



Evolution of the solid electrolyte interphase on tin phosphide anodes in sodium ion batteries probed by hard x-ray photoelectron spectroscopy



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ABSTRACT

In this work the high capacity anode material Sn_4P_3 for sodium ion batteries is investigated by electrochemical cycling and synchrotron-based hard x-ray photoelectron spectroscopy (HAXPES) in order to elucidate the solid electrolyte interphase (SEI) properties during the first 1.5 cycles. The electrochemical properties of tin phosphide (Sn_4P_3) when used as an anode material are first established in half cells versus metallic sodium in a 1 M NaFSI in EC:DEC electrolyte including 5 vol% FEC as SEI forming additive. The data from these experiments are then used to select the parameters for the samples to be analysed by HAXPES. A concise series of five cycled samples, as well as a soaked and pristine sample, were measured at different states of sodiation after the initial sodiation and after the following full cycle of sodiation and desodiation. Our results indicate that the SEI is not fully stable, as both significant thickness and composition changes are detected during cell cycling.

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1. Introduction

Sodium-ion battery (SIB) technology is a fast growing field both in science and in industry due to the inherent advantages concerning material abundance and price [1]. Within the field, researchers are still exploring if and how knowledge from the well advanced field of lithium ion batteries (LIBs) can be transferred to and utilized in SIBs. While a lot of materials are compatible with both sodium and lithium ions, there are issues regarding graphite not being able to intercalate sodium to any practical extent [2]. Anode materials in sodium-based cells have therefore generally been restricted to the use of soft or hard carbon allotropes instead of graphite. While graphite has a capacity of 372 mAh g^{-1} in LIBs, hard carbon usually attains between a capacity of 250–300 mAh/g in SIBs [3–5]. Furthermore, the volumetric capacity of carbon anodes remains problematic due to the low density of hard carbons. Thus, there is a drive for novel anode materials to improve the both the gravimetric and volumetric capacity of SIBs while reducing the problems with high initial irreversible capacity and poor rate capability of carbon anodes.

Possible alternatives to carbon based electrodes range from phosphorous [6,7] to tin [8] and antimony [9]. These materials, however, suffer from issues such as poor capacity retention, large volume expansion and/or significant over-potentials. In this work, we take a closer look at tin phosphide (Sn_4P_3). Sn_4P_3 has managed to take a significant leap towards a practical anode material by enabling stable cycling, which has previously been shown to be extremely difficult to obtain with either tin or phosphorous alone [10]. Although Sn_4P_3 has a practical capacity that is lower than phosphorous ($\sim 1800 \text{ mAh g}^{-1}$) and roughly equivalent to tin ($\sim 550\text{--}750 \text{ mAh g}^{-1}$), this still places it in the top tier of anode materials [11]. In terms of the volumetric energy density, Sn_4P_3 compares favourably to hard carbons with a volumetric capacity of 700 mAh. cm^{-3} and 465 mAh. cm^{-3} respectively assuming 300 mAh. g^{-1} capacity and a density of 1.55 g. cm^{-3} for hard carbon [12]. Furthermore, the bulk capacity of Sn_4P_3 displays a fairly linear sloping voltage profile between 1 – 0.1 V vs. Na^+/Na . This is an advantageous property since issues with sodium plating on the anode during charge are unlikely in this voltage range, as compared to the flat plateau of phosphorous anodes close to 0V vs. Na^+/Na [6].

As a battery anode, Sn_4P_3 undergoes electrochemical reactions to form alkali-phosphorus compounds such as Na_3P and alkali-tin alloy particles during the first sodiation [10,12,13,14]. The advantage of such kind of phase change is that the starting material forms nanocrystals of tin within a phosphorous matrix

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when it is sodiated, thereby avoiding agglomeration of tin particles during cycling in parallel with mitigating the issue of poor electrical conductivity associated with phosphorus [14]. Although Sn_4P_3 has a volume expansion that can reach 100% when fully sodiated, the distribution of material within the electrode increases the capability of handling volume expansion than previously mentioned materials [15].

Due to the potential range in which Sn_4P_3 operates, it is imperative that a solid electrolyte interphase (SEI) forms, which in turn can stop the electrolyte from decomposing at the anode surface. Previous SEI studies on SIBs have shown that the SEI formation and composition are far from trivial, and the formed SEI has more pronounced stability issues than what is experienced from analogous lithium systems [16–19]. The volume expansion of Sn_4P_3 makes it extra challenging to ensure that the SEI prevents consumption of electrolyte and sodium ions, as the surface layer must not only be stable with regards to solubility and applied electrochemical potentials but also robust enough to deal with repeated swelling and contraction of particles during sodiation and desodiation. Although several studies have shown more than 100 cycles with good capacity retention in half cells comprising Sn_4P_3 [10,14,15,20], this does not guarantee that the SEI is truly functional. It should be mentioned that in these prototype cells aimed for research, the amount of electrolyte is often highly exaggerated, and the effects of electrolyte consumption might therefore go unnoticed.

To enable this material to take the necessary steps towards true practical use, it is vital to characterize and understand the surface reactions in order to achieve a stable SEI composition. In this work, we have chosen to use the combination of sodium bis(fluoro-sulfonyl)imide (NaFSI) salt in a mixture of ethylene carbonate (EC) and diethyl carbonate (DEC) with 5 vol% fluoroethylene carbonate (FEC) additive. While the solvent mixture and FEC additive are established electrolyte components for materials that possess significant volume change during cycling, the FSI^- anion is a relatively innovative salt component and commonly praised for its high electrochemical stability and ability to form a robust SEI [21–24]. These properties should be very beneficial to this demanding battery chemistry and is the motivation for our choice. One of the most suitable techniques for SEI studies is X-ray photoelectron spectroscopy (XPS) since the surface sensitivity of this technique matches the typical SEI thickness. Therefore, the chemical composition of the SEI can be evaluated without significant bulk contribution. In sodium ion batteries, the thickness of the SEI often exceeds the probing depth of standard in-house XPS instruments which means that higher energy hard-XPS (HAXPES) is required for a complete view of the SEI as it enables greater analysis depths. The combined use of two excitation energies (2005 eV and 6015 eV) in this work also enables a coarse thickness determination of the SEI in combination with the ability to ascertain information about composition of the SEI as a function of depth. To this end, we hereby present our HAXPES results on cycled tin phosphide to map the influence of volume expansion and evaluate SEI composition and thickness, as well as, *in-operando* x-ray diffraction (XRD) to investigate structural changes of tin-phosphide electrodes.

2. Experimental

2.1. Sample preparation

The active Sn_4P_3 material was obtained as powder by ball milling metallic tin (Aldrich $\geq 99\%$) together with red phosphorous (Alfa Aesar 325 mesh 98.9%) in a 4:3 stoichiometric mix. Ball milling was performed on 2 grams of sample for one hour in a SPEX 8000 M MiXER/MILL using two 20 mm stainless steel balls weighing 30 grams each. Electrodes were produced by mixing Sn_4P_3 with

Super P carbon (Erachem) and sodium carboxymethylcellulose (NaCMC)(Sigma-Aldrich) binder in an 8:1:1 weight ratio into a slurry using water as solvent in a planetary ball mill. The slurry was then bar coated on copper foil from which 13 mm diameter disks were punched and subsequently dried at 120 °C under vacuum for 12 h. The mass loading for the prepared electrodes varied between 2.30 and 2.63 mg/cm² of active material. Metallic sodium anodes were prepared in a glovebox by rolling a thin foil from which 14 mm diameter disk shaped electrodes were punched. For the *in operando* X-ray diffraction (XRD) experiment the slurry was instead coated into an aluminium mesh in order to obtain a mass loading of 9.3 mg.cm⁻². The electrolyte was prepared in an argon glovebox by first mixing ethylene carbonate (EC) and diethyl carbonate (DEC) (both BASF) in a 1:1 mixture. To this mixture, 5 vol % of fluoroethylene carbonate (FEC, Aldrich 99%) was added before the addition of sodium bis(fluorosulfonyl)imide (NaFSI, Solvionic) thoroughly dried under vacuum at 100 °C for 20 h resulting in a 1 M clear solution. Tin phosphide–sodium pouch cells were assembled under an argon atmosphere. Solupor separator was used with copper as current collector for the tin phosphide. All non-XRD cells had 100 μL electrolyte added and were cycled galvanostatically with a current density of 50 mA.g⁻¹ at room temperature. The *in operando* cell consisted of aluminium current collectors arranged in parallel to create a space where the X-ray beam could pass through unimpeded, the cell was cycled at 10 mA.g⁻¹ and contained 150 μL of electrolyte.

2.2. Characterization:

Powder XRD measurements were performed on pure Sn_4P_3 powder in transmission mode on a Stoe & Cie GmbH Stadi X-ray powder diffractometer equipped with a Ge monochromator (single wavelength $\text{Cu K}_{\alpha 1}$). A Mythen 1 K Si strip detector was operated in sweeping mode with an angular resolution of 0.015° 2 θ . *In operando* X-ray diffraction (XRD) measurements (*i.e.* measured on an operating battery) were carried out in transmission mode through an unmodified pouch cell on the same diffractometer. The cell was oriented such that the beam passed through the pouch material, a thin piece of sodium metal, separator and the positive electrode composite including aluminium mesh. Here the detector was operated in stationary mode, positioned to cover a 19° 2 θ range. Each data set was collected for 20 min resulting in 400 diffraction patterns collected over the whole discharge-charge cycle. Rietveld refinements were performed with the Rietveld method [25] in the JANA2006 software [26]. All electrochemical measurements were carried out using a Digatron Battery Testing System. The tin phosphide cells were cycled between 0.01 and 2.5 V vs. Na⁺/Na for long term cycling and between 0.01 and 2 V vs. Na⁺/Na for HAXPES samples. Prior to the HAXPES characterisation, all cycled samples were allowed to reach the desired point in the cycling curve before being promptly disassembled and gently washed. Washing was performed by applying 3 drops of DMC to the electrode followed by a short wait whereupon the DMC was decanted and the procedure was repeated one time. The pristine sample used was treated to the same as other samples with the exception of not being introduced to a pouch cell. The samples were stored briefly in an Ar-filled glovebox after washing before being vacuum sealed for transport to the synchrotron facility. HAXPES measurements were performed at the HIKE instrument (KMC-1 beamline) at the synchrotron facility BESSY II at Helmholtz-Zentrum Berlin. The samples were characterized using photon energies of 2005 and 6015 eV. All sample preparation and introduction was performed in argon atmosphere avoiding exposure of the samples to atmospheric conditions. To ensure that radiation damage was not affecting the result, the measurements started and ended with identical sweeps of the F1 s spectra.

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