Full paper

Superior reversible tin phosphide-carbon spheres for sodium ion battery anode

Xiulin Fan\textsuperscript{a}, Tao Gao\textsuperscript{a}, Chao Luo\textsuperscript{a}, Fei Wang\textsuperscript{a}, Junkai Hu\textsuperscript{b}, Chunsheng Wang\textsuperscript{a,}\textsuperscript{c}

\textsuperscript{a} Department of Chemical and Biomolecular Engineering, University of Maryland, College Park, MD 20742, USA
\textsuperscript{b} Department of Chemistry & Biochemistry, University of Maryland, College Park, MD 20742, USA

ARTICLE INFO

Keywords:
Sodium ion batteries
Anodes
Coulombic efficiency
Tin phosphate

ABSTRACT

Sodium ion batteries (SIB) have potential for large scale renewable energy storage due to geopolitical abundance of Na. However, the high capacity Na-ion anodes still suffer from poor cycling stability and low Coulombic efficiency (CE). Herein, uniform Sn\textsubscript{4}P\textsubscript{3}@C spheres were synthesized by a facile aerosol spray-pyrolysis-phosphidation method. By tuning the electrolyte, a reversible capacity of ~ 800 mAh/g with an extremely low capacity decay rate of 0.09% per cycle was achieved with a record-high initial CE (~ 90%) and high cyclic CE (~ 99.9%). The Sn\textsubscript{4}P\textsubscript{3}@C in the stable ether-based electrolyte shows the highest accumulated cycling capacities in the reported SIB anodes.

1. Introduction

The challenges for sodium ion batteries (SIB) are the low energy density and short cycle life. Extensive efforts have been devoted to explore high capacity and long cycling cathode and anode materials for SIBs [1–5]. For the anodes, the alloying materials such as phosphorus- and Sn-based materials [6–13] have very high gravimetric capacities and volumetric capacities and proper charge/discharge potentials, which are ideal for SIB anodes. However, high capacities generate large volume changes, which pulverize the anode material and result in SEI breaking/reforming during charge/discharge cycles. The SEI breaking/reforming reduces Coulombic efficiency (CE) during cycling and consume the electrolyte and Li-ion source from cathode, resulting in poor cycling life of Na-ion full cells [14].

Nanostructured materials have been adopted to reduce the pulverization of alloy anodes, thus successfully extending the cycle life of anode materials [15,16]. However reducing the anode materials into nanoscale increases surface area between electrode and electrolyte, lowering the CE in the first several charge/discharge cycles. Although adding SEI-stabilizing FEC additives into the electrolyte can enhance cycling stability by forming a thick and dense SEI [14], it also further reduces the initial CE. P/Carbon nanotube anodes only show a low initial CE of 69% in FEC-added carbonate electrolyte [6], although a high reversible capacity of > 700 mAh/g was achieved in 30 cycles. We significantly extended the cycling life of P/Carbon nanotube anode to 2000 cycles using the vaporization-condensation synthesis method [11]. However, the initial CE is still very low (~ 68%). Alloing P with Sn to form Sn\textsubscript{4}P\textsubscript{3} compounds can slightly increase the initial CE to 75–77% in FEC-added electrolytes [7,10]. The cycling life of Sn\textsubscript{4}P\textsubscript{3}/C can be largely extended by reducing the particle size to nanoscale. However, the initial CE of Sn\textsubscript{4}P\textsubscript{3}/C nanocomposites were significantly reduced to 40–50% [17,18]. It is very challenging to achieve both the long cycle life and high CE for high capacity anodes.

To accomplish a long cycling performance and a high CE, the ideal anode materials should have micro-sized primary particles consisting of nano-sized secondary high capacity active materials and nanopores in a carbon matrix, so that SEI only forms on the primary particle surface, while the electronic conductive nanoporous composite can well maintain integration during charge/discharge cycles. Herein, we report such a high capacity anode, pomegranate-structured Sn\textsubscript{4}P\textsubscript{3}/C spheres, which were synthesized by a facile method of aerosol spray-pyrolysis and subsequent low temperature phosphidation. We demonstrated that such Sn\textsubscript{4}P\textsubscript{3}/C spheres could deliver a highly reversible capacity of > 700 mAh/g with record-high initial CE of ~ 90% and cycling CE of ~ 99.9% in the ether-based electrolyte, achieving both long cycle life and high CE. The pomegranate-structured Sn\textsubscript{4}P\textsubscript{3}/C spheres show the highest “accumulated capacities” in all reported Na-ion anodes. The accumulated capacities at Nth cycles (N is the cycle number) was defined and calculated by multiplying the capacity at Nth cycles with all the CEs before Nth cycles, which is utilized to convert the capacity of anode tested in half-cell to the true anode capacity in a full cell.

\textsuperscript{*} Corresponding author.
E-mail address: cswang@umd.edu (C. Wang).
2. Synthesis of pomegranate-structured Sn₄P₃@C spheres

Fig. 1a illustrates the detailed synthesis process for the pomegranate-structured Sn₄P₃@C spheres. First, monodisperse well-defined SnO₂/C microspheres were facilely fabricated by aerosol-spray-pyrolysis method in the presence of sucrose and sulfuric acid in water-ethanol solution (Scheme S1). Then, these SnO₂/C microspheres were hand milled with NaH₂PO₂ and heated at 280 °C for 10 min, during which SnO₂ nanoparticles were reduced and in situ chemically transformed into Sn₄P₃ nanoparticles, resulting in uniform Sn₄P₃@C spheres. The amorphous carbon content in the SnO₂/C template is about 19 wt% as measured by TGA analysis (Fig. 1b). The X-ray diffraction (XRD) pattern in Fig. 1c identified the tetragonal phase of SnO₂ (JCPDS No. 41-1445) after aerosol-pyrolysis. As shown in SEM, TEM and HRTEM in Fig. S1, these template SnO₂/C spheres are ideal features should ensure a good electrochemical cycling performance for Sn₄P₃@C anode.

3. Electrochemical performance of Sn₄P₃@C spheres

CE is one of the most important parameters for the high capacity anodes (Fig. S3). We evaluated electrochemical reduction stability of several electrolytes with different solvents (Fig. S4) from 1.5 V to 0.0 V vs. Na⁺/Na⁺⁺. A broad reduction peak in a wide potential range of 0.0–1.5 V was observed in NaPF₆-EC/DMC electrolyte and a large peak at 0.4 V appears in NaPF₆-EC/DMC+10%FEC. However, no obvious peaks were detected in the electrolyte of NaPF₆-DME and the reaction current is less than half of values in carbonate electrolytes, which demonstrates that NaPF₆-DME is much stable at a low potential, thus can significantly increase the initial CE. The small and quickly reduced current with charge/discharge cycles in NaPF₆-DME electrolyte should be attributed to minor reduction of electrolyte and impurity in the electrolyte (Fig. S4c and S4d). Fig. 3a shows the first cycle charge/discharge curves for the Sn₄P₃@C electrode using three different electrolytes at a current of 50 mA/g. The obvious plateau in the discharge at 1.2 V in LiPF₆-EC/DMC+10%FEC electrolyte with a lowest CE of 59.8% could be attributed to the decomposition of FEC forming dense SEI layers, which is consistent with the electrochemical stability test (Fig. S4b) and previous reports [18]. Removing the FEC from the carbonate electrolyte, the first CE increases to 72.7%, but still much lower than that in DME electrolyte. A significantly high initial CE of 90.7% is observed for the Sn₄P₃@C in DME electrolyte, demonstrating one of the highest CE in all Sn and P compounds reported to date [9,10,18]. The small amount of irreversible capacity is possibly due to the impurities in the electrolyte and the formation of thin SEI layer.
The galvanostatic discharge/charge profiles of different cycles for Sn₄P₃@C in NaPF₆-DME electrolyte are shown in Fig. 3b. The discharge voltage profiles of Sn₄P₃@C show two plateaus located at ~ 0.25 V and 0.01 V vs. Na⁺/Na, which is well consistent with the previous work, and could be attributed to the formation of NaₓP and NaₓSn [10,18]. The sodiation and desodiation reactions follow the subsequent equations:

In the initial sodiation step:

\[
\text{Sn}_4\text{P}_3 + 24\text{Na}^+ + 24e^- \rightarrow \text{Na}_{15}\text{Sn}_4 + 3\text{Na}_3\text{P} \quad (1)
\]

The subsequent charging/discharging cycles can be characterized by reversibly alloying and de-alloying Na₃P and Na₁₅Sn₄ [9,10,18]:

\[
\text{Na}_{15}\text{Sn}_4 \leftrightarrow 4\text{Sn} + 15\text{Na}^+ + 15e^- \quad (2)
\]

\[
\text{Na}_3\text{P} \leftrightarrow \text{P} + 3\text{Na}^+ + 3e^- \quad (3)
\]

As shown in Fig. 3c, the Sn₄P₃@C anode in NaPF₆-EC/DMC shows fast capacity decay from 700 mAh/g in the third cycle to 380 mAh/g after 110 cycles. Yet, it is still much stable compared to the previously reported tin phosphide composites [9,10], which may be due to unique pomegranate-structure of Sn₄P₃@C spheres. As the FEC was added into the electrolyte, much better cycling performance was observed. A reversible capacity of 580 mAh/g can be obtained after 120 cycles, with a capacity retention of 95% from the 2nd to 120th cycle. This indicates that thick SEI layers formed from reduction of the FEC additive can prevent the continuous side reactions of the electrolyte and the electrode [21], resulting in better cycling performance. As the electrolyte changes to NaPF₆-DME, the cycling stability is similar to the EC/DMC + 10%FEC system, but shows a much higher reversible capacity. After 120 cycles, the Sn₄P₃@C anode in NaPF₆-DME electrolyte still delivers a reversible capacity of over 700 mAh g⁻¹, which is one of the highest specific capacities for Sn-based anode materials. The mechanism for the high capacity in NaPF₆-DME electrolyte was investigated using electrochemical impedance spectroscopy (EIS). The semicircles at the high frequency range in EIS (Fig. 3d) represent the total interfacial resistance from SEI and the charge transfer resistance. The Sn₄P₃@C in DME electrolyte has a lowest interfacial resistance of ~ 250 Ω (vs. ~ 750 Ω for EC/DMC + 10% FEC). This phenomenon illustrates that much better electrode stability and more favorable sodiation/desodiation kinetics can be achieved for pomegranate-structured Sn₄P₃@C in DME electrolyte, which is confirmed by the much better rate capability for the Sn₄P₃@C in NaPF₆-DME electrolyte (Fig. S5). The electrochemical performance of ball milled Sn₄P₃/C composite was also evaluated. As shown in Fig. S6, the capacity of the ball milled Sn₄P₃/C composite decays very fast in the 1 M NaPF₆ DME electrolyte, demonstrating that the pomegranate structure plays a significant role in stabilizing the cycling performance.
Fig. 3. Electrochemical performance of pomegranate-structured Sn$_4$P$_3$@C composite. (a) Initial galvanostatic charge-discharge voltage profiles of composite at a current density of 50 mA/g using three different electrolytes. (b) Galvanostatic charge-discharge voltage profiles of pomegranate-structured Sn$_4$P$_3$@C composite at a current density of 50 mA/g using 1 M NaPF$_6$ in DME as the electrolyte. (c) Cycling performances of pomegranate-structured Sn$_4$P$_3$@C nanospheres at the 100 mA/g using different electrolytes. (d) Nyquist plots for Sn$_4$P$_3$@C composite cycled in three different electrolytes after 10 cycles. (e) Coulombic efficiency for the pomegranate-structured Sn$_4$P$_3$@C composite cycled in three different electrolytes. (f) Accumulated cycling performance for the pomegranate-structured Sn$_4$P$_3$@C composite cycled in three different electrolytes considered the Coulombic efficiency.

Fig. 3e shows the cyclic CE of the Sn$_4$P$_3$@C in these three electrolytes at the 100 mA/g. For EC/DMC and EC/DMC-10%FEC electrolytes, the Sn$_4$P$_3$@C electrode possesses a CE of 99.6% and 99.8% after about 10 charge/discharge cycles, respectively. The CE of Sn$_4$P$_3$@C quickly increases to 99.9% after 6 cycles in relatively stable NaPF$_6$-DME electrolyte, which is the highest cyclic CE ever reported for alloying anode materials for SIBs (Table S1). The high CE for Sn$_4$P$_3$@C in DME electrolyte is consistent with the electrochemical stability tests (Fig. S3) and small interfacial resistance (Fig. 3d). The thin and spatially confined SEI on Sn$_4$P$_3$@C in DME electrolyte highly increases the CE.

The morphology and elemental distribution on Sn$_4$P$_3$@C spheres after charging/discharging in three electrolytes for 10 cycles was directly characterized using SEM, TEM and XPS, shown in Fig. 4 and Fig. S7. All of the spherical structures are well preserved for these samples cycled in the three different electrolytes (Fig. 4a, f, and j), indicating that the pomegranate architecture ideally accommodate the volume expansion during sodiation as we expected. For the Sn$_4$P$_3$@C cycled in EC/DMC + 10% FEC, a thick and relatively dense layer mainly containing Na and F were observed (Fig. 4d, e, k, l and m). No Sn- or P-containing particles can be observed. The red dash arc in Fig. 4e shows that the Na concentrated in the out layer of the sphere. As for Sn$_4$P$_3$@C cycled in EC/DMC, porous layer on the surface of the spheres were detected, the red arrows in Fig. 4j illustrate the pores in the SEI layer. The uniform distribution of Na (Fig. 4f, and i) indicates the SEI layer in 1 M NaPF$_6$-DME electrolyte is much thinner than that cycled in carbonate electrolytes. The primary Sn- or P-containing nanoparticles can still be observed in the spheres encapsulated by the thin carbon layer (Fig. 4f). XPS shows that small amount of NaF can be observed on the surface of Sn$_4$P$_3$@C in DME.
electrolyte, which is formed by reduction of the electrolyte on the Sn4P3@C surface (Fig. 4l and m). Formation of much thinner SEI on Sn4P3@C in DME solvent electrolyte than that in EC/DMC and EC/DMC + 10% FEC electrolytes was also confirmed by C 1s signals before and after sputtering (Fig. S7).

Due to excess of electrolytes and Na source of Na metal in Na/Sn4P3@C half-cell, cycling stability of Na/Sn4P3@C in half cells cannot reveal the stability of full cells (Fig. S3). The consequent implication of the low CE is that these anodes can only be assembled into a cell with a much excess of the cathode materials to offset the every cycle’s depletion of the ions, which will dramatically lead to a lower energy density for the full cell and therefore is not practical for the SIB
industry. Hence, meaningful capacity of an electrode at Nth (N is the cycle number) cycles should be calculated by multiplying the electrode capacity at Nth cycles with all CEs before Nth cycle. We define this meaningful capacity as an "accumulated capacities", which reflects the anode capacity in a full cell. Here, we compared the Sn4P3@C electrode cycled in three different electrolytes based on the "accumulated capacities" (as shown in Fig. 3f), which is calculated based on the following equation:

\[
\text{Capacity}_{\text{accumulated}} = \text{Capacity}_{\text{cycle}} \times \text{Capacity}_{\text{cycle}} \times \text{Capacity}_{\text{cycle}} \times \text{CE}_{i} \times \text{CE}_{j} \times \text{CE}_{k} \]

(4)

For the Sn4P3@C cycled in NaPF6-DME, an accumulated capacity of over 570 mAh/g can be obtained after 120 cycles, which is more than two and three times higher than cycled in EC/DMC-10% FEC (230 mAh/g) and in EC/DMC (148 mAh/g), respectively. The Sn4P3@C in relatively stable NaPF6-DME electrolyte shows the highest accumulated capacity in all anodes ever reported (Fig. 5) for SIBs

4. Methods

4.1. Synthesis of SnO2/C nanospheres

The template of SnO2/C nanospheres were synthesized by a facile and low-cost aerosol-spray pyrolysis route. In a typical synthesis process, SnSO4 (3 g), sucrose (1 g) and sulfuric acid (2 mL, 98%) were dissolved into a 100 mL mixture of ethanol and distilled water (1:1). The solution was atomized by Ar flow with a collision-type nebulizer (Atomizer Aerosol Generator ATM 220, TOPAS, Germany), and the aerosols that were generated subsequently entered a tubular furnace at 600 °C. The flow rate of the precursor solution vapor was about 200 cm^3 s^-1. During the pyrolysis, SnSO4 was in situ decomposed to SnO2 nanoparticles and the sucrose transformed to carbon at the catalysis of sulfuric acid.

4.2. Synthesis of pomegranate-structured Sn4P3@C nanospheres

To prepare pomegranate-structured Sn4P3@C nanospheres, the as-synthesized SnO2/C nanospheres were hand milled with NaH2PO2. The molar ratio of Sn to P was 1:5. Subsequently, the mixture was heated at 280 °C for 5 min with a heating rate of 10 °C min^-1. After cooling down, Sn4P3@C spheres were collected by washing the mixtures with diluted HCl aqueous solution (0.05 mol/L), water and ethanol, respectively.

4.3. Synthesis of Sn4P3/C composite

The Sn4P3/C composite were prepared by ball milling under an argon atmosphere. The active materials (Sn and P): carbon black weight ratio was set to 76:24. The Sn:P ratio was 4:3 by molar ratio. The weight ratio of milling balls to powder was 40:1. The rotation speed of the mill was set to 400 rpm for 24 h.

4. Materials characterization

The crystalline structure of the materials was characterized by powder X-ray diffraction (XRD) on a Bruker Smart1000 diffractometer with a Cu Kα radiation. The morphology and microstructure of the sample was investigated by scanning electron microscopy (SEM, Hitachi SU-70) and transmission electron microscopy (TEM, JEM 2100 LaB6, 200 keV). X-ray photoelectron spectroscopy (XPS) was conducted on a high sensitivity Kratos AXIS 165 X-ray photoelectron spectrometer with Mg Kα radiation. All binding energy values were referenced to the C 1s peak of carbon at 284.6 eV. Before the XPS characterizations, the cycled electrodes were washed with the corresponding solvents (DME for the 1 M NaPF6-DME electrolyte, and DMC for 1 M NaPF6-EC/DMC electrolyte and 1 M NaPF6-EC + FEC electrolyte) for several times to remove the salts. Thermogravimetric analysis was carried out using a TA Q600 (USA) in air at a heating rate of 5 °C min^-1. Pore size distributions, specific surface areas and pore volumes of the samples were characterized by N2 adsorption by means of a Micromeritics ASAP 2020 Porosimeter Test Station. Samples were degassed (in a vacuum) at 180 °C for 12 h before the test. The specific surface areas were calculated using the Brunauer–Emmett–Teller (BET) method from the adsorption branch. The porosity distribution was calculated from adsorption branch using the BJH (Barrett–Joyner–Halenda) equation.
4.5. Electrochemical measurements

Electrolytes are prepared by adding NaPF₆ into various anhydrous solvents (DMF, EC/DMC, EC/DMC + 10% FEC). All the solvents were dried by molecular sieves (4 Å, Sigma-Aldrich) to make sure the water content to be lower than 10 ppm, which is tested by Karl-Fisher titrator (Metrohm 899 Coulometer). The charge-discharge performances of the electrode materials were examined by 2032 type coin cells. The Sn₄P₃@C composite with carbon black and sodium alginate dissolved in water were mixed at a weight ratio of 70:15:15 to form a slurry, which was then pasted on the Cu foil and dried to obtain working electrodes. Pure Na foil was used as counter and reference electrode. The electrochemical performance of pomegranate-structured Sn₄P₃@C spheres for the Na⁺ ion insertion/de-insertion was investigated in different electrolytes. A three-electrode “T-cell” was utilized to test the stability window of the different electrolytes with a polished stainless steel as the working electrode, Na foils as the reference and counter electrodes. Cyclic voltammetry (CV) testing with voltages ranging from 0 to 1.5 V under a scan rate of 10 mV/s was recorded using a Gamry 1000E electrochemical workstation (Gamry Instruments, USA). All the cells were assembled in a glove box with oxygen content lower than 2 ppm and tested at room temperature. The galvanostatic charge/discharge test was conducted on Arbin battery test station (BT2000, Arbin Instruments, USA). Na₅V₂(PO₄)₃ (NVP) was used as cathode in a full cell to couple with our pomegranate-structured Sn₄P₃@C composite. A conventional solid-state reaction was used to prepare NVP according to the previously reported protocol.

Acknowledgements

This work was supported as part of the Nanostructures for Electrical Energy Storage (NEES), an Energy Frontier Research Center funded by the U.S. Department of Energy, Office of Science, Basic Energy Sciences under Award number DESC0001160.

Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.nanoen.2017.06.014.

References

**Dr. Fei Wang** received his B.S. and Ph.D. in Physical Chemistry from Fudan University in 2015. He is currently a co-advised postdoctoral Research Associate in U.S. Army Research Lab and University of Maryland, College Park, USA. His research interests focus on energy storage devices including electrode materials, electrolyte, electrochemistry for rechargeable batteries and aqueous batteries.

**Dr. Junkai Hu** is a Post-Doctoral Associate at the University of Maryland, College Park. He graduated with BS (2006) and MS (2009) degrees in Chemistry from Fudan University, Shanghai, China, and obtained his Ph.D. degree in Chemistry at the University of Maryland, College Park in 2015. His research interests include the synthesis of heterogeneous mesoporous materials for electrochemical energy storage devices and hazard gas adsorption/decomposition.

**Prof. Chunsheng Wang** is a full professor at University of Maryland College Park (UMCP). He was educated in materials science and trained in electrochemistry, and got his Ph.D. degree from Zhejiang University. He has more than 150 peer-reviewed journal publications and more than 25 years of experience in battery research. His Li-ion battery research has been highlighted in EFRC news by DoE in 2012, and by Chemical & Engineering News in 2013. He is a recipient of the University of Maryland Outstanding junior Researcher Award.