Nanospheres of a New Intermetallic FeSn₅ Phase: Synthesis, Magnetic Properties and Anode Performance in Li-ion Batteries

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ABSTRACT: We synthesized monodisperse nanospheres of an intermetallic FeSn₅ phase via a nanocrystal-conversion protocol using preformed Sn nanospheres as templates. This tetragonal phase in P4/mcc space group, along with the defect structure Fe₀.₇₄Sn₅ of our nanospheres, has been resolved by synchrotron X-ray diffraction and Rietveld refinement. Importantly, FeSn₅, which is not yet established in the Fe–Sn phase diagram, exhibits a quasi-one dimensional crystal structure along the c-axis, thus leading to interesting anisotropic thermal expansion and magnetic properties. Magnetization measurements indicate that nanospheres are superparamagnetic above the blocking temperature $T_B = 300$ K, which is associated with the higher magnetocrystalline anisotropy constant $K = 3.33$ kJ m⁻³. The combination of the magnetization measurements and first-principles density functional theory calculations reveals the canted antiferromagnetic nature with significant spin fluctuation in lattice $a-b$ plane. The low Fe concentration also leads Fe₀.₇₄Sn₅ to enhanced capacity as an anode in Li ion batteries.

- INTRODUCTION

Nanocrystal conversion chemistry is evolving as a powerful general strategy for synthesizing complex solids.¹,² The concept involves utilizing preformed simple nanostructures as templates to promote compositional and morphological attributes on final products through, for instance, galvanic-replacement reactions and diffusion-based methods.

One good example is the conversion of compositionally simple tin nanocrystals into several complex tin-based intermetallics whose shapes (nanocubes, nanospheres, or nanorods) and sizes are directed by these tin templates.³ It is fascinating that these intermetallics form so readily by this route, in contrast to bulk systems (e.g., FeSn₂ and CoSn₃) that are difficult to prepare via conventional high-temperature metallurgy. According to their phase diagrams, these compounds pass through different structures on cooling down from the liquid phase before attaining their ultimate ground states.⁴ Instead, this conversion chemistry approach provides a new ‘bottom-up’ route to synthesize low-temperature phases of intermetallic nanostructures that are otherwise energetically difficult to synthesize. We reproduced the tin intermetallics conversion synthesis and generated M–Sn (M = Fe, Cu, Co, Ni) nanospheres as high-capacity anode materials in Li ion batteries.⁵ The second metal M in tin intermetallics is believed to play a key role in enhancing the cell performance by buffering the volume change, stabilizing the integration, and improving the electronic conductivity.⁶–⁸ In practice, the merit of our ability to control both the shape and the size of these nanoparticles by conversion chemistry enables us to compare their intrinsic cell performance and identify the best composition in this important category of tin-based intermetallic electrodes.

Interestingly, during our preparation of the Fe–Sn system, we found that while the FeSn₂ phase prevailed over a wide range of the molar ratio of Fe and Sn precursors (i.e., $n(\text{FeCl}_3)/n(\text{SnCl}_2) = 0.3–1$), as we lowered it to 0.1, we obtained uniform nanospheres with a new FeSn₃ intermetallic phase that was not previously established in the existing Fe–Sn phase diagram. These nanospheres have Fe vacancies and exhibit a single-crystal Fe₀.₇₄Sn₅/amorphous Fe–Sn–O core–shell nanostructure.

Moreover, the lack of magnetization data in the literature for FeSn₅/FeSn₂ nanoparticles, combined with the fact that monodisperse single-crystalline nanoparticles may potentially have promise as materials for high-density magnetic recording devices, has motivated us to study the magnetic properties of Fe₀.₇₄Sn₅ nanospheres and compare it with the known-phase FeSn₃ nanospheres.

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We are also interested in its performance as an anode material in Li ion batteries. FeSn2 has been found as the best composition among M–Sn (M = Fe, Cu, Co, Ni) nanospheres. However, the presence of Li storage-inactive Fe in FeSn2 suppresses the theoretical capacity (804 mAh g⁻¹) as compared with pure Sn (993 mAh g⁻¹). Fe₀.₇₄Sn₅ has a theoretical capacity of 929 mAh g⁻¹, which, to our knowledge, is the highest to date for the demonstrated M–Sn intermetallic anodes, where M is electrochemically inactive.

**EXPERIMENTAL SECTION**

**Chemicals.** SnCl₂ (anhydrous, 99% min, Alfa), FeCl₃ (anhydrous, 97%, Aldrich), polyvinylpyrrolidone (PVP, MW = 360 000, Aldrich), and poly(2-ethyl-2-oxazoline) (PEtOx, MW = 50 000, Alfa) as surface stabilizers; tetraethylglycol (TEG, 99%, Alfa) as the solvent; and NaBH₄ (98%, Alfa) as the reducing agent.

**Synthesis.** We obtained the Fe₀.₇₄Sn₅ nanospheres by two reaction steps in the typical mode of conversion chemistry. The first step involved synthesizing templates of uniform tin nanospheres by the reduction of SnCl₂ using NaBH₄ in TEG; we used PVP and PEtOx as surface stabilizers. In 11.25 mL of TEG, 0.525 g of PVP and 0.225 g of PEtOx were dissolved. Then the solution was heated to 170 °C for 10 min, and then held at 205 °C for 2 h. The synthesis was performed while vigorously stirring the suspension in a three-neck flask filled with argon atmosphere via a Schlenk line. We collected the resulting nanoparticles by centrifugation and washed them with ethanol.

**Characterization.** The X-ray diffraction experiments on the synthesized Fe–Sn nanospheres were carried out on beamline X14A (λ = 0.72958 Å) of the National Synchrotron Light Source (NSLS) at Brookhaven National Laboratory. The diffraction patterns were collected in a Q-range from 0.5 to 8.7 Å⁻¹, with a Si strip detector at a step size. XRD patterns were analyzed using the software Jade 6.5 (Materials Data Incorporated). Jana 2006 (Petricek, V., Dusek, M., and Palatinus, L., 2006), and Superflip,¹⁰ a program for solving structures using the charge-flipping method.¹¹ The low-temperature experiments were conducted with a displex cryostat (ADP Cryogenics). The XRD patterns were collected using a Ge (111) analyzing crystal and a point detector at X14A beamline. The lattice parameters were obtained by fitting the XRD data using software TOPAS-Academic V4.1 (Coelho Software, Brisbane, 2007). The wavelength is 0.77599 Å, and the estimated stand deviations for lattice a and c are 0.0001 Å and 0.0002 Å, respectively.

A Hitachi S-4800 scanning electron microscope (SEM) and a JEM-2100F transmission electron microscope (TEM) with an energy dispersive X-ray spectroscopy (EDS) detector were used for the nanomaterial characterization. The EDS measurement was performed in the scanning TEM (STEM) mode with a spot size of 0.7 nm. Differential thermal analysis (DTA) was conducted using a Diamond TG/DTA Instruments (Perkin-Elmer).

To explore the magnetic properties of our new intermetallic nanoparticles, we measured the temperature and field dependencies of the dc magnetization at temperatures from 2 to 300 K and in a magnetic field of 50 kOe, using the Quantum Design magnetic property measurement system (MPMS). For temperatures 300–850 K, we employed a vibrating sample magnetometer in a Quantum Design physical property measurement system (PPMS). We dispersed about 10 mg of nanoparticles in paraffin and contained them in gelatin capsules fastened in plastic straws for immersion into the MPMS. For the high-temperature measurements in PPMS we used a gold foil to contain the sample. We subtracted the diamagnetic signal from the paraffin and the container from the magnetization data. The magnetization was normalized to the total mass of Fe atoms within each sample.

The electrode films consisted of Fe₀.₇₄Sn₅ nanospheres, carbon black (Super P Li, TIMCAL), and sodium carboxymethyl cellulose (CMC, MW ~ 90 000, Aldrich) binder with the weight composition of 80:10:10 on copper foils (0.025 mm thick, Schlenk). The composition of FeSn₂ electrode was FeSn₂ (64 wt %), carbon black (16 wt %), and poly(vinylidene fluoride) binder (PVDF, Alfa, 20 wt %). The electrolyte solution was 1.0 M LiPF₆ in ethylene carbonate/dimethyl carbonate (1:1 by volume, Novolyte). The Celgard 2320 membrane served as the separator. We fabricated laminated 2032-type coin cells with an electrode...
The crystal structure was solved from synchrotron powder XRD data using the charge-flipping method, which has been successfully applied to a structural solution from powder XRD data (Figure 1a). Briefly, the space group and lattice constants were obtained from the indexing of XRD pattern of synthesized Fe−Sn compound. With these parameters from the indexing, atomic coordinates were determined through structural solution by the charge-flipping method. A Rietveld refinement of the XRD pattern was then performed using the solved structure, during which the lattice parameters, thermal factors, atomic coordinates, and occupancies were allowed to be refined.

Differing from known Fe−Sn phases (including room-temperature FeSn and FeSn2 phases and high-temperature Fe5Sn3 and Fe3Sn2 phases), this new FeSn5 phase has a tetragonal lattice in the P4/mcc space group. The lattice parameters of Fe0.74Sn5 were refined as \(a = b = 6.91369 \text{ Å}, c = 5.88967 \text{ Å}\), and \(\alpha = \beta = \gamma = 90^\circ\), with a weighted R-factor \(R_w\) < 3.0%. The atomic coordinates of the Fe and Sn atoms are as follows: Fe (1/2, 1/2, 1/4), Sn1 (0, 0, 1/2), and Sn2 (0.190, 0.607, 1/2). In addition, the Rietveld refinement of Fe occupancy in our sample also yielded a Sn/Fe molar ratio of 6.8, indicative of the presence of vacancies at Sn sites. This nonstoichiometry is further supported by our findings from scanning transmission electron microscopy-energy dispersive X-ray spectroscopy (STEM-EDS) with a spot size of 0.7 nm, which return a similar Sn/Fe of 7.0. Moreover, the fact that there are not any extra peaks in the XRD pattern suggests that Fe vacancies are disordered. The calculated partial reflection table containing the index, d-spacing, and relative intensity information of Fe0.74Sn5 is given in Table 1.

In our present experimental conditions, the pure intermetallic FeSn5 nanoparticles always come with a large number of Fe vacancies. Upon increasing Fe ratio in the precursors, a mixture with few FeSn2 vacancies results. This means the FeSn5 is energetically preferable when excess of Fe available, implying strongly that the FeSn5 structure is only stable in the presence of large numbers of Fe vacancies.

It is interesting to find that the crystal structure of FeSn5 shares a lot of similarities with that of FeSn2. Besides the same tetragonal lattice and similar lattice constants (for FeSn2, \(a = b = 6.534 \text{ Å}\) and \(c = 5.326 \text{ Å}\), there is only one Fe position in each structure. In both cases, each Fe atom is surrounded by eight Sn atoms that form an Archimedean square antiprism (cf. Figure 1a−d; for clarity, only the bonds between Fe atoms and nearest Sn atoms are shown); the distances between the Fe and Sn atoms are similar (2.70347 Å for FeSn5 and 2.79582 Å for FeSn2). Moreover, the distances between two nearest Fe atoms in FeSn2 are both \(c/2\), i.e., FeSn2 has a non-interconnected 1D network along the c-axis. The structure of FeSn5 is then stabilized by space filling Sn atoms that hold the antiprisms in place. As to be shown below, such a weakly interconnected 1D network naturally leads to strong quasi-1D characteristics in both structural and magnetic properties of this new material, drastically different from the 3D case of FeSn2.

Looking at the two crystal structures, it seems that in FeSn5, if we substitute the eight corner Sn atoms and the four edge Sn atoms on the c-axis with eight edge Fe atoms on the c-axis (two Fe atoms on one edge), the crystal structure of FeSn5 may evolve into that of FeSn2. The change of the atom number in the unit cell also supports this evolution; there are in total one corner Sn atom and one edge Sn atom (considering the share of atoms among neighboring unit cells) in FeSn5 that are replaced by two edge Fe atoms, which results in four Fe atoms and eight Sn atoms in the new unit cell, i.e., FeSn2. In this sense, FeSn5 probably is one intermediate phase between Sn and FeSn2.

The low-temperature synchrotron XRD experiments unveiled that the Fe0.74Sn5 lattice (also obtained by the same Rietveld refinement) expands, upon warming up, much more along the a-axis than along the c-axis, as shown in Figure 1e. As a result, the tetragonality (indicated by \(c/a\)) increases monotonically with temperature. This is in great contrast to the tetragonal FeSn2 nanosystem with few appreciable change in tetragonality.
makes us interested in studying the magnetic properties of our Fe$_{0.74}$Sn$_{0.26}$, which is characteristic of this quasi-1D structure and the anisotropic thermal expansion.

We have measured the field $H$ and temperature $T$ dependencies of the magnetization $M$ of Fe$_{0.74}$Sn$_{0.26}$ and FeSn$_2$ nanospheres with similar diameters (45 ± 11 nm for Fe$_{0.74}$Sn$_{0.26}$ and 39 ± 7 nm for FeSn$_2$). Powders of nanospheres with both compositions were diluted in paraffin to minimize interparticle interactions for the low-temperature measurements. The magnetization measurements were carried out between 2.0 and 300 K using a Quantum Design MPMS and at higher temperatures 300–1000 K using a vibrating sample magnetometer (VSM) in a Quantum Design PPMS.

The temperature dependencies of $M$ for Fe$_{0.74}$Sn$_{0.26}$ and FeSn$_2$ nanoparticles are presented in Figure 3a and b showing the separation below the blocking temperature $T_B$ of the zero field cooled (ZFC) and field cooled (FC) magnetizations that are typical of small magnetic particles when their superparamagnetic fluctuations freeze or that become slower than the measurement time. ZFC and FC magnetizations were measured in an applied field of 500 Oe. The separation of ZFC and FC magnetizations below $T_B$ indicates that there is an energy barrier $\Delta E$ proportional to $k_B T_B$ for the reorientation of a net nanoparticle moment that is much larger for Fe$_{0.74}$Sn$_{0.26}$ ($T_B$ ~300 K) than for FeSn$_2$ ($T_B$ ~125 K). Generally, $\Delta E$ depends on both the nanoparticle volume $V$ and the magnetocrystalline anisotropy $K$, so that $\Delta E \sim KV$. Since the outermost 3 nm of the nanoparticles is amorphous, we will assume that it does not contribute to the nanoparticle magnetization, which is ascribed entirely to the remaining 33 nm diameter core in FeSn$_2$ and 39 nm in Fe$_{0.74}$Sn$_{0.26}$. We estimate that the Fe$_{0.74}$Sn$_{0.26}$ nanospheres have $K = 3.33$ kJ m$^{-3}$, which is larger than the $K = 2.29$ kJ m$^{-3}$ calculated for the FeSn$_2$ nanospheres. For equal nanoparticle dimensions, it is more difficult to reorient the entire moment of an Fe$_{0.74}$Sn$_{0.26}$ nanoparticle than that of an FeSn$_2$ nanoparticle. The larger anisotropy of Fe$_{0.74}$Sn$_{0.26}$ that is inferred from this measurement likely reflects robust bonding along the $c$-axis but weaker $a-b$ plane bonding. We note that the values of the magnetocrystalline anisotropy constants of our samples are several magnitudes less than for FePt nanoparticles.

The observation of superparamagnetic behavior implies that each nanoparticle has a net moment. While true long-range order with diverging correlation lengths and time scales cannot be realized in finite sized systems such as nanoparticles, the net nanoparticle moment implies that at least some of the individual moments making up the nanoparticle have fixed relative orientations and are in this sense magnetically ordered below a transition temperature.

We have measured the field dependencies of the magnetization in Fe$_{0.74}$Sn$_{0.26}$ and FeSn$_2$ at 2, 150, and 300 K (Figure 3c and d). In both cases, the magnetization is comprised of two temperature-dependent components. The first is reminiscent of a bulk ferromagnet, being highly nonlinear at low fields and saturating at high fields. A small coercive field of 180 ± 9 Oe is found for Fe$_{0.74}$Sn$_{0.26}$ and a larger value of 750 ± 11 Oe for FeSn$_2$, both at 2 K. The magnitude of this ferromagnetic component of the magnetization shrinks with increasing temperature, vanishing completely above 2 K for FeSn$_2$ but remaining substantial at temperatures at least as large as 300 K for Fe$_{0.74}$Sn$_{0.26}$ which validates our identification of 300 K as the blocking temperature for this sample. The second component of the magnetization is linear in field and is positive for both types of nanoparticles at 2 K and at

Figure 2. (a) SEM and (b) TEM images of Fe$_{0.74}$Sn$_{0.26}$ nanospheres.

The anisotropic thermal expansion phenomenon has been previously reported in several systems, and one explanation is based on the change in the tilt angle of interpolyhedra in the crystal structures with temperature. The dramatically different behavior in the case of Fe$_{0.74}$Sn$_{0.26}$ as compared with FeSn$_2$, on the other hand, originates from the quasi-1D nature of the structure. Since the bonding between the antiprotons is much weaker than the direct connection within the 1D network along the $c$-axis, the anharmonic regime of the internetwork bonding can be easily reached (thermally) in the $a-b$ plane, leading to a strong thermal expansion in the plane, as illustrated in Figure 1g and h. This also provides the system additional flexibility to relax without compromising the more robust direct connections within the antiproton along the $c$-axis, leading to a negligible thermal expansion in comparison. Interestingly, a similar anisotropic thermal expansion is observed in L1$_1$ FePt with large magnetic anisotropy energy (MAE), most likely resulting similarly from the very sensitive separation below the blocking temperature $T_B$ of the zero field cooled (ZFC) and field cooled (FC) magnetizations that are typical of small magnetic particles when their superparamagnetic fluctuations freeze or that become slower than the measurement time. ZFC and FC magnetizations were measured in an applied field of 500 Oe. The separation of ZFC and FC magnetizations below $T_B$ indicates that there is an energy barrier $\Delta E$ proportional to $k_B T_B$ for the reorientation of a net nanoparticle moment that is much larger for Fe$_{0.74}$Sn$_{0.26}$ ($T_B$ ~300 K) than for FeSn$_2$ ($T_B$ ~125 K). Generally, $\Delta E$ depends on both the nanoparticle volume $V$ and the magnetocrystalline anisotropy $K$, so that $\Delta E \sim KV$. Since the outermost 3 nm of the nanoparticles is amorphous, we will assume that it does not contribute to the nanoparticle magnetization, which is ascribed entirely to the remaining 33 nm diameter core in FeSn$_2$ and 39 nm in Fe$_{0.74}$Sn$_{0.26}$. We estimate that the Fe$_{0.74}$Sn$_{0.26}$ nanospheres have $K = 3.33$ kJ m$^{-3}$, which is larger than the $K = 2.29$ kJ m$^{-3}$ calculated for the FeSn$_2$ nanospheres. For equal nanoparticle dimensions, it is more difficult to reorient the entire moment of an Fe$_{0.74}$Sn$_{0.26}$ nanoparticle than that of an FeSn$_2$ nanoparticle. The larger anisotropy of Fe$_{0.74}$Sn$_{0.26}$ that is inferred from this measurement likely reflects robust bonding along the $c$-axis but weaker $a-b$ plane bonding. We note that the values of the magnetocrystalline anisotropy constants of our samples are several magnitudes less than for FePt nanoparticles.

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Figure 3. The temperature dependencies of the zero field cooled (ZFC) and field cooled (FC) magnetizations in applied fields of 0.05 kOe for (a) Fe$_{0.74}$Sn$_5$ and (b) FeSn$_2$ nanospheres. The magnetic field dependencies of the magnetizations for (c) Fe$_{0.74}$Sn$_5$ and (d) FeSn$_2$ nanospheres, where the insets are expanded views of the same magnetizations but at lower fields. The high-temperature part of the ZFC magnetizations in an applied field of 1 kOe for (e) Fe$_{0.74}$Sn$_5$ and (f) FeSn$_2$ nanospheres, where the dashed lines indicate the melting points determined from DTA measurements.

higher temperatures becomes much weaker for FeSn$_2$ and Fe$_{0.74}$Sn$_5$ nanoparticles. This linear magnetization is found in many magnetic nanoparticle systems and is generally ascribed to uncompensated moments that cannot be saturated in field, located perhaps at the particle surface or at the core–shell interface. These uncompensated moments are presumably responsible for the large Curie tail that is evident in both the FC and ZFC $M(T)$ for Fe$_{0.74}$Sn$_5$ and more weakly in FeSn$_2$, where it is present only in the FC magnetization.

The observation of superparamagnetic behavior in both Fe$_{0.74}$Sn$_5$ and FeSn$_2$ nanoparticles is definitive proof that some part of each order at temperatures above 300 K, but it is not a priori evident what the nature of this order is in these multicomponent core–shell particles. For instance, surface atoms are responsible for the paramagnetic contribution in ferri- and ferromagnetic nanoparticles, while in antiferromagnetic nanoparticles, the surface atoms instead are the source of a nonlinear contribution to the magnetization due to a complex magnetic structure with an uneven number of sublattices. We have carried out measurements of the magnetization of the Fe$_{0.74}$Sn$_5$ and FeSn$_2$ nanoparticles above 300 K to search for the onset of long-ranged ferromagnetic or antiferromagnetic order. Since the compound has not been synthesized previously, we have no results from measurements on bulk FeSn$_2$ to constrain this search. DTA shows that the melting temperatures ($T_m$) of the two compounds are very similar, 776 ± 10 K for FeSn$_2$ and 790 ± 14 K for Fe$_{0.74}$Sn$_5$. Note that nanoparticles can agglomerate and grow together at temperatures below $T_m$.

The high-temperature magnetization has very similar properties in the two compounds (Figure 3e and f). It decreases slowly as the temperature is raised above 300 K, and a sharp peak is seen in Fe$_{0.74}$Sn$_5$ at $\sim$700 K. We associate this peak with the onset of antiferromagnetic order in the Fe$_{0.74}$Sn$_5$ cores. There is no overt sign of magnetic order in $M(T)$ for FeSn$_2$, except several slope changes between 450 to 700 K. Since magnetic blocking is observed in FeSn$_2$ and a saturating component of the magnetization is evident at temperatures as large as 300 K, we conclude that FeSn$_2$ orders antiferromagnetically above 300 K. Our measurements have revealed that Fe$_{0.74}$Sn$_5$ and FeSn$_2$ are mostly likely antiferromagnetic, but that the formation of a moment bearing component via moment canting, sublattice formation, or uncompensated surface moments provides coupling to the external field. We will see below that the theoretical calculations support the presence of antiferromagnetic order in the crystal structures of both FeSn$_2$ and FeSn$_3$.

First-principles density functional theory calculations were carried out to gain additional insight into the magnetic characters of FeSn$_2$ and Fe$_{0.74}$Sn$_5$. Since our nanoparticles are relatively large, we assume that finite-size effects will provide only small corrections to the bulk electronic structures but not dramatically change the magnetic ground state. We thus calculated the total energy of various magnetic configurations (cf. Table 2 and Figure 4) within the local spin density approximation plus Hubbard U (LSDA+U) approach for three reasonable sets of parameters ($U$, $J$) and found consistent qualitative trends for all the parameters sets.

Interestingly, our results in Table 2 show that the lowest energy states in the bulk FeSn$_2$ and FeSn$_3$ are with antiferromagnetic correlation in the plane ($a$–$b$ plane). FeSn$_2$ is found to have ferromagnetic correlations out of the plane (along $c$-axis), as previously observed experimentally. On the other hand, FeSn$_3$ prefers antiferromagnetic correlation out of the plane. Please see Figure 4c and e for the lowest energy states of FeSn$_4$ and FeSn$_3$, respectively. Also, FeSn$_3$ appears to have much weaker in-plane coupling from the small energy difference between the second and the fourth rows in Table 2. This can be easily understood from the large in-plane Fe–Fe distance in the quasi-1D structure. In other words, for FeSn$_3$, the magnetic structure is hard along $c$-axis and soft in $a$–$b$ plane. This is also reminiscent of the hard (i.e., less expansive) $c$-axis and soft $a$–$b$ plane during thermal expansion.

These theoretical results support our experimental observations. First, existing experiments on bulk FeSn$_2$ indicate that it is a canted antiferromagnet, and as we explain above, this is likely for the nanoscale version of FeSn$_2$ studied here as well. While there are no measurements of the magnetization of bulk FeSn$_2$, both our theoretical results and measurements on nanoscaled Fe$_{0.74}$Sn$_5$ support the conclusion that it is also a canted antiferromagnet. Moreover, the relatively weak in-plane coupling of FeSn$_2$ would lead to stronger in-plane spin fluctuations and consequently accounts for the weaker coercive field, larger observed fluctuation.
Table 2. For FeSn$_2$ and FeSn$_5$, Calculated Electronic Total Energy of Various Magnetic Configurations and ($U, J$) in the Scheme of DFT with LSDA+$U$

<table>
<thead>
<tr>
<th>magnetic configurations</th>
<th>electronic total energy, meV</th>
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<tr>
<td>lowest energy state</td>
<td>$U = 2$ eV, $J = 0.7$ eV</td>
</tr>
<tr>
<td>FeSn$_2$</td>
<td>FM in plane (a–b plane)</td>
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<tr>
<td></td>
<td>−53.591</td>
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<tr>
<td>FeSn$_5$</td>
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<td>−226.706</td>
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* All the energy values are relative to the non-magnetic configuration. One ferromagnetic and three mostly possible antiferromagnetic orders are chosen in our modeling. FM and AF in this table stand for ferromagnetic and antiferromagnetic, respectively.

Figure 4. Schematic diagrams of the antiferromagnetic configurations considered in Table 2. Figures (a–c) correspond to the 2nd to 4th rows in Table 2, and (d–f) correspond to the 6th to 8th rows. Only Fe atoms are shown here for simplicity. The box in each diagram is not exactly the chemical unit cell but is meant for better visualization. The vertical axis is the c-axis in their tetragonal lattice. Red and blue Fe atoms carry opposite spins.

Figure 5. Reversible capacities of Fe$_{0.74}$Sn$_5$ and FeSn$_2$ nanospheres as anodes in Li ion batteries.

moments, the coexistence of weak ferromagnetic hysteresis and antiferromagnetism, and the disappearance of the nonlinearity in the $M$–$H$ curve at much lower temperatures.

In our current theoretical scheme, we cannot exclude that the almost one-quarter iron vacancies might change magnetic correlation especially along c-axis (although, the additional electronic scattering resulting from the Fe vacancy is unlikely to favor ferromagnetic coupling). The weaker antiferromagnetic coupling in the a–b plane should be less sensitive to Fe content. More sophisticated theoretical treatment of the vacancies is now on going.

We also studied the cell performance of Fe$_{0.74}$Sn$_5$ nanospheres as an anode in Li-ion batteries. Its 929 mAh g$^{-1}$ theoretical capacity is the highest to date for the reported M (electrochemically inactive)–Sn intermetallic anodes (the next one is the 852 mAh g$^{-1}$ for CoSn$_3$), and is higher than most of the reported systems, where M is active (with exception of Mg$_2$Sn where Mg can form the solid solution with Li in Mg atomic percentage between 0 and $\sim$70%). NaSn$_6$ (962 mAh g$^{-1}$, inactive), K$_4$Sn$_23$ (940 mAh g$^{-1}$, inactive), and CaSn$_4$ (1028 mAh g$^{-1}$, active) have higher theoretical capacities, but their application as anode materials has not yet been verified.

Because of the low (yet sufficient) Fe concentration, a higher capacity of Fe$_{0.74}$Sn$_5$ has been achieved as compared with that of FeSn$_2$. As shown in Figure 5, the value stabilizes at around 750 mAh g$^{-1}$ for 15 cycles, while it is around 500 mAh g$^{-1}$ in the case of FeSn$_2$. The initial Coulomb efficiency also increases to 72% for Fe$_{0.74}$Sn$_5$ from 50% for FeSn$_2$. If we consider the suppression of capacity due to the presence of surface oxidized layer (EDS analysis indicates that the Sn mass percentages in the nanospheres are 89.1% and 75.2% for Fe$_{0.74}$Sn$_5$ and FeSn$_2$, respectively) and assume that Sn in this layer is active$^2$, then the theoretical capacities of these nanospheres become respective 886 mAh g$^{-1}$ (Fe$_{0.74}$Sn$_5$) and 747 mAh g$^{-1}$ (FeSn$_2$). Therefore, Fe$_{0.74}$Sn$_5$ nanospheres can achieve 85% of its theoretical capacity, but FeSn$_2$ can realize only 67%.

**CONCLUSION**

In conclusion, we synthesized nanospheres of a new intermetallic FeSn$_5$ phase by converting preformed Sn nanosphere templates. The nanospheres show a single crystal Fe$_{0.74}$Sn$_5$/amorphous Fe–Sn–O core–shell structure. FeSn$_5$ has an interesting quasi-1D crystal structure and may serve as one intermediate
phase between Sn and FeSn2. The thermal expansion of the lattice constants of Fe0.74Sn5 nanospheres is highly anisotropic. The magnetization measurements indicated that the blocking temperature (T_B) of the nanospheres is as high as 300 K, due to their high magnetocrystalline anisotropy constants. Moreover, magnetization measurements suggest that the magnetic state of the Fe0.74Sn5 nanospheres is best described as a canted antiferromagnet. The thermal expansion of the Fe0.74Sn5 nanospheres is best described as a canted antiferromagnet both in a-b plane and along c-axis and confirmed that FeSn3 has rather weak in-plane magnetic coupling. Both the expansion anisotropy and the magnetic properties are attributed to the FeSn3 quasi-1D structure with the strong c-axis and weak a-b plane bondings. Moreover, lowering the Fe concentration is effective in enhancing the cell performance of Fe-Sn intermetallic anodes in Li ion batteries.

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REFERENCES