

# Synthesis and characterization of Al-ion battery material as a potential substitute to Li-ion battery material

Advaith Kaikini\*, Nishant M. George, Dalton Pinto, Reghu. V. R

Mechanical Engineering, Christ (Deemed to be University), Bangalore, India

\*email for communication: advaith.kaikini@btech.christuniversity.in

## ABSTRACT

Li-ion battery is the most popular secondary battery at present. Introduced in the market three decades ago, it is still facing many challenges. Difficulties in handling due to its high reactivity, environmental and over-heating issues, power density and energy density related challenges are some of them. Moreover, the limited global supply of Lithium demands substantial and sustained research works to find a substitute for lithium that possesses the desired electro-chemical characteristics to serve the battery materials research field.

After extensive literature survey on synthesis of anode materials, a potential anode composite material was identified that comprised of a compound based on antimony (Sb), graphite(C) and aluminium (Al). The chosen composition was weighed accurately and ball milled for 60 hours with the goal to synthesize a newer material phase by mechanical alloying. Samples were removed after ball milling for 20 hours, 40 hours and 60 hours. In order to characterize the change in the ball milled powder particle morphologies with ball milling time, the particles were analyzed with respect to milling time by using a Scanning Electron Microscope (SEM); phase change if there was any was assessed by X-Ray diffractometry (XRD), and the homogeneity of the composition based on the progressive milling was inspected by using Energy Dispersive Spectroscopy (EDS) associated with the SEM. The electronic conductivity is expected to increase when the particle size becomes finer and the composition becomes homogeneous. The results showed very encouraging morphological changes with progress in milling time. The samples will go through electronic conductivity test using an impedance analyser, and the suitability as an electrode for a high capacity secondary battery would be analysed at later stages in this research work and are not included in this paper.

**Keywords** – Aluminium-ion battery, ball milling, material characterization, scanning electron microscopy, XRD

## 1. INTRODUCTION

Lithium-ion battery electrodes and hence batteries made by using them as electrodes have reached their “operational potential limit” in their current carrying capacity and the energy density characteristics. Additionally, Lithium (Li) is found in limited quantities and is a major challenge to recycle and extract Li-metal. Furthermore, as the most reactive metal, Li-metal poses many safety hazards and operational risks. A need for a more efficient and cheaper battery with same functionalities is a global need. One compound that offers such advantages is based on antimony, graphite and aluminium [1].

Aluminium is one of the most abundant materials on the earth’s crust, donating a maximum of 3 electrons per atom to aid the materials properties. Graphite is an excellent anode material [1, 2, 3, 4] and Antimony shows promise as a metalloid anode material, hence a composite produced as a compound with these constituents has the potential to act as an effective anode material if it satisfies all the performance qualification tests [5,6]. Good electronic conductivity and capability to form a half cell when coupled with a suitable

electrolyte are some of the major characteristics of an appropriate anode material. In the process to experiment and to make and test a new anode material, the morphological changes introduced into the constituents of the newer compound attempted to be synthesized during progressive ball milling experiment is discussed in this paper

## 2. EXPERIMENTAL WORK

Based on the literature survey a material composition consisting of antimony (Sb), graphite (C), and aluminium (Al) was selected [1, 2]. All the chemicals were of nearly 99% purity and from reputed lab chemical suppliers. Antimony and aluminium, constituted 75% and graphite constituted 25%, on weight basis. 75% of antimony and aluminium constituted equal moles of each chemical (i.e. in 25 g of powder composite prepared, antimony was 15.34 g, graphite was 6.25 g and aluminium was 3.41 g). The chemicals were ball milled by using agate jars and agate balls with a proportion of 10 times the weight of the chemicals to be ground (250 g of balls were added for 25g of the powder composite).

The mixing jar with agate balls is shown in Fig. 1 and a photograph of the planetary ball mill that was used to ball mill the constituent powders is shown in Fig.2. Before adding the chemicals, both the agate jars and balls were carefully decontaminated using ultrasonicator, nitric acid and distilled water. Also, the jars and balls were dried thoroughly using a hot air blast to make sure that the powder will not stick to the jar surface or on balls. The constituents were dry ground without using any liquid media in the ball mill. The ball mill was operated at 300 RPM.



Fig.1: Agate mixing jar with agate balls



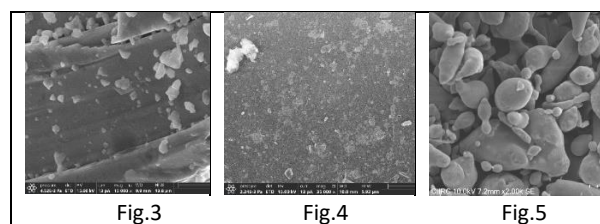
Fig 2: Planetary ball mill

Around two grams of the ball milled powders were removed at the end of 20, 40 and 60 hours of grinding. The powder particles were ultrasonically treated for segregation (removal of agglomerates) and studied under a Field Emission Scanning Electron Microscope (FESEM) to determine the morphological changes in the powder particles that occurred during ball milling. Energy Dispersive X-Ray Spectroscopy (EDS) associated with the SEM was employed to study the chemical composition. The powders were also analyzed for structural phases by using X-ray Diffraction method.

XRD was employed to determine if any compound formation occurred during ball milling or any change in the diffraction pattern was found to occur, that could be suggestive of morphological changes.

### 3. RESULTS AND DISCUSSION

SEM Micrographs of the raw materials antimony, graphite, and aluminium are shown in figures 3, 4 and 5 respectively

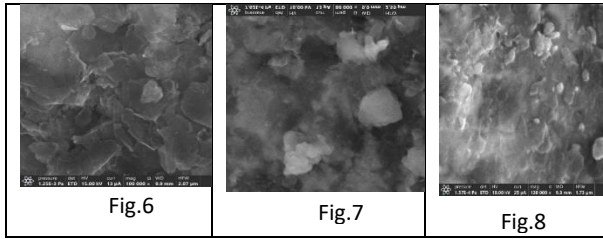


SEM micrograph of raw materials: Fig. 3 antimony (Scale 5μm), Fig. 4: graphite (Scale 2 μm), Fig.5: aluminium (scale 20 μm)

The most important feature observed in the three SEM micrographs, pertaining to the raw materials is that the grains (powder particles) were fairly coarse grained, were consistently much larger than few microns in particle size. The coarser the particle sizes, the reactivity among the constituents are expected to be low. Ball milling processing was expected to significantly reduce the particle sizes and thereby improve the reactivity [7] and also the electronic conductivity of the composite which is a very important property to perform as an electrode in a high capacity battery. The rounded edges of aluminium particles also is clearly evident from the micrograph

Figures 6, 7 and 8 show the SEM micrographs of the ball milled powder after completion of 20, 40 and 60 hours of ball milling respectively. For the convenience of comparison all the micrographs were obtained at the same magnification of 100,000X (500 nm scale).

Significant reduction in the particle sizes of the constituent raw material powders were observed even after 20 hours of ball milling process, the compound showed presence of large number of sub-micron particles. Although the fineness of the particles was evident, 20 hours of ball milling did not exhibit significant change in the particle morphologies. Both antimony and graphite particles retained their angular morphologies.



SEM micrograph of ball milled materials: Fig. 6: 20 h ball milled Fig 7: 40 h ball milled, Fig.8: 60 h ball milled (Scale 500 nm)

The SEM micrograph of the 40 hours ball milled composite shows abundant number of subzero particles with rounded edges. When ball milling progresses, at 60 hours of ball milling the micrograph points the possibility of the smaller particles to merge together to produce bigger particles [7]. The effects of this phenomenon on the behaviour of electronic conductivity to be investigated.

EDS patterns pertaining to the ball milled compositions are shown in Figures 9, 10 and 11.

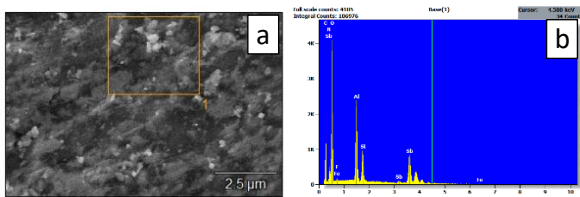


Fig 9: SEM micrograph showing location of analysis and EDS pattern of 20 hr ball milled constituents

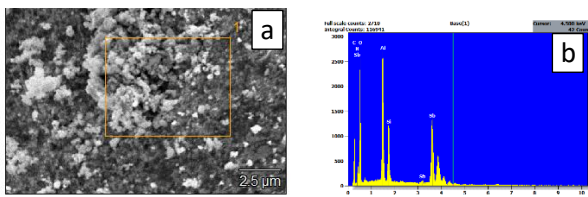


Fig 10: SEM micrograph showing location of analysis and EDS pattern of 40 hr ball milled constituents

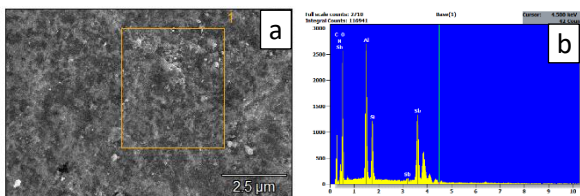


Fig 11: SEM micrograph showing location of analysis and EDS pattern of 60 hr ball milled constituents

In TABLE 1, EDS pattern results after progressive ball milling (elements by weight basis) up to 60 hours is shown. The impurities given by the analysis are removed

for better clarity. The EDS was done at a lower magnification to capture maximum number of elements in the field of observation.

TABLE 1: Distribution of major elements based on EDS pattern (weight %)

Sr. No.	Ball milling hours	Antimony	Graphite (Carbon)	Aluminium
1	20	41.1	10.96	12.11
2	40	47.35	7.99	11.29
3	60	51.96	7.41	9.36

The EDS comparison of relevant elements of the composites undergone 20, 40 and 60 hrs of ball milling shows the consistency of the elemental presence. The EDS pattern showed a % weigh reduction of antimony and graphite from the selected area. This may be due to the problem of sticking these materials on the jar surface in a very fine layer form which will not be removed by balls. In the future works, this will be overcome by adopting wet grinding for better uniformity.

The EDS patterns produced after 40 hours and 60 hours of ball milling show the consistency with 20 hours ball milled pattern for the distribution of the chemicals during ball milling process. Though the ball milling is not expected to change the chemical composition drastically, the EDS pattern showed the presence of a good amount of oxygen in the pattern which has to be analyzed and preventive actions to be taken if oxide formation is taking place during the process.

The XRD patterns of the starting materials, antimony, graphite and aluminium are shown in figure 12. The figure also illustrates the XRD patterns of the ball milled powders. All the patterns are placed in one figure and the scale in the x-axis is aligned so that one to one comparison amongst the raw material and ball milled powder could be established. The sharpness of the patterns confirmed the crystallinity of the materials evaluated. The ball milled powders appeared to match well with the XRD pattern of antimony, this was anticipated because graphite and aluminium were added in smaller quantities to antimony proportion. Also, it may be due to the retainment of crystalline structure by antimony after ball milling. The clearly defined sharp peaks disappeared for graphite and aluminium due to its

responses to ball milling and formation of nanosized material. Ball milling at 40 and 60 hours began to exhibit some introduction of amorphous nature. The interesting observation from the XRD patterns of the ball milled composite is that the 40 hr and 60 hr ball milled composites showed almost the similar pattern but peaks with slightly lowered intensity. This finding is suggestive of the crystallinity of powder particles being affected by ball milling; Narrower particle sizes indicate that the particle sizes could be nano sized. This finding indicates that the raw materials could be in a stage of transition from crystalline phase to amorphous phase during the ball milling progresses. The impact of this on the electronic conductivity of the milled product is yet to be investigated (not being discussed in this paper)

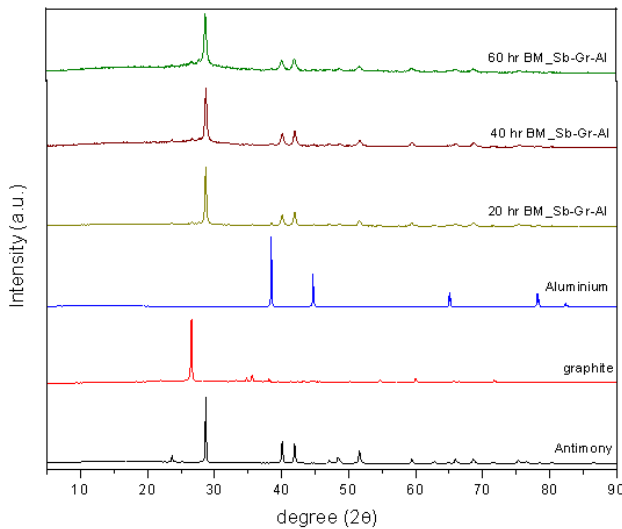


Fig 12: XRD pattern of starting materials and the powders after 20, 40 and 60 hours of ball milling

The significance of the progressive reduction in the intensity of the XRD patterns while they were being ball milled is further highlighted in Figure 16.

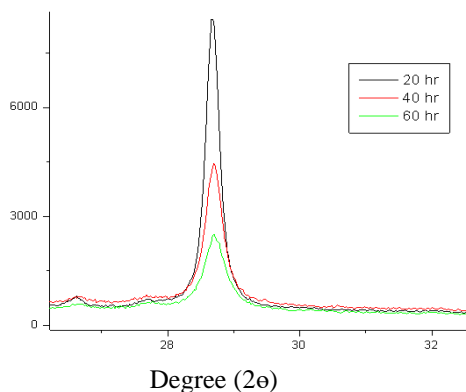


Fig 16: XRD pattern of ball milled powder

The sharpness and intensity of the peaks appeared to rease with increased ball milling which was clear ication of the tendency of the powder particples to be used to nano powders. This effect was also confirmed the line broadening exhibited by the powder ball led for 40 and then for 60 hours.

#### 4. CONCLUSIONS

Antimony, graphite and aluminium powders were ball milled with a goal to determine if the powders formed an alloy during the ball milling process which could enhance the electrical/ electronic properties. Ball milling was found to significantly reduce the particle sizes of the powder particles. Even 20 hours of ball milling of the raw materials showed remarkable morphological and particle size related changes. 40 hours of ball milling produced more submicron particles with rounded edges which are expected to improve the electronic properties of the material. When the powder was ball milled for more than 40 hours, the sub-micron particles showed the tendency to agglomerate. The impact of this on electronic conductivity is yet to be investigated. XRD revealed that the ball milled powders to be comprised of only antimony. While graphite is too fine and small quantity to be detected in the pattern, the reason for the absence of aluminium in the pattern is not known. Though the EDS pattern is confirming the presence of aluminium and graphite in the selected area, those may have lost some of its crystalline structure and so did not create a well-defined pattern No new phase was formed even after 60 hours of ball milling, which confirmed the absence of mechanical alloying. Grinding the powder in presence of a liquid medium may enhance the scope for the formation of mechanically alloyed compound. Though the XRD patterns of the three, ball milled powder show the phases, i.e. antimony, the intensity and sharpness of the peaks were reduced on progressive milling. This shows the conversion of some of the material to be converted into finer sizes due to continuous grinding, which resulted in formation of nano particles and the pattern line broadening. The effect of this on electronic conductivity to be investigated.

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