Carbon Nanotubes for High-Performance Lithium-Ion Batteries

David Ensling¹, Alberto Varzi², Martin Kreis³, Corina Täubert², Sebastian Schebesta¹

¹ VARTA Microbattery GmbH
² FutureCarbon GmbH
³ Zentrum für Sonnenenergie- und Wasserstoff-Forschung (ZSW)
Outline

- Introduction
  - Project
  - Lithium-Ion Battery
  - Processing
- Material Evaluation
  - Anode
  - Cathode
- Conclusions
CarboPower

- Evaluation of Carbon Nanotubes (CNT) as conductive agent for next-generation lithium ion batteries
  - Improved **energy density** due to smaller amounts of conductive additives
  - Increased **power density** due to high conductivity
CNT Manufacturing and Refinement Processes

**CCVD Process for Base Material Synthesis** *(Catalytic Assisted Chemical Vapor Deposition)*

Current Production Capacity: ~ 1 ton per year
Short-term upscaleable to >10 tons per year, depending on demand
**CNT Properties**

- MWCNTs (5 to 9 walls)
- Average outer diameter: 13 nm
- Length: 1-100 µm
- BET: ~ 290 m^2/g

**CNT-Dispersions**
- Water (CMC-binder)
- NMP / NEP (PVDF-binder)
Preparation of Electrodes for Lithium-Ion Batteries

Composite Electrodes:
- Active material, i.e. LiCoO$_2$, Graphite (90%)
- Conductive agents, i.e. carbon black, CNTs (5%)
- Binder, i.e. PVDF, CMC (5%)

Process steps:
1. Mixing of components
2. Coating on Al- or Cu-foil (10 – 20 µm)
3. Cutting of electrodes
4. Calendaring
Typical processes during cell fabrication

Example: stacked cell
1. Stacking of single electrodes and separator
2. Tagging of current collectors
3. Packing in Pouch
4. Filling with electrolyte
5. Formation (first charging)
Lithium-ion battery

Composite electrodes: active material/binder/conductive agent

Solid-electrolyte interphase (SEI)

Graphite

Layered TM-Oxide

CNT: active anode material

CNT: conductive agent in anode and cathode
Negative Electrodes - MWCNTs as Lithium Host

Graphite (BET: ca. 4 m² g⁻¹)

MWCNTs (BET: ca. 300 m² g⁻¹)

- Different insertion mechanism compared to graphite (absence of a charge/discharge plateau) – still unclear due to difficulty in determining the Li storage sites
- Huge irreversible capacity due to **Solid Electrolyte Interphase (SEI)** → proportional to surface area!

Not suited as active anode material!
**Negative Electrodes - MWCNTs as Conductive Agent**

**Long-term cycling**

NMC/CNT vs. Graphite/CNT

Graphite anode: 0.05 – 0.35V

- Very good cycling stability, but unacceptable initial losses (<1V)

TiO$_2$/CNT vs. Li

TiO$_2$ anode: 1.0 - 1.8V

- Capacity is retained up to 80% after 1000 cycles in the potential window 1-3V
Positive Electrodes - MWCNTs as Conductive Agent

Long-term cycling stability of half cells (NMC vs. Li)

- MWCNTs avoid the contact loss between the particles providing a capacity retention up to 75% after 250 cycles at 2C
Full-cells

- Promising results for CNT-cathodes
- combination with standard anode in full cell

Experiment
- Variation of conductive additives
  (CNT, carbon black)

<table>
<thead>
<tr>
<th>Anode</th>
<th>Cathode</th>
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<tbody>
<tr>
<td>A</td>
<td>Graphite NMC + carbon / reference</td>
</tr>
<tr>
<td>B</td>
<td>Graphite NMC + „more“ carbon</td>
</tr>
<tr>
<td>C</td>
<td>Graphite NMC + CNT</td>
</tr>
</tbody>
</table>

CB = carbon black
Positive Electrodes - MWCNTs as Conductive Agent

Rate Capability of full cells (NMC/CNT vs. C)

C-rate:
C (mA) = Cap. (mAh)/h

<table>
<thead>
<tr>
<th>Capacity</th>
<th>3C</th>
<th>5C</th>
<th>8C</th>
</tr>
</thead>
<tbody>
<tr>
<td>(A) Reference</td>
<td>74%</td>
<td>45%</td>
<td>14%</td>
</tr>
<tr>
<td>(B) High Carbon</td>
<td>77%</td>
<td>56%</td>
<td>22%</td>
</tr>
<tr>
<td>(C) CNT</td>
<td>82%</td>
<td>61%</td>
<td>36%</td>
</tr>
</tbody>
</table>

→ improved rate performance for CNT electrodes
→ only slight improvement with high carbon content over reference
Positive Electrodes - MWCNTs as Conductive Agent

Long-term cycling stability of full cells (NMC/CNT vs. C)

<table>
<thead>
<tr>
<th>Capacity</th>
<th>250</th>
<th>500</th>
<th>750</th>
</tr>
</thead>
<tbody>
<tr>
<td>(A) Reference</td>
<td>92%</td>
<td>89%</td>
<td>86%</td>
</tr>
<tr>
<td>(B) High Carbon</td>
<td>94%</td>
<td>91%</td>
<td>89%</td>
</tr>
<tr>
<td>(C) CNT</td>
<td>96%</td>
<td>93%</td>
<td>90%</td>
</tr>
</tbody>
</table>

→ better cycling stability for CNT electrodes than for reference
→ comparable to high carbon content electrodes (energy density)
The aim was to
• further improve the electrochemical performance
• completely replace common additives with the lowest CNT amount possible

In principle
• use of CNTs result in lower percolation threshold than carbon black and/or graphite

In practice
• MWCNTs have strong tendency to agglomerate leading to poor connection of the active materials particles

The Strategy: functionalization

- Chemical oxidation
  - MWCNTs-COOH (better dispersibility in polar solvents)

- CNTs unbundling
  - Improved particle-particle connection

- pristine MWCNTs (highly agglomerated)
NCM-based cathodes (~ 10µm)

90 wt% active material, 2 wt% Conductive Agent, 8 wt% Binder
LiFePO$_4$-based cathodes (~ 500nm)

90 wt% active material, 2 wt% Conductive Agent, 8 wt% Binder
NCM-based cathodes

- Improved connection network among the active particles, however dramatic fade of electrochemical performance.
- Electrochemical performance appears to be affected by surface passivation reaction.

LiFePO₄-based cathodes

- MWCNTs-COOH provide an enhanced connection network among the nano-sized LFP particles thus improving the capacity.
- For LFP cathodes the electrode kinetics appears to be mainly dominated by resistivity issues.
Conclusions

Cathodes

- Significant increase of long-term cycling stability
- Improvement of rate capability (power density)

Anodes

- Increase of rate capability
- Increase of long-term cycling stability
- However, large initial losses for graphite due to SEI formation
  - Stable above 1V vs. Li/Li\(^+\) (e.g. TiO\(_2\)); Problem with graphite

Processability

- More difficult than “classic” conductive agents (e.g. carbon black, graphite particles)
- Use of CNTs requires modification of processing
Comparison

- CNT as conductive additive

![Graph showing comparison of different categories such as Energy density, Power density, Processability, Cycle life, Cost, consumer, EV, Power tools, HEV, Automotive, Grid storage. The graph compares Standard and CNT versions.]
Thank you!