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$Sn\text{-}Fe_5(PO_4)_4(OH)_3.2H_2O$/graphene: A new electrode for superior rate applications in Li/Na ion batteries

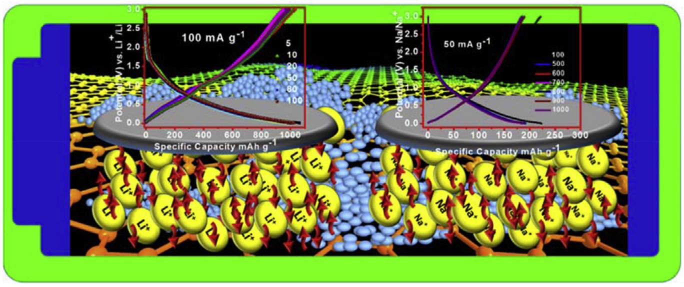
V. Mani, G.N. Suresh babu, N. Kalaiselvi*

ECPS Division, CSIR- Central Electrochemical Research Institute, Karaikudi 630003, India

HIGHLIGHTS

- Sn $Fe_5(PO_4)_4(OH)_3.2H_2O$/Graphene composite has been newly identified.
- Recommended as an alternative anode for LIBs and SIBs.
- An appreciable capacity of 750 mAh g^{-1} has been exhibited up to 300 cycles in LIBs.
- Demonstrated excellent rate capability and reversibility up to 5 A g^{-1} condition.
- 195 mAh g^{-1} of capacity at 50 mA g^{-1} up to 1000 cycles has been observed for SIBs.

GRAPHICAL ABSTRACT



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ABSTRACT

A novel $Sn\text{-}Fe_5(PO_4)_4(OH)_3.2H_2O$, otherwise known as (Sn-FeHP) is prepared by hydrothermal method and subsequently, Sn-FeHP/G composite containing graphene is obtained by adopting a simple mechanothermal approach. Not requiring the addition of surfactant or template, the currently adopted hydrothermal strategy produces flower like morphology with a polyhedral rod assembly. When it is explored as Li-ion battery anode, a steady state capacity of 1000 mA h g^{-1} is demonstrated by Sn-FeHP/G under the influence of 100 mA g^{-1} current density with an excellent Coulombic efficiency of 99% up to 100 cycles. The title anode demonstrates its suitability for high capacity and high rate applications by exhibiting appreciable capacity values of 520, 450, and 350 mA h g^{-1}, under the influence of 2, 3 and 5 A g^{-1} respectively. Further, Sn-FeHP/G composite anode demonstrates the suitability for Na-ion batteries by exhibiting 195 and 160 mA h g^{-1} of capacity under the influence of 50 and 100 mA g^{-1} up to 1000 and 100 cycles respectively. The study recommends Sn-FeHP/G composite for its exploitation as an alternative anode for high-performance lithium-ion and sodium-ion batteries.

1. Introduction

In the twenty-first century, energy storage has become one of the critical challenges requiring immediate attention, due to the rapid depletion of fossil fuels and the increasingly worsening environmental pollution [1–3]. Owing to certain advantages such as high energy density, long cycle life, safety and good environment compatibility [4,5] lithium-ion batteries (LIBs) have attracted a great deal of research interest as potential energy storage system. The increasing consumer market demand for lithium batteries has provoked the search for alternative electrode materials with high capacity and good cycling stability. As a result, plentiful research attempts are being made to explore newer electrode materials and to design novel nanostructures of electrode materials [6–10]. In this context, if LIBs are to gain a significant place in the future, increasing demand for Li metal would become unavoidable, resulting in serious concerns about the increasing cost and

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* Corresponding author.
E-mail address: kalaiselvicecri@gmail.com (N. Kalaiselvi).

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limited abundance of Li. Alternatively, sodium-ion batteries (SIBs) is a possible substitute to LIBs, owing to its low cost and high natural abundance of sodium, particularly when large scale applications are considered.

Of late, iron phosphate-based materials have received more and more interest due to their application in catalysis [11,12] electrocatalysis [13]corrosion protection [14] and lithium batteries [15,16] In the past few decades, iron phosphate and similar category nanostructured metal phosphates have been widely studied, because of their encouraging electrochemical performance in applications such as catalysis and lithium batteries. Similarly, the non-lithiated hydroxyl phosphate, viz. $Fe_5(PO_4)_4(OH)_3.2H_2O$ represented as FeHP has gained attention from researchers recently. For example, Y. Song et al. [17] have studied the magnetic properties and battery applications of FeHP, isostructural with lipscombite. G. L. et al. [18] have synthesized FeHP with different shapes by varying synthesis parameters, such as reaction time, temperature, amount of H_2O_2, types of precursors and pH values. Similarly, H. Ming et al. [19] varied the ratio of reducing agent and lithium acetate to prepare FeHP with different size, shape and morphology. On the other hand, S. W. Cao et al. [20] studied the photoluminescent properties and D. L. et al. [11] compared the catalytic activity of FeHP with and without H_2O_2. The high catalytic activity could be attributed to an interesting mechanism, viz., activation of H_2O_2 by Fe (III) in FeHP by a Fenton-like pathway. Further, FeHP with single-crystalline hyperbranched nanostructures is reported to possess biocompatibility and excellent capability for isolation of phosphorylated peptides from a proteolytic digest mixture [12], thus inviting interest from life science researchers also. However, explanation of FeHP for energy storage applications has not been studied extensively.

With the advent of graphene as a potential additive to prepare composites for energy storage applications, FeHP/G composite has been reported as a cathode material for lithium battery applications [15]. It is well known that graphene as a two-dimensional (2D) carbon material has fascinated great deal of research interest due to its high conductivity, large surface area, high mechanical strength and appreciable chemical and thermal stability [21]. Benefiting out of these unique characteristics, graphene has been widely chosen as a conductive material to prepare composites with numerous metal oxides and phosphates rather than an electrode material by itself to exhibit better electrochemical performance in energy storage applications. Further, graphene can effectively prevent the volume expansion/extraction and the aggregation of metals or metal oxides during discharge/charge processes [22]. Based on these reasons, graphene has been chosen to prepare the title composite of the present study.

It is recently understood and published by our team that with the newly identified composition of stannates, which could be represented using the general formula Li_2SnO_3. $A_xB_{y,}$ where A-metal and B-polyanionic matrix, one can demonstrate their suitability as anodes for application in high capacity and high rate lithium-ion batteries [23,24]. Intrigued by such attempts, we have extended our study further to understand whether the concept of Li_2SnO_3 stabilized anodes could be made applicable to non-lithiated polyanionic metal derivatives also. Towards this direction, we intended to introduce tin along with the carefully selected FeHP matrix, bestowed with the cost effective and environmentally benign advantages to exhibit better anode property, wherein graphene has been included as a conducting as well as compositing additive. Basically, tin in the newly formulated composite is expected to impart and to improve the anode behaviour of FeHP and the added graphene to facilitate enhanced conductivity related benefits. In other words, the title composite anode enjoys the synergistic effect involving the combination of insertion, conversion and alloying/dealloying mechanism, which is found to be responsible for the improved electrochemical behaviour. Fascinatingly, there has been no report found on Sn-FeHP/G as anode for lithium and sodium battery applications till date (Table S1). Further, the title composite, despite possessing crystal water in the compositional matrix exhibits appreciable electrochemical behaviour and such an observation is in line with the literature reports stating the beneficial role of crystal water in improving the electrochemical behaviour of closely related electrode materials deployed in lithium-ion and sodium-ion batteries [25–30] (Table S2).

In other words, our present work that deals with the investigation of hydrothermally synthesized nano crystalline Sn-FeHP/G as a high capacity and high rate anode material for LIBs and SIBs is first of its kind to report on the possibility of extracting a high specific capacity of 1000 $\mathrm{mA\,h\,g^{-1}}$ under 100 $\mathrm{mA\,g^{-1}}$ conditions. Further, the suitability of Sn-FeHP/G anode for high rate (5000 $\mathrm{mA\,g^{-1}}$ or 5 $\mathrm{A\,g^{-1}}$) LIB applications has also been demonstrated in this communication. More importantly, possibility of exploiting FeHP framework for energy storage application in SIBs has also been demonstrated, thereby providing extended scope to investigate wide variety of metal hydroxy phosphates as alternative anode candidates in lithium-ion and sodium-ion battery applications.

2. Experimental

To synthesise Sn-$Fe_5(PO_4)_4(OH)_3$, stoichiometric amount of precursors, namely 0.250 g of $Na_2HPO_4{\cdot}4H_2O$ (Alfa Aesar), 0.681 g of Na_2SO_4 (Alfa Aesar), 0.202 g of $FeCl_3{\cdot}6H_2O$ (Alfa Aesar), and 0.2 ml of $SnCl_4$ (Alfa Aesar), were dissolved in 80 ml of Milli Q water and subjected to mechanical stirring until a pale yellow turbid solution was obtained. Then the whole content was transferred into a 100 ml Teflon-lined stainless steel autoclave. Subsequently, the autoclave was sealed and slowly heated at 1 °C/min to 220 °C and the temperature was maintained for about 48 h. Further, it was cooled down to room temperature, subjected to centrifugation and repeated washing with Milli Q water and ethanol to obtain a pale green powder. The powder thus obtained was dried at 60 °C for 24 h in vacuum oven, and the resultant product is labeled as Sn-FeHP.

To prepare Sn-FeHP/G composite with 5 wt % of graphene (Sn-FeHP-0.95 g and G-0.05 g), the as received Sn-FeHP powder was mixed and sonicated with ethanol for 1 h. After sonication, the mixture was kept in oven (60 °C) for solvent evaporation and the mixture was heated to 500 °C for 2 h in Ar atmosphere. To ensure perfect adherence of added graphene and preferably to obtain a good conducting network on the surface of nano crystalline Sn-FeHP particles, such a mechanothermal method has been used to prepare Sn-FeHP/G composite consisting of conducting graphene additive.

3. Electrode preparation and coin cell assembly

The electrode was prepared from a combination of 70 wt % active composite material, 20 wt % super P carbon and 10 wt % polyvinylidene flouride (PVdF) binder. The PVdF binder was first dissolved in N-methylpyrrolidone, and the mixture of active composite material with super P carbon has been added to the solution to get a homogenous slurry. The slurry was coated on a Cu foil (current collector), dried under vacuum at 80 °C for 12 h and pressed with 3 ton pressure. Such a hot roll pressed electrode was cut in to circular shape (14 mm) and the electrodes typically had an active material content of 3 mg, including graphene and Sn-FeHP. The specific capacity was calculated based on the total mass of the active composite material. The electrode was further dried under vacuum at 80 °C for 3 h prior to the assembling of cells in an argon filled glove box. Electrochemical characterization was carried out with the freshly fabricated 2032 coin cells consisting of nano Sn-FeHP/G composite anode. In these coin cells, 1 M $LiPF_6$ in a mixture of ethylene carbonate and diethyl carbonate (EC:DEC) (1:1 V/V) was used as electrolyte for LIB assembly and 1 M $NaClO_4$ in a mixture of ethylene carbonate and propylene carbonate (EC:PC) (1:1 V/V) was used as electrolyte for SIB assembly. Polypropylene was used as a common separator and Li or Na foils were used as counter electrode respectively in the LIB and SIB assembly.