Tunable Core-Shell Single-Walled Carbon Nanotube-Cu₂S Networked Nanocomposites as High-Performance Cathodes for Lithium-ion Batteries

Xiangbo Meng[†], Shannon C. Riha[‡], Joseph A. Libera[†], Qingliu Wu[§], Hsien-Hau Wang[‡], Alex B.

Martinson[‡], and Jeffrey W. Elam^{†*}

[†]Energy Systems Division, [‡]Materials Science Division, and [§]Chemical Sciences and Engineering Division, Argonne National Laboratory, 9700 South Cass Avenue, Argonne, IL 60439, USA

*Corresponding author: jelam@anl.gov

Abstract:

In this study, nanoscale copper(I) sulfide (n-Cu₂S) was deposited over networks of single-walled carbon nanotubes (SWCNTs) by atomic layer deposition (ALD). This synthetic route provides a high degree of control for tuning the materials properties. The resulting core-shell SWCNT-n-Cu₂S composite structure ensures an intimate contact between the two components while maintaining a high porosity for efficient transport of charges. Indeed, electrochemical testing demonstrates that these nanocomposites are promising as cathodes in lithium-ion batteries (LIBs), exhibiting excellent stability over 200 discharge-charge cycles with a sustainable, high capacity of 260 mAh g⁻¹ (92% of the theoretical value in terms of Cu₂S) and >99% Coulombic efficiency. This work establishes a general strategy for developing high-performance nanoscale electrode materials.

Keywords: Cu₂S, Cathode, Atomic layer deposition, Lithium-ion battery

1. Introduction

Among the many competing technologies for energy storage, lithium-ion batteries (LIBs) have emerged to dominate the consumer portable electronics market [1, 2]. Current LIBs utilize an intercalation-based graphite anode coupled with a lithium-transition oxide or phosphate cathode. However, due to limitations in energy density, cost, and safety, LIBs are inadequate for powering electrical vehicles and smart grids [3, 4]. These limitations have motivated the search for alternative electrodes, and conversion-based metal oxides were found to offer higher capacities than the traditional insertion-based metal oxide electrodes [5]. Following these discoveries[6], metal sulfides and fluorides were also found to have exceptional electrochemical properties as conversion materials for LIB electrodes[5].

In the metal sulfide family, CuS is regarded as a promising cathode, boasting a theoretical capacity of 560 mAh g⁻¹. As a consequence, CuS has been fabricated into various nanostructures [7-12] and evaluated as a LIB cathode. Unfortunately, severe capacity fading was observed due to the partial dissolution of lithium sulfide formed through electrochemical cycling[13]. Different mechanisms have been proposed for the electrochemical reactions in these earlier CuS studies [7, 13, 14]. Combining transmission electron microscopy (TEM) and *in situ* X-ray diffraction (XRD), the team led by Tarascon provided solid evidence that these reactions proceed in two steps[13]:

In agreement with Equation (1) and (2), two discharge plateaus are commonly observed, occurring at 2.0-2.2 and 1.5-1.8 V (vs. Li/Li⁺), respectively [7, 8, 10-15]. In this two-step mechanism, the intermediate Cu₂S product can itself serve as a cathode material, and it has a theoretical capacity of

337 mAh g⁻¹ [15]. Compared to the many studies of CuS [7-11, 13-15], reports of Cu₂S are relatively rare. Only recently, micro-sized Cu₂S (μ-Cu₂S) was investigated by Jache et al [15] and Ni et al [16]. Jache et al mainly studied the effects of electrolytes and current collectors on the electrochemical characteristics of both Cu₂S and CuS, while Ni et al developed Cu₂S as a cathode for thin film batteries. However, there have been no reports on nanoscale Cu₂S for LIBs.

While there are numerous methods for synthesizing nanoscale materials, atomic layer deposition (ALD) has some unique advantages, particularly for fabricating nanoscale composites. ALD is a thin-film technique used mainly in microelectronics manufacturing [17], but in the past decade its capabilities have expanded into new domains including sustainable energy [18, 19], catalysis [20], and biomedical technologies [21, 22]. By its very nature, ALD enables film growth in a layer-by-layer mode at the atomic-scale. ALD utilizes alternating exposures between precursor vapors and a solid surface, where the precursors react individually and in a self-limiting, surface-controlled fashion. Furthermore, ALD enables conformal deposition within high-aspect-ratio and porous nanostructures [23]. As a consequence, ALD has become a novel and powerful tool for nanofabrication [20, 24, 25]. Beyond its wide successes in oxides, ALD now is making great strides for other categories of functional materials such as sulfides, fluorides, and nitrides. To date, there have been 16 metal sulfide materials deposited using ALD [26-28]. In particular, we recently developed a Cu₂S ALD process for applications in photovoltaics, and demonstrated this technique for preparing thin films on planar, two-dimensional substrates [29-32].

In this study, we utilized Cu₂S ALD to prepare unique composites by depositing nanosized Cu₂S (n-Cu₂S) over networks of single wall carbon nanotubes (SWCNTs) to produce core-shell

SWCNT-n-Cu₂S networked composites. These materials are highly tunable by controlling the Cu₂S deposition parameters, and provide intimate contact between the two distinct nanomaterials to ensure a high concentration of three-phase (electron, ion, and electrode) regions. Electrochemical testing revealed excellent performance for these nanoscale composites as LIB cathodes, which we attribute to their nanoscale dimensions, porous structure, and intimate SWCNT-Cu₂S contact.

2. Experimental

2.1 ALD Cu₂S

The ALD Cu₂S was deposited on networked 1D SWCNTs (Sigma-Aldrich, USA) at 135 °C using a Savannah 200 ALD reactor (Cambridge Nanotech), using alternating exposures to Bis(N,N'-disec-butylacetamidinato)dicopper(I) (CuAMD, Dow Chemical Company, USA) and 1% H₂S (balanced by N₂, Matheson Tri-gas, USA). The ALD reactor was coupled to a N₂-filled glove box. Prior to the Cu₂S ALD, SWCNT powders were loaded into a porous container and placed in the reactor. The reactor was then purged using ultrahigh purity (UHP, 99.999%) nitrogen carrier gas at 10 sccm and a pressure of ~0.4 Torr. Next, the SWCNTs were functionalized using a 9-min O₃ treatment (5% in 500 sccm ultrahigh purity oxygen). The Cu₂S ALD was performed using a static (or exposure) mode where the Cu and S precursors were supplied alternatively with a purging period of pure N₂ flow between each exposure. The ALD timing sequence is designated as: t₁ - t₂ - t₃ - t₄, corresponding to the durations of the CuAMD exposure, first N₂ purge, H₂S exposure, and second N₂ purge, respectively, with all times in seconds (s). Two different timing sequences were used in this study: 2.0 - 20.0 - 0.1 - 20.0 s for coating small quantities (≤ 5 mg) of SWCNTs, and 40.0 - 90.0 - 2.0 - 90.0 s for coating larger quantities (100 mg) of SWCNTs. To boost the CuAMD vapor pressure, the solid compound was heated to 150 °C in a temperature-controlled, stainless steel

cylinder. The SWCNT samples were coated using 50 - 600 ALD cycles to adjust the thickness of the Cu₂S films.

2.2 Characterization

The SWCNT-n-Cu₂S composites were characterized using a field emission scanning electron microscope (FE-SEM, Hitachi S4700) equipped with energy dispersive X-ray spectroscopy (EDX) for elemental analysis. Transmission electron microscopy (TEM, JEOL 2100F) was utilized to evaluate the Cu₂S coating thickness and microstructure. X-ray diffraction (XRD, Bruker D-8) was used to characterize the crystallinity of the SWCNT-n-Cu₂S composites as well as a commercial micro-sized Cu₂S powder (μ -Cu₂S, Sigma-Aldrich), and the pristine SWCNTs. Room temperature Raman spectra (Renishaw) were recorded at a resolution of 1 cm⁻¹ in back scattering (180°) configuration using 632.8 nm excitation. Thermogravimetric analyses (TGA) were performed on a NETZSCH STA 449F3 thermogravimetric analyzer where the samples were analyzed from room temperature to 900 °C in an Al₂O₃ crucible pan at a heating rate of 5 °C min⁻¹ in air.

2.3 Electrochemical measurements

For the electrochemical measurements, the SWCNT-n-Cu₂S composite powder was mixed with Super P carbon black and polyvinylidene fluoride (PVDF, Sigma-Aldrich) using a ratio of 8:1:1 and suspended in N-methyl-2-pyrrolidone (NMP, Sigma-Aldrich) to ensure homogenous mixing. The resultant slurry was cast onto a Cu foil and expanded into a laminate using a 100 μ m doctor blade. The laminate was then dried in a furnace at 80 °C within an Ar-filled glove box for 24 hours. Next, the dried laminate was punched into 7/16 inch circular electrodes and subsequently assembled into CR2032 LIB coin cells in an Ar-filled glove box with H₂O and O₂ levels below 1 ppm. Li metal

was used as the counter/reference electrode, a Celgard 2325 membrane was used as the separator, and 1.2 M LiPF₆ in ethylene carbonate/ethyl methyl carbonate (EC:EMC = 3:7 by weight, Tomiyama) was used as the electrolyte. The discharge-charge testing was performed on an Arbin 2043 electrochemical tester using a voltage window of 0.01 - 3.00 V for the SWCNT-n-Cu₂S electrodes. In addition, control samples were assembled and tested following the same procedures described above using laminates prepared from the pristine SWCNTs, μ -Cu₂S powder, and a mixture of the two in a ratio of 1:1 (i.e., SWCNT- μ -Cu₂S). All of the electrochemical testing was performed at room temperature.

3. Results and discussion

The pristine SWCNTs characteristics have been detailed in our previous study [33], but some of their salient features are described herein. The SEM image in figure 1(a) shows that the CNTs are mainly less than 10 nm in diameter and that they form a 3D structured network with numerous contact points yet maintaining an open porosity. High-resolution TEM (HR-TEM) in figure 1(b) further reveals that the CNTs are predominantly bundled, consistent with previous observation [34]. The single-walled nature of the pristine SWCNTs was confirmed by Raman analysis, as illustrated by the black traces in figure 1(c) and 1(d). The radial breathing mode (RBM) [35-37] of SWCNTs, typically in the range of 100 - 400 cm⁻¹, was observed at 196, 218, 258, and 282 cm⁻¹. The RBM at 196 cm⁻¹ can be assigned to metallic tubes while the ones at 258 and 282 cm⁻¹ are attributed to semiconducting tubes. Thus, the SWCNTs are a mixture of metallic and semiconducting tubes. Furthermore, the RBM at 218 cm⁻¹ indicates the presence of bundles [37]. For isolated SWCNTs, the correlation [35, 38] between nanotube diameter (d_t) and breathing mode frequency (ω_{RBM}) is $d_t = 248 \text{ cm}^{-1} \text{ nm} / \omega_{\text{RBM}} \text{ cm}^{-1}$. The RBM features at 196, 258, and 282 cm⁻¹ indicate nanotubular

diameters of 1.3, 1.0, and 0.9 nm, respectively. In addition, the SWCNTs exhibited a D band at 1306 cm^{-1} , G band at 1552 and 1592 cm^{-1} , M band at 1720 and 1920 cm^{-1} , and G' band at 2607 cm^{-1} [35-37]. The presence of the D band implies an abundance of defects that should provide reactive nucleation sites for the Cu_2S ALD [35-37]. However, our initial attempts to deposit Cu_2S directly on the pristine SWCNTs yielded poor results. Consequently, we treated the SWCNTs with O_3 for 9 minutes in order to create a higher concentration of active sites. Raman measurements of the SWCNTs following the O_3 treatment revealed an increase in the D band while the G band nearly remained intact (red traces in figure 1(c) and 1(d)) suggesting that the density of oxygen-containing defects was increased by O_3 treatment [39-42]. The O_3 treatment enabled the facile nucleation and growth of the ALD Cu_2S on the SWCNTs, and was used for the remainder of the study.

Figure 2(a-d) shows SEM images of the O_3 -treated SWCNTs after performing Cu_2S ALD using 100, 200, 400, and 600 cycles, respectively. It is apparent that the ALD Cu_2S morphology evolved with increasing ALD cycles from discontinuous nanoparticles of $\sim 15\text{ nm}$ (figure 2(a)) into coalesced nanoparticles of $\sim 30\text{ nm}$ (figure 2(b)) and finally into continuous films (figure 2(c,d)). As anticipated, the Cu_2S loading can be precisely controlled by adjusting the number of Cu_2S ALD cycles. It is interesting that the thinner ALD Cu_2S films deposited as discrete particles despite the O_3 -treatment. Evidently, the active site density for the Cu_2S ALD is still low (estimated to be $\sim 10^{11}\text{ cm}^{-2}$ from figure 2a), or the Cu_2S de-wets the SWCNT surface. In our previous work, ALD Cu_2S films deposited on planar silicon samples under comparable conditions also form isolated agglomerates of similar dimensions [29]. Nevertheless, the 600-cycle ALD Cu_2S treatment produced a dense and relatively uniform coating (figure 2(d)) and yielded a core-shell SWCNT-n- Cu_2S networked composite. EDX mapping in figures 3(b - d) for the C, Cu, and S

concentrations, respectively after 200 Cu₂S ALD cycles (SEM image in figure 3(a)), also indicate the uniform covering of Cu and S over the SWCNT networks, consistent with our observation in figure 2(b).

XRD analysis of the 200-cycle SWCNT-n-Cu₂S (black trace in figure 4) disclosed a series of peaks that can be referenced to hexagonal chalcocite Cu₂S (JCPDS PDF No. 09-0328). The commercial micro-sized Cu₂S (μ -Cu₂S) (shown by the red trace in figure 4) was also consistent with crystalline Cu₂S (JCPDS PDF No. 03-1071). The SWCNTs showed no peaks in XRD as expected due to their single-walled nature. TEM images in figure 5(a,b) verified that, after 100-cycle Cu₂S ALD, the n-Cu₂S particles are ~15 nm in size and are chained by SWCNTs. The HR-TEM image in figure 5(c) clearly shows the crystalline Cu₂S lattice with an inter-plane distance of 3.6 Å corresponding to the characteristic planes of (260).

To prepare a sufficient quantity of the SWCNT-n-Cu₂S composite for electrochemical testing, we deposited Cu₂S on a large, 100-mg batch of SWCNTs using 200 ALD Cu₂S cycles. In order to quantify the electrochemical results we must know the Cu₂S loading of the composite materials, and this was determined using TGA. As controls, both the pristine and O₃-treated SWCNTs were analyzed as well. As illustrated in figure 6, the SWCNTs were thermally stable up to 400 °C, and the TGA weight loss profiles (the red and blue traces) each exhibited a single-step degradation. During the pronounced mass loss, the SWCNTs exhibited a much smaller loss due to the oxidation of amorphous carbon [34, 43, 44]. The pristine SWCNTs oxidation was greatest at ~530 °C, as shown by the red derivative trace in the inset to figure 6. In comparison, the O₃-treated SWCNTs showed a slightly faster and earlier oxidation of the amorphous carbon, and also an earlier

maximum for the SWCNT oxidation at ~ 480 °C, (blue trace in inset to figure 6). The TGA revealed $\sim 10\%$ residual weight at 900 °C for the SWCNTs, probably from the growth catalysts [34, 43, 44].

Compared to the SWCNTs, the TGA trace for the commercial μ -Cu₂S powder (magenta trace in figure 6) is more complex and reflects the larger number of chemical transformations occurring. Based on previous studies of Cu₂S [11, 45, 46], the initial mass uptake from 300 to 450 °C results from oxidation: $\text{Cu}_2\text{S} + 1.5\text{O}_2 \rightarrow \text{Cu}_2\text{O} + \text{SO}_2$ and $\text{Cu}_2\text{O} + \text{O}_2 + \text{SO}_2 \rightarrow \text{CuO} \cdot \text{CuSO}_4$. The mass drop between 700 and ~ 825 °C signals decomposition of the sulfate: $\text{CuO} \cdot \text{CuSO}_4 \rightarrow 2\text{CuO} + 2\text{SO}_2 + 0.5\text{O}_2$ and $\text{Cu}_2\text{O} + 0.5\text{O}_2 \rightarrow 2\text{CuO}$, and the final mass drop from 700 to ~ 825 °C results from $\text{CuO} \rightarrow 0.5\text{Cu}_2\text{O} + 0.25\text{O}_2$. The residual weight was 89% and is consistent with the overall transformation: $\text{Cu}_2\text{S} \rightarrow \text{Cu}_2\text{O}$.

As expected, the TGA profile for the 200-cycle SWCNT-n-Cu₂S composite (green trace in figure 6) shows contributions from both the SWCNTs and Cu₂S oxidation. The 200 - 300 °C mass loss reflects oxidation of amorphous carbon, and the 300 - 350 °C mass gain results from oxidation of Cu₂S to copper sulfate. The first large mass drop at 350 - 500 °C signals oxidation of CNTs and decomposition of copper sulfate to CuO, while the second 670 - 760 °C mass drop results from the final CuO to Cu₂O conversion. It appears from the TGA that the nanoscale n-Cu₂S in the composite oxidizes more easily than the commercial μ -Cu₂S. Based on these analyses the $\sim 45\%$ weight remaining from the SWCNT-n-Cu₂S sample implies a loading of 44 wt.% Cu₂S in the composite.

In figure 7(a-d), we compared the first three discharge-charge profiles for the pristine SWCNTs (a), μ -Cu₂S (b), mechanically mixed 1:1 SWCNT- μ -Cu₂S (c), and ALD deposited SWCNT-n-Cu₂S (d)

in the potential range of 0.01-3.00 V at room temperature. The corresponding dQ/dV profiles are shown in the insets to figure 7(a-d). SWCNTs have been widely investigated as anode materials in LIBs [47-51]. In figure 7(a), the 1st discharge for the pristine SWCNTs shows a plateau at ~0.8 V and a sloping decrease below 0.25 V (red trace). The ~0.8 V plateau is commonly attributed to the decomposition of liquid electrolytes and the simultaneous formation of solid state interphase (SEI), while the slope below 0.25 V is believed to be Li insertion into the SWCNTs [47, 50-53]. The 1st discharge of the SWCNTs reached a capacity of 1525 mAhg⁻¹. In contrast, the 1st charge profile does not show any evident plateau but rather a sloping increase. In other words, the Li extraction was almost uniform from 0.01 - 3.00 V, implying a large hysteresis between Li insertion and extraction. The 1st charge achieved a capacity of 390 mAh g⁻¹, yielding a Coulombic efficiency (CE) of only 26% and an irreversible capacity of 1135 mAh g⁻¹. This large capacity loss is due to extensive SEI formation on the large surface area of the SWCNTs, 2630 m² g⁻¹ theoretically [54]. In contrast, the 2nd (blue) and 3rd (magenta) discharges showed a fast voltage drop from 3.00 to 0.25 V with no plateau, and a declining slope below 0.25 V and yielded capacities of 380 and 340 mAh g⁻¹, respectively. The 2nd and 3rd charges demonstrated a uniform voltage increase, with capacities of 295 (CE = 78%) and 286 mAh g⁻¹ (CE = 84%), respectively. The dQ/dV profiles in the inset of figure 7(a) show the evolution of reduction and oxidation reactions in the first two discharge-charge cycles of the SWCNTs. The reduction peak at ~0.8 V in the 1st discharge stems from the irreversible SEI formation reaction. Following the plateau at ~0.8 V, dQ/dV declined with a sloping profile, and the majority of Li was inserted into the SWCNTs below 0.25 V. The absence of a plateau below 0.25 V indicates the lack of a well-defined insertion stage [51]. The dQ/dV profile for the 1st charge showed weak oxidation peaks at 1.2, 2.4, and 3.0 V. The peak at 1.2 V was attributed to Li extraction from the inner cores of the SWCNTs while the peaks at > 2.4 V were due to the

extraction of Li bonded to the surface functional groups[47]. In comparison to the dQ/dV profile for the 1st cycle, the 2nd cycle was absent the SEI peak at 0.8 V but otherwise similar.

Figure 7(b) shows the discharge-charge profiles of the commercial μ -Cu₂S in the first three cycles. The 1st discharge (red) was dominated by a declining plateau at ~ 1.7 V while the 1st charge quickly increased to ~ 1.9 V and plateaued, and afterwards showed staircase increases with several plateaus at 2.3, 2.4, and 2.6 V. It is noteworthy that the charging characteristics during the 1st cycle resemble very much the charging behavior of CuS as described by Tarascon et al [13]. The 1st cycle exhibited capacities of 392 and 329 mAh g⁻¹ for discharge and charge, respectively. The 1st discharge capacity exceeded the theoretical value of 337 mAh g⁻¹ by 55 mAh g⁻¹ indicating SEI formation. Upon this point, the 1st dQ/dV profile in the inset of figure 7(b) disclosed that, beside a strong reduction peak at 1.7 V due to Cu₂S reduction, there is a weak peak at 0.6 V ascribed to the SEI formation [11, 16]. The sloping profile below 0.5 V has been attributed to the formation of elemental Cu [16]. Corresponding to the 1st charge, the 1st dQ/dV profile showed a series of oxidation peaks at 1.9, 2.0, 2.3, 2.4, and 2.6 V. The irreversible capacity accounted for 63 mAh g⁻¹ in the 1st cycle, yielding CE $\sim 84\%$. The 2nd discharge (blue) exhibited a sloping plateau at ~ 2.0 V, flat plateaus at ~ 1.9 and 1.5 V, and a sloping plateau below 0.5 V. Evidently, the 2nd discharge behaved very different from the 1st discharge, and exhibited characteristics of CuS [13]. Similar to the 1st charge, the 2nd charge showed a fast voltage increase to 1.9 V and exhibited plateaus at 1.9, 2.2, and 2.37 V. The 2nd discharge and charge achieved capacities of 320 and 260 mAh g⁻¹, respectively so that CE $\sim 81\%$. The 3rd cycle (magenta) demonstrated very similar discharge and charge behaviors to the 2nd cycle, but showed a further evolution in the voltage plateaus. In addition, the capacities for discharge and charge continued to drop to 306 and 210 mAh g⁻¹, respectively. As a consequence, the CE further

diminished to 69% in the 3rd cycle. The dQ/dV profiles for the 2nd cycle, as shown in the inset of figure 7(b), clearly demonstrated the evolution of discharge and charge behaviors, showing three reduction peaks at ~2.0, 1.9, and 1.5 V and three oxidation peaks at 1.9, 2.2, and 2.37 V. Based on these results, we conclude that following the 1st discharge, the commercial μ -Cu₂S, exhibited the reduction-oxidation behavior for CuS as described in Equations (1) and (2). Moreover, the 1st discharge followed the reaction in Equation (2) so that in the following cycles some of the Cu remained in the metallic state. The capacity fading observed in the first three cycles might result from the partial dissolution of Li₂S [8, 10].

Figure 7(c) and (d) show the discharge-charge features for the SWCNT- μ -Cu₂S and SWCNT-n-Cu₂S composites, respectively. In figure 7(c), the 1st discharge (red) of the SWCNT- μ -Cu₂S showed plateaus at 1.7 and 0.8 V, and a slope below 0.25 V while the 1st charge exhibited two plateaus at 1.9 and 2.35 V. Apparently, the mechanically mixed SWCNT- μ -Cu₂S demonstrated the electrochemical characteristics of both the SWCNTs and the commercial μ -Cu₂S during the 1st cycle. The 1st discharge and charge achieved capacities of 909 and 321 mAh g⁻¹, respectively. These values are close to the expected capacities for the 50-50 mixture of 958 and 359 mAh g⁻¹ for discharge and charge, respectively, if one assumes that the SWCNTs and the μ -Cu₂S components contribute equally in the composite. This was further substantiated in the later cycles. We observed voltage plateaus at 2.0 and 1.5 V and a slope below 0.25 V which we attribute to the SWCNTs in the 2nd discharge (blue). The 2nd charge demonstrated some evolution in voltage plateaus, as also seen for the μ -Cu₂S in the 2nd discharge in figure 7(b). The dQ/dV curves in the inset of figure 7(c) show clearly the reduction and oxidation peaks of Cu₂S in the first two cycles. The 3rd cycle (magenta) is quite similar to the 2nd, except for some evolution in the plateaus. The 2nd

cycle showed a capacity of 375 mAh g⁻¹ for discharge and 301 mAh g⁻¹ for charge while the 3rd cycle showed 339 mA g⁻¹ for discharge and 296 mAh g⁻¹ for charge. As a consequence, the CE progressively improved from 35% in the 1st cycle to 80% in the 2nd and 87% in the 3rd cycle. In comparison to the pure μ -Cu₂S in figure 7(b), the SWCNT- μ -Cu₂S exhibited a much higher CE, and this likely results from the boost in electrical conductivity imparted by the SWCNTs.

Similar to the SWCNT- μ -Cu₂S, the SWCNT-n-Cu₂S also displayed the electrochemical characteristics of both the SWCNTs and n-Cu₂S (figure 7(d)). It is noteworthy that the 1st discharge (red) showed two discharge plateaus at ~1.7 V from the lithiation of n-Cu₂S, and ~0.8 V due to the decomposition of the electrolyte. In addition, there was a slope below 0.25 V in the 1st discharge, ascribed to lithiation of the SWCNTs and the formation of elemental Cu. Besides a continuous increase due to the SWCNTs, the 1st charge showed plateaus at 1.9 and 2.35 V due to the delithiation of Li₂S. As a consequence, the 1st cycle realized a capacity of 709 mAh g⁻¹ for discharge and 239 mAh g⁻¹ for charge. By simply adding the capacities from 44% Cu₂S and 56% SWCNTs, we predict values of 1026 and 363 mAh g⁻¹ for the 1st discharge and charge, respectively. These large deviations from the expected capacity values indicate that SWCNTs and Cu₂S do not act individually in the ALD SWCNT-n-Cu₂S as we saw for the SWCNT- μ -Cu₂S composite. This unexpected behavior may result from the conformal ALD n-Cu₂S coating over the SWCNT scaffold that greatly reduces the exposed surface of the SWCNTs for lithiation. In other words, the capacity contribution from SEI formation on the SWCNTs has decreased. In contrast, the mechanically produced SWCNT- μ -Cu₂S composite did not have intimate contact between the SWCNTs and the Cu₂S so that the very high SWCNTs surface area was preserved. Further evidence for this interpretation is that the charge due to SEI formation on the SWCNT-n-Cu₂S (451 mAh g⁻¹) was

significantly below the pure SWCNTs (815 mAh g^{-1}), and the SWCNT- μ -Cu₂S (744 mAh g^{-1}). The 2nd (blue) and 3rd (magenta) cycles for the SWCNT-n-Cu₂S also exhibited a combination of the electrochemical characteristics of both the SWCNTs and n-Cu₂S, similar to the SWCNT- μ -Cu₂S. The 2nd cycle showed capacities of 275 and 221 mAh g^{-1} for discharge and charge, respectively. In comparison, the 3rd cycle achieved 249 and 220 mAh g^{-1} for discharge and charge, respectively. Thus, the CE for the first three cycles was improved from 34% in the 1st cycle to 80% in the 2nd cycle and 88% in 3rd cycle.

Following the initial electrochemical studies of the four samples, we next investigated their long-term cyclability (figure 8). The SWCNTs (black) exhibited fast capacity fading over the first 25 cycles followed by relatively stable cycling with a capacity of $\sim 220 \text{ mAh g}^{-1}$ for the remainder of the 200 cycles, although some fluctuations were observed. In contrast, the μ -Cu₂S (red) showed very rapid capacity fading in the first ten cycles, followed by a gradually increasing capacity to reach 126 mAh g^{-1} at the 200th cycle. Previous studies have documented similar capacity increases for CuS [12] and Cu₂S [16]. Moreover, the initial capacity drop in the first ten cycles has been widely observed and was attributed to the partial dissolution of Li₂S into the electrolyte and disintegration of the μ -Cu₂S leading to a loss of electrical contact to the carbon filler. The subsequent slow recovery might result from a rearrangement of the Cu₂S that proceeds once material is sufficiently pulverized that restores electrical contact [55]. In our study, the excess metallic Cu remaining after the 1st discharge could also improve the electrical conductivity. Furthermore, recent studies [15] using Cu current collectors revealed the beneficial trapping of sulfide species on the Cu. The metallic Cu in our materials might also serve this function.

The SWCNT- μ -Cu₂S (blue) showed a fast capacity fade in the first ten cycles followed by further slow degradation up to the 200th cycle at which point the capacity was 200 mAh g⁻¹. The lack of capacity recovery compared to the μ -Cu₂S suggests that perhaps the material is too dense to allow a rearrangement in the electrode composition. In contrast, the SWCNT-n-Cu₂S (green) did show capacity recovery up to the 150th cycle, followed by a plateau at 260 mAh g⁻¹ that persisted to the 200th cycle. The capacity recovery of the SWCNT-n-Cu₂S might stem from increasing access to the SWCNT surfaces allowing more extensive SWCNT lithiation, but a rearrangement of the electrode composition, as hypothesized for the μ -Cu₂S, might also contribute. We note that figure 8 also plots the CE of the four samples and in all cases CE ~99% after the first few cycles.

To evaluate the fraction of Cu₂S that actively contributes to the storage capacity in the different cathodes, we subtracted the SWCNT contribution at the 200th cycle from the discharge capacities for the μ -Cu₂S, SWCNT- μ -Cu₂S, and SWCNT-n-Cu₂S. The resulting Cu₂S-only discharge capacities were: 127 (μ -Cu₂S), 182 (SWCNT- μ -Cu₂S), and 311 mAh g⁻¹ (SWCNT-n-Cu₂S). Compared to the theoretical capacity of 337 mAh g⁻¹ for Cu₂S, it is apparent that the addition of SWCNTs greatly improves the Cu₂S capacity from 38% (μ -Cu₂S) to 54% (SWCNT- μ -Cu₂S) of the theoretical value. Moreover, reducing the Cu₂S to nanoscale dimensions further improves the capacity to 92% (SWCNT-n-Cu₂S) of the theoretical value.

In summary, the ALD SWCNT-n-Cu₂S networked composite proved to be the best material for harvesting the full storage capacity of the Cu₂S. We attribute the high performance of the SWCNT-n-Cu₂S to: (1) the nanoscale ALD Cu₂S coatings offer short electronic and ionic conducting pathways; (2) the conducting SWCNT scaffold provides electrical continuity to the

matrix; and (3) the open and “sponge-like” network allows wetting by the electrolyte while also trapping sulfides providing a robust support. Using fluidized-bed or rotary ALD [18], furthermore, the production of the SWCNT-n-Cu₂S is potentially able to scale up. However, it also needs to point out that, in spite of the benefits associating with the SWCNT-n-Cu₂S composites, there may exist difficulties in practice for applying them into real batteries, such as their low volumetric density and high percentage of SWCNTs. Additionally, the wide voltage range of 0.01-3.00 V was rarely used in reality and a more suitable one should be explored.

4. Conclusions

We have demonstrated a new route for fabricating nanostructured cathode materials for LIBs using ALD. The resulting nanoscale composites exploit the excellent electrical conductivity and open pore structure of the SWCNTs networks, while the precise and conformal ALD Cu₂S coatings maximize the crucial interface to the SWCNTs while maintaining the porosity for contact to the electrolyte. As a result, these nanocomposites provide an optimal structure to harvest the intrinsic properties of the active material. The core-shell SWCNT-n-Cu₂S composites achieved 92% of the theoretical capacity for Cu₂S, and did not show capacity fade over 200 cycles. Using the same methodology, we plan to fabricate nanoscale composites using a wide variety of materials amenable to ALD processing with the ultimate goal of improving LIB performance to levels suitable for electric vehicles and grid-scale energy storage.

Acknowledgements

This work was supported as part of the Center for Electrical Energy Storage: Tailored Interfaces, an Energy Frontier Research Center funded by the U.S. Department of Energy, Office of Science,

Office of Basic Energy Sciences. Electron microscopy was performed at the Electron Microscopy Center for Materials Research (EMCMR) at Argonne National Laboratory. Use of the EMCMR was supported by the U. S. Department of Energy, Office of Science, Office of Basic Energy Sciences, under Contract No. DE-AC02-06CH11357 operated by UChicago Argonne, LLC. X. Meng appreciates the funding support of an NSERC Postdoctoral Fellowship, Canada. S. C. Riha was supported in part by the Department of Energy (DOE) Office of Energy Efficiency and Renewable Energy (EERE) Postdoctoral Research Awards under the EERE Solar Program administered by the Oak Ridge Institute for Science and Education (ORISE) for the DOE. ORISE is managed by Oak Ridge Associated Universities (ORAU) under DOE contract no. DE-AC05-06OR23100.

References

- [1] J.M. Tarascon, Philosophical Transactions of the Royal Society a-Mathematical Physical and Engineering Sciences, 368 (2010) 3227-3241.
- [2] M.M. Thackeray, C. Wolverton, E.D. Isaacs, Energy Environ. Sci., 5 (2012) 7854-7863.
- [3] J. Liu, J.G. Zhang, Z.G. Yang, J.P. Lemmon, C. Imhoff, G.L. Graff, L.Y. Li, J.Z. Hu, C.M. Wang, J. Xiao, G. Xia, V.V. Viswanathan, S. Baskaran, V. Sprenkle, X.L. Li, Y.Y. Shao, B. Schwenzer, Adv. Funct. Mater., 23 (2013) 929-946.
- [4] Z.G. Yang, J.L. Zhang, M.C.W. Kintner-Meyer, X.C. Lu, D.W. Choi, J.P. Lemmon, J. Liu, Chem. Rev., 111 (2011) 3577-3613.
- [5] J. Cabana, L. Monconduit, D. Larcher, M.R. Palacin, Advanced Materials, 22 (2010) E170-E192.
- [6] P. Poizot, S. Laruelle, S. Grugeon, L. Dupont, J.M. Tarascon, Nature, 407 (2000) 496-499.
- [7] J.S. Chung, H.J. Sohn, Journal of Power Sources, 108 (2002) 226-231.
- [8] Y. Han, Y.P. Wang, W.H. Gao, Y.J. Wang, L.F. Jiao, H.T. Yuan, S.X. Liu, Powder Technology, 212 (2011) 64-68.
- [9] L. Zhao, F.Q. Tao, Z. Quan, X.L. Zhou, Y.H. Yuan, J.C. Hu, Mater Lett, 68 (2012) 28-31.
- [10] Y.H. Chen, C. Davoisne, J.M. Tarascon, C. Guery, J Mater Chem, 22 (2012) 5295-5299.
- [11] R. Cai, J. Chen, J.X. Zhu, C. Xu, W.Y. Zhang, C.M. Zhang, W.H. Shi, H.T. Tan, D. Yang, H.H. Hng, T.M. Lim, Q.Y. Yan, J Phys Chem C, 116 (2012) 12468-12474.
- [12] Y.P. Du, Z.Y. Yin, J.X. Zhu, X. Huang, X.J. Wu, Z.Y. Zeng, Q.Y. Yan, H. Zhang, Nature Communications, 3 (2012).
- [13] A. Debart, L. Dupont, R. Patrice, J.M. Tarascon, Solid State Sciences, 8 (2006) 640-651.
- [14] Y.R. Wang, X.W. Zhang, P. Chen, H.T. Liao, S.Q. Cheng, Electrochim. Acta, 80 (2012) 264-268.
- [15] B. Jache, B. Mogwitz, F. Klein, P. Adelhelm, Journal of Power Sources, 247 (2014) 703-711.
- [16] S.B. Ni, T. Li, X.L. Yang, Thin Solid Films, 520 (2012) 6705-6708.
- [17] G.N. Parsons, J.W. Elam, S.M. George, S. Haukka, H. Jeon, W.M.M. Kessels, M. Leskela, P. Poodt, M. Ritala,

- S.M. Rossnagel, J. Vac. Sci. Technol. A, 31 (2013).
- [18] X. Meng, X.Q. Yang, X. Sun, Adv. Mater., 24 (2012) 3589-3615.
- [19] J.A. van Delft, D. Garcia-Alonso, W.M.M. Kessels, Semicond Sci Tech, 27 (2012).
- [20] C. Detavernier, J. Dendooven, S.P. Sree, K.F. Ludwig, J.A. Martens, Chem Soc Rev, 40 (2011) 5242-5253.
- [21] S.A. Skoog, J.W. Elam, R.J. Narayan, Int Mater Rev, 58 (2013) 113-129.
- [22] H. Im, N.J. Wittenberg, N.C. Lindquist, S.H. Oh, J Mater Res, 27 (2012) 663-671.
- [23] S.M. George, Chem Rev, 110 (2010) 111-131.
- [24] C. Bae, H. Shin, K. Nielsch, Mrs Bulletin, 36 (2011) 887-897.
- [25] H. Kim, H.B.R. Lee, W.J. Maeng, Thin Solid Films, 517 (2009) 2563-2580.
- [26] X. Meng, J.A. Libera, T.T. Fister, H. Zhou, J.K. Hedlund, P. Fenter, J.W. Elam, Chem. Mater., 26 (2014) 1029-1039.
- [27] X. Meng, D.J. Comstock, T.T. Fister, J.W. Elam, Acs Nano, 8 (2014) 10963-10972.
- [28] L.K. Tan, B. Liu, J.H. Teng, S. Guo, H.Y. Low, K.P. Loh, Nanoscale, 6 (2014) 10584-10588.
- [29] A.B.F. Martinson, J.W. Elam, M.J. Pellin, Appl Phys Lett, 94 (2009) 123107.
- [30] E. Thimsen, Q. Peng, A.B.F. Martinson, M.J. Pellin, J.W. Elam, Chem Mater, 23 (2011) 4411-4413.
- [31] A.B.F. Martinson, S.C. Riha, E. Thimsen, J.W. Elam, M.J. Pellin, Energy & Environmental Science, 6 (2013) 1868-1878.
- [32] S.C. Riha, S. Jin, S.V. Baryshev, E. Thimsen, G.P. Wiederrecht, A.B.F. Martinson, Acs Applied Materials & Interfaces, 5 10302-10309.
- [33] X. Meng, K. He, D. Su, X. Zhang, C. Sun, Y. Ren, H.-H. Wang, W. Weng, L. Trahey, C.P. Canlas, J.W. Elam, Advanced Functional Materials, 24 (2014) 5435-5442.
- [34] M.F. Zhang, M. Yudasaka, A. Koshio, S. Iijima, Chemical Physics Letters, 364 (2002) 420-426.
- [35] M.S. Dresselhaus, G. Dresselhaus, A. Jorio, A.G. Souza, R. Saito, Carbon, 40 (2002) 2043-2061.
- [36] S.S. Islam, K.A. Shah, H.S. Mavi, A.K. Shaukla, S. Rath, Harsh, B Mater Sci, 30 (2007) 295-299.
- [37] F. Hennrich, R. Krupke, S. Lebedkin, K. Arnold, R. Fischer, D.E. Resasco, M. Kappes, J Phys Chem B, 109 (2005) 10567-10573.
- [38] A. Jorio, M.A. Pimenta, A.G. Souza, R. Saito, G. Dresselhaus, M.S. Dresselhaus, New J Phys, 5 (2003).
- [39] J.M. Simmons, B.M. Nichols, S.E. Baker, M.S. Marcus, O.M. Castellini, C.S. Lee, R.J. Hamers, M.A. Eriksson, Journal of Physical Chemistry B, 110 (2006) 7113-7118.
- [40] K. Peng, L.Q. Liu, H.C. Li, H. Meyer, Z. Zhang, Carbon, 49 (2011) 70-76.
- [41] J.L. Bahr, J.M. Tour, J Mater Chem, 12 (2002) 1952-1958.
- [42] D.B. Mawhinney, V. Naumenko, A. Kuznetsova, J.T. Yates, J. Liu, R.E. Smalley, Journal of the American Chemical Society, 122 (2000) 2383-2384.
- [43] D. Bom, R. Andrews, D. Jacques, J. Anthony, B.L. Chen, M.S. Meier, J.P. Selegue, Nano Letters, 2 (2002) 615-619.
- [44] H.P. Li, N.Q. Zhao, C.N. He, C.S. Shi, X.W. Du, H.J. Li, Materials Science and Engineering a-Structural Materials Properties Microstructure and Processing, 473 (2008) 355-359.
- [45] S.E. Perez-Fontes, M. Perez-Tello, L.O. Prieto-Lopez, F. Brown, F. Castillon-Barraza, Miner Metall Proc, 24 (2007) 275-283.
- [46] M. Perez-Tello, H.Y. Sohn, J. Lottiger, Miner Metall Proc, 16 (1999) 1-7.
- [47] B. Gao, A. Kleinhammes, X.P. Tang, C. Bower, L. Fleming, Y. Wu, O. Zhou, Chemical Physics Letters, 307 (1999) 153-157.
- [48] E. Frackowiak, F. Beguin, Carbon, 40 (2002) 1775-1787.
- [49] B.J. Landi, M.J. Ganter, C.D. Cress, R.A. DiLeo, R.P. Raffaele, Energy & Environmental Science, 2 (2009) 638-654.

- [50] B.J. Landi, M.J. Ganter, C.M. Schauerma, C.D. Cress, R.P. Raffaele, J Phys Chem C, 112 (2008) 7509-7515.
- [51] J. Eom, H. Kwon, J Mater Res, 23 (2008) 2458-2466.
- [52] S.-L. Chou, Y. Zhao, J.-Z. Wang, Z.-X. Chen, H.-K. Liu, S.-X. Dou, The Journal of Physical Chemistry C, 114 15862-15867.
- [53] J.Y. Eom, H.S. Kwon, J. Liu, O. Zhou, Carbon, 42 (2004) 2589-2596.
- [54] Y.P. Wu, E. Rahm, R. Holze, Journal of Power Sources, 114 (2003) 228-236.
- [55] J.-S. Do, C.-H. Weng, Journal of Power Sources, 146 (2005) 482-486.

List of Figure Captains

Figure 1. (a) SEM and (b) HR-TEM images of the pristine SWCNTs; (c) and (d) Raman spectra of the pristine and O₃-treated SWCNTs.

Figure 2. SEM images of the ALD-coated SWCNTs following (a) 100, (b) 200, (c) 400, and (d) 600 Cu₂S ALD cycles.

Figure 3. (a) SEM image and (b-d) EDX elemental maps for C, Cu, and S, respectively, of the 200-ALD cycle SWCNT-n-Cu₂S.

Figure 4. XRD patterns of the pristine SWCNTs, μ -Cu₂S, and 100-ALD cycle SWCNT-n-Cu₂S.

Figure 5. (a,b) TEM and (c) HR-TEM images of the 100-ALD cycle SWCNT-n-Cu₂S.

Figure 6. TGA weight loss profiles of the pristine SWCNTs, O₃-treated SWCNTs, and 200-ALD cycle SWCNT-n-Cu₂S. The inset shows the corresponding derivative weight percentage curves with temperature.

Figure 7. Discharge-charge characteristics of the first three cycles at a current density of 100 mA g⁻¹ from 0.01-3.00 V: (a) the pristine SWCNTs, (b) μ -Cu₂S, (c) SWCNT- μ -Cu₂S, and (d) 200-ALD cycle SWCNT-n-Cu₂S. Insets show the corresponding dQ/dV profiles for in the first two cycles.

Figure 8. Cycling performance and CE of the pristine SWCNTs, μ -Cu₂S, SWCNT- μ -Cu₂S, and 200-ALD cycle SWCNT-n-Cu₂S with discharge-charge cycles at a current density of 100 mA g⁻¹ from 0.01-3.00 V.

Figures

Figure 1

Figure 2

Figure 3

Figure 4

Figure 5

Figure 6

Figure 7

Figure 8