



## Study of multi-walled carbon nanotubes for lithium-ion battery electrodes

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### ABSTRACT

The potential use of multi-walled carbon nanotubes (MWCNTs) produced by Chemical Vapor Deposition (CVD) as conductive agent for electrodes in Li-ion batteries has been investigated.  $\text{LiNi}_{0.33}\text{Co}_{0.33}\text{Mn}_{0.33}\text{O}_2$  (NCM) has been chosen as the active material for positive electrodes, and a nano-sized  $\text{TiO}_2$ -rutile for the negative electrodes. Also the MWCNTs ability of reversibly inserting Li has been characterized. The electrochemical performances of the electrodes are studied by galvanostatic techniques and cyclic voltammetry. In particular the influence of the nanotubes on the rate capability is evaluated. The addition of MWCNTs significantly enhances the rate performances of NCM-based cathodes at all investigated C-rates. The 1 wt.% MWCNTs in  $\text{TiO}_2$  rutile-based anodes accounts for an increase in the rate capability when the electrodes are cycled in the potential range 1.0–3.0 V. The range extension to more negative potentials (i.e. 0.1–3.0 V), however, causes a capacity fading especially at higher current rates. The obtained results demonstrate that the addition of MWCNTs to the electrode composition, even in low amounts, enables an increase in both energy and power densities of a Li-ion battery.

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### 1. Introduction

Since their discovery, the interest around carbon nanotubes (CNTs) has grown continuously. Particularly in the last decade, both their electrical and mechanical properties have become an area of interest for Li-ion battery applications.

Carbon nanotubes can be considered as one-dimensional structures and schematically viewed as cylinders comprised of rolled-up graphene layers. They are commonly classified depending on the number of layers that constitute their walls. Only one graphene layer defines the so-called single-walled carbon nanotubes (SWCNTs), while multi-walled carbon nanotubes (MWCNTs) are made by several sheets. SWCNTs have been extensively studied both theoretically and experimentally. They can be entirely described (except for their length) by a single vector (i.e. chiral vector) which defines the way in which the layers are rolled-up, thus determining their properties. Among these, the electronic conductivity is one of the most affected by the structure of the nanotubes. SWCNTs show either metallic or semiconductive behavior, depending on the band structure, and the energy gap of the semiconducting ones is related to the chirality [1]. Regarding MWCNTs, an accurate description of the relation between structure and properties is anything but a trivial matter. In fact, by increasing the number of

concentric tubes, the complexity of the problem increases too. In spite of that, there are different models describing MWCNTs, which are in a good agreement with the experimental results [1].

There are mainly two features that make CNTs interesting for Li-ion battery applications. The high electronic conductivity compared to carbon blacks makes them suitable as conductive agent for electrodes. On the other hand, their ability to insert Li ions might allow them to be used as anode active material [2].

Many works have investigated the addition of CNTs as a conductive agent for positive electrodes, using several active materials such as  $\text{LiCoO}_2$  [3–5],  $\text{LiNi}_{0.7}\text{Co}_{0.3}\text{O}_2$  [6],  $\text{MnO}_2$  [7],  $\text{LiMn}_2\text{O}_4$  [8,9],  $\text{LiFePO}_4$  [10–13], and  $\text{LiMnPO}_4$  [13]. According to these studies, CNTs can not only provide higher conductivity and thus better capability at high C-rates, 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 interesting active materials because they can insert Li ions in a way similar to graphite. Due to their big aspect ratio they can reach a capacity higher than  $372 \text{ mAh g}^{-1}$ , which is the theoretical capacity of graphite. Depending on the structure and shape of the CNTs, Li can not only be inserted in the inner space of the tube but also on the outer surface as well as on the edges of the rolled-up graphene layers [14]. However, the high irreversible capacity at the first cycle and the poor cycling stability hinder a real application as active material for anodes.

For these kinds of applications, the cost plays a key role and is presently the main factor hindering an extensive use in commercial

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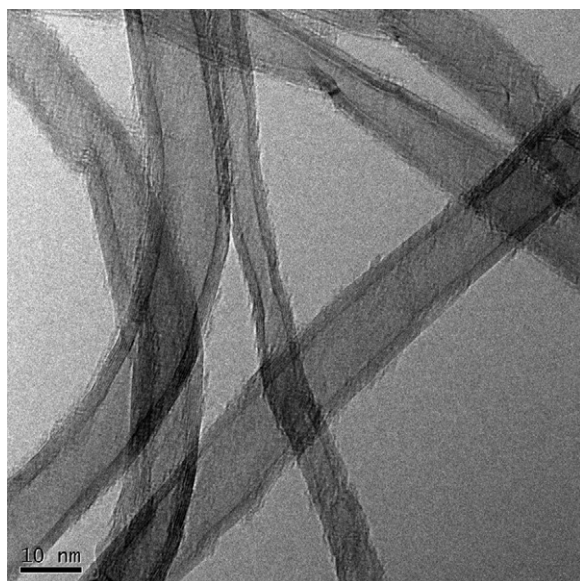


Fig. 1. TEM image of MWCNTs produced by CVD from FutureCarbon GmbH.

devices. SWCNTs have the biggest gap to fill as their price is 50–100 times higher than that of MWCNTs.

In this work we evaluated MWCNTs as conductive agent for both cathode and anode electrodes in Li-ion batteries, with the aim of partially replacing the classical carbon black and/or graphite and thus enhancing the electrochemical performances.  $\text{LiNi}_{0.33}\text{Co}_{0.33}\text{Mn}_{0.33}\text{O}_2$  (NCM) has been chosen as active material for the positive electrodes, and a nano-sized  $\text{TiO}_2$ -rutile for the negative electrodes. Especially the influence of MWCNTs on the rate capability has been evaluated. Also the ability of the MWCNTs to reversibly insert Li has been investigated.

## 2. Experimental

### 2.1. Electrode preparation and characterization

The CNTs used in this work were multi-walled (MWCNTs, from FutureCarbon GmbH), produced via Chemical Vapor Deposition (CVD) on a metal catalyst (Fe). They had an average outer diameter of about 8–17 nm and consisted of 5–9 walls (see Fig. 1); their length is in the range of several micrometers (1–10  $\mu\text{m}$ ). The iron catalyst residue was removed using an acid purification, and the obtained nanotubes were dispersed in anhydrous N-methyl-2-pyrrolidone (NMP) by successive high energy and high shearing force steps.

MWCNTs tend to agglomerate during production and to re-agglomerate in dispersions. Thus high shearing forces are helpful for breaking up the agglomerations. Low energy methods are usually not successful while “brute force” methods like ball milling might pulverize the nanotubes.

The positive electrodes were fabricated from  $\text{LiNi}_{0.33}\text{Co}_{0.33}\text{Mn}_{0.33}\text{O}_2$  (hereinafter called NCM) with the fol-

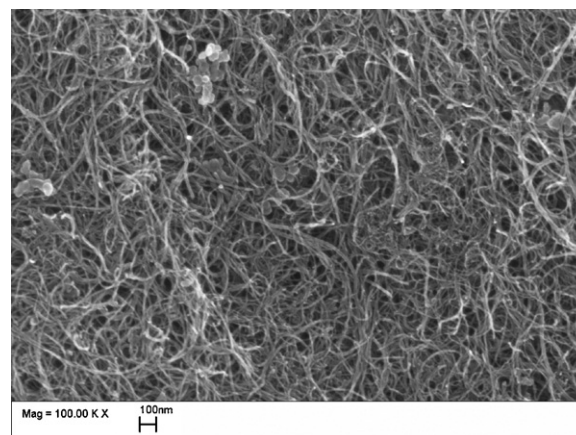


Fig. 2. SEM micrograph of a MWCNTs-based electrode.

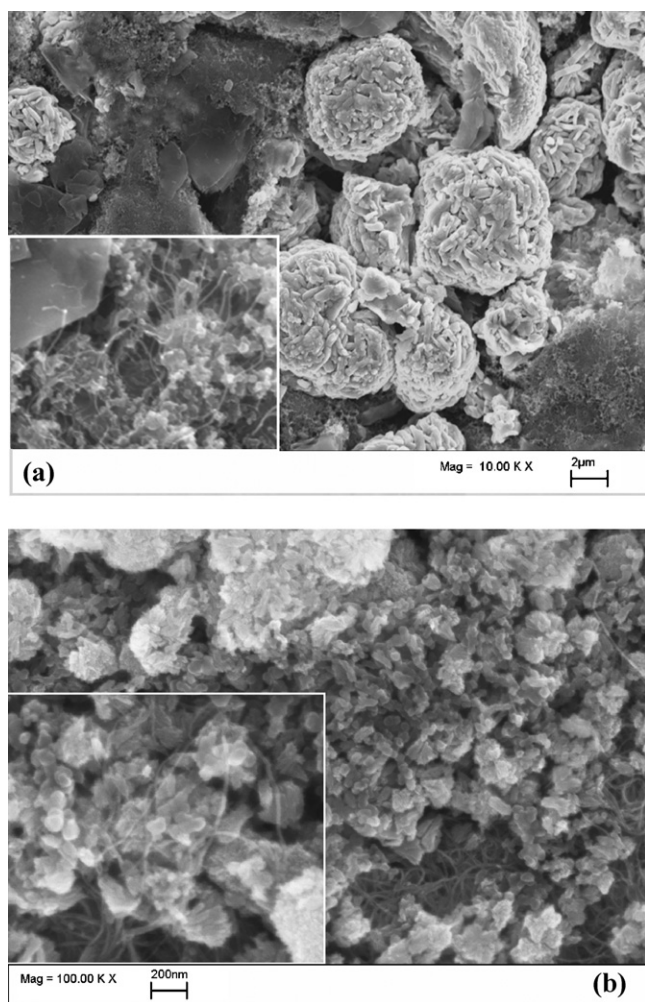
lowing standard composition: 84 wt.% NCM, 6 wt.% carbon black (SuperP, Timcal), 2 wt.% graphite (SFG6, Timcal), and 8 wt.% poly (vinylidene fluoride) (PVDF) binder (Solvay). The active material for the negative electrodes was a nano-sized  $\text{TiO}_2$  rutile (synthesized at the Institute of Inorganic Chemistry I of the University of Ulm, from the group of Prof. Hüsing), with the electrodes containing 76 wt.%  $\text{TiO}_2$  rutile, 12 wt.% carbon black (SuperP), and 12 wt.% PVDF binder (Solvay). Starting with these formulations, 1 wt.% of MWCNTs was added to the electrodes' composition to replace 4 wt.% of carbon black in the NCM-based electrodes and 1 wt.% in the  $\text{TiO}_2$  rutile-based one, respectively. Electrodes with MWCNTs as active material contained 85 wt.% MWCNTs, 10 wt.% carbon black (SuperP), and 5 wt.% PVDF binder (Solvay). Table 1 gives an overview of the electrode formulations which were characterized. The slurries were coated by using the “doctor-blade” technique on Al (positive electrodes) or Cu (negative electrodes) foils. The obtained electrodes were very homogeneous. The loadings of the NCM-based electrodes were slightly different for the MWCNTs-containing electrodes compared to the standard composition. A reason for this could be the different electrode formulations in the two cases. However, the densities had similar values of about 1.9–2.0  $\text{g cm}^{-3}$ . In the case of the  $\text{TiO}_2$  rutile-based electrodes both those with and those without MWCNTs had similar loadings and densities (0.6  $\text{g cm}^{-3}$ ). Figs. 2 and 3 show the SEM micrographs (collected on a LEO 1530 VP) of the MWCNTs-containing electrodes studied in this work.

### 2.2. Electrochemical characterization

The electrochemical characterization has been carried out in Swagelok three-electrode cells with Li as the counter and reference electrode. Before cell assembly in an Ar-filled glove box (MBraun), the electrodes were dried at 130 °C overnight in order to remove traces of water and solvent. Glass microfiber (Whatman, GF/A) was used as a separator. The electrolyte consisted of 1 M  $\text{LiPF}_6$  in ethylene carbonate and dimethyl carbonate (EC:DMC 1:1

Table 1  
Overview of the electrode formulations characterized in this work.

	Active material (wt.%)	Conductive agent			Binder (wt.%)
		Carbon black (wt.%)	Graphite (wt.%)	MWCNTs (wt.%)	
NCM	84	6	2	–	8
NCM + CNTs	87	2	2	1	8
$\text{TiO}_2$ rutile	76	12	–	–	8
$\text{TiO}_2$ rutile + CNTs	76	11	–	1	8
MWCNTs	85	10	–	–	5



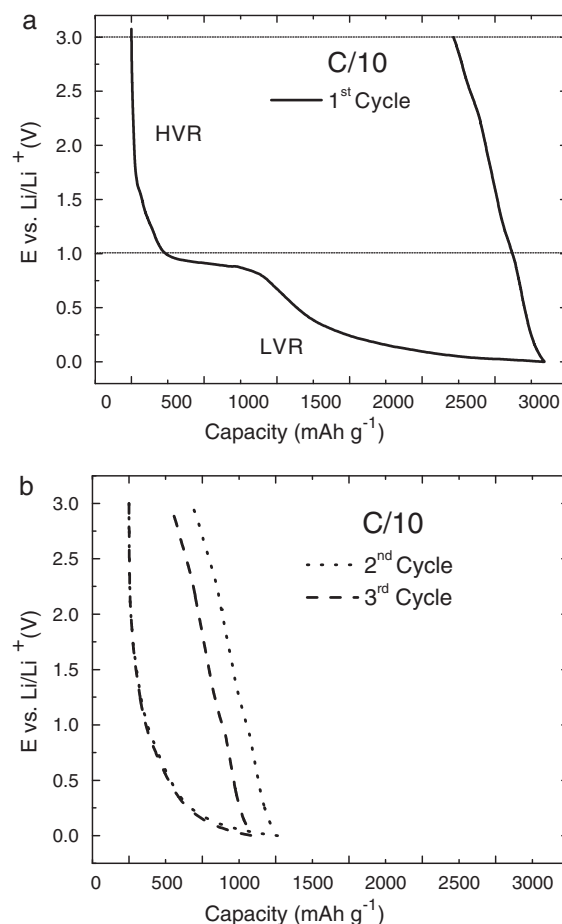
**Fig. 3.** SEM micrographs of electrodes containing MWCNTs as conductive agent: (a) NCM (positive) and (b) TiO<sub>2</sub> rutile (negative).

by w/w) from Ube, Japan. Another electrolyte composed of 0.7 M LiBOB in a mixture of EC and ethyl methyl carbonate (EC:EMC 1:1 by w/w) was used for investigating the SEI film formation on the electrodes with MWCNTs as active material. All the measurements were performed at room temperature with a VMP multi-channel potentiostat/galvanostat (Bio-logic Science Instrument), equipped with an EC-Lab<sup>®</sup> software. Galvanostatic cycling with potential limitation and cyclic voltammetry were the electrochemical techniques used in this work. The positive electrodes were tested in the potential window 3.0–4.3 V, while the negative ones both between 1.0–3.0 V and 0.1–3.0 V vs. Li/Li<sup>+</sup> (TiO<sub>2</sub> rutile-based), or 0–3.0 V vs. Li/Li<sup>+</sup> (MWCNTs-based). Charge always refers to delithiation, while discharge refers to lithiation. The applied current rates were calculated taking into account the following theoretical capacities: NCM = 278 mAh g<sup>-1</sup>; TiO<sub>2</sub> rutile = 335 mAh g<sup>-1</sup>; MWCNTs = 372 mAh g<sup>-1</sup>. Specific capacity values (mAh g<sup>-1</sup>) are obtained considering only the active material mass of the electrodes. All potentials are reported vs. Li/Li<sup>+</sup>.

### 3. Results and discussion

#### 3.1. MWCNTs as active material for Li insertion

Electrodes with MWCNTs as active material were characterized with two aims: (i) to determine their potential for reversible Li insertion and (ii) to observe their electrochemical behavior in the



**Fig. 4.** Voltage profile of the (a) first and (b) second and third discharge/charge cycles at a C/10 rate of MWCNTs-based electrodes in 1 M LiPF<sub>6</sub> in EC-DMC.

potential range 0–2.0 V in which anodes are usually active, and thus to find out if they are suitable as conductive agent for negative electrodes in Li-ion batteries.

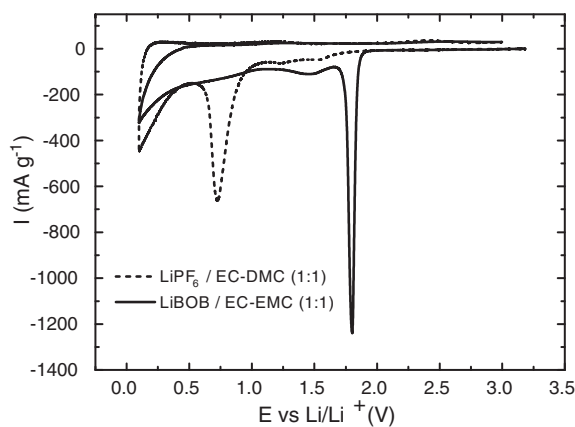
The electrochemical behavior of CNTs upon galvanostatic cycling has been extensively investigated and is known to be dependent on the kind and shape of the tubes [15]. Previous works in the literature have demonstrated through several techniques (XRD, <sup>7</sup>Li NMR, micro-Raman) that Li insertion starts in CNTs below 0.1 V. If it starts at more positive potentials, it proceeds without any electronic transfer [16–18]. The complete lithiation is reached only at potentials very close to 0 V [17].

A typical feature of CNTs is a significant irreversible capacity loss in the first cycle, which is usually greater in the case of opened CNTs in comparison to the closed ones. This was attributed to the SEI film formation occurring below 1 V vs. Li/Li<sup>+</sup> (usually 0.7–0.9 V) in LiPF<sub>6</sub> or LiClO<sub>4</sub>-based electrolytes [19,20]. Fig. 4 presents the first three discharge/charge galvanostatic cycles in the potential range 0–3.0 V at a rate of C/10 (calculated considering the theoretical capacity of graphite, 372 mAh g<sup>-1</sup>).

After a first steep decay (usually called high voltage region (HVR)), the potential reaches a large pseudo-plateau at about 0.9 V which can be related to electrolyte decomposition and SEI formation. This plateau can be observed only in the first cycle (see Fig. 4a).

The assumption that this corresponds to SEI film formation could be confirmed by cyclic voltammetric experiments carried out on MWCNTs electrodes in a LiBOB-based electrolyte (Fig. 5). LiBOB is known for its ability to form a stable film on the graphite surface [21–24]. In comparison to LiPF<sub>6</sub>, film formation in LiBOB starts at more positive potentials – i.e. about 1.8 V (see the peak in Fig. 5,





**Fig. 5.** Cyclic current-potential curves for MWCNTs electrodes, recorded at  $0.05 \text{ mV s}^{-1}$ . The first cycles in  $\text{LiPF}_6/\text{EC-DMC}$  (1:1) (dashed line), and  $\text{LiBOB}/\text{EC-EMC}$  (1:1) (solid line) are compared.

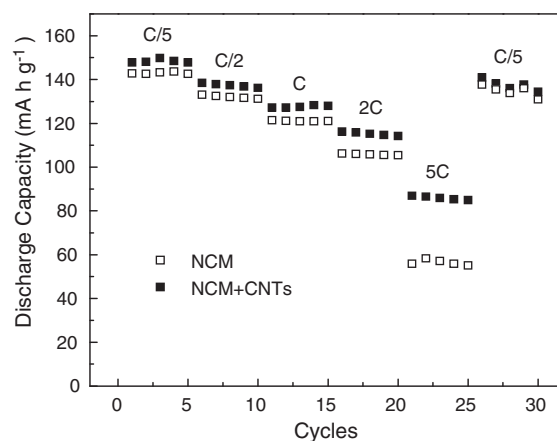
solid line). In the  $\text{LiPF}_6$ -based electrolyte a clear defined peak can be observed at  $0.75 \text{ V}$  (see the dashed line in Fig. 5).

Li insertion in MWCNTs occurs only in the lower potential region (LVR) and it clearly differs from the case of graphite. While the typical discharge curve of the latter usually shows a staging phenomenon characterized by several potential plateaus, in the former case such behavior is not observed. Though much work has been done to understand the lithium storage mechanisms in CNTs, there are still no conclusive studies on this topic. In general, because of the morphological complexity of the CNTs, the identification of the Li storage sites remains the main hindrance for elucidating the mechanism of Li insertion. Indeed, different from graphite, Li storage in CNTs is much more affected by the presence of so called “3D defects”, such as cavities and pores of several shapes and dimensions [25].

The irreversible capacity observed in the first cycle is about  $2200 \text{ mAh g}^{-1}$  and considerably larger than the results reported in the literature for MWCNTs [19,26]. A possible explanation for such kind of behavior is the high ratio of open-ended MWCNTs. As described in Section 2, the MWCNTs used in this work underwent an acid treatment in order to remove the metal catalyst residues. Besides removing Fe particles, the acid attacks the defects as well (most of them usually being located at the ends of the nanotubes) and most likely causes an opening of the tubes. Phenomena associated to SEI film formation (e.g. electrolyte reduction) can cause a high irreversible capacity loss in the first discharge. The higher the surface area, the more significant the film formation can be. Open MWCNTs can provide a greater available surface in comparison to closed MWCNTs (or SWCNTs) and thus exhibit higher irreversible capacity [19,20]. Another possibility is that, as Frackowiak et al. suggested in Ref. [27], Li could be adsorbed (and trapped) at the edges of pseudo-graphitic aromatic layers present at the opened ends of the tubes or at micro-textural irregularities. Furthermore, CNTs have the tendency to form bundles, thus conferring a higher porosity to the electrode (see also Fig. 2). Hence, the electrolyte can better access the active surface and decompose to form the passive SEI layer [28].

### 3.2. MWCNTs as conductive agent for NCM-based cathodes

The feasible application of Li-ion batteries as power sources for electrical engines in the automotive field necessarily requires them to have high power performances. In order to achieve this, the electrodes should possess a high electronic conductivity. Electrode formulations always contain conductive additives in different amounts (usually 2–10 wt.%) since most of the electrode materials



**Fig. 6.** Rate capability of NCM-based electrodes in a  $\text{LiPF}_6$  electrolyte at different charge/discharge rates ranging between C/5 and 5C – comparison between electrodes without MWCNTs and with 1 wt.% MWCNTs.

(especially for cathodes) have a poor electronic conductivity. In the case of cathodes, these additives (e.g. carbon black, graphite) do not contribute to the capacity since they are electrochemically inactive for Li insertion at the typical working potentials of a positive electrode. A high amount of conductive agents would mean a lower amount of active material, thus penalizing the energy density. Due to their excellent electronic conductivity, 0.5–1 wt.% CNTs can theoretically completely replace the commonly used conductive agents. More conductive electrodes would also mean better rate capability and thus higher power. Hence, using CNTs could improve both the power and energy densities of Li-ion batteries.

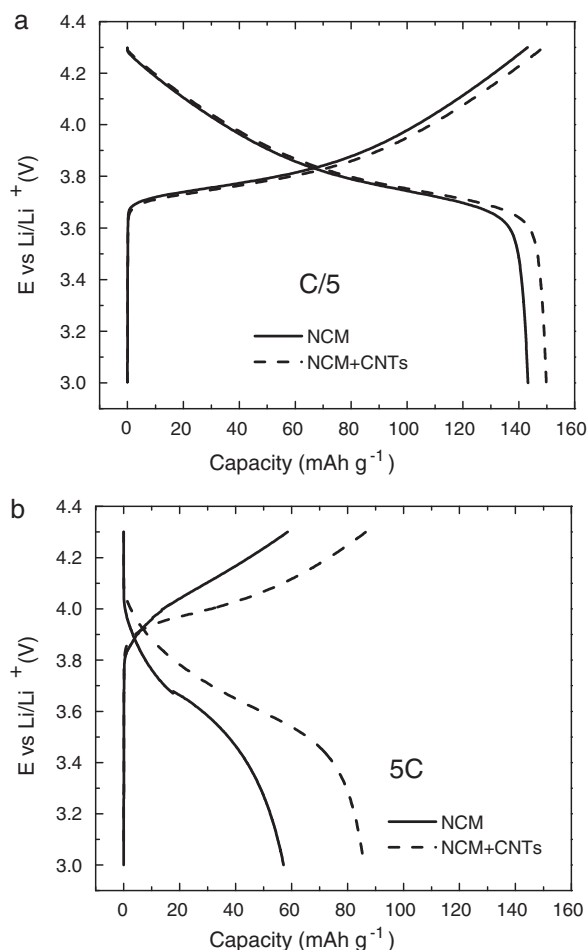
$\text{LiCoO}_2$  is still one of the most used cathode materials in commercial batteries for portable applications, mostly due to its good electrochemical properties and high energy density. It suffers, however, from a relative low thermal stability, which can cause safety problems. Among the layered metal oxides, NCM seems to be a very promising cathode material because of better thermal safety characteristics with respect to  $\text{LiCoO}_2$ , good capacity in a wide potential range and small volume changes upon cycling [29–31].

The effect of MWCNTs addition on the electrochemical performances of NCM-based cathodes has been investigated by galvanostatic tests at different C-rates between C/5 and 5C.

As shown in Fig. 6, the specific discharge capacities delivered by the cathodes containing MWCNTs are at all investigated C-rates higher than those of the electrodes containing only the classical conductive agents. The difference becomes more significant at rates higher than 2C. The addition of MWCNTs to the electrode considerably improves the capacity especially at 5C:  $87 \text{ mAh g}^{-1}$  in comparison to only  $58 \text{ mAh g}^{-1}$  with the commonly used conductive agents. Also after cycling at relatively high currents, and returning to C/5, the capacity values are almost the same as the initial ones. Misleading values of discharge capacity can be obtained when charging with a very low current. Indeed, it is worth to notice that, in this work all the galvanostatic measurements have been performed applying the same current rates both for charge and discharge.

Fig. 7 depicts the voltage curves for NCM electrodes recorded at C/5 and 5C rates. The slope-like voltage profile is typical for Li insertion/extraction from a layered oxide [29,30], and at the higher C-rate the lower polarization clearly reflects improved electrode kinetics.

Several studies relate the better rate capability to an improved electronic conductivity of the electrodes due to the CNTs [3–8,10–12]. This might be the case when replacing the classical conductive agents with the same amount of CNTs. However, in the present work the total amount of conductive agents has been



**Fig. 7.** Charge/discharge voltage profiles at a rate of (a) C/5 and (b) 5C – comparison between NCM electrodes without (dashed line) and with MWCNTs (solid line).

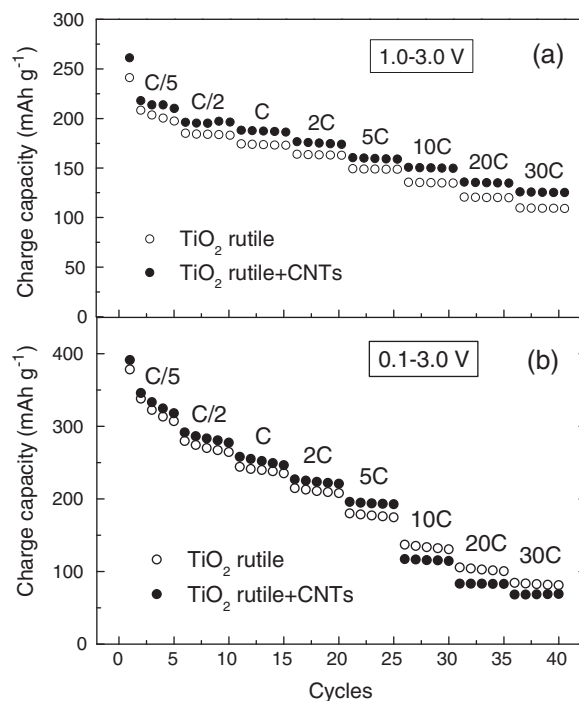
reduced, while the amount of active material has been increased. Therefore electronic conductivity measurements using the van der Pauw technique (results not reported) did not show a significant improvement. The authors believe that the presence of MWCNTs also influences the electrode structure, in particular the porosity. A better pore distribution can improve the electrolyte access and thus the Li ions diffusion into the active material particles.

### 3.3. MWCNTs as conductive agent for TiO<sub>2</sub> rutile-based anodes

Many studies in the literature concerning Li-ion batteries dealt with the use of CNTs as Li host at the negative side [15–18,32]. Recently, they have also been investigated for application as a kind of buffer against electrode expansion/contraction occurring during the alloying/de-alloying reactions of Li-alloy materials such as Li<sub>x</sub>Si<sub>y</sub> [33,34].

Carbonaceous materials (such as graphite and hard carbons) are the most commonly used anode materials for commercial Li-ion batteries. However, they can suffer from poor rate performances and low thermal stability. The demand for high power batteries with improved safety in the last years has led the research to faster materials with higher thermal stability and thus safety. In these terms, a promising anode material is TiO<sub>2</sub> rutile [35] because of its excellent rate capability, high stability and last but not least non-toxicity [36,37].

The main advantage of both TiO<sub>2</sub> anatase and rutile is that the Li insertion occurs in the potential stability window of the standard electrolytes (above 1 V vs. Li/Li<sup>+</sup>). On the other hand, such a high



**Fig. 8.** Rate capability of TiO<sub>2</sub> rutile-based negative electrodes in a LiPF<sub>6</sub> electrolyte in two different voltage windows: (a) 1.0–3.0 V and (b) 0.1–3.0 V – comparison between electrodes without (empty dots) and with MWCNTs (filled dots).

anode potential strongly penalizes the overall energy of the battery. Extending the potential window to more negative values allows a gain in terms of capacity but also affects the rate capability [36]. Even though the MWCNTs are known to be active toward the formation of an SEI film at potential below 1 V, a small amount of them could theoretically improve the rate capability without affecting the other electrochemical properties too much.

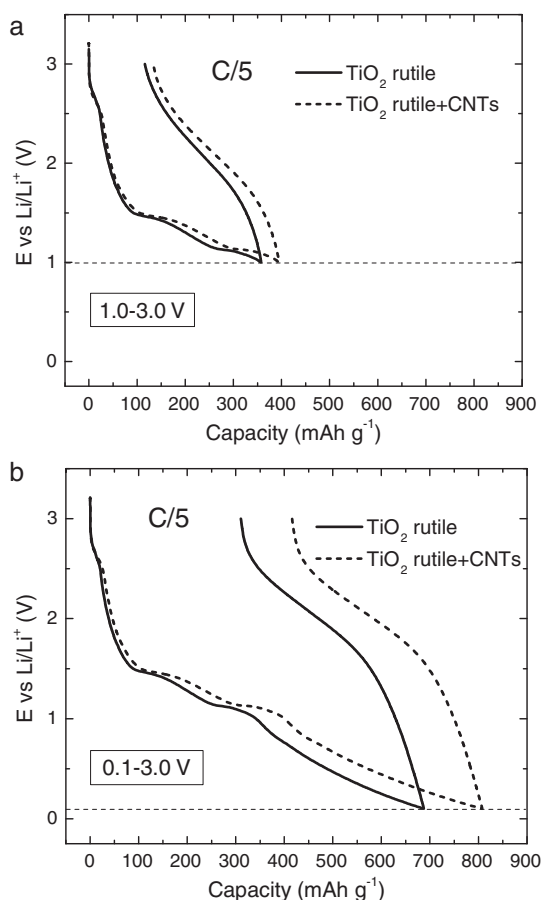
For the present study, a new nano-sized TiO<sub>2</sub> rutile has been used as active material. In the case of carbonaceous materials, the electrode conductivity has never been a great issue. On the contrary, TiO<sub>2</sub> rutile needs a certain amount of conductive agents since the material itself is a semiconductor.

The MWCNTs were added to the slurry formulations to partly replace SuperP and the resulting electrodes were electrochemically characterized. In particular the influence of the cut-off potential on the performances was investigated. Fig. 8 shows the rate capability of TiO<sub>2</sub> rutile-based composite electrodes with SuperP as unique conductive agent and with the SuperP+MWCNTs combination. Different C-rates between C/5 and 30C were employed for discharge/charge the electrodes.

At all investigated C-rates the addition of MWCNTs leads to an increase in the specific capacity when cycling in the potential range 1.0–3.0 V. Extending the potential window to 0.1 V, a certain capacity fading can be observed for current rates higher than 5C (see Fig. 8b). In Fig. 9 the voltage profiles during the first discharge/charge in both investigated potential windows are reported.

If we compare the profiles in the two cases, it is quite clear that a deeper discharge of the composite electrode (up to 0.1 V) significantly increases the first cycle irreversible capacity loss, regardless if the electrodes contain nanotubes or not (see Table 2 for the exact values).

In a previous work, Pfanzelt et al. [36] investigated the electrochemical properties of TiO<sub>2</sub> rutile with the same electrolyte. They suggested that the film formation (at potentials lower than 0.8 V) could be a possible explanation for the first cycle higher irreversible capacity in the broader potential window.



**Fig. 9.** Voltage profiles for the first Li insertion/extraction of  $\text{TiO}_2$  rutile-based negative electrodes in two different voltage windows: (a) 1.0–3.0 V and (b) 0.1–3.0 V. Electrodes without (solid line) and with MWCNTs (dashed line) are compared.

**Table 2**

First cycle irreversible capacities of  $\text{TiO}_2$  rutile-based electrodes.

CUT-OFF (V vs. $\text{Li/Li}^+$ )	$\text{TiO}_2$ rutile ( $\text{mAh g}^{-1}$ )	$\text{TiO}_2$ rutile + CNTs ( $\text{mAh g}^{-1}$ )
1–3 V	116	133
0.1–3 V	310	416

As expected, the presence of MWCNTs in the  $\text{TiO}_2$  rutile-based electrodes brings an additional contribution to irreversible capacity in both potential windows. When cycling in the potential range 0.1–3.0 V the irreversible capacity associated with the CNTs increases substantially from  $17 \text{ mAh g}^{-1}$  to  $106 \text{ mAh g}^{-1}$ .

This behavior might partially be attributed to Li ions irreversibly trapped by the tubes. However, according to literature, no Li insertion should occur in the nanotubes at potential more positive than 0.1 V, or at least only in a negligible part. It is more likely that this difference arises from the SEI formation in the case of the MWCNTs-containing electrodes. In principle, a less conductive SEI might also affect the rate capability at high C-rates causing the fading shown in Fig. 8b. Further investigations are required in order to support this hypothesis.

#### 4. Conclusions

The addition of a small amount of MWCNTs as conductive agent has been evaluated with both positive and negative electrode materials for Li-ion batteries. Also, the ability of MWCNTs to reversibly insert Li has been investigated.

The addition of 1 wt.% MWCNTs enhanced the rate capability of NCM-based cathodes at all investigated C-rates. The effect is more significant at high current rates – i.e. about 50% higher specific capacity at 5C.

The replacement of only 1 wt.% of SuperP with the same amount of MWCNTs in  $\text{TiO}_2$  rutile-based anodes results in an increase in the rate capability if the electrodes are cycled in the potential range 1.0–3.0 V. When extending the range to more negative potentials (0.1–3.0 V) a pronounced capacity fading is observed, especially at higher C-rates. Also, the irreversible capacity loss in the first cycle becomes more significant. A tentative explanation of this phenomenon can be the formation of a thicker/less conductive SEI film on the electrodes containing MWCNTs.

The very significant irreversible capacity loss in the first cycle ( $2200 \text{ mAh g}^{-1}$ ), together with their poor reversibility, make the investigated MWCNTs not suitable for Li insertion.

CNTs are a fascinating tool for enhancing the power density of Li-ion batteries by improving rate capability of both positive and negative electrodes. Their ability to insert Li and the formation of a SEI film on their surface must be considered when choosing the right working potential window. This is very important especially when using CNTs as conductive agents for negative electrodes, otherwise the electrode performances can suffer.

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#### References

- [1] T. Belin, F. Epron, Mater. Sci. Eng. B B 119 (2005) 105–118.
- [2] B.J. Landi, M.J. Ganter, C.D. Cress, R.A. DiLeo, R.P. Raffaele, Energy Environ. Sci. 2 (2009) 638–654.
- [3] W. Guoping, Z. Qingtang, Y. Zuolong, Q. Meizheng, Solid State Ionics 179 (2008) 263–268.
- [4] Z. Qing-Tang, Q. Mei-Zhen, N. Hong, Y. Zuo-long, New Carbon Mater. 22 (4) (2007) 361–364.
- [5] K. Sheem, Y. Hee Lee, H.S. Lim, J. Power Sources 158 (2006) 1425–1430.
- [6] X. Li, F. Kang, W. Shen, Electrochem. Solid-State Lett. 9 (3) (2006) A126–A129.
- [7] H. Yue, X. Huang, Y. Yang, Mater. Lett. 62 (2008) 3388–3390.
- [8] S. Chen, C. Mi, L. Su, B. Gao, Q. Fu, X. Zhang, J. Appl. Electrochem. 39 (2009) 1943–1948.
- [9] S-B. Ma, K-W. Nam, W-S. Yoon, S-M. Bak, X-Q. Yang, B-W. Cho, K-B. Kim, Electrochem. Commun. 11 (2009) 1575–1578.
- [10] X. Li, F. Kang, X. Bai, W. Shen, Electrochem. Commun. 9 (2007) 663–666.
- [11] Y. Liu, X. Li, H. Guo, Z. Wang, W. Peng, Y. Yang, R. Liang, J. Power Sources 184 (2008) 522–526.
- [12] B. Jin, E. Mei Jin, K-H. Park, H-B. Guo, Electrochem. Commun. 10 (2008) 1537–1540.
- [13] L. Kavan, R. Bacsa, M. Tunckol, P. Serp, S.M. Zakeeruddin, F. Le Formal, M. Zúkalova, M. Graetzel, J. Power Sources 195 (2010) 5360–5369.
- [14] Y. Matsumura, S. Wang, J. Mondori, Carbon 33 (1995) 1457–1462.
- [15] Z. Yang, Y. Feng, Z. Li, S. Sang, Y. Zhou, L. Zeng, J. Electroanal. Chem. 580 (2005) 340–347.
- [16] F. Leroux, K. Méténier, S. Gautier, E. Frackowiak, S. Bonnamy, F. Béguin, J. Power Sources 81–82 (1999) 317–322.
- [17] G. Maurin, Ch. Bousquet, F. Henn, P. Bernier, R. Almairac, B. Simon, Chem. Phys. Lett. 312 (1999) 14–18.
- [18] G. Maurin, Ch. Bousquet, F. Henn, P. Bernier, R. Almairac, B. Simon, Solid State Ionics 136–137 (2000) 1295–1299.
- [19] Z. Yang, H. Wu, Solid State Ionics 143 (2001) 173–180.
- [20] A.S. Claye, J.E. Fischer, C.B. Huffman, A.G. Rinzler, R.E. Smalley, J. Electrochem. Soc. 147 (8) (2000) 2845–2852.
- [21] C. Täubert, M. Fleischhammer, M. Wohlfahrt-Mehrens, U. Wietelmann, T. Buhrmester, J. Electrochem. Soc. 157 (6) (2010) A721–A728.
- [22] J.-C. Panitz, U. Wietelmann, M. Wachtler, S. Ströbele, M. Wohlfahrt-Mehrens, J. Power Sources 153 (2006) 396–401.
- [23] K. Xu, S. Zhang, B.A. Poesse, T.R. Jow, Electrochem. Solid-State Lett. 5 (2002) A259–A262.

- [24] M. Wachtler, M. Wohlfahrt-Mehrens, S. Ströbele, J.-C. Panitz, U. Wietelmann, J. Appl. Electrochem. 36 (2006) 1199–1206.
- [25] N.A. Kaskhedikar, J. Maier, Adv. Mater. 21 (2009) 2664–2680.
- [26] Z. Yang, H. Wu, Chem. Phys. Lett. 343 (2001) 235–240.
- [27] E. Frackowiak, S. Gautier, H. Gaucher, S. Bonnamy, F. Béguin, Carbon 37 (1999) 61–69.
- [28] E. Frackowiak, F. Béguin, Carbon 40 (2002) 1775–1787.
- [29] S.-H. Kang, D.P. Abraham, W.-S. Yoon, K.-W. Nam, X.-Q. Yang, Electrochim. Acta 54 (2008) 684–689.
- [30] H. Kobayashi, Y. Arachi, S. Emura, H. Kageyama, K. Tatsumi, T. Kamiyama, J. Power Sources 146 (2005) 640–644.
- [31] J.-M. Kim, H.-T. Chung, Electrochim. Acta 49 (2004) 3573–3580.
- [32] G.T. Wu, C.S. Wang, X.B. Zhang, H.S. Yang, Z.F. Qi, P.M. He, W.Z. Li, J. Electrochem. Soc. 146 (5) (1999) 1696–1701.
- [33] J. Lee, J. Bae, J. Heo, I.T. Han, S.N. Cha, D.K. Kim, M. Yang, H.S. Han, W.S. Jeon, J. Chung, J. Electrochem. Soc. 156 (11) (2009) A905–A910.
- [34] T. Kim, Y.H. Mo, K.S. Nahm, S.M. Oh, J. Power Sources 162 (2006) 1275–1281.
- [35] Y.S. Hu, L. Kienle, Y.-G. Guo, J. Maier, Adv. Mater. 18 (2006) 1421–1426.
- [36] M. Pfanzelt, P. Kubiak, M. Wohlfahrt-Mehrens, Electrochem. Solid-State Lett. 13 (7) (2010) A91–A94.
- [37] P. Kubiak, M. Pfanzelt, J. Geserick, U. Hörmann, N. Hüsing, U. Kaiser, M. Wohlfahrt-Mehrens, J. Power Sources 194 (2009) 1099–1104.