CARBON NANOTUBES AS CONDUCTIVE AGENT FOR LITHIUM-ION BATTERIES ELECTRODES

Alberto Varzi[a], Corina Täubert[a], Margret Wohlfahrt-Mehrens[a]
Martin Kreis[b], Walter Schütz[b]

[a]ZSW - Center for Solar Energy and Hydrogen Research,
Helmholzstraße 8, D-89081 Ulm, Germany
[b]FutureCarbon GmbH,
Gottlieb-Keim-Straße 60, D-95448 Bayreuth, Germany

Introduction

Carbon nanotubes (CNTs) have a wide range of properties which make them highly suitable for several high-tech applications. Especially during the last years they attracted a lot of interest in the field of electrochemical devices and in particular as possible application in lithium-ion batteries and supercapacitors [1, 2].

For hybrid, plug-in and electric vehicles applications, Li-ion batteries with high power capability are required. Without any doubt, highly conductive electrodes are a key factor for achieving high power batteries. Many works investigated the addition of CNTs as conductive agent for positive electrodes, using several active materials such as $LiCoO_2$ [2-4], $LiNi_{0.7}Co_{0.3}O_2$ [5], MnO_2 [6], $LiFePO_4$ [7, 9]. CNTs can provide not only higher conductivity and thus better capability at high C-rates than the commonly used conductive agents, but they could also improve the capacity retention upon cycling by avoiding contact loss between the active particles.

Regarding the negative side in lithium-ion batteries, CNTs are considered as interesting active materials because they can insert Li ions in a similar way as graphite. Depending on the structure and shape of the CNTs, Li can be inserted not only in the inner space of the tube but also on the outer surface and on the edges of the rolled-up graphene layers [10]. However, the high irreversible capacity at the first cycle and the poor cycling stability hinder a real application as active materials for anodes.

In the present work we evaluated MWCNTs as conductive agents for both cathode and anode electrodes for Li-ion batteries, with the aim of replacing the classical carbon black and/or graphite and thus increasing the electronic conductivity. $LiNi_{0.33}Co_{0.33}Mn_{0.33}O_2$ (NCM) has been chosen as active material for positive electrodes and a nano-sized TiO_2 rutile for the negative electrodes.

Experimental

The CNTs used in this work were multi-walled (MWCNTs, FutureCarbon GmbH), produced by means of chemical vapor deposition (CVD) process on a metal catalyst. They have an average outer diameter of about 13 nm and 5 to 9 walls; their length is in the range of several micrometers (see Fig. 1). The iron catalyst residue was removed via an acid purification and the nanotubes were dispersed in anhydrous N-Methyl-2-pyrrolidone (NMP) by successive high energy and high shearing force steps.

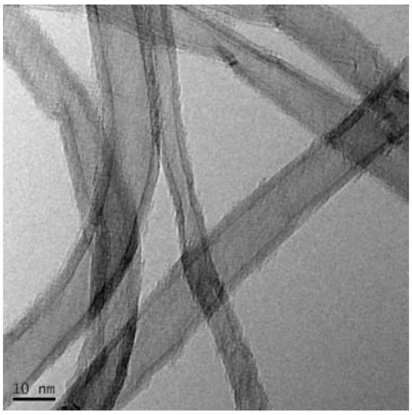

Fig. 1 TEM image of MWCNTs produced by CVD from FutureCarbon GmbH.

The electrodes have been fabricated by coating slurries containing the active materials (NCM or TiO_2 rutile), conductive agents (carbon black, graphite, MWCNTs) and a PVDF binder in NMP. Al and Cu foils were used as current collectors.

The electrochemical characterization has been carried out in three-electrode cells with Li as counter and reference electrodes. The cells were assembled in an Ar-filled glove box with glass microfiber separators and a $LiPF_6$ electrolyte. All measurements have been performed at room temperature with a VMP multi-channel potentiostat/galvanostat (Bio-logic Science Instrument). The main used electrochemical characterization technique was galvanostatic cycling with potential limitation. The potential range for the positive electrodes was 3.0-4.3 V vs. Li/Li^+. For the negative electrodes two potential ranges were tested: 1.0-3.0 V and 0.1-3.0 V. All potentials are reported vs. Li/Li^+.

Results and Discussion

Due to their shape, MWCNTs can ensure a better contact between the active particles in comparison to the classical conductive agents (e.g. carbon blacks or graphite). Also, their flexibility contributes to a better cyclability.

The addition of a relative low amount of MWCNTs (1-2 wt %) significantly improved the rate capability of the NCM-based positive electrodes at all investigated C-rates, as Fig. 2 shows. Especially at currents as high as 5C the improvement in the capacity was of about 30 mA h/g (see Fig. 3).

Most of the studies investigated CNTs as conductive agents for positive rather than negative electrodes. In the present work we evaluated the influence of CNTs addition on the electrochemical performance of a nano-sized TiO_2 rutile, a very promising active material for anodes that is well known for its excellent rate capability. The electrochemical characterization has been carried out at different C-rates up to 30C, and with different cut-off potentials. In the potential range 1.0-3.0 V the addition of CNTs has proven to have a beneficial effect on the rate capability of the electrodes. If the cut-off is extended to 0.1 V, the electrodes containing CNTs show a substantial capacity fading (see Fig. 4). As demonstrated by the voltage profiles reported in Fig 5, a deeper discharge of the composite electrode also increases dramatically the first cycle irreversible capacity. This can be due both to the SEI formation and Li insertion into the CNTs.

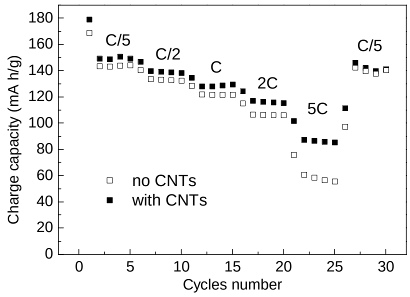

Fig. 2 Rate performance of NCM electrodes at different charge/discharge rates – comparison between the "classical" conductive agents and MWCNTs.

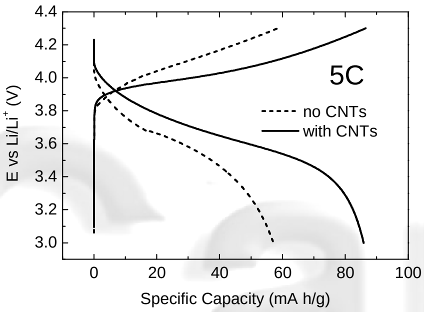

Fig. 3 Charge and discharge voltage profiles at high current rate (5C) of NCM electrodes: with (solid line) and without the addition of MWCNTs (dashed line).

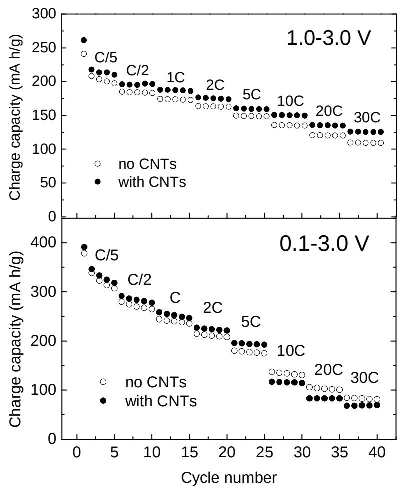

Fig. 4 Rate performance of TiO_2 electrodes at various charge/discharge rates in two different potential ranges - comparison between the "classical" conductive agents and MWCNTs.

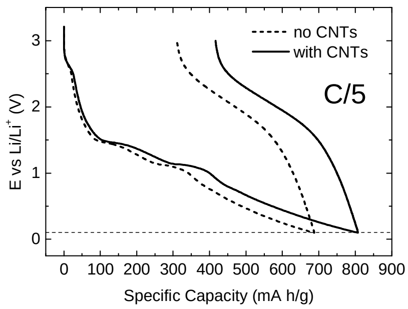

Fig. 5 First cycle discharge and charge voltage profiles of TiO_2 rutile electrodes: with (solid line) and without the addition of MWCNTs (dashed line).

Conclusions

In this work one of the most promising applications of CNTs concerning the field of Li-ion batteries has been investigated. Both positive and negative electrodes containing MWCNTs as conductive agent showed higher performances in terms of specific capacity, even if in the case of TiO_2 anodes the cut-off potential plays an important role. Since SEI formation could occur differently in the case of CNTs-containing anodes, this can be an explanation of the higher irreversible capacity observed during the first cycle in the potential range 0.1-3.0 V. A less conductive/thicker SEI film can also cause the capacity fading observed at high C-rates.

Acknowledgments. This work was done in the frame of the "CarboPower" project (Inno.CNT) with the support of Germany's Federal Ministry for Education and Research (BMBF). The authors wish also to thank Dr. Pierre Kubiak and Manuel Pfanzelt (ZSW) and the group of Prof. Hüsing (Institute of Inorganic Chemistry I, University of Ulm).

References

[1] B.J. Landi, M.J. Ganter, C.D. Cress, R.A. DiLeo and R.P. Raffaelle, Energy and Environmental Science 2009;22:638-654.

[2] W. Guoping, Z. Qingtang, Y. Zuolong, Q. MeiZheng, Solid State Ionics 2008;179:263-268.

[3] Z. Qing-Tang, Q. Mei-Zhen, N. Hong, Y. Zuo-long, New Carbon Materials 2007;22(4):361-364.

[4] K. Sheem, Y. Hee Lee, H.S. Lim, Journal of Power Sources 2006;158:1425-1430.

[5] X. Li, F. Kang and W. Shen, Electrochemical and Solid State Letters 2006;9(3):A126-A129.

[6] H. Yue, X. Huang, Y. Yang, Materials Letters 2008;62:3388-3390.

[7] X. Li, F. Kang, X. Bai, W. Shen, Electrochemistry Communications 2007;9:663-666.

[8] Y. Liu, X. Li, H. Guo, Z. Wang, W. Peng, Y. Yang, R. Liang, Journal of Power Sources 2008;184:522-526.

[9] B. Jin, E. Mei Jin, K-H. Park, H-B. Guo, Electrochemistry Communications 2008;10:1537-1540.

[10] Y. Matsumura, S. Wang and J. Mondori, Carbon 1995;33:1457-1462.