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Melt-Spun Fe-Sb Intermetallic Alloy Anode for Performance Enhanced Sodium-Ion Batteries

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ABSTRACT:

Owing to the high theoretical sodiation capacities, intermetallic alloy anodes have attracted considerable interest as electrodes for next-generation sodium-ion batteries (SIBs). Here we demonstrate the fabrication of intermetallic Fe-Sb alloy anode for SIBs *via* a high-throughput and industrially viable melt-spinning process. The earth-abundant and low-cost Fe-Sb based alloy anode exhibits excellent cycling stability with nearly 466 mAh g⁻¹ sodiation capacity at a specific current of 50 mA g⁻¹ with 95% capacity retention after 80 cycles. Moreover, the alloy anode displayed outstanding rate performance with ~300 mAh g⁻¹ sodiation capacity at 1 A g⁻¹. The crystalline features of the melt-spun fibers aid in the exceptional electrochemical performance of the alloy anode. Further, the feasibility of the alloy anode for real-life applications was demonstrated in a sodium-ion full-cell configuration which could deliver a sodiation capacity of over 300 mAh g⁻¹ (based on anode) at 50 mA g⁻¹ with more than 99% coulombic efficiency. The results further exhort the prospects of melt-spun alloy anodes to realize fully functional sodium-ion batteries.

Alarming depletion and related aggravating environmental issues of fossil fuels call for the implementation of sustainable energy resources such as solar, wind and wave. In this regard, it is vital to develop efficient, low-cost electrochemical energy storage systems (EES) to facilitate the large-scale implementation of these renewable energy resources¹⁻². The predominant lithium-ion battery (LIB) technology seems to be inadequate to meet the skyrocketing demands, as the existing lithium reserves are sparse and limited-calling for “beyond-LIB” research³⁻⁴. In this context, sodium-ion batteries (SIBs) have received a renewed interest in the recent past in view of the abundant and low-cost of active materials (sodium) as well as the close similarity in operation mechanisms to LIBs⁵⁻⁶. However, the larger size and mass of Na presents the challenge of finding suitable insertion hosts and the higher redox potential projects ~15% penalty in energy density compared to LIBs^{2, 7}. Nonetheless, recently significant progress has been made in the development of suitable SIB cathodes with performance at par with the LIB cathodes^{6, 8-9}. However, the research progress to find a suitable anode capable of performance in full-cell configuration is still slow-paced.

The ideal Na metal anode poses serious safety hazards due to its low melting point (97.7 °C) and high reactivity along with issues of dendrite formation that can lead to short circuit. In addition, graphite- the conventional anode for LIBs, is found to be inapt for SIBs, while non-graphitic hard carbons have been shown to accommodate Na ions¹⁰⁻¹². However, the sodiation potential of these disordered carbons are minimal which is close to that of metallic sodium, causing further safety concerns such as plating and dendrite formation¹³. Moreover, the low tap-density of these carbon materials would severely lower the volumetric energy density- impeding the application in practical SIBs. Insertion anodes also suffer from limited insertion sites for the Na ions which would lead to limited sodiation capacity¹⁴⁻¹⁵.

On the other hand, alloy anodes such as tin, antimony and phosphorus possess high theoretical sodiation capacities at appropriate potential and are expected to aid the commercialization of SIBs¹⁶. However, these alloy anodes possess the challenges of huge volume changes during cycling- leading to pulverization and abrupt capacity fade^{13, 16}. Antimony-based anodes have been investigated as SIB anodes due to the high sodiation capacity of 660 mAh g⁻¹ and ideal sodiation potential to eliminate dendrite formation and safety issues¹⁷⁻¹⁸. Many approaches have been undertaken to mitigate the issues of poor cycling stability of bare Sb anode, including the nano-structuring of active material, use of a carbon matrix, active/inactive buffer in the form of intermetallics, and so on¹⁹⁻²⁴. However, most of these strategies seem to be inappropriate for practical applications owing to their poor-scalability and throughput. Our approach was to develop a high-performance anode material for SIBs through a commercial process which could further find its potential in full-cell configurations.

Herein we present large-scale and industrially-viable melt-spinning process based production of intermetallic Fe-Sb alloy ribbons and investigate the electrochemical performance of these new alloys in sodium-ion batteries. Melt-spinning is a scalable, high-yield, rapid solidification process with high quench rates of $\sim 10^6$ K s⁻¹ which imparts the alloys with nano-crystalline/amorphous features and intriguing material traits²⁵⁻²⁶. The Fe-Sb alloy anodes exhibited outstanding cycling performance along with the exceptional rate capability. In addition, a full-cell configuration was also fabricated and its electrochemical studies were carried out to demonstrate the potential of these Fe-Sb alloy anodes for real-world applications. The preliminary electrochemical results suggest the suitability of these intermetallic Fe-Sb alloy anodes for practical next-generation performance enhanced SIBs.

Results and Discussions:

The fabrication of the Fe-Sb alloy ribbons via melt-spinning is schematically illustrated in **Scheme 1 and Supporting Information section 1.1**. Briefly, the Fe and Sb metal powders are intimately mixed in a mortar and pestle and then cold pressed into a pellet. The pellet is then loaded in a quartz tube with slit nozzle and melted via induction heating in argon atmosphere. The melt is forced down the quartz tube nozzle by pressurized argon gas and the alloy ribbons are formed when the melt falls upon the rotating water-cooled copper wheel. The melt-spinning process can deliver high yields of these alloy ribbons, making the process highly scalable.

Scheme 1. a) Graphical illustration of the preparation of melt-spun Fe-Sb alloy ribbons, b) Digital images and c) microscopic images showing appearance of freshly prepared alloy ribbons.

Although iron is electrochemically inactive with respect to sodium, it can serve as a highly conductive matrix to host antimony and aid in the buffering of volume changes during the sodiation and desodiation processes²⁷⁻²⁸. Fe-Sb alloy was prepared via melt spinning with Fe:Sb 1:2 molar ratio and is hereafter denoted as MS_FeSb. Alloy ribbons of dimensions $\sim 20 \times$

0.8 x 0.05 mm (length x width x thickness) were obtained with more than 90% yield in the melt-spinning process. The melt-spun Fe-Sb alloy ribbons were characterized by X-ray diffraction (XRD) as shown in Figure 1a. The sharp diffraction peaks attest the crystallinity of the alloy ribbons and the absence of any oxide impurities is also confirmed from the diffraction pattern. Furthermore, the diffraction peaks were Rietveld refined to analyze the phases present in the alloy ribbons. Figure 1b shows FeSb₂ and FeSb unit cell configurations and based on the obtained data the alloy composition was characterized and identified with a composition of 88.38% FeSb₂ and 11.62% FeSb respectively (Figure 1c).

Figure 1. a) XRD pattern of the as-obtained Fe-Sb alloy ribbons (PDF numbers: 01-075-1498 34-1184 (FeSb₂), 34-1053 (FeSb)); b) Crystal structures of FeSb₂ and FeSb alloys²⁹ c) Phase composition of the melt-spun alloy.

Next, we examined the surface topography of the Fe-Sb alloy ribbons using high-resolution transmission electron microscopy (HR-TEM) and field emission scanning electron microscopy (FESEM) (Figure 2). Figure 2a & b shows HR-TEM images of flakes of Fe-Sb alloy. Analysis of an individual block shows lattice fringes with d -spacing of 0.285 nm corresponding to the orthorhombic phase of FeSb₂ alloy (Figure 2b). A crystalline configuration of Fe-Sb could be generated *via* rapid cooling ($\sim 10^4$ - 10^7 K s⁻¹) of the molten composite during the melt-spinning process which effectively arrests further nucleation and grain growth. In contrast to the conventional solution-based growth processes and strategies intended for nanostructuring of active materials, melt-spinning can aid in the rapid processing of crystalline alloy segments with comparatively higher yield. Furthermore, FE-SEM images of the flakes with ~ 0.76 mm width (Figure S2a) which were in contact with the copper wheel (Scheme 1) appeared smooth (Figure S2a & b) while the exposed surface appeared irregular (Figure S2c & d). Figure 2c-g shows images corresponding to the energy dispersive X-ray spectroscopy (EDX) analysis of a single flake of Fe-Sb alloy on silicon substrate. Figures 2d and 2e show uniform distribution of Sb (labelled blue) and Fe (labelled as red) and an overlay of the images indicates binary phase intermetallic alloy formation with minimum clustering. Figure 2h shows the corresponding EDX spectra of elements upon scanning a selected area on the surface of Fe-Sb flakes.

Figure 2. (a), (b) HR-TEM images of MS_Fe-Sb alloy flakes. (c)-(g) SEM-EDX micrographs showing mapping of the flakes (blue label represents Sb; red label represents Fe). h) Elemental map obtained for a selected area.

The electrochemical performance of the MS_Fe-Sb alloy ribbons was preliminarily evaluated in Na-ion half-cell assembly. Prior to cell assembly, the electrodes were prepared by a slurry-coating technique on copper foil (the Supporting Information section 1.3). The electrodes were punched out into circular discs of ~14 mm diameter (~1.5-2 mg cm⁻² active mass loading) and assembled into CR2016 coin cells with Na metal as the counter electrode and 1M NaClO₄ in propylene carbonate (PC) with 5 vol.% fluoroethylene carbonate (FEC) as the electrolyte. For comparison, a set of Fe-Sb metal powders physically mixed electrodes were also investigated for the cycling stability. Figures 3(a) shows the capacity retention plot and the MS_Fe-Sb alloy ribbons outperformed the physically mixed electrode counterparts in terms of cycling stability. The MS_FeSb alloy delivered a sodiation capacity of ~555 mAh g⁻¹ for the first cycle with initial coulombic efficiency of 81.3% and maintained 97-99% coulombic efficiency in the subsequent cycles. Interestingly, the alloy anode retained ~95% of the second sodiation capacity after 80 cycles. Figure S3 shows comparison of cycling performance delivered by pristine Sb, MS_Fe-Sb alloy and its physically mixed counter parts. Thus, the performance enhancement observed in MS_Fe-Sb alloy electrode could be attributed to the crystalline features inherited during intermetallic alloy formation through the melt-spinning process. In addition to this, the melt spun Fe-Sb electrodes exhibited excellent rate performances (Figure 3b) with sodiation capacities of ~300 mAh g⁻¹ at high current rate of 1 Ag⁻¹ (Figure S4 shows corresponding GCD curves). This further attests the highly conductive milieu and the fast diffusion pathways realized by high-temperature alloying of active materials of the electrode by means of the melt-spinning process.

Figure 3. (a) Galvanostatic cycling at 50 mA g⁻¹ (b) Rate performance of MS_FeSb at different specific currents from 50-1000 mA g⁻¹. c) Cyclic voltammogram of MS_FeSb at 0.1 mV s⁻¹ in the potential window 0.005-2.5 V vs. Na

The cyclic voltammetry (CV) studies as shown in Figure 3c demonstrate the enhanced sodiation/desodiation behavior of the MS_Fe-Sb alloys over the pristine Sb powder. Figure S5 shows CV curves obtained by using pristine Sb powder for comparison. During the first sodiation process, both MS_Fe-Sb alloy as well as pristine Sb exhibited a prominent peak at ~ 0.25 V vs. Na for Sb and close to 5 mV vs. Na for MS_Fe-Sb. This can be attributed to the formation of the solid electrolyte interphase and the initial sodiation of the active material³⁰⁻³¹. In the following desodiation process, a prominent peak was observed at ~ 1 V vs. Na for Sb and ~ 0.86 V vs. Na for MS_Fe-Sb corresponding to the de-alloying process. The overlapping peaks during the subsequent cycles attest the improved stability of the MS_Fe-Sb anode when compared to the rapid fading observed in the case of pure Sb electrode. After the initial formation cycles, the alloy exhibited three sodiation peaks at ca. 0.64, 0.47, 0.33 V vs. Na. and the peak currents were found to increase in the consequent cycles. This is a classical observation in alloy and conversion type materials and can be attributed to the decrease of the particle size and restructuration of the active material during the first sodiation process³².

The *ex-situ* XRD studies of the alloy anode after first and second sodiation process have been conducted. Figure 4 shows the changes in XRD pattern during sodiation/desodiation processes. The formation of poorly crystallized Na₃Sb phase was observed during sodiation, corresponding to the diffraction peaks at 19.1°, 21.3°, 38.7° (JCPDS no. 741,162).³² Similarly, the peaks corresponding to Na₃Sb were absent in the desodiated electrodes. The constituent FeSb and FeSb₂ alloys progressively transform during cycling into Fe rich Fe_xSb phase with the extrusion of Sb and the formation of Na₃Sb and amorphous Fe matrix which was not detected in XRD³². Further, the electrochemically inactive Fe matrix would serve as a highly conductive

pathway and buffer matrix to aid in the cycling stability of the electrochemically active Sb. Thus, the first sodiation cycle of the Fe-Sb alloy can be described as follows³²:

During desodiation, the electrochemically inactive Fe serves as the conductive matrix and the following reaction takes place³²:

Figure 4. *Ex-situ* XRD of the electrodes at the cut-off potentials for the first and second cycles.

The sodiation/desodiation kinetics of the MS_Fe-Sb was investigated by gauging the electrochemical response at increasing scan rates (Figure 5a). As the scan rates were increased

from 0.1-2 mV s^{-1} , significant peak shifts were observed and the corresponding peak currents were plotted based on the power law:

$$\log i_p = b \log v + \log a \quad (3)$$

where i_p is the peak current, v is the scan rate, a and b are constants.

Figure 5. (a) Cyclic voltammogram of MS_FeSb anode at different scan rates (b) $\log(i)$ vs. $\log(v)$ relationship of peaks 1-3 (c) EIS spectra of MS_FeSb fresh electrode and after 80 cycles.

Figure 5b shows the linear relationship between $\log(i)$ and $\log(v)$ for the peak currents. The ' b ' values deduced from the slope of the line are 0.72, 0.73 and 0.56 for peaks 1, 2 and 3

respectively. While ‘ b ’ value close to 1 reveals pseudocapacitive behavior, b values in the range ~ 0.5 - 0.7 indicate a combination of solid-state diffusion and pseudocapacitive contributions and the excellent rate capability of the MS_Fe-Sb anode possibly stems from this synergistic combination³³. Furthermore, electrochemical impedance spectroscopy (EIS) confirms the formation of a stable solid-electrolyte interphase (SEI) without significant increase in the charge transfer resistance during cycling as observed from the diameter of the semicircle in the high-frequency region of the Nyquist plot (Figure 5c inset). The sloping tail in the low-frequency region can be ascribed to the Warburg impedance and is characteristic for Na^+ ion diffusion into the electrode³⁴.

The excellent cycling performance and rate capability of the melt-spun Fe-Sb alloy motivated us to further investigate its full-cell performance and examine the feasibility of the anode for real-world applications. In this regard, we coupled the MS_FeSb with a sodium manganese oxide (NMO) cathode. The NMO cathode in half-cell assembly delivered a stable capacity of $\sim 160 \text{ mAh g}^{-1}$ over 50 cycles (Figure S6) with high coulombic efficiency. The details of the full-cell assembly and the procedure for preparation is given in Supporting Information Section 1.4. The preliminary investigation of the NMO/Fe-Sb full cell in coin-cell assembly delivers promising performance, as the cell delivered an initial capacity of 350 mAh g^{-1} (based on anode mass) and over 99% coulombic efficiency and retained $\sim 79 \%$ of the initial capacity. Figure 6a shows the potential profile of electrodes employed in the full-cell assembly. Full-cell exhibits stable cycling stability (Figure 6b) and we demonstrated the potential of full cell to power a white LED lamp (Figure 6c). Further tests are in progress to improve the cycling stability of the full cell as well as the performance evaluation in pouch-cell configuration to investigate the prospective scalability of MS_Fe-Sb alloy anode.

In conclusion, Fe-Sb alloy anodes were fabricated by a scalable and industrially viable melt-spinning process. The alloy anode exhibited exceptional cycling capability and rate performances in sodium-ion half-cell assembly. Nearly 466 mAh g⁻¹ sodiation capacity was attained at 50 mA g⁻¹ in the second sodiation, with ~95% capacity retention after 80 cycles. Moreover, the alloy anode displayed promising electrochemical performance in full-cell sodium-ion battery configuration as well as delivered a sodiation capacity of ~300 mAh g⁻¹ (based on the anode) at 50 mA g⁻¹, with more than 99% coulombic efficiency. The results attest the suitability of the MS_Fe-Sb alloy anode for future sodium-ion batteries for practical applications as well as emphasize the need for further extended studies on alloy anodes.

Figure 6. Full cell performance of MS_FeSb alloy ribbons coupled with NMO cathode (a) Potential profile and (b) Cycling stability at specific current of 50 mA g⁻¹ and (c) photograph showing LED powered by NMO/MS_FeSb couple.

ASSOCIATED CONTENT

Supporting Information. A Supporting Information is available for this manuscript. Details of electrode preparation, electrochemical characterization and morphological analysis of active materials are incorporated.

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