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Electrophoretic Deposition of Tin Sulfide Nanocubes as High Performance Lithium-Ion Battery Anodes

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Abstract: Here we report the use of assemblies of SnS nanocubes as Lithium ion battery anodes. The particles are deposited in dense, conductive thin films with high gravimetric capacity using electrophoretic deposition, negating the requirement for binders or conductive additives. While SnS nanocube ensembles display both alloying and conversion modes, a significant benefit to capacity retention during long term cycling was observed by limiting the upper cutoff voltage to 1 V. In this alloying only regime that is more realistic for practical use, a discharge capacity of 552 mAh\(^{-1}\) was delivered with a loss of only 0.08 %/cycle observed over the 400 charge/discharge cycles. We further show that Li-S formation that occurs in the first lithiation acts as a buffer to the expansion and contraction though crucially this effect is optimized if this species is not cycled further (>1V). The SnS nanocube electrodes are tested in both half cell (HC) and full cell (FC) configurations and analyzed using ex-situ SEM and EIS analysis. Finally, the electrophoretic deposition of SnS nanocubes onto a 3D textured current collector is demonstrated to increase the mass loadings.

Introduction
The increasingly widespread usage of electric vehicles and the intermittency of renewable energy sources have driven a growing global requirement for more energy dense secondary batteries. This will necessitate the development of high-performance materials to replace the current commercially-used graphite anodes in Li-ion batteries (LIBs). Many Li alloying materials with higher theoretical gravimetric capacities than graphite (372 mAh/g), such as silicon (3.579 mAh/g), germanium (1.384 mAh/g) and tin (994 mAh/g), have been proposed; however problems with cost, scalability and/or long-term stability have thus far largely prevented commercialisation.\(^{[1-3,4]}\) Tin offers a significant enhancement of gravimetric capacity, combined with material safety and relative abundance.\(^{[5-7]}\) Furthermore, the slightly higher discharge voltage of tin (0.4 – 0.75 V) when compared with Si/Ge means that potential safety problems associated with electroplating of Li are avoided.\(^{[8]}\)

The major barrier preventing the widespread use of tin-based anodes is significant capacity loss experienced during extended cycling.\(^{[5,6]}\) This loss is largely attributed to the volume expansion and contraction during lithium insertion/de-insertion, causing pulverization/delamination and loss of electrical contact.\(^{[9]}\) Several approaches have been undertaken to overcome this deficiency, of which nanostructuring and the utilization of tin in sulfide form are discussed here. The use of nanostructured battery electrodes has been demonstrated to mitigate material pulverization through enhanced mechanical strain accommodation and the provision of void space to buffer expansion.\(^{[10,11]}\) Furthermore, the high surface area to volume ratio of nanostructures increases the number of electrochemically active sites while maintaining short Li\(^+\) diffusion lengths, enhancing rate capability and energy efficiency.\(^{[12]}\) Zero dimensional Sn nanocrystals have shown particular promise, combining the advantages of nanostructuring with relatively simple and scalable fabrication processes.\(^{[9]}\)

Typically, battery anodes consisting of films of nanoparticles are fabricated by the initial synthesis of nanoparticles followed by deposition onto a suitable current collector. A number of deposition methods are possible, including self-assembly\(^{[13,14]}\) and more notably EPD, in which nanoparticles dispersed in a solvent are driven to, and assembled at, the current collector by an applied electric field.\(^{[15-23]}\) Although not widely studied in nanostructured battery anode fabrication, this method is particularly advantageous in terms of enhanced film densification, conductivity and adhesion, while eliminating the need for binder and conductive additives which reduce active mass.\(^{[24-28]}\)

Crucially, EPD also enables uniform deposition onto 3-D current collectors,\(^{[21]}\) which provide reduced Li\(^+\) diffusion lengths,\(^{[29,30]}\) enhanced conductivity and better expansion accommodation than their 2-D counterparts.\(^{[31,32]}\)

The utilization of tin in sulfide form brings about a combined alloying and conversion lithiation process, involving the (usually poorly reversible)\(^{[33-35]}\) though not always\(^{[36]}\) formation of Li-S during the first lithiation. This Li-S then acts as a chemically inactive amorphous “buffer” during subsequent cycling of the alloying stage. The presence of this buffer has been reported to reduce pulverization during expansion/contraction,\(^{[35,37-42]}\) thereby increasing capacity retention during extended cycling. Indeed, the use of Sn in sulfide form has been demonstrated to significantly increase capacity retention during extended cycling.\(^{[39]}\) However, most reports perform extended cycling of tin sulfide over a wide voltage range e.g. 0 – 2.5/3 V vs Li/Li\(^+\)\(^{[33,36-43]}\) This typically achieves the highest possible initial capacity by including both processes,\(^{[44,47,48]}\) however given the irreversibility of the conversion process (Equation 1), the benefit of its inclusion is often short-lived or even limited to a single cycle.\(^{[54,49,50]}\) To our knowledge, no examinations into how cycling the Li-S material affects its role as a buffer have been performed.

Tin can be synthesized in both monosulfide (SnS) and disulfide (Sn\(_{2}\)S\(_{2}\)) forms.\(^{[50,42]}\) SnS maximizes the reversible portion of the capacity, and undergoes lithiation via the following two-step mechanism:

\[
\text{SnS} + 2 \text{Li} \rightarrow \text{Sn} + \text{Li}_2\text{S} \quad (\text{Eq 1}) \quad 353 \text{ mAh/g} \quad \text{(Conversion, > 1 V vs. Li/Li\(^+\))}
\]

\[
\text{Sn} + 4.4 \text{Li} \rightarrow \text{Li}_{4.4}\text{Sn} \quad (\text{Eq 2}) \quad 778 \text{ mAh/g} \quad \text{(Alloying, < 1 V vs. Li/Li\(^+\))}
\]

This results in a total Li storage capacity of 1,131 mAh/g, with 778 mAh/g generally considered reversible. An often overlooked concept is the varying energy densities that can be extracted from each process, given the wide voltage ranges over which they occur. Despite the significant contribution to gravimetric capacity that conversion processes can make, the characteristic high voltages (vs. Li/Li\(^+\)) reduce their contribution to energy density (when compared with low voltage alloying processes).

Furthermore, typical Li-ion batteries output at a high and narrower
voltage range, 3.5 – 3.7 V,[2,5,1] necessitating anodes which discharge at a low (< 1 V vs. Li/Li⁺) and relatively constant voltage. Here we report a facile, scalable method of fabricating dense thin films of SnS NCs. These films are assessed for their suitability as Li-ion battery anodes in both HC and FC configurations. In particular, we focus on optimization of cycling voltage range to maximize energy density and capacity retention during long term cycling, demonstrating the key role this understudied aspect can play. We design strategies to investigate the mechanism(s) of capacity loss of this material, involving electrochemical impedance spectroscopy (EIS), ex-situ SEM, and a new “intermittent cycling” test. Finally, we take advantage of the unique EPD method to construct 3D textured electrodes with high mass loadings with superior capacity retention profiles.

Results and Discussion
A schematic detailing the fabrication process of a SnS battery anode is shown in Figure 1a. Monodisperse SnS NCs were synthesized by hot injection using a previously reported protocol,[26] after which they were washed with anti-solvent to remove unwanted residual solvent/ligands. The NCs were then dispersed in a toluene bath, and electrophoretically deposited onto a Cu foil electrode using a 300 V electric field. Typically, uniform films of approximately 500 nm in thickness were formed. A cross sectional SEM image of such a film is shown in Figure 1b. XRD and Raman analysis (Figure S1) confirmed the presence of single-phase orthorhombic SnS.

![Figure 1a](image1a.png)
(a) Schematic detailing the battery electrode fabrication process. (b) Cross-sectional SEM image of electrophoretically deposited SnS film. (c) Cyclic voltammetry (sweep rate = 0.1 mV/s) of SnS anode in a half-cell configuration.

In order to both improve the conductivity and reduce the inactive mass of the electrode, the films on Cu foil were subjected to a facile ligand removal treatment,[26] involving a short exposure to a solution of ammonium sulfide in methanol. This replaced the long-chain organic ligands (hexadecylamine) with sulfide anions, thereby reducing interparticle distance and improving electrode conductivity.[24,25] Additionally, this treatment brought about the formation of a thin film of Cu₂S on the surface of the copper current collector.[26]

The electrochemical lithiation characteristics were assessed using cyclic voltammetry from 0 – 3 V in a HC. Cycles 1, 2 & 5 are shown in Figure 1c. Through comparison with previous reports for SnS,[35,40,45,54] (as well as analysis of SnS NC and Cu₂S films alone, Figure S2), the CV peaks were assigned to the relevant lithiation/delithiation processes. Cycle 1 cathodic (lithiation) peaks were attributed to conversion-mode lithiation of the Cu₂S film and SnS (1.65 V and 1.2 V), and the formation of a Li₂Sn alloy (0.2 V). Anodic (delithiation) peaks were observed at 0.55 V, 1.2 V, 1.9 V & 2.3 V, attributable to the de-alloying of LiSn and the reformation of SnS and Cu₂S. Lithiation processes can therefore be separated by type (alloying < 1 V and conversion > 1 V) and by material involved (Sn/SnS at 0 – 2 V, and Cu₂S at 1.5 – 3 V). This concept is shown graphically in Figure 1c. The peaks relating to the Cu₂S film significantly reduced in intensity over the first 5 cycles, confirming its rapidly diminishing impact on measured capacity.

The rapid reduction in intensity of CV peaks occurring> 1.5 V observed in Figure 1c, and the poor reversibility in the formation of Li₂S noted previously,[38,45,55] suggests a large variation in stability of the alloying and conversion processes. In order to maximize reversible capacity, and to better understand the relative contribution of the alloying and conversion processes, the cycling voltage range of HCs was varied to isolate and examine these processes individually. Here, three ranges are presented. Firstly, the 0 – 2 V range encompassed all SnS lithiation activity (alloying and conversion reactions, Eq 1 & Eq 2), however this also initially included some contribution from the Cu₂S film. Secondly, a 0 – 1.5 V range excluded all processes related to Cu₂S. Thirdly, limiting the range to 0 – 1 V constrained lithiation activity to the Li₃Sn alloying/de-alloying process alone (Eq 2, here Li₂S is formed during the first lithiation and remains in that form in subsequent cycles). This alloying process provides the majority of the capacity of SnS at a voltage that is most valuable for use as an anode material (i.e. close to 0 V vs. Li/Li⁺), both in terms of energy density and suitability for integration into existing battery technologies. Three equivalent HCs were cycled over these voltage ranges at 200 mA/g (Figure 2a).

![Figure 2a](image2a.png)
(a) Gravimetric discharge (delithiation) capacities of three identical SnS electrodes in HCs cycled over varying voltage ranges at 200 mA/g. DCPs for cells cycled in the range (b) 0 – 1 V, (c) 0 – 1.5 V, and (d) 0 – 2 V.
The initial discharge capacities varied as a function of the voltage window width (1.149 mAh/g vs. 657 mAh/g vs. 552 mAh/g for 0-2 V, 0-1.5 V and 0-1 V respectively), due to the inclusion of the extra delithiation process(es). However, this advantage quickly reversed during continued cycling, with the 0 – 1 V cell outperforming the 0 – 1.5 V and the 0 – 2 V cells by cycle 10 and 23 respectively. The observed capacity loss of the 0 – 2 V and 0 – 1.5 V cells was attributed to (a) the rapidly decaying contribution from the CuPcS film, and (b) poor reversibility in the formation of Li2S (Eq 1). It may have been expected that the capacities of the three cells would then converge as cycling continued, as the alloying process becomes the sole contributor to capacity. As a result, the subsequent superior capacity retention displayed by the 0 – 1 V cell (reaching a 40 % advantage over the 0 – 1.5 V cell after 250 cycles) is notable. This phenomenon suggests that not only is the conversion process poorly reversible (and not appropriate for use in existing battery technology due to an unsuitable discharge voltage), but also that cycling in this higher voltage region (> 1 V) further destabilizes the electrode itself, reducing the capacity retention capability of the low voltage alloying process.

The capacity retention trends can be understood more effectively by examining the DCPs, shown in Figures 2b, c & d for the 3 voltage ranges. The single de-alloying anodic peak visible in all 3 DCPs at approximately 0.5 V gradually evolved into 3 distinct peaks, indicating progression into a multistage de-alloying involving the formation of intermediate phases such as Li23Sn/Li15Sn (this may also be indicative of a lithiation-induced phase change in the Sn material). Notably, this progression was most rapid in the cells cycled over the wider ranges. The other anodic peaks (at 1.2 V and 1.9 V, corresponding to reformation of SnS and CuPcS) rapidly disappeared, eliminating the initial capacity advantage of the larger voltage ranges. A more detailed study of the DCPs for the 0 – 2 V cell (Figure S3) indicates that almost all processes > 1 V have ceased by cycle 20, indicating that some reversibility in the conversion processes extends to this number of cycles. It is important to note that the benefit of the narrower voltage range to capacity retention was not simply a consequence of the initially lower level of expansion/contraction experienced by the 0 – 1 V cell (due to its initially lower capacity). This was demonstrated by fabrication of another HC in which the voltage range was further constrained 0 - 0.75 V. This cell experienced an even lower level of contraction during delithiation, however no further benefit to capacity retention was observed (Figure S4). Rather the exclusion of the conversion processes involving the Li2S buffer was the key differentiating factor. It seems likely that an optimum morphology of this material for high capacity retention is established after the first lithiation and associated Li2S formation, and that cycling of the conversion process beyond this point brings about undesirable morphological evolution. While the buffer role played by Li2S has been well established, little study has focused on the effect of its formation and deformation (during the initial stage of partial reversibility) on overall electrode performance. This implies that despite the high initial capacity of the wider voltage ranges, it was in fact disadvantageous to include them in long term cycling. It is important to note that the majority of studies to date of this and similar materials that combine alloying and conversion processes (SnSx, ZnS, GeS, AlSx) have only tested over wide voltage ranges, and may therefore be underestimating the capacity retention of these materials by negatively impacting the more stable alloying process. In order to demonstrate the viability of this processing technique to form dense, conductive films, the rate capability was examined by cycling a HC at rates of 0.2, 0.5, 1, 2, 5 & 10 A/g for 5 cycles each, followed by a further 5 cycles at 0.2 A/g (Figure 3a). The electrode maintained a relatively high capacity of 402 mAh/g at a rate 2 A/g, however cycling at higher rates led to more severe reduction in capacity. This did not appear to damage the electrode in any way, however, as evidenced by the capacity recovery to 541 mAh/g when the rate was returned to 0.2 A/g. To more fully assess the materials suitability for integration into existing battery technologies, an electrode was tested in a FC with a LCO cathode. A voltage range of 3.9 to 3.0 V was chosen as a voltage output of > 3 V is typical of commercial secondary batteries. The capacity during extended cycling is shown in Figure 3b (see Figure S5 for energy density). The superior initial capacity of this cell (622 mAh/g) when compared with the equivalent HC may be indicative of superior Li extraction from/insertion into LCO. Additionally, the actual voltage range experienced by the SnS electrode is more difficult to control in a FC (no reference electrode was present), so it possible that higher voltage processes were making a contribution to the capacity in the first few cycles. This cell followed a capacity profile similar to that of the HC cycled between 0 – 1 V, however after approx. 300 cycles the decay rate significantly increased. This may reflect the limited cyclable Li available in this configuration, as well as any additionally capacity loss brought about by degradation of the LCO cathode. The coulombic efficiency for the test is provided in Figure S6.

It is important to differentiate between degradation mechanisms associated with repeated cycling (e.g. pulverization, loss of electrical contact) and those associated with storage/time (e.g. SEI formation, electrolyte leakage). To investigate this, we compared two equivalent HCs, one (Cell A) cycled in the standard manner and the other (Cell B) which undergoes a 10 hour rest period at approximately 1 V (open circuit) after every cycle. Figure 4a shows the voltage profiles of these two cells, while the capacities during extended cycling are shown both as a function of cycle number (Figure 4b) and total time since fabrication.
Two distinct stages can be observed in the capacity retention trend of Cell B in Figure 4b. Firstly, an increased rate of capacity loss was observed over the first 50 cycles when compared with the Cell A (0.47 %/cycle vs. 0.25 %/cycle, respectively), suggesting the existence of capacity draining chemical interactions between electrolyte and anode while stored at open circuit. This extra capacity loss was 7 % at cycle 50, at which point Cells A & B were 269 and 725 hours old, respectively. Subsequently, the capacity of Cell B was quite stable over cycles 50 – 100, undergoing little capacity loss, whereas Cell A continued to decay at 0.075 %/cycle over the same period. This can be interpreted as Cell A “catching up” and completing its time dependent degradation. Conversely, when the capacities were compared with respect to time since fabrication (Figure 4c), they match quite well up to 1,000 hours. Beyond this point, Cell A degrades more rapidly, indicating the dominance of cycling related decay during this later stage. By 1,250 hours, an extra cycling-related capacity loss of 5 % was observed, at which point cells A and B had undergone 268 and 87 cycles, respectively. This indicates that capacity fade mechanisms are initially largely time-dependent (anode/electrolyte interactions e.g. SEI formation), but that cycling (morphology evolution, pulverization) subsequently becomes the dominant factor.

The mechanisms behind capacity loss was further analyzed by examining the evolution in electrode material morphology. An ex-situ SEM study was undertaken on electrodes in HCs cycled at 200 mA/g in the range 0 – 1 V vs. Li/Li⁺. Figure 5 shows top-down SEM images of SnS films pre-cycling (Figure 5a), cycled for 10 (Figure 5b and 5c) and 100 (Figure 5d and 5e) cycles, before and after the solid electrolyte interphase (SEI) was removed by immersion in acetic acid. Cracks in the layer formed during observation (caused by the effect of the electron beam on the SEI layer) enabled observation of the layer underneath (Figure 5b and 5d). After 10 cycles, the SEI appeared largely as a film completely covering the intact SnS nanocrystals beneath (i.e. the SEI had not yet penetrated into the SnS layer). The morphology at this point was similar to the SEI provides mechanical stability to the active material, while parasitic Li consumption associated with its formation was minimized. Additionally, the nanoporosity and surface area of the active material is maintained (Figure 5c). However, after 100 cycles, no discernible layer separation between SEI and active material was evident (Figure 5d), and active material porosity had been significantly reduced (Figure 5e). It appears that this gradual evolution in SEI/active material morphology (HC and FC), and the loss of cyclable Li associated with extensive SEI formation (FC only), were significant degradation mechanisms.

The growth of an SEI layer is established to be the most significant degradation mechanism for existing batteries, and is particularly dramatic for those with nanostructured anodes. The sequential SEI formation observed here (attributed to the dense film) suggests that EPD may offer a route towards achieving an SEI layer which provides mechanical stability while minimizing cyclable Li loss. While this offers potential, the eventual SEI penetration throughout the layer requires further work to overcome.

In order to analyze the effects of extended cycling and morphological evolution on electrode resistance, EIS measurements were performed on HCs. Three features were...
observed in the spectra: the high frequency x-axis intercept denoting the series resistance, a large depressed semi-circle representing the charge transfer resistance at the electrode, and the low frequency line representing the Warburg impedance of Li-diffusion in the electrolyte. Spectra were obtained over the course of the first lithiation of a HC at three voltages (Figure 6a), representing the three stages of active material lithiation, namely (i) SnS (1.5 V), (ii) Sn + LiS (1 V), and (iii) Li2Sn + Li2S (0.1 V). The charge transfer resistance ($R_{ct}$) increased significantly from 1.5 V to 1.0 V, due to the replacement of conductive SnS with insulating Li$_2$S. Figure 6b shows spectra obtained at 1.0 V during extended cycling. $R_{ct}$ was remarkably stable (550 Ω ± 50 Ω) over the first 100 cycles, demonstrating that the time-dependent SEI formation and morphological changes observed in Figure 5 did not substantially affect the electrical properties of the electrode. After 500 cycles $R_{ct}$ had approx. doubled to 982 Ω, due to the reduction in electrical contact between Sn particles caused by volume expansion/contraction.

Although the electrophoretically deposited SnS films offer an advantage over graphite in terms of gravimetric capacity, greater mass loadings are needed. In order to investigate this, the mass deposited during EPD was elevated by simply increasing the concentration of NCs in the EPD bath. To enhance the performance at these higher loadings, a 3D textured current collector (pressed Cu foam, SEM image in Figure 7a) was also used, and compared with standard planar Cu foil. Figures 7b and 7c shows the capacity (gravimetric and areal) during extended cycling of these HC electrodes. On planar Cu, the higher mass loading exhibited poor capacity retention when compared with low mass loading, falling to < 100 mAh/g after just 30 cycles. Notably the areal capacity fell below that of the lower mass loading after just 15 cycles. This likely reflects a greater mean particle to current collector distance, as well as poorer adhesion of outer NCs. Conversely, on Cu foam, the high mass loading maintained a significant advantage in areal capacity over the low mass loading up to 250 cycles. In general, films deposited on Cu foam offered greater gravimetric capacities than the corresponding films on planar Cu, and this advantage was most significant at higher mass loadings. This indicates that the morphology of the current collector will play a pivotal role in achieving commercial level areal capacities. The combination of a 3-D structured electrode and EPD allowed high areal capacities to be achieved without binders or conductive additives.

**Figure 6:** (a) Impedance spectra for a HC obtained at three voltages during its first lithiation. Inset is the equivalent circuit used for analysis. (b) Impedance spectra obtained at 1 V for HCs during extended cycling.

**Figure 7:** SEM images of pristine (a) and SnS-coated (b) Cu foam. (c) Cross sectional image of SnS film on Cu foam. (d) Gravimetric and (e) Areal capacities for foam and planar Cu current collectors for two mass loading levels. Cycling of the high mass loading cell on planar Cu was stopped after 100 cycles due to low capacity.

**Conclusions**

We have developed a facile method for fabricating nanostructured SnS electrodes for Li-ion battery anodes, utilizing electrophoretic deposition. This enabled the formation of dense, well-adhered films on both planar and 3D textured current collectors, with controllable mass loadings. A stable discharge capacity of 552 mAh g$^{-1}$ was achieved when cycling was limited to alloying alone (< 1 V) with <0.08 % capacity loss per cycle observed. We show that not only is there poor reversibility of the conversion reaction (1 – 2 V vs. Li/Li$^+$), but that cycling in this region damaged the electrode. Through analysis of capacity loss mechanisms during extended cycling, it was revealed that capacity fade was initially time-dependent, after which cycling-related effects became dominant. We have tested the performance of these SnS nanoparticle ensembles in real-world battery conditions (half and full cell batteries, scalable fabrication, realistic voltage ranges, elevated mass loadings) to show their viability for scalable lithium ion.
Experimental Section

All chemicals were purchased from Sigma Aldrich unless otherwise stated.

SnS NC Synthesis. The NCs were synthesized according to a previously published protocol.[12] Briefly, 38 mg SnCl₂ was mixed with 2 g hexadecylamine (HDA) in a 3-neck flask, which was flushed with Argon before being heated to 100 °C for 15 min. 1 ml tri-butyl phosphine was then injected, after which the temperature of the mixture was raised to 150 °C for 60 min. In a separate vial, 290 mg thiourea was dissolved in 2.2 g HDA by stirring and heating to approx. 100 °C for 30 min. 2 ml of this was then injected into the 3-neck flask, and the heating mantle was immediately removed. Upon cooling to 100 °C, the product was dispersed into a vial. The NCs were isolated by washing with toluene and acetone several times (further details on the washing procedure can be found in the supporting information), before being redispersed in toluene.

Electrophoretic Deposition. The baths for EPD were created by adding a volume of the NC dispersion into 5 ml anhydrous toluene. Pieces of Cu foil (planar or foam) held approx. 5 mm apart were immersed in the bath and a voltage of 300 V was applied for 5 mins. Almost all the NCs present were deposited by this time (as judged by solution clarity), and so deposition mass could be controlled by altering the initial concentration of NCs in the bath. Typically, a bath concentration of 0.06 mg/ml was used to achieve 0.1-0.2 mg/cm².

Ligand Removal. After deposition, electrodes were dried and weighted to determine active material mass, before (unless otherwise stated) being immersed in a 20 mM solution of ammonium sulfide in methanol to remove the long-chain organic ligands, followed by rinsing in methanol for 30 s. For electrodes with higher (> 0.2 mg/cm²) mass loading, a slower drying (post ligand removal) in a saturated methanol atmosphere was necessary to avoid film cracking and delamination.

Characterization. Scanning electron microscopy (SEM) was performed with a Hitachi SU-70 system equipped with an Oxford Instruments EDS detector, X-Ray diffraction (XRD) with a PANalytical X’Pert PRO MPD instrument with a Cu Kα radiation source (λ = 1.5418 Å) with a 1-D X-celerator strip detector. Raman spectroscopy was carried out using a Horiba Labram 300 spectrometer system equipped with a 633 nm laser.

Electrochemical Measurements. The electrochemical performance of the electrodes was evaluated by assembly of a Swagelok-type two-electrode cell in an argon-filled glovebox. The SnS electrodes were placed opposite either elemental Li (in a HC configuration) or LCO (in a FC configuration), with a separator (Celgard) in between. LCO cathodes (NEI corporation) consisted of a 0.64 cm² electrode on Al foil with a capacity of 555 µAh. The electrolyte used for all tests was a 1 M solution of LiPF₆ in ethylene carbonate/dimethyl carbonate (1:1 v/v) with 3 % vinylene carbonate as an additive. The specific currents and capacities were determined based on the mass deposited during EPD and included ligands adsorbed on the NC surface as well as excess HDA (which were subsequently removed). Thus the values of gravimetric capacity quoted represent an approx. 20% underestimate of the actual values. Due to the formation of the Cu₂₃S film concurrent with ligand removal,[48] it was impossible to determine the actual mass of active SnS deposited, and so the conservative capacity values were used. EIS was performed using an Autolab PGSTAT100 potentiostat, applying an AC voltage with an amplitude of 10 mV over the frequency range 1 MHz to 0.01 Hz.

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Keywords: Li-ion battery • Electrophoretic Deposition • Tin Sulfide • Lithium Alloying Material

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