

Specialty Multi-Walled Carbon Nanotubes for Advanced Li-ion Battery Cathodes

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ABSTRACT

In order to meet global goals to reduce fuel consumption and harmful emissions, there is a tremendous effort in the US to develop and produce alternatively powered vehicles such as all-electric vehicles (EVs) where the intent is to power them by domestically developed and manufactured lithium ion (Li-ion) batteries. However, it is believed that the current batteries being produced to address this market will not fully meet the needs of high power applications in the future due to the insufficient characteristics of the materials from which the battery cathodes are made. Currently used conductive material in these cathodes often cannot handle the constant charge and discharge cycles placed upon it and can degrade over time, damaging the battery performance. To address this issue, it has been proposed that carbon nanotubes be incorporated into these batteries because they are highly conductive and have large aspect ratios which are capable of creating networks that can better withstand the stresses placed upon them during the lifetime of a battery.

THEORY

Existing Li-ion cathodes incorporate conductive carbon particles (typically carbon black) in a composite electrode to provide an electrically conductive network to the active lithium metal oxide or phosphate material from the current collector. For high power applications, the weight loading of these conductive additives can be as high as 10%. However, the low aspect ratio of currently used carbon particles does not result in sufficiently robust conductive networks that allow the composite to withstand the resulting electromechanical stresses during cycling. As evidenced by the work of Sheem *et al.*, it is believed that carbon nanotubes (CNTs) can better withstand the constant charging and discharging experienced by battery electrodes because they possess higher intrinsic electronic conductivity and dramatically higher aspect ratios than currently used carbon particles [1]. A visual representation of this idea can be seen in Figure 1. In addition, replacing these current carbon particles with CNTs can lead to higher conductivity at much

lower weight loadings, allowing more active Lithium material to be used per unit weight or volume of cathode material, thus improving the energy storage capacity of these batteries. Also, CNT networks provide more efficient and robust thermal properties and heat conduction pathways, which allow for better heat transfer and reduce the thermal decomposition of lithium metal nano-crystal structures. Therefore, in order to experience the improvements in capacity, cyclability, and rate, it is important to develop cathode materials incorporating CNTs.

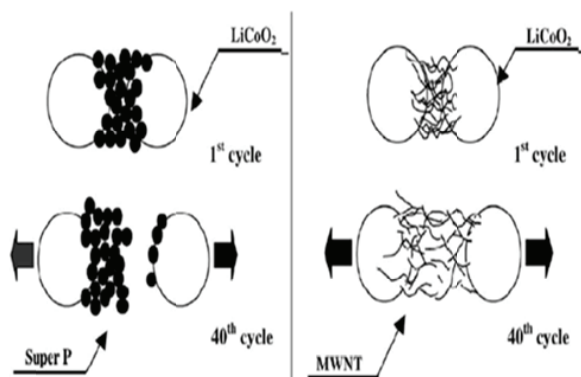


Figure 1 – Illustration of cathode battery degradation during several charge-discharge cycles (Taken from K. Sheem *et al.*¹⁾)

CARBON NANOTUBE PROPERTIES

Multi-walled carbon nanotubes (MWCNTs) exist as concentric rings of carbon nanotubes (**Error! Reference source not found.**) with a distance between walls of approximately 0.37 nm. Commercial MWCNTs have more than 10 walls (sometimes up to 30+ walls). SWeNT has developed a particular category of multi-walled nanotubes, called specialty multi-walled (SMWTM), whereby the number of walls is controlled to vary between three and eight walls while maintaining CNT lengths greater than 3

μm. This leads to an aspect ratio in the 350 – 550 range.

The lower number of walls results in

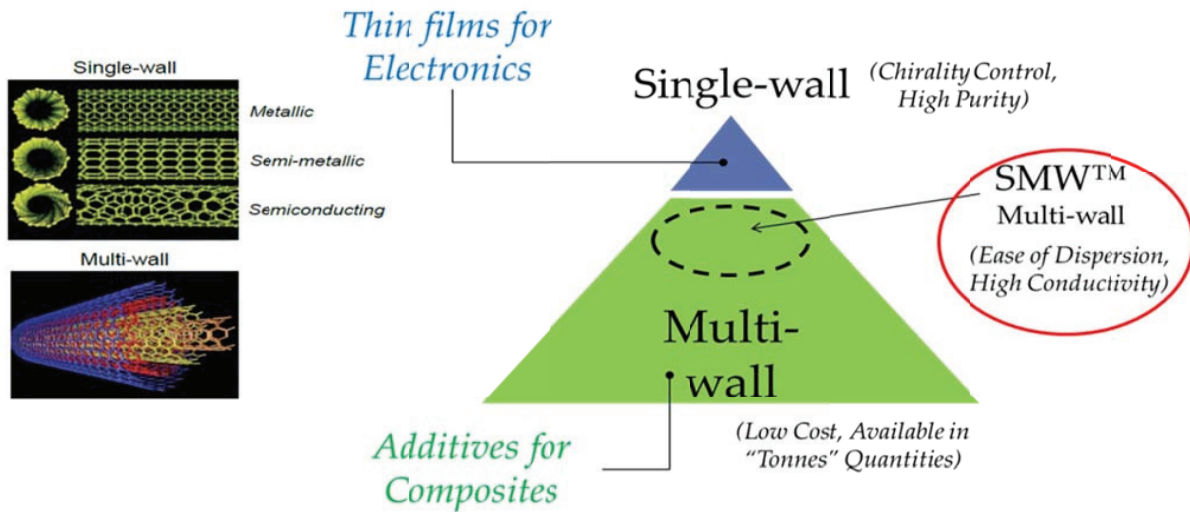


Figure 2 – Examples of carbon nanotube categories (SWCNTs, SMW™, and MWCNTs)

less structural defects, higher purity (> 98% CNTs), and less waste of carbon material, while straight and longer tubes provide better overall CNT morphology (Figures 3 and 4 and Table 1). Compared to other conventional MWCNTs on the market, this combination of properties yields a material that is easier to disperse and demonstrates improved conductive and mechanical properties for advanced applications like conductive polymers or Li-ion battery cathodes.

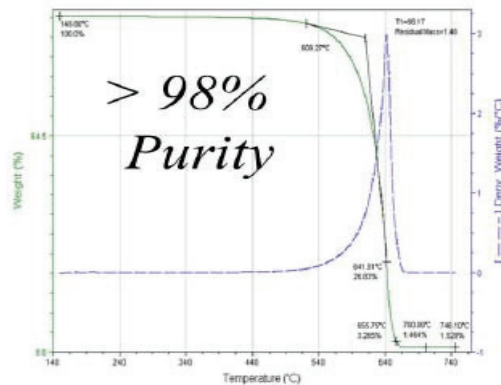


Figure 4 - TGA Analysis corresponding to SMW™ CNT

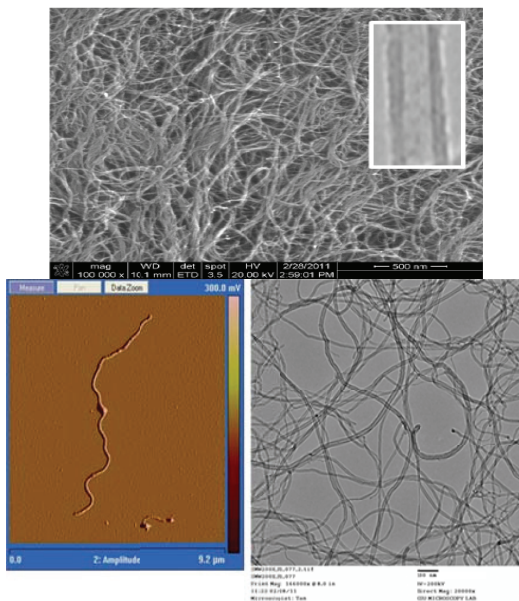


Figure 3 - SEM, AFM and TEM Analyses of SMW™ CNT

Outer Diameter	10±1 nanometers
Inner Diameter	4.5±0.5 nanometers
Number of Tube Walls	6-8 tube walls
Aspect Ratio (L/D)	350-550

Table 1 - Physical properties of SMW™ CNT

EXPERIMENTAL RESULTS

Figure 5 shows a comparison of conductivity data for SWeNT's SMW™ products versus other commercially available MWCNT materials. Measuring the sheet resistance of CNT Bucky Paper (a thin solid film created by filtration of 0.15 g of CNT/m²) shows that as expected, a SWCNT material (in this case SG76) has the lowest resistivity value. But significantly, the SMW200-X purified material is more than twice as conductive when compared to the best MWCNT material investigated (Competitor A). Interestingly, the SMW200-X NanoHybrid (NH-SMW200-X) material only contains about 70 – 75% CNTs, but shows conductivity that is comparable or better than the Competitor A material.

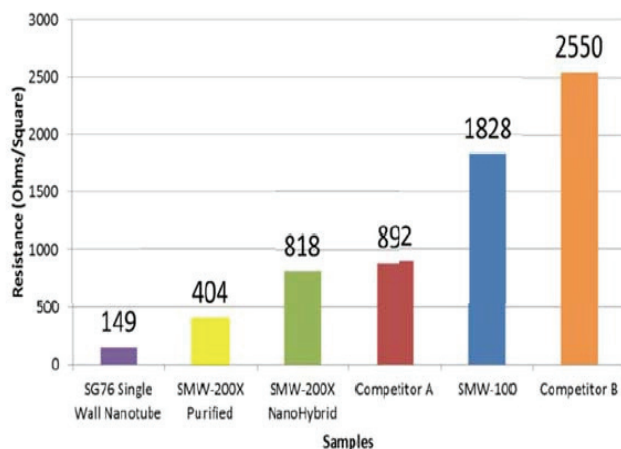


Figure 5 – Bucky Paper resistivity measurements of various MWCNTs including SMW™ products

Figure 6 compares sheet resistance Bucky Paper data for different products as a function of the CNT aspect ratio (L/D), as determined by AFM and TEM analysis. One can note the trend of lower sheet resistance with higher aspect ratios, with SMW200-X having the best conductivity properties. In addition to the CNT aspect ratio, we have also

observed that the morphology of the tubes is another key factor that strongly influences the conductivity of the tubes. A lower number of defects in the tubes results in higher electrical conductivity capacity.

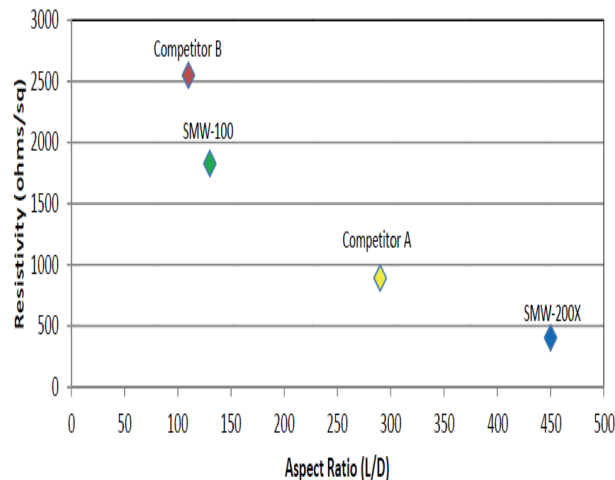


Figure 6 – Variation of Bucky Paper resistivity as a function of the CNT aspect ratio

To realize the potential benefits of incorporating CNT materials in next generation cathodes for Li-ion batteries, Figure 7 shows results after the incorporation of SMW200-X into Li-ion batteries specifically designed to form efficient and robust conductive networks at lower weight percent loadings than any other carbon material. Standard battery performance tests were conducted with this new CNT material and the results were compared under the same experimental conditions with typical conductive carbon material. The results show that 1wt% SMW200-X can replace 6 wt% conductive carbon, resulting in improved cycle life. Other benefits include increased specific energy, improved performance in rate capability, and lower impedance in high power electrodes. These performance benefits are attributed to an optimal control of CNT structure and high levels of purity as previously mentioned. From these results, it is clear that SMW™ CNTs are promising materials for next generation advanced Li-ion battery cathodes.

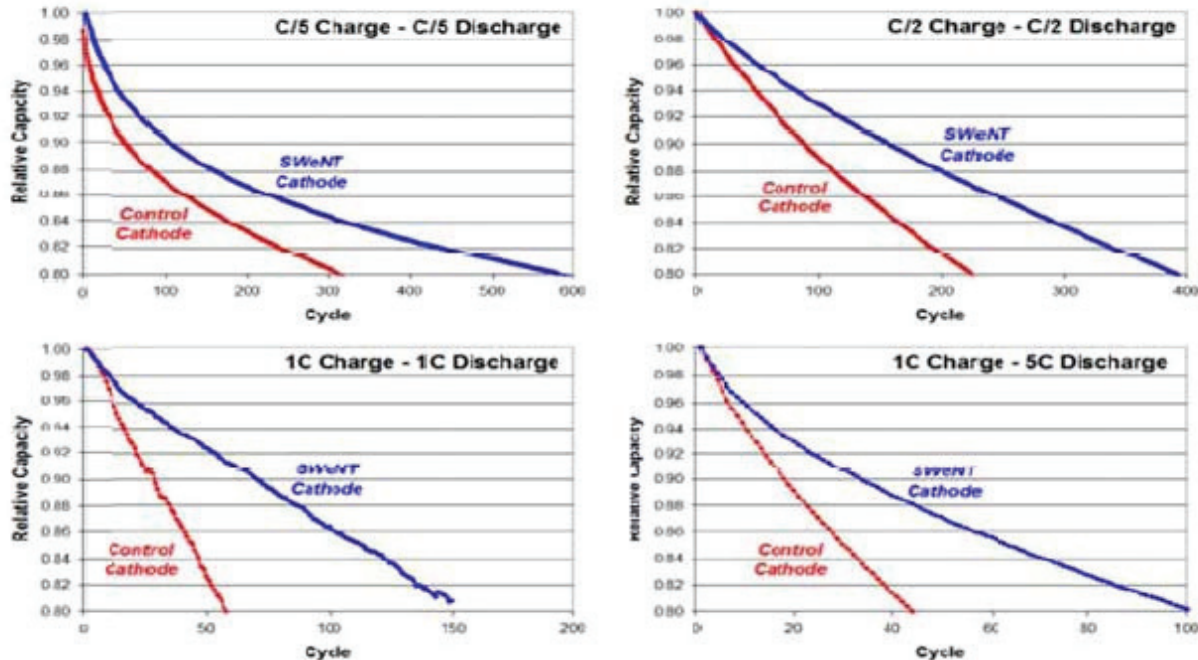


Figure 7 – Cycle life comparison at different charge/discharge rate conditions

CONCLUSIONS

The results of this work clearly show that 1 wt% SWeNT specialty multi-walled CNT is as effective as 6 wt% of standard conductive carbon-P material currently used in Li-ion battery cathode formulation. Replacing the standard material with SWeNT's CNTs also results in improved cycle life, increased specific energy, improved performance in rate capability, and lower impedance in high power electrodes. These performance benefits are attributed to an optimal control of CNT structure (morphology, higher aspect ratio (L/D), fewer number of walls, lower structural defects) and high levels of purity. In addition, SWeNT's specialty multi-wall CNTs allow for a greater ease of dispersion and higher electrical conductivity than any other multi-wall CNTs produced in commercial quantities. Based on these characteristics and the previously mentioned testing results, it is clear that SMWTM CNTs are a promising material that can be a key component for next generation advanced Li-ion battery cathodes.

REFERENCES

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ACKNOWLEDGEMENTS

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