reduced this voluminous waste through open field burning wherein the ash turned into crystalline silica which is known hazardous to the human respiratory system when inhaled. Aside from the crystalline form of silica, amorphous SiO_2 can also be extracted from RH by controlled temperature treatment. Likewise, in order to obtain high purity of silica, pre-and-post treatment processes on raw RH must also be considered [6, 8].

Though the use of silica from RH has been extensive research for decades, its application is still limited to conventional utilization in low-value agricultural items, heat, and energy sources, additives in construction materials, and many others [7]. Some researchers from other countries also investigated the potential of silica and silicon extracted from RH for semiconductor, solar technology, and even as electrode material for both Li and LIB applications [2, 9]. With the abundance of waste RH in the Philippines [6], renewable and cheap source of AnS for the development of anode material is very promising.

In this present study, AnS synthesized from Philippine waste RH as an anode raw material for Li battery by doping or incorporating it with electronically conductive material

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Email address: easm022808@yahoo.com, rb.cervera@coe.upd.edu.ph was investigated. The microstructure and initial electrochemical performance of the prepared working anode electrode were evaluated.

2. Materials and methods

2.1. Materials

The precursor material used was AnS synthesized from Philippine waste RH which was prepared by calcination, leaching, and acid precipitation methods [8]. Other raw materials used were: iron acetate ($Fe(C_2H_3O_2)_2$, Sigma-Aldrich); carbon black (CB, Emfutur); polyvinylidene fluoride (PVDF, Sigma-Aldrich); lithium foil (LF, Sigma-Aldrich); 1 M of lithium hexafluorophosphate ($LiPF_6$, Sigma-Aldrich) solution in 1:1 EC:DMC volume ratio; and N -Methyl 2-pyrrolidinone (NMP, J.T. Baker) liquid solvent.

2.2. Fe doping of the AnS via solid-state reaction

Since bulk silica has low electronic conductivity and electrochemically inactive material [3], the conductivity of the AnS material was enhanced by doping or incorporation of 5 mol % of Fe. The mixture was prepared by solid-state reaction. The stoichiometric amounts of each material were calculated from the molecular weights and mole ratio of the materials with the assumption that the AnS is 100 % pure silica and the $Fe(C_2H_3O_2)_2$ is 95 % pure (according to package). About 0.1927 grams of $Fe(C_2H_3O_2)_2$ is to 1.2 grams of AnS were the computed gravimetric amounts. The weighed amounts of $Fe(C_2H_3O_2)_2$ and AnS were mixed and ground in an agate mortar and pestle for around one hour to ensure homogenous mixing of the two different materials. Then, the mixture was subjected to annealing at 400^{o}C in an electric furnace for one hour with 10 ^{o}C/min ramping rate. The annealed mixture is referred to as the Fe-doped AnS.

2.3. Working electrode preparation

The method of preparing the working anode electrode and materials ratio was adopted from [2]. The materials proportion was as follows: Fe-doped AnS as active material; 60 weight %; CB as an electronic conductor 20 weight %; and PVDF as the binder 20 weight % [2]. The weighed materials were mixed and were homogenized by continuous grinding for 1 hour. Small drops of NMP liquid solvent were added to the homogenized dry materials and again ground until a semi-viscous solution was achieved.

The semi-viscous solution was dispersed into a pre-weighed current collector (about 1 cm diameter) by brushing. The current collector with dispersed anode material was dried in an oven at 100 - 160 ^{o}C for at least 1 hour. The target amount of dried active materials deposited onto the current collector was ~ 3 mg/cm^2 [1].

A battery was assembled using a Swagelok as a cell and was performed inside an argon-filled glove box. The battery cell consisted of the following: the prepared anode materials deposited in a current collector as the anode electrode, a paper as the separator, the LF as the counter electrode (cathode), and 1M $LiPF_6$ solution in 1:1 EC:DMC volume ratio as the electrolyte.

2.4. Characterizations

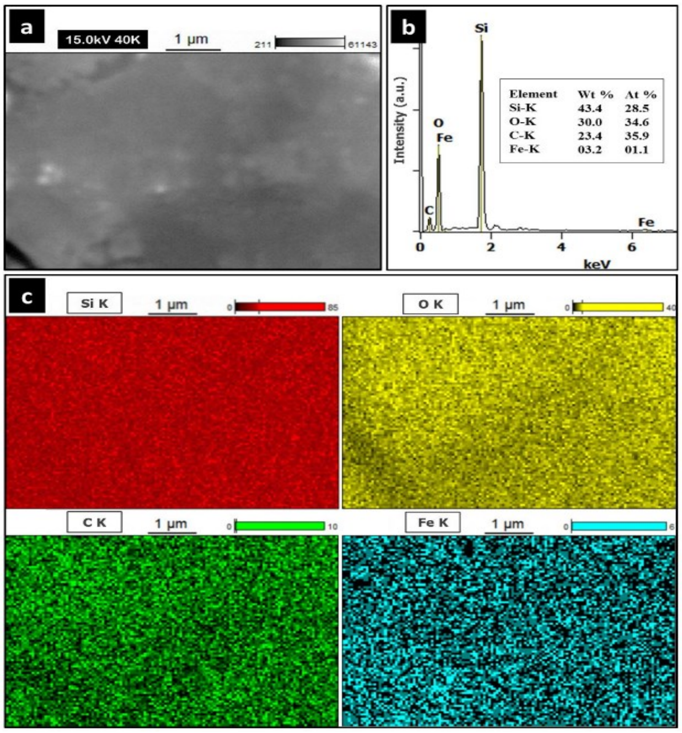
The morphology of the Fe-doped AnS was determined by SEM and the composition was obtained by the EDS. The structure is characterized by the XRD technique. The occurrence of the functional bands in the sample was determined using FTIR.

The initial electrochemical property of the Fe-doped AnS sample was evaluated by galvanostatic charge-discharge and cyclic voltammetry (CV) methods in an electrochemical work station (VMP-300, BioLogic Science Instruments). The prepared battery cell consisted of the following materials: anode electrode prepared from Fe-doped AnS, CB, and PVDF (60:20:20 ratio); LF as cathode; and 1 M $LiPF_6$ solution in 1:1 EC:DMC volume ratio as electrolyte. The voltage profile of the assembled battery cell was measured between 0 to 3 V vs. Li/Li$^+$ at 23.15 mA/g for both discharge and charge. Initial CV measurements were performed at two different scan rates (10 mV/s and 0.5 mV/s) and both at scan voltages of 0 - 3 V.

3. Results and discussion

3.1. SEM-EDS analysis of the Fe-doped AnS

The SEM micrograph of the Fe-doped AnS at x40k magnification is shown in Figure 1a. The EDS pattern (Figure 1b) revealed that the elements present in the sample are silicon (Si), oxygen (O), carbon (C), and iron (Fe) with 43.4, 30.0, 23.4, and 3.2 wt. %, respectively. The EDS elemental mapping analyses of Si, O, C, and Fe are shown in Figure 1c. revealing a homogeneous distribution of elements as evidently shown in the map.



Element	Wt %	At %
Si-K	43.4	28.5
O-K	30.0	34.6
C-K	23.4	35.9
Fe-K	03.2	01.1

Figure 1. SEM a) micrograph at x40k magnification, b) EDS pattern and elemental composition, and c) EDS elemental mapping of the Fe-doped AnS.

3.2. XRD analysis of the Fe-doped AnS

Figure 2 shows the XRD pattern of the Fe-doped AnS. The appearance of a broad peak centered at 21.84 (2 theta) degrees is a characteristic of amorphous SiO2 or short-range nanocrystallite structure. The broad peak beside the amorphous SiO_2 at about 23.8 and 43.4 (2 theta) degrees can be attributed to the presence of amorphous C in the sample [10]. Also, the peaks at 30.18 (220), 35.54 (311), 42.18 (400), 54.02 (422), 57.48 (511), and 63.02 (440) (2 theta) degrees are characteristics of γ-Fe_2O_3 nanoparticles annealed at 400 °C [11].

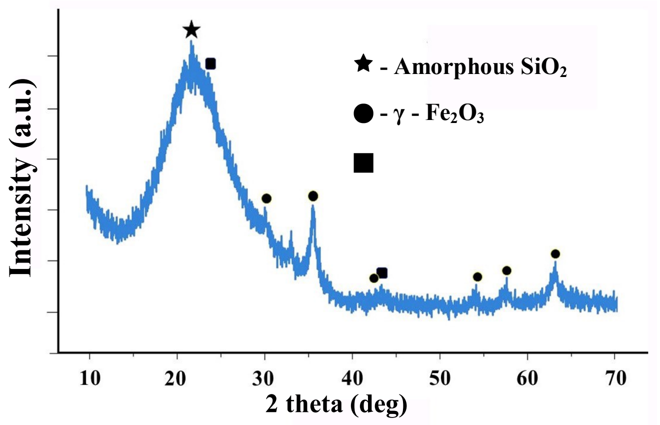


Figure 2. XRD pattern of the Fe-doped AnS.

3.3. FTIR Analysis of Fe-doped AnS

Figure 3 shows the FTIR spectrum of the Fe-doped AnS. The absorbance peaks that appeared at 439, 802, 1049 cm^{-1} are associated with the bending vibrations, symmetric stretching, and asymmetric stretching of Si-O-Si chains, respectively [8]. The absorbance peak that appeared at 1632 cm^{-1} can be associated with the presence of some aromatic C=C vibrations which were activated by the neighboring oxygen groups [12]. The absorbance peaks observed at 3393 and 1632 cm^{-1} are due to the presence of surface hydroxyls and chemically absorbed water in the sample [13].

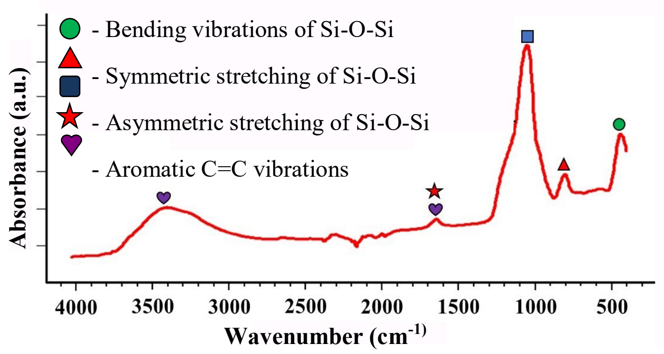


Figure 3. FTIR spectrum of the Fe-doped AnS.

3.4. Charge-discharge profile of the prepared working electrode

The voltage profile of the assembled battery cell from the prepared working electrode vs. Li/Li$^+$ at 0 to 3 V was determined. The voltage profile of the galvanostatic test of the working electrode from the prepared Fe-doped AnS anode material is shown in Figure 4.

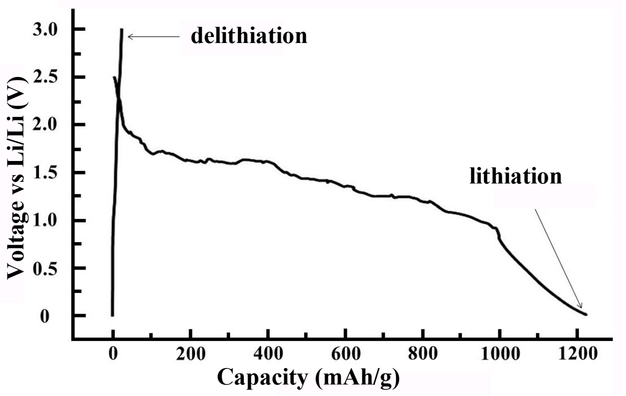


Figure 4. The voltage profile of the galvanostatic test on the prepared Fe-doped AnS anode material.

The lithiation (discharging) and delithiation (charging) capacity of the assembled battery cell were evaluated at a current density of 23.15 mAh/g. The current density was calculated based on the current (0.05 mA) and the active materials (AnS) in the anode electrode (about 0.00216 g). The specific capacity was also calculated based on the current density and the time used in lithiation and delithiation. The lithiation capacity result is considerably high at about 1232 mAh/g. However, the delithiation capacity curve is very steep resulting in only 8 mAh/g capacity and a low coulombic efficiency of about 0.65 % only.

The successive small plateaus in the potential range of 1.7 to 1.2 V during lithiation are due to intercalation of the Li into the Fe_2O_3 structure and also the conversion of iron from Fe(III) to Fe(II) to Fe(0) [14]. The possible reaction happens on AnS reduced to silicon and forming as well Li_2O during lithiation/delithiation and this can be rewritten as in Eq. 1a, Eq. 1b, and Eq. 2 [15]:

$$SiO_x + yLi^+ + ye^- \rightarrow Si + Li_yO_x \qquad (1a)$$

$$yLi^+ + SiO_x + ye^- \rightarrow Li_ySiO_x \qquad (1b)$$

$$yLi^+ + Si + ye^- \leftrightarrow Li_ySi \qquad (2)$$

The reaction in Eq. 1a and Eq. 1b are irreversible capacity while the reaction in Eq. 2 corresponds to the reversible capacity.

3.5. Cyclic voltammetry measurement of the prepared working electrode

Initial CV measurements of the assembled battery cell with Fe-doped AnS working electrode (anode) versus Li/Li$^+$ were performed at two different scan rates and scan voltage of 0 - 3 V. The cyclic voltammogram of the sample was measured by the following conditions: first cycle - open-circuit voltage (OCV) to 0 V and from 0 V to 3 V at 10 mV/s rates; and second cycle - open-circuit voltage (OCV) to 0 V and from 0 V to 3 V at 0.5 mV/s rates.

Figure 5 shows the cyclic voltammogram of the Fe-doped AnS anode material at 10 mV/s. The battery cell has an OCV of 0.389 V. As can be observed in the figure, there is no reaction happening in the oxidation and reduction voltages during the first cycle. However, in the second cycle, a pair of silicon lithiation at 0.50 V and delithiation at 0.24 V occurred [15].

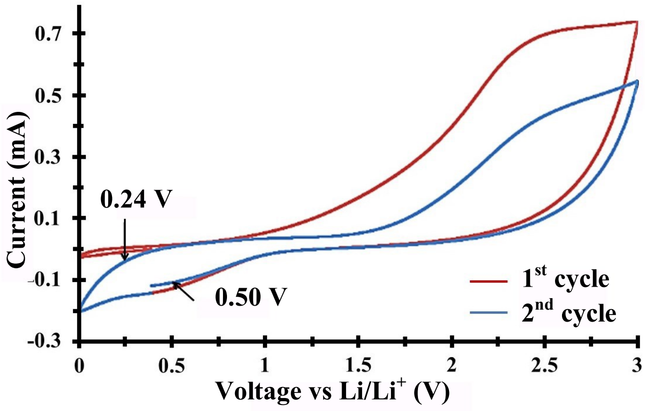


Figure 5. The cyclic voltammogram of Fe-doped AnS anode material at 10 mV/s.

Figure 6 shows the cyclic voltammogram of the Fe-doped AnS anode material at 0.5 mV/s. The battery cell has an OCV of 0.426 V. The oxidation and reduction voltage peaks occurred in the sample at its first cycle. The reduction peak at 0.07 V is associated with the lithiation of silica while the oxidation peaks at 0.37 and 0.65 V can be related to the delithiation of silica [15].

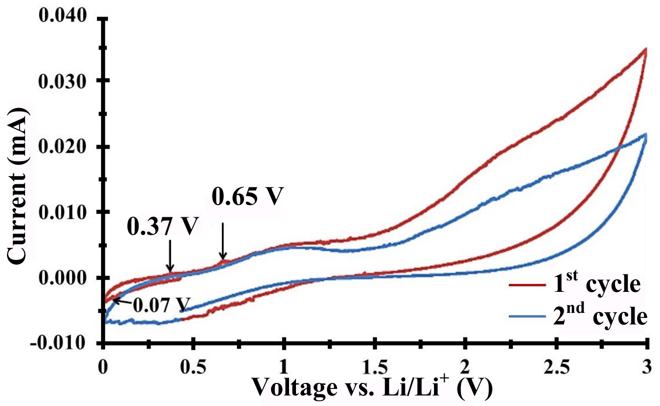


Figure 6. The cyclic voltammogram of Fe-doped AnS anode material at 0.5 mV/s.

4. Conclusions

The AnS synthesized from the PWRH was successfully incorporated with Li as evident from the results of XRD, SEM-EDS and FTIR analyses. EDS mapping revealed the elemental distribution in the samples.

The initial investigation on the electrochemical performance of the 5 mol % Fe-doped AnS revealed a specific capacity of 1232 mAh/g upon lithiation; however, only 8 mAh/g upon delithiation. The lithiation capacity is almost four times more as compared to the commercial graphite anode. This indicates that AnS synthesized from PWRH is a potential anode raw material for lithium batteries production.

Further study on the amount of Fe dopant in the amorphous silica and detailed analysis and enhancement on the charge and discharge results are recommended.

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