High-Purity, CO_2-Derived Multiwall Carbon Nanotube Formulations for Realizing High-Energy and High-Power Lithium-Ion Cells

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Abstract
Multiwall carbon nanotubes (MWCNTs) generated from permanent CO_2 capture, utilization, and sequestration (CCUS) are discussed in the context of advanced conductive additives for lithium-ion battery (LIB) electrodes. An electrochemical molten carbonate electrolysis process is employed to generate the MWCNTs (30-50 nm diameter), and a high-efficiency (95%) thermochemical CO_2 uptake is used to regenerate the lithium carbonate electrolyte for new tube growth. The MWCNTs are then post-processed to remove excess electrolyte, purified to remove metal catalyst, and pre-dispersed in solvent (water or N-methylpyrrolidone) before making the final electrode dispersions. LIB cathode performance data with $LiNi_{0.6}Mn_{0.2}Co_{0.2}O_2$ (NMC 622) is discussed along with Si/graphite anode formulations for realizing simultaneous energy and power density increases. These cathode formulations contain only 10-26% substitution of the baseline conductive carbon black with MWCNTs, which corresponds to 0.50-0.62 wt% MWCNTs in the final electrode coating. The substantial capacity increases for the improved cathodes within the 1-3C discharge range are highlighted, and plans for boosting Si/graphite anode performance with 30 wt% Si and 1.0-2.5 wt% MWCNTs are introduced.

Key Words
Lithium-ion batteries; multiwall carbon nanotube (MWCNT) additives; high power density; extreme fast charging; molten carbonate electrolysis; CO_2 capture, utilization, and sequestration (CCUS)

Introduction
SkyNano, LLC is a domestic woman-owned small business that produces ***low cost***, high-purity multiwall carbon nanotubes (MWCNTs) from CO_2 pollution via molten carbonate electrolysis and thermochemical electrolyte regeneration with atmospheric or point-source-capture CO_2.[1-4] This carbon negative technology enables SkyNano to produce MWCNTs at about $1/10^{th}$ the cost of state-of-the-art chemical vapor deposition methods. SkyNano battery grade MWCNTs have high CNT purity, high C content (99.90-99.95%), tunable diameter within the range of 10-100 nm, and typical aspect ratios between 100-200. SkyNano's CO_2-derived MWCNTs are well-poised to supplement or replace state-of-the-art carbon black conductive additives in lithium-ion battery (LIB) applications for improved performance that meets the demands of today's warfighter.

These CO_2-derived MWCNTs have been demonstrated to substantially improve high discharge-rate cathode $LiNi_{0.6}Mn_{0.2}Co_{0.2}O_2$ (NMC 622) performance in lithium-ion battery (LIB) pouch cells produced at the DOE Battery Manufacturing R&D Facility (BMF) at Oak Ridge National Laboratory (ORNL) when 10% of the carbon black conductive additive was replace with SkyNano MWCNTs. Increases of 21% at 2C, 62% at 3C and 52% at 5C in discharge capacity were observed over the control cathode with no MWCNTs. For warfighters in the field, this advancement means: 1) higher energy at higher discharge rates (higher peak power density); or 2) increased usage per charge for a given discharge rate, which will improve communication ability, device performance in the field, unmanned ariel vehicle / unmanned underwater vehicle (UAV/UUV) mission duration and maneuverability, and military base grid independence.

Results and Discussion
In these prior efforts to integrate our CNTs into LIBs, we studied the partial replacement of state-of-the-art carbon black (CB) with our CNTs in NMC622 cathodes, a material commonly used in EV and other high energy batteries. Industrially relevant slot-die-coated electrodes were fabricated using a Frontier Industrial Technology Dynacoat pilot slot-die coating line to best mimic commercial processing. **Table 1** below shows the three cathode formulations that were studied. The anode used was the ORNL BMF standard Superior Graphite SLC 1520T material at an active material loading of 92 wt%, a CB loading of 2 wt%, and a PVDF binder loading of 6 wt%. The 95-wt% NMC 622 slurry (formulation "F8") needed to be thickened substantially from 46% solids to 65% solids during the mixing protocol to achieve a viscosity that would allow for slot-die coating, which subsequently taught us *another value proposition of using CNTs as a partial replacement of CB – less solvent use in electrode fabrication*. Single layer pouch cells were

Table 1. NMC622 cathode compositions with SkyNano MWCNTs partially substituted for carbon black.

Formulation	CNT (%)	CB (%)	Total C (wt%)	NMC 622 (wt%)	PVDF (wt%)	Slurry Solids Loading (wt%)
Control 2	0	100	4	91	5	46
F7	10	90	4	91	5	46
F8	26	74	2.4	95	2.6	60

constructed (five replicates for each cell configuration) using these three coatings, which had an average rated capacity of 134 ± 10 mAh. **Figure 1** shows the rate capability data ***normalized to total cathode mass*** for these cell groups, and it is seen that both CNT formulations (F7 and F8) outperform the Control 2 at all discharge rates above 0.5C (below 0.5C all cells perform comparably). The scaled F7 pouch cells performed better than their half coin cell counterparts and significantly outperformed Control 2 (***20.5%, 62.7%, and 46.7% capacity improvements at 2C, 3C, and 5C discharge rates, respectively), showing that only a small amount of CNTs is required to realize large improvements in cathode rate capability***. When examining the performance of the 95-wt% NMC622 formulation (F8) in Figure 1, it is seen that no further improvement in performance was realized over that of the 91-wt% NMC622 one (F7) on a total cathode mass basis except at the low C rates (high energy conditions). Once the discharge rate was increased above 1C, the C/binder network established with the lower mass fractions became performance limiting and electronic conductivity limitations were reached at the higher discharge rates. ***This result demonstrates the need for a fully optimized CNT dispersion network that will be critical for ultra-high active-material loadings of 95-97 wt%, and helps to motivate the proposed tasks in this scope of work.*** **Figure 1** also shows the power densities obtained from the rate capability study. The 91-wt% formulation significantly increased the power density magnitude over Control 2 for the 2-5C discharge rates; however, performance limitations of the 95-wt% formulation are evident here, and underscore the remaining critical challenges related to CNT dispersion optimization for enabling higher active material loadings.

The pouch cells tested for rate capability (discussed above) were immediately subjected to accelerated degradation testing by cycling them at 1C/-2C for 1000 cycles. The capacity retention profiles for Control 2 (91 wt% NMC 622 with no CNTs), formulation F7 (91 wt% NMC 622 with 0.4 wt% CNTs), and formulation F8 (95 wt% NMC 622 with 0.63 wt% CNTs) are shown in **Figure 2** through 500 cycles. The associated capacity results were normalized to the **total cathode mass** for a direct comparison between the 91-wt% (F7) and 95-wt% (F8) NMC 622 cathodes. It is seen that the capacity retention of all cells retained 80% of their initial 1C/-2C capacity over the 500 cycles. However, the capacity magnitudes where substantially higher after 500 cycles for both formulations with SkyNano CNTs (13% improvement), and the error bars (2σ standard deviation) were smaller. Also seen in Figure 2 (lower plot) is the performance of a larger 266-mAh cell with the 91-wt% NMC 622 formulation (F7) subjected to the Department of Energy Vehicle Technologies Office (DOE VTO) extreme fast charging (XFC) 6C/

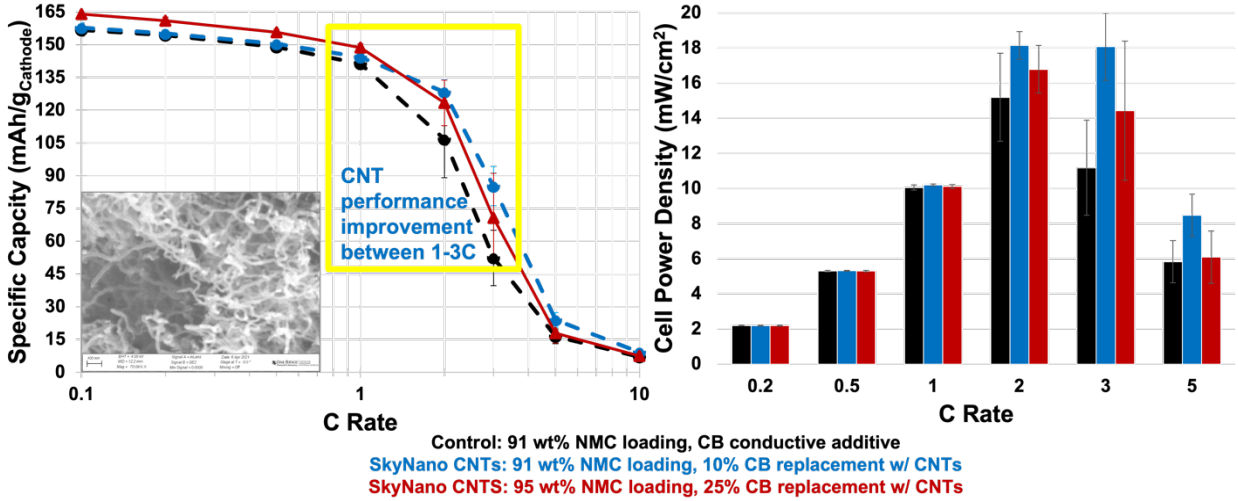

Figure 1. Rate capability (left) and power density (right) of pouch cells enabled with SkyNano CNTs

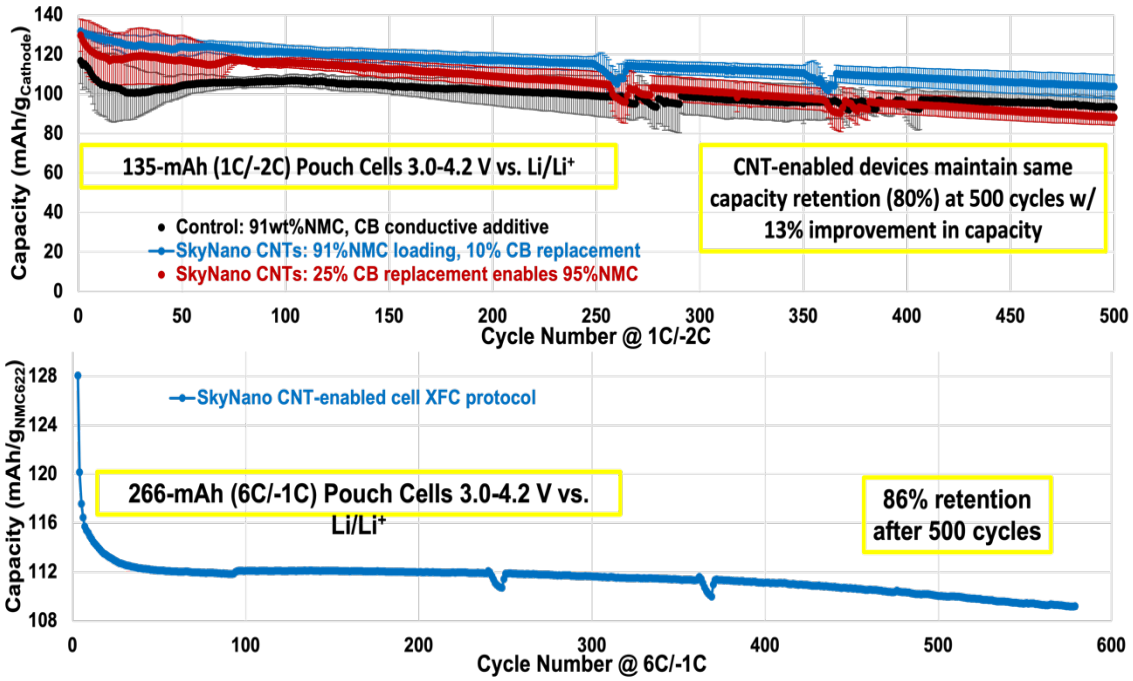

Figure 2. Cycling data of pouch cells enabled with SkyNano CNTs

-1C protocol. It was observed that the XFC cell performed extremely well under these conditions showing 72% of rated capacity (formation capacity at 0.05C) at the onset of cycling, which leveled off at 88% capacity retention after 80 6C/-1C cycles and retained its capacity well at 86% after 500 cycles.

Nanoscale integration of low-cost, electrochemically manufactured MWCNTs into highly loaded, Si based anodes is a major focus of SkyNano's LIB R&D, but there is a great deal of front-end research that needs to occur to create a sub-micron network of spherical primary Si/SiO nanoparticles and MWCNTs in a finished electrode coating. In addition, a network of this type is highly beneficial to Si mechanical and surface chemical stability during long-term cycling (at 4C/-1C) by establishing a scaffold-type structure of individual MWCNTs that encases individual Si/SiO secondary particles. SkyNano MWCNTs have unique surface chemistry compared to conventionally produced materials via chemical vapor deposition (CVD) using methane or ethylene carbon sources, which will be exploited to achieve this anode microstructure with individually dispersed MWCNTs among Si/SiO and carbon black (CB) aggregates. Two control anode compositions will be used, which are 30:55:2.5:4.5:8 and 30:55:1:6:8 compositions of Si/graphite/MWCNT/CB/LiPAA. The VTO Si Anode

Consortium baseline materials will be used with SkyNano MWCNTs such as MSE Supplies 150-nm Si/SiO, Superior Graphite SLC 1520T, Denka CB, LiPAA for aqueous colloids, and polyimide for NMP colloids (see Figure 3 for schematic of desired anode microstructure).

Current obstacles for MWCNT integration into advanced batteries are that cost is too high (4-10 times higher than carbon black), the physical properties (diameter, length, and wall thickness) have not been optimized for high-rate performance (i.e., 2C discharge and 4C charge rates), and CNT co-dispersion with Si nanoparticles is difficult. The latter will feature 30 wt% Si anodes, which is equal to the VTO Si Anode Consortium target loading. Enabling the widespread commercialization of high-energy, advanced batteries with low cost for transportation electrification, renewable energy storage, and portable electronics will result in substantially reduced CO_2 emissions, increased mobility, and ubiquitous opportunity for connectivity for the modern warfighter and the U.S. military in general. In addition, SkyNano produces its MWCNTs through the consumption of ambient or flowing CO_2 streams, which will contribute to slowing the increase in CO_2 emissions and ultimately reducing the current atmospheric content of 421 ppm. MWCNTs provide many commercial advantages in advanced batteries: 1) using thicker, higher-energy electrodes by minimizing electronic conductivity losses; 2) higher power density (i.e., higher capacity at high discharge rates); 3) integrating structured electrode architectures; 4) higher loadings of Si at the anode by forming a more mechanically

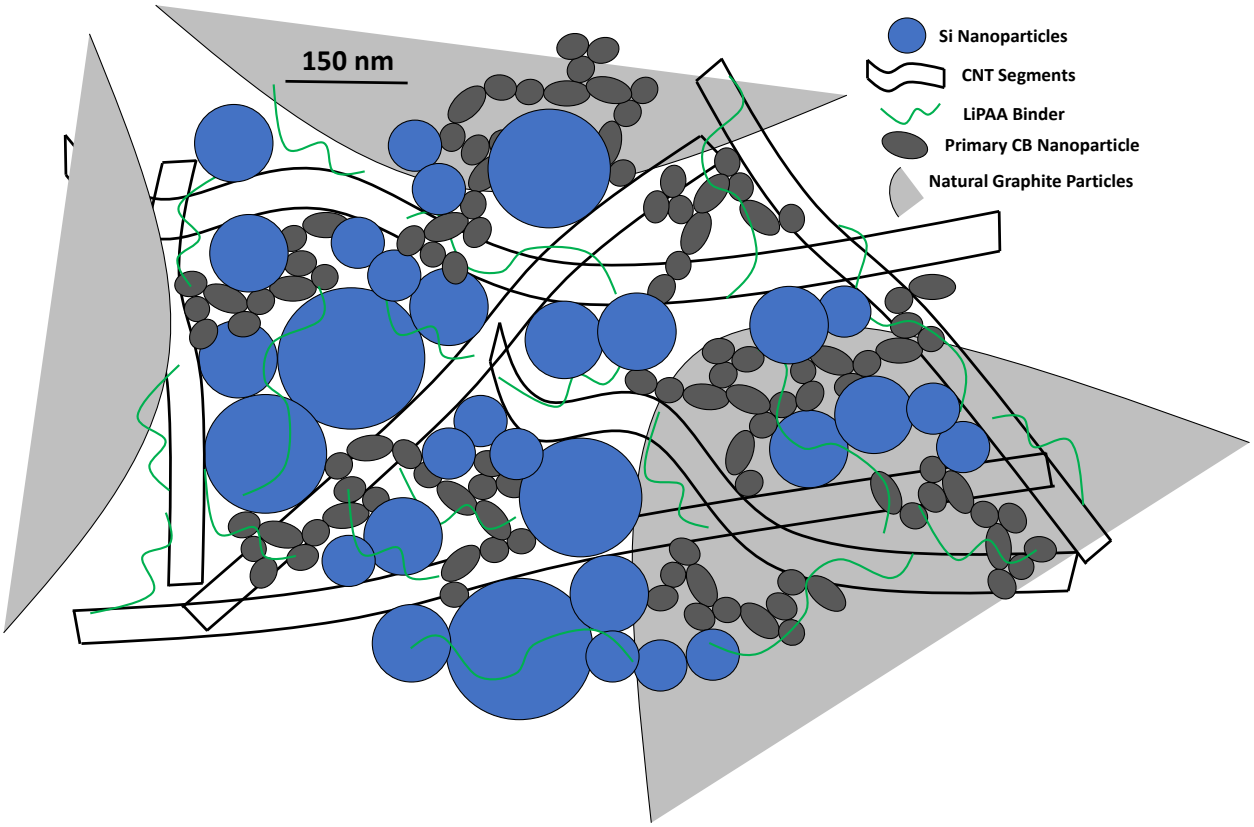

Figure 3. Schematic (to scale) of proposed Si-C anode nanoscale architecture with example composition of 40:40:5:5:10 Si/graphite/MWCNT/CB/LiPAA enabled by micro-dispersion of MWCNTs where Si nanoparticles are encased in a monodispersed MWCNT network.

stable composite with graphite during electrochemical cycling; and 5) faster charging rates approaching 4-6C. In addition, SkyNano MWCNTs at scale will be much less expensive than those produced using the high-vacuum conditions of chemical vapor deposition (CVD), and the material properties may be tailored for the type of electrode of interest. The electrode designs discussed here rely on the use of conventional electrolytes, widely available active materials, and conventional electrode manufacturing approaches and require no capital expenditures to integrate into current manufacturing lines.

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