A lithiation/delithiation mechanism of monodispersed MSn₅ (M = Fe, Co and FeCo) nanospheres†

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A designed Sn based alloy host as a higher capacity and longer cycle life next generation lithium-ion battery, consisting of monodisperse nanospheres of intermetallic MSn₅ (M = Fe, Co and FeCo) phases was synthesized by a nanocrystal conversion chemistry method using preformed Sn nanospheres as templates. The same crystal structure, identical particle surface morphology and the similar particle size distribution (30–50 nm) of these intermetallic MSn₅ (M = Fe, Co and FeCo) phases are ideal for comparison of the electrochemical performance, reaction mechanism, thermodynamics and kinetics during lithiation/delithiation. Importantly, MSn₅ (M = Fe, Co and FeCo) phases with defect structures Fe₀.₇₄Sn₅, Co₀.₈₃Sn₅ and Fe₀.₃₅Co₀.₃₅Sn₅ exhibit the highest theoretical capacity of >917 mA h g⁻¹ among the reported M–Sn (M is electro-chemically inactive) based intermetallic anodes. The ex situ XRD and XAFS illustrate the complete reversibility of MSn₅ (M = Fe, Co and FeCo) phases during lithium insertion/extraction for the first cycle. The Fe₀.₃₅Co₀.₃₅Sn₅ anode can take advantage of both high capacity of Fe₀.₇₄Sn₅ and long cycle life of Co₀.₈₃Sn₅, providing 736 mA h g⁻¹ and maintaining 92.7% of initial capacity after 100 cycles with an average capacity loss of only 0.07% per cycle. The excellent electrochemical performance of the Fe₀.₃₅Co₀.₃₅Sn₅ system is attributed to higher reversibility, lower reaction resistance. This work provides a novel insight toward designing and exploring an optimal Sn based alloy anode for next generation Li-ion batteries.

1. Introduction

Rechargeable lithium-ion batteries have attracted much attention because they have been widely used in mobile communication devices, portable electronic devices, and may play a critical role in emerging electric vehicles (EV) and large-scale renewable energy storage. To satisfy the high energy requirement of EV, substantial improvements in energy density of current Li-ion batteries are required. One of the promising electrode materials that can potentially meet these requirements is M (electrochemically inactive)–Sn intermetallic materials, which have the advantage of high theoretical mass capacity and volumetric capacity over the state-of-the-art graphite anodes (372 mA h g⁻¹ and 883 mA h cm⁻³). Most importantly, the beneficial role of M is to offer a “buffer zone” to compensate the volume fluctuation during lithiation/delithiation, which avoids the pulverization or aggregation of the Sn particles, stabilizes the solid electrolyte interphase (SEI) and thus improves the cycling stability.

Among M–Sn intermetallics, a considerable effort has been devoted to develop high capacity Fe–Sn, Co–Sn, and Fe–Co–Sn systems in academia and industry. Recently, our research group has synthesized nonequilibrium new intermetallic compounds, Fe₀.₇₄Sn₅ and Co₀.₈₃Sn₅ with theoretical capacities of 929 and 918 mA h g⁻¹ respectively, which are different from Mike Thackeray’s patent and have the highest capacities to date among the reported Sn based binary intermetallic anodes. Although Fe₀.₇₄Sn₅ and Co₀.₈₃Sn₅ share the same crystal structure, their electrochemical performance is quite different. Fe₀.₇₄Sn₅ has a high capacity of 750 mA h g⁻¹, but poor cycle life, while Co₀.₈₃Sn₅ has long cycling stability but low capacity (500 mA h g⁻¹). Due to the lack of knowledge on the lithiation/delithiation mechanism of Fe₀.₇₄Sn₅ and Co₀.₈₃Sn₅, the difference in electrochemical performance between them and the effect of M (Fe, Co) element in the alloy are not fully understood. Since the electrochemical performance of MSn₅ (M = Fe, Co and FeCo) is very sensitive to particle size and the crystal structure,
the comparison study on the electrochemical performance and the reaction mechanism of MSn₅ (M = Fe, Co and FeCo) should be conducted using MSn₅ with the identical particle size, structure and morphology. However, it is very difficult to synthesize FeSn₅, CoSn₅ and Fe₀.₅Co₀.₅Sn₅ intermetallic phases with an identical structure, composition and particle size using traditional synthesis techniques (such as chemical vapor deposition, electroplating, ball milling, carbothermal reduction and arc-melting) due to the large difference in melting points between Sn, Co and Fe. Nanocrystal conversion chemistry promotes compositional and morphological attributes on final products, which is a powerful approach for synthesis of homogeneous nano-sized materials with well-defined shapes and structure.

Since MSn₅ (M = Fe, Co and FeCo) phases with defect structures Fe₀.₇₄Sn₅, Co₀.₈₃Sn₅ and Fe₀.₃₅Co₀.₃₅Sn₅ are currently absent in the equilibrium Fe–Sn, Co–Sn, and Fe–Co–Sn phase diagram and have the highest theoretical capacities of 929, 918, and 931 mA h g⁻¹, respectively, among the reported M (M is electrochemically inactive)–Sn intermetallic anodes in this work, we have successfully synthesized FeSn₅, CoSn₅ and Fe₀.₅Co₀.₅Sn₅ intermetallic phases with the same crystal structure, identical particle surface morphology and the similar particle distribution (30–50 nm) from the same Sn nanoparticle templates using a unique nanocrystal conversion chemistry method. Moreover, we systemically investigated the lithiation/delithiation reaction mechanism of MSn₅ (M = Fe, Co and FeCo), and compared the reaction thermodynamics, reaction kinetics and electrochemical performance among these three compounds. The insight obtained from this work also provides guidance for the design of other Sn-based compounds for next generation Li-ion batteries.

2. Experimental section

2.1 Chemicals and synthesis

Tin(II) chloride (SnCl₂, anhydrous, 99%, Alfa), iron(III) chloride (FeCl₃, anhydrous reagent grade, 97%, Aldrich), cobalt(II) chloride hexahydrate (CoCl₂–6H₂O, 99.9% metal basis, Alfa), polyvinylpyrrolidone (PVP, MW = 360 000, Aldrich), poly(2-ethyl-2-oxazoline) (PEtOx, MW = 50 000, Alfa), tetraethylene glycol (TEG, 99%, Alfa) and sodium borohydride (NaBH₄, 98%, Alfa) were used as starting materials.

The preparation of Fe₀.₅Co₀.₅Sn₅ nanospheres was carried out under an argon atmosphere via a Schlenk line following the procedure developed by Chou et al. First, 30–50 nm Sn nanoparticles were synthesized in a three necked flask and used them as a template to obtain Fe₀.₅Co₀.₅Sn₅. As surface stabilizers, 1.57 g of PVP and 0.66 g of PEtOx were added into 35 mL of TEG. After the mixture was totally dissolved in TEG via vigorous stirring at the temperature of 170 °C, a 0.3 g of SnCl₂ was added into 4 mL of PVP–PEtOx–TEG. After dropping of 0.6 g NaBH₄ as a reducing agent for 15 min, tin nanoparticles were precipitated turning the suspension solutions from colorless to turn black. To synthesize Fe₀.₅Co₀.₅Sn₅ nanospheres from the tin nanoparticle template, the temperature of the suspensions was increased to 200 °C under argon, FeCl₃ and CoCl₂ solution (0.01930 g of FeCl₃ and 0.0094 g of CoCl₂–6H₂O in 8 mL of TEG) was injected into the tin nanosphere suspension drop by drop until the molar ratio of (Fe + Co) to (Sn) reach 0.1. After 1.5 hours at 200 °C, the samples were cooled down to room temperature, Fe₀.₅Co₀.₅Sn₅ nanospheres were harvested by centrifugation and washed with ethanol several times before drying under vacuum overnight. The FeSn₅ and CoSn₅ nanospheres were synthesized through a similar conversion chemistry process.

2.2 Structural characterization

The synchrotron powder X-ray diffraction (XRD) pattern were performed using beamline BL14B1 (λ = 1.2398 Å) of the Shanghai Synchrotron Radiation Facility (SSRF) with a Naïl point detector at a step rate of 0.02 degrees. The XRD patterns of the materials were analyzed using the software Jade 6.5 (Materials Data Incorporated), Jana 2006 (Petricek, V., Dusek, M., and Palatinus, L., 2006), and Superflip. The lattice parameters were obtained by fitting the XRD data using software TOPAS-Academic V4.1 (Coelho Software, Brisbane, 2007). The Sn K-edge XAFS spectra were collected in transmission mode at beamline BL14W using a Si (311) detector. The reference spectrum of the Sn element for the energy calibration was simultaneously collected with the corresponding Sn metal foils. The samples were characterized by scanning electron microscopy (FESEM and HR-SEM, Hitachi, S-4800) using an operating voltage of 8 kV and transmission electron microscopy (TEM, Tecnai F20 and JEOL 2100) with an energy dispersive X-ray spectroscopy (EDS) detector.

2.3 Electrochemical measurements

The working electrode films were composed of the active materials, carbon black and a binder with the weight composition of 80 : 10 : 10 on copper foils. The active material loading weight was ~0.5 mg cm⁻² and the films were dried in a vacuum oven at 110 °C overnight. Lithium foil served as both the counter and reference electrodes under ambient temperature. Carbon black (Super P) is from TIMCAL and the sodium carboxymethyl cellulose (CMC, MW ~ 90 000) binder is from Alfa Aldrich. The Celgard 2320 membrane was used as the separator and the Li metal as a counter and a reference electrode. 1.0 M solution of LiPF₆ in ethylene carbonate/dimethyl carbonate/ethyl methyl carbonate EC/DMC/EMC, 1 : 1 : 1 in volume (CAPCHEM) was used as the electrolyte solution. The 2032-type coin cells were fabricated in an argon-filled glove box with both moisture and oxygen contents below 0.1 ppm. All galvanostatic charging-discharging and GITT tests were conducted on a multichannel battery-testing system (BT2000, Arbin Instruments, USA) with the voltage range of 0.01–1.5 V at room temperature at the current rate of C/20 (i.e., the time for full charge or discharge of the theoretical capacity was 20 h). Cyclic voltammetry (CV) between 0.01 and 2 V at a scan rate of 0.02 mV s⁻¹ and EIS of anodes were recorded using an electrochemical workstation (1470E, UK).
3. Results and discussion

3.1 Material synthesis and characterizations

Monodisperse FeSn₅, Fe₀.₅Co₀.₅Sn₅, and CoSn₅ nanospheres were obtained by using Sn nanospheres as templates. The formation mechanism of MSn₅ (M = Fe, Co and FeCo) nanospheres is shown in Fig. 1a, and illustrated in detail in Experimental section. The similar particle distribution (30–50 nm) of these three compounds is demonstrated using electron microscope images in Fig. 1b, e and h. Moreover, the high-resolution transmission electron microscopy (HRTEM) images revealed that all FeSn₅, Fe₀.₅Co₀.₅Sn₅, and CoSn₅ nanospheres had a core–shell structure consisting of a ~30 nm single-crystalline intermetallic core and a ~4 nm amorphous oxide shell (Fig. 1c, f and i). The STEM EDS elemental mapping images in Fig. 1d, g and j clearly demonstrated that transition metals (Fe or Co) and Sn in the nanospheres were homogeneously distributed. Moreover, the ratios of Sn to transition metals are about 7 : 1, 7 : 1, and 6 : 1 for the Sn/Fe, Sn/Fe + Co and Sn/Co respectively as evidenced by transmission electron microscopy energy dispersive X-ray spectroscopy (TEM-EDS). The ratio deviation from 5 : 1 in MSn₅ indicated the existence of Co/Fe vacancies in FeSn₅, Fe₀.₅Co₀.₅Sn₅, and CoSn₅ phases, which confirm that nonstoichiometry always existed in alloy materials.

Since MSn₅ did not exist in the equilibrium diagram, we characterized the detailed structures of three MSn₅ compounds using synchrotron powder X-ray diffraction (XRD) patterns (Fig. 2a). The crystal structures including refined lattice parameters, thermal factors, atomic coordinates, occupancies, d spacing, and relative intensity were resolved by the charge-flipping method. The FeSn₅, Fe₀.₅Co₀.₅Sn₅, and CoSn₅ nanospheres from the β-Sn nanosphere template were chemically pure with a highly crystalline tetragonal phase in the P4/mcc space group. With increase in the proportion of Fe from CoSn₅, Fe₀.₅Co₀.₅Sn₅, to FeSn₅, a and b axes were slightly reduced (summarized in Table S1†). Meanwhile, the lattice parameter c was elongated by 1.68% in comparison with the original phase due to the volume expansion from phase CoSn₅ (278.8 Å³) to FeSn₅ (281.5 Å³) because the crystal radius of Fe is a little larger than that of Co. The refine analysis demonstrated that the Fe

![Fig. 1](image-url)
and Co atoms partially occupied the 2c sites in FeSn$_5$, Fe$_{0.5}$Co$_{0.5}$Sn$_5$, and CoSn$_5$ phases, revealing the existence of vacancies, which were also evidenced by TEM-EDS. Accordingly, the real compositions of these nanospheres are Fe$_{0.74}$Sn$_5$, Fe$_{0.35}$Co$_{0.35}$Sn$_5$, and Co$_{0.83}$Sn$_5$. Fig. 2b shows a representative set of Fourier transforms (FTs) of the synchrotron X-ray absorption fine structure (XAFS) spectra at the Sn K-edge, which confirmed that Fe$_{0.74}$Sn$_5$, Fe$_{0.35}$Co$_{0.35}$Sn$_5$, and Co$_{0.83}$Sn$_5$ had the same MSn$_5$ structure. The Sn atoms in these samples formed the first coordination shell, with a Sn─Fe (Co) bond length, and Sn and Sn atoms formed the second coordination shell similar to that in Sn foil.

### 3.2 Electrochemical performance of FeSn$_5$, Fe$_{0.5}$Co$_{0.5}$Sn$_5$, and CoSn$_5$ nanospheres

As far as we know, intermetallic FeSn$_5$, CoSn$_5$, and Fe$_{0.5}$Co$_{0.5}$Sn$_5$ phases with the defect structures (Fe$_{0.74}$Sn$_5$, Co$_{0.83}$Sn$_5$ and Fe$_{0.35}$Co$_{0.15}$Sn$_5$) have the highest theoretical capacities of 929, 918 and 931 mA h g$^{-1}$ among the reported M─Sn (M is electrochemically inactive) binary and ternary intermetallic anodes.$^{21}$ The charge–discharge behaviors of the three MSn$_5$ anodes at 0.05 C between 0.05 V and 1.5 V in the 1, 2 and 5 cycles are shown in Fig. 3a–c. All three MSn$_5$ cathodes show a similar lithiation/delithiation behavior. The plateaus at 0.7 V and 1.3–1.7 V in the first lithiation were associated with the reduction of the amorphous Sn oxide shell and electrolyte decomposition on the surface of the nanospheres, resulting in the irreversible discharge capacity.$^{40,41}$ In the following lithiation cycles, the voltage plateaus at 1.3–1.7 and at 0.7 V dispersed and the voltage profile shifted to left. The delithiation profiles mainly exhibited 2 plateaus at $\sim$0.5 V and $\sim$0.65 V, as well as a slanted plateau above 0.75 V. The detailed lithiation/delithiation behavior of FeSn$_5$, Fe$_{0.5}$Co$_{0.5}$Sn$_5$, and CoSn$_5$ nanospheres was investigated with cyclic voltammetry (CV) measurements using...
lithium as the reference/counter electrode. The CV curves of three MSn5 anodes in the first five cycles measured at a scan rate of 0.02 mV s⁻¹ between 0.01 V and 2.0 V are shown in Fig. S1. During the first lithiation, there were two broad cathodic peaks at around 1.7 V and 1.3 V which could be attributed to the formation of solid–electrolyte interface (SEI) films and/or the irreversible lithiation of the surface oxidized layer, since these two peaks disappeared in the following lithiation. A broad-peak centered at 0.3 V and a small-peak centered at 0.55 V were associated with the phase change in the alloy process. In the delithiation process, three broad oxidation peaks at around 0.47 V, 0.63 V and 0.75 V corresponded to the reversible phase change in the de-alloying process. The CV curves were in good agreement with the charge–discharge curves.

Fig. 3d illustrates the cycling stability of FeSn5, Fe₀.₅Co₀.₅Sn5, and CoSn5 nanospheres upon cycling at a 0.05 C rate. Fe₀.₇₄Sn5 could deliver a high capacity of ~750 mA h g⁻¹, but the capacity quickly dropped after 15 cycles. On the other hand, Co₀.₈₃Sn5 nanospheres had only a capacity of 500 mA h g⁻¹ but it could maintain a similar capacity for 100 cycles. The Fe₀.₃₅Co₀.₃₅Sn5 had both high capacity as Fe₀.₇₄Sn5 and long cycling stability as Co₀.₈₃Sn5. The capacity of Fe₀.₃₅Co₀.₃₅Sn5 increased with initial cycles to 736 mA h g⁻¹ at cycle 25, and maintained 92.7% of the initial capacity after 100 cycles. The average capacity loss was only 0.07% per cycle. The increase in cycle capacity early in the cycling of Fe₀.₃₅Co₀.₃₅Sn5 may be due to: (i) the formation and stabilization of the SEI; (ii) an activation process of the electrode (especially for high capacity electrodes with large volume changes) in initial few lithium uptake/removal cycles; (iii) the improvement of Li insertion/extraction kinetics. Given the almost identical crystal structure and nanostructure, this significant difference in cell performance could be closely tied to the difference in composition (i.e., Fe and Co). Based on these findings, the presence of Fe could lead to high capacity, while the presence of Co resulted in superior stability.

Further, the lithiation and delithiation mechanisms of three MSn5 compounds were investigated using ex situ X-ray diffraction (XRD) and X-ray absorption fine structure (XAFS). The phase evolution at different lithiation and delithiation levels marked in the first charge–discharge curves (a–g, a₀–g₀ and a₀₀–g₀₀ in Figs. 4a, d and g) was identified using ex situ XRD and XAFS. The ex situ XRD patterns at marked lithiation/delithiation levels in Fig. 4a, d and g are shown in Fig. 4b, e and h respectively. The XAFS at the corresponding lithiation/delithiation levels are shown in Fig. 4c, f and i. At open circuit potential (a, a₀, a₁), XRD patterns could be indexed to the tetragonal structure of FeSn5, Fe₀.₅Co₀.₅Sn5 and CoSn5 in the P4/mcc space group. The Sn amorphous oxides layer could not...
be detected by XRD. During initial lithiation from open circuit potential to 0.7 V, no obvious change in XRD patterns could be observed (a–c, a′–c′, a″–c″), suggesting that the potential plateau may be associated with the reduction of the amorphous Sn oxide shell and the formation of the solid electrolyte interphase on the surface of the MSn₅ nanospheres. Reduction of Sn oxide and the formation of the SEI at a potential above 0.7 V had been reported.  

During lithiation from 0.7 to 0.3 V (c and d, c′ and d′, c″ and d″), XRD remained unchanged but slightly shifted, demonstrating the potential formation of an intermediate solid solution of LiₓMₓSn₅ (M = Fe, Co and FeCo, voltage ≥ 0.3 V). With further lithiation from 0.3 V to 0.01 V (d and e, d′ and e′, d″ and e″), transition metals were extruded from MSn₅ compounds and Li with Sn yields a Li–Sn alloy phase. At the point of e (e′ or e″), the peaks of XRD patterns became very weak and almost not visible, which might be attributed to the complete decomposition of MSn₅ (M = Fe, Co and FeCo) phases to form amorphous or nano-sized Li–Sn alloys. The reversible reaction mechanisms during the first lithiation could be described as:

\[
x\text{Li} + M_y\text{Sn}_5 \rightarrow \text{Li}_xM_y\text{Sn}_5 \\
(M = \text{Fe, Co and FeCo}, 0.7–0.3 \text{ V}); \quad (1)
\]

\[
z\text{Li} + Li_xM_y\text{Sn}_5 \rightarrow Li_{x+z}\text{Sn}_5 \rightarrow yM \quad (x + z \leq 22, 0.3–0.01 \text{ V}); \quad (2)
\]

In the charge process, at the point of f, f′, and f″ (0.65 V), weaker XRD diffraction peaks of LiₓMₓSn₅ appeared again (especially in f′ and f″). On further delithiation to 1.5 V, the reformation of MSn₅ (M = Fe, Co and FeCo) peaks could be observed, which illustrated the high reversibility of lithiation/delithiation reaction. The reaction mechanisms during delithiation could be expressed as follows:

\[
\text{Li}_{x+z}\text{Sn}_5 \rightarrow x\text{Li} + Li_xM_y\text{Sn}_5 \\
(x + z \leq 22, \text{voltage} \geq 0.65 \text{ V}); \quad (3)
\]

\[
Li_xM_y\text{Sn}_5 \rightarrow x\text{Li} + M_y\text{Sn}_5 \\
(M = \text{Fe, Co and FeCo}, \text{voltage} \geq 1.5 \text{ V}); \quad (4)
\]

The lithiation/delithiation mechanisms of the FeSn₅, Fe₀.₅Co₀.₅Sn₅ and CoSn₅ nanospheres electrode proposed based on XRD are also supported by the Sn K-edge XAFS spectra taken during the first cycle at Li insertion to 0.01 V and Li removal to 1.5 V (Fig. 4c, f and i). Correspondingly, XAFS patterns at point e, e′, and e″ (0.01 V) could be associated with the formation of a Li–Sn alloy phase. Moreover, in the three electrodes, after the following full delithiation (g, g′, g″), the phase could be indexed to the original tetragonal structure FeSn₅, Fe₀.₅Co₀.₅Sn₅, and CoSn₅ in the P4/nm space group, illustrating the complete reversibility of these three MSn₅ compounds.

Due to the large volume change, the morphology of MSn₅ also changed with lithiation/delithiation cycles. The uneven distribution of FeSn₅ nanoparticles could be clearly observed (Fig. 5a) after the first cycle, which was caused from massive volume change in lithium insertion/extraction, while Fe₀.₅Co₀.₅Sn₅ and CoSn₅ could almost maintain the original morphology (Fig. 5c and e). Moreover, the 3–4 nm of the amorphous oxide shell on a single-crystalline intermetallic MSn₅ core became blurred or disappeared (Fig. 5b, d and f) after one cycle. These results showed the irreversible lithiation reaction of the amorphous Sn based oxide shell. The EDS spectrum (Fig. S2†) illustrates that the ratios of Sn/Fe, Sn/Fe + Co, and Sn/Co in FeSn₅, Fe₀.₅Co₀.₅Sn₅ and CoSn₅ nanocrystals were still maintained at 7 : 1, 7 : 1 and 6 : 1 after one charge–discharge cycle.

The structure and composition stability of the FeSn₅, CoSn₅ and Fe₀.₅Co₀.₅Sn₅ nanocrystals after extended 100 cycles were also analyzed. From the TEM images, the FeSn₅ anode material could still keep the morphology of nanocrystals; however, they had a wide range of size with tens to hundreds of nanometers (Fig. 6a). However, the morphology of the CoSn₅ anode significantly changed from the spherical to cubic structure (Fig. 6d). Fe₀.₅Co₀.₅Sn₅ nanocrystals had both the cubic structure and small sphere nanoparticles after 100 cycles (Fig. 6g). Selected-area electron diffraction (SAED) patterns of the three compounds demonstrate that both cubic and sphere particles
were in crystal structures (Fig. 6b, e and h). Further, the EDS image (Fig. 6c) shows that Fe and Sn elements in FeSn$_5$ nanoparticles were completely separated, and only Fe was found in the TEM investigated region (Fig. 6a). The separation of Fe from Sn and aggregation of Sn particles may result in quick capacity decline of FeSn$_5$ (Fig. 3d). In contrast, Sn/Co with the ratio close to 2 : 1–4 : 1 existed in CoSn$_5$ cubic particles (Fig. 6f). Similarly, all Fe, Co and Sn elements appeared in Fig. 6i where the cubic particle was a Co–Sn alloy (Fig. S3†) and small particles were Fe. These may be the reason why Fe$_{0.5}$Co$_{0.5}$Sn$_5$ could retain good cycling stability as CoSn$_5$ did.

To investigate the effect of transition metals on the thermodynamic property of MSn$_5$, the equilibrium potentials of three MSn$_5$ compounds at different delithiation levels were measured using the galvanostatic intermittent titration technique$^{47}$ by applying a current pulse of 20 mA g$^{-1}$ for 0.5 h and then relaxed for 4.0 h to reach quasi-equilibrium potentials. The delithiation equilibrium potentials of the FeSn$_5$, Fe$_{0.5}$Co$_{0.5}$Sn$_5$ and CoSn$_5$ compounds at different delithiation states (normalized capacity) are shown in Fig. 7a. As expected, the three compounds had a similar equilibrium potential due to the same crystal structure and similar properties of Co and Fe. Three potential plateaus were clearly observed in all three compounds corresponding to successive phase change during the dealloying process. The equilibrium potentials of MSn$_5$ showed three plateaus between 0.0 V and 0.7 V, which could be assigned to the delithiation of Li from Li$_x$Sn alloys and react with local M to form Li$_x$MSn$_5$ compounds. Further delithiation from 0.7 V to 1.2 V, the Li$_x$MSn$_5$ would change back to MSn$_5$. The equilibrium potential of three MSn$_5$ almost overlapped each other except for capacity at the second potential plateau at 0.65 V where CoSn$_5$ showed a slightly higher capacity than FeSn$_5$ and Fe$_{0.5}$Co$_{0.5}$Sn$_5$ lay between them.

The reaction resistances are determined by dividing over-potential with pulse current in GITT measurement. Fig. 7b shows the evolution of reaction resistance during lithiation/delithiation of three MSn$_5$ compounds and the corresponding GITT curves are shown in Fig. S4†. The reaction resistance of three compounds during charge and discharge also showed a similar trend. The reaction resistance decreased in the beginning of lithiation, then stabilized but periodically changed with successive phase transformation and finally decreased again towards the end. Periodical change in reaction resistance during the phase change was observed in graphite,$^{48}$ which was attributed to gradually increasing diffusion length in each phase transformation process. The decrease in reaction resistance in initial and final lithiation could be due to the volume expansion reducing the interfacial resistance and increasing the
conductivity of the compounds. In these three MSn5 compounds, CoSn5 showed the lowest lithiation reaction resistance, and FeSn5 had the highest lithiation reaction resistance and Fe0.5Co0.5Sn5 lay between them. The calculated resistances for Fe0.74Sn5 anode materials at 25%, 50% and 75% SOCs during lithiation were 4.5, 4.0 and 4.0 Ω g respectively and for Co0.83Sn5 nanospheres, corresponding resistances were 3.6, 2.8 and 2.8 Ω g at 25%, 50% and 75% SOCs. As compared, the reaction resistances of the Fe0.35Co0.35Sn5 system during lithiation were 4.0, 3.6 and 3.2 Ω g. During delithiation, the reaction resistances of three compounds were similar. They increased in the beginning, stabilized afterwards and spiked towards the end.

Since the electrochemical impedance spectroscopy (EIS) could provide individual reaction resistances in the total reaction resistance determined by GITT, EIS was applied to these three compounds after being discharged to 0.3 V at 20 mA g\(^{-1}\) in the 5th cycle and being relaxed for 2 h shown in Fig. 7c. The EIS consisted of a depressed semicircle in the high frequency and slop line in the low frequency region. The high-frequency semicircle was related to interfacial (SEI and charge-transfer) resistances. The interface resistance of FeSn5 was larger than CoSn5 and Fe0.5Co0.5Sn5 lay between them, which were in good agreement with the total reaction resistance measured using GITT. Based on the GITT and EIS results, the FeSn5 anodes had higher reaction resistance, lower reversibility than CoSn5 and Fe0.5Co0.5Sn5 lay between them. The high reaction resistance and low reversibility of FeSn5 might lead to separation of Fe to Sn and Sn aggregation, thus quickly capacity decay. The Fe0.5Co0.5Sn5 system could effectively tune the reaction resistance and cycling stability, thus retained good cycling stability as CoSn5 did, with high specific capacity due to the presence of Fe.

4. Conclusions

In conclusion, intermetallic MSn5 (M = Fe, Co and FeCo) phases with the same structure, particle surface morphology and similar particle size distribution were synthesized using the nanocrystal conversion chemistry method for the comparison study on the mechanism of lithiation/delithiation, capacity decline and reaction kinetics. Fe0.74Sn5 has high capacity and Co0.83Sn5 has long cycling stability, while the Fe0.35Co0.35Sn5 anode can take advantage of both high capacity of Fe0.74Sn5 and long cycle life of Co0.83Sn5, providing 736 mA h g\(^{-1}\) and maintaining 92.7% of initial capacity after 100 cycles with an average capacity loss of only 0.07% per cycle. The ex situ XRD and XAFS indicate that MSn5 (M = Fe, Co and FeCo) phases are almost completely reversible for the first charge–discharge cycle. Upon further charging–discharging to 100 cycles, Sn in FeSn5 is gradually separated from Fe aggregated into large particles, resulting in quick capacity decay. However, Sn in CoSn5 still alloys with Co although the ratio of Sn to Co decreases from 6 : 1 to 4 : 1, demonstrating a high cycling stability. The exceptional electrochemical property of the Fe0.5Co0.5Sn5 electrode is attributed to coexistence of Fe and Co–Sn. In addition, Fe0.5Co0.5Sn5 also inherits the low reaction resistance of CoSn5. The thorough understanding on the origins of excellent electrochemical performance of intermetallic MSn5 (M = Fe, Co and FeCo) phases provides new opportunities for exploring other high capacity and long cycle life Sn-based anode materials.

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