SWCNT vs MWCNT and Nanofibers. Applications in Lithium-Ion Batteries and Transparent Conductive Films

Mikhail Predtechenskiy, Alexander Bezrodny, Oleg Bobrenok, Andrey Kochnev, Andrey Kosolapov, Nina Krechetova, Vladimir Saik

OCSiAl Group, 1804 Embarcadero Rd., Suite 202, Palo Alto, California, 94303, USA
bezrodny.ae@ocsial.com

ABSTRACT

Due to their unique electrical properties, carbon nanotubes are used as conductive additives in various applications. In our study single-walled carbon nanotubes (SWCNTs), carbon black and nanofibers are evaluated as conducting agents in a cathode in a Li-ion cell. We also compared properties of transparent conductive coatings on the surface of polymer film produced of SWCNT and MWCNT. The results show that SWCNTs are feasible alternative to conductive agents currently used in Li-ion batteries and transparent conductive films.

Keywords: single-walled carbon nanotube, multi-walled carbon nanotube, CNT, lithium-ion battery, transparent conductive film.

1 INTRODUCTION

Exceptional electrical properties of single-walled carbon nanotubes (SWCNTs) make them promising alternatives to conductive agents. SWCNTs have a diameter of 1.5-2 nm and a length of about 5 microns. In addition to the high electrical conductivity, SWCNTs possess high strength, elastic, thermal and other properties. However, because of the high cost, their use in industrial processes, until recently, have not been considered so far. The appearance of the Tuball™ (SWCNTs produced by OSCiAl www.ocsial.com) made use of SWCNTs cost-effective. In our study, we focused on application of SWCNTs in lithium-ion batteries and transparent conductive films.

2 LITHIUM-ION BATTERIES

As a rule, the electrical conductivity of the electrode active material of a Li-ion battery is low. To improve the conductivity of electrodes, conductive carbon materials are used as additives. Such additives create a conductive network, which maintains stability of the battery conductive properties after repeated cycling.

In our study SWCNTs (Tuball™ produced by OcSiAl www.ocsial.com), carbon black (SuperP) and nanofibers (VGCF-H, Showa Denko) are evaluated as conducting agents in a cathode in a Li-ion cell.

VGCF-H nanofibers have an average diameter of 150 nm, and length of 10 – 20 μm (Fig. 1). NMC 1:1:1 (MTI Corp.) and LFP P2 (Clariant) were used as active materials for making Li-ion battery cells. Basic composition for the both cathode materials contained 3% of a conductive additive Super C65, PVDF being used as a binder. Conductive additives Super C65 and VGCF-H were added to the slurry in the form of a powder. For introduction into matrix of the cathode material, SWCNTs were dispersed in NMP using ultrasound. To prepare a suspension, 100 mg of SWCNTs and 200 mg of PVP were added to 100 g of NMP. The mixture was sonicated with power density of up to 1 W·h/ml. Then PVPF and the cathode material were sequentially added to the suspension and stirred for 1 hour to obtain homogeneous slurry. Cathode slurries were applied on the surface of an aluminum foil with a thickness of 20 microns using the doctor blade method. The full loadings were 14 mg / cm^2 for the LFP electrode, and 20 mg / cm^2 for the NMC electrode. Graphite SMG A3 was used as the anode. Cells

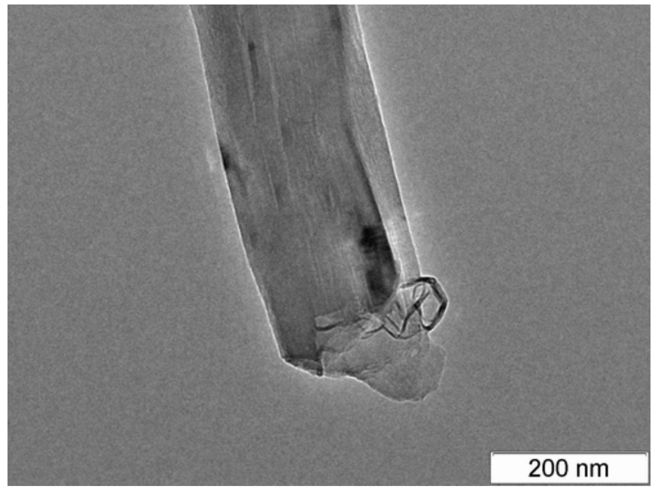

Figure 1: High resolution TEM image of nanofibers VGCF-H.

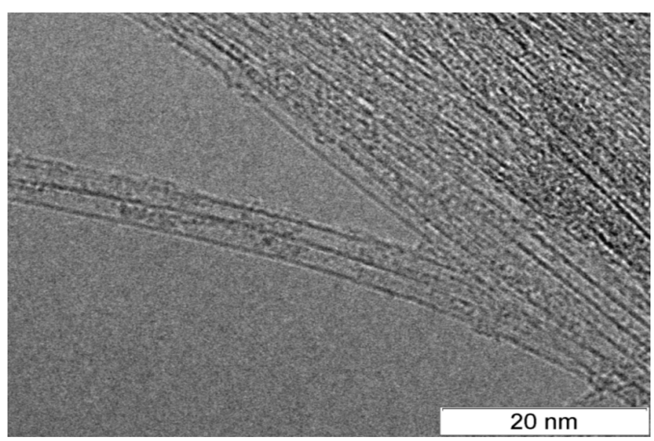

Figure 2: High resolution TEM image of SWCNT.

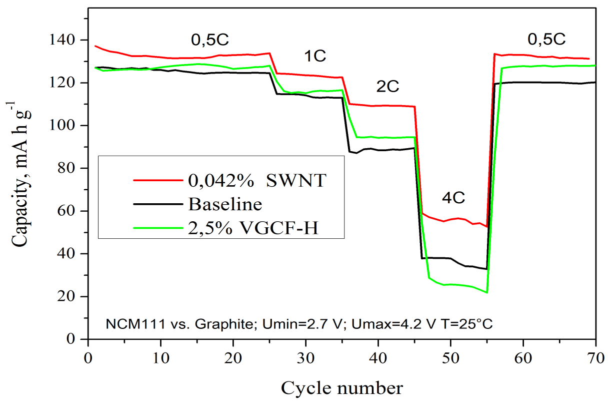

Figure 3: Rate capability of NCM-based electrodes at different charge/discharge rates.

with NMC were subjected to cycling with different discharge currents.

Figure 3 shows that the cathode containing only 0.042% of SWCNTs without other conductive additives demonstrates superior discharge characteristics than the cell with the basic cathode and the cathode containing nanofibers. After 70 cycles the basic electrode degradation is observed at the level of 8% of the initial capacity at the current 0.5C, whereas the cells with nanofibers and SWCNTs have an insignificant degradation. It is worth noting that in the SWCNTs electrode a weight fraction of the conductive agent is almost 60 times smaller than in the cathode with nanofibers and 70 times smaller than the basic cathode.

A similar effect of nanotubes on the properties of the cells was also observed using LFP as the cathode material. Figure 4 shows electrochemical impedance measurements of cells obtained immediately after their formation. It can be seen that replacement of 3% Super C65 with the same amount of nanofibers leads to a double decrease of the cell resistance, and the use of 0.2% SWCNTs decreases the cell resistance more than 7 times.

The cycling of cells with the LFP cathode was carried out at a discharge current 1C. The cells containing nanotubes exhibited the best stability.

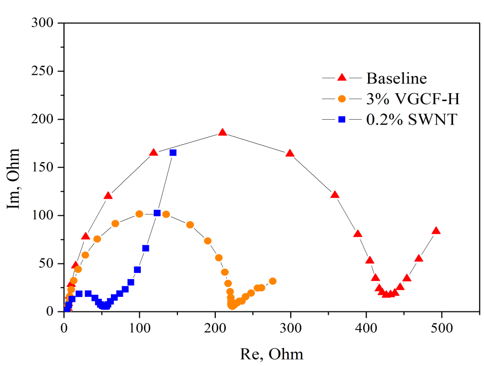

Figure 4: Electrochemical impedance spectra of cells measured at full charge state.

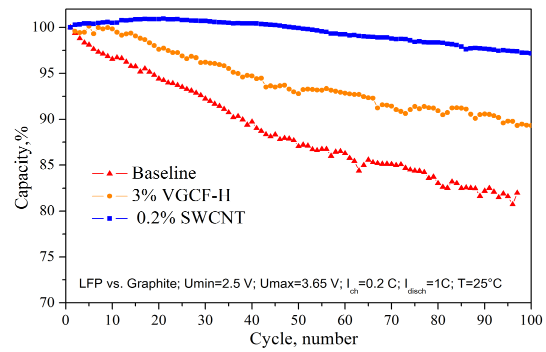

Figure 5: The cyclic performance of LFP cells.

The use of VGCF-H as a conductive additive also improves the cells cycling as compared to the basic composition.

Our experiments on studying the possibility of using SWCNTs as a conductive additive to the cathodes in Li-ion batteries have shown the promise of this approach. Use of nanotubes can reduce loading of the conductive agent in the cathode to the fraction of 1% while improving such properties as resistance and the cells cycling. Reduction of a conductive agent content allows increasing an active material loading, which, in its turn, results in enhance of the overall energy cathode capacity. Such an effect of the use of nanotubes is attributable to the formation of a conductive 3D network in the cathode. Nanofibers form a similar conductive network in the cathode material. The fact that the effect of nanotubes can be observed at significantly lower concentrations may be explained by the nanotube diameter which is more than 100 times smaller than the diameter of the nanofibers.

3 TRANSPERANT CONDUCTIVE FILMS

There are several applications of thin transparent conductive films (TCF) in electronics, including touch-panels, OLEDs, solar cells, smart windows etc. Carbon nanotubes are considered to be promising materials as a replacement of ITO in TCF production /1,2/. In order to replace ITO, the CNT-based TCF should exhibit a high light transmittance and low surface resistance. Recent industrial standards correspond to the sheet resistance less than 100 Ohm/square and 90% transmittance.

We used SWCNT Tuball™ and commercially available multi-walled CNTs (MWCNTs) for TCF preparation, both spray coating and doctor blade techniques being used. We prepared suspension of SWCNT in DIW for spray-coating, with the mass concentration of Tuball being equal to 0.01%. SDBS was used as the surfactant. Its concentration was equal to 0,1%.

As it's seen from the chart (Fig. 6), the TCF made of SWCNT clearly exhibits superior performance in terms of high transparency and low resistance by about two orders of magnitude. The best results for TCF obtained by the use of doctor blade

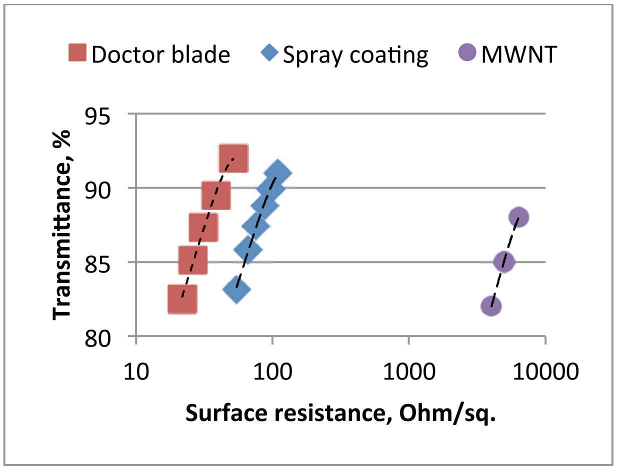

Figure 6: The dependence of transmittance upon the resistance of the TCF made of SWCNT and MWNT on PET.

The sonication with total energy density of 2 W*hour/ml was sufficient in order to obtain the dispersion. The suspension was separated on centrifuge for 1 hour at 8000 rpm. For doctor blade technique the concentration of SWCNTs was 0.2% and SDBS - 1%.

After TCF was applied on PET substrate, the film was washed with DIW, dried and placed into a vapor of nitric acid for one hour. The transmittance of TCFs was measured by Shimadzu UV 3600 spectrometer at 550 nm. The surface resistance measurements for TCF were performed by 4-points probe in accordance with ASTM F1711-96R08.

For the performance of TCF the most important is its high transparency and low sheet resistance. There is well known the relationship between them for the TCF [2]. We compared the dependences of the transmittance vs. the resistance for the SWCNT and commercially available MWNT. The results are presented at fig. 6. The SEM image of Tuball™ SWCNT is presented at the figure 7.

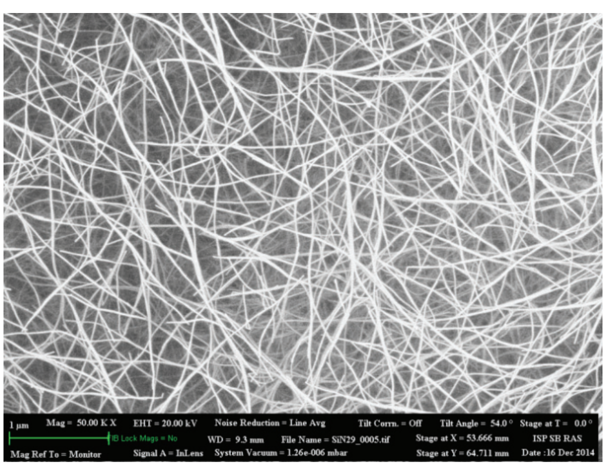

Figure 7: High resolution SEM image of TCF made of suspension of SWCNTs

4 CONCLUSION

The comparative study of properties of lithium-ion batteries and transparent conductive films have shown that single-walled carbon nanotubes are feasible alternative to conductive agents currently used in Li-ion batteries and transparent conductive films.

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