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Energy

Range

HEV:



P/E = >15

Portable Energy Challenge

Energy demand generally exceeds supply

- Increase Energy Density (carry more)
- Fast Recharge (refill often)
- Device Energy Efficiency (use wisely)



VILI

Lithium ion batteries are optimized either for high energy or high power

Can nanomaterials address this limitation?



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Application of CNTs in Li⁺ Batteries



Carbon Nanotube Properties





- High electricaly conductivity
- Nanoscale porosity
- Electrochemical and thermal stability

Application of Carbon Nanotubes

CNTs can be used as an additive material due to high aspect ratio and conductivity: percolation network at low wt. loadings

CNTs can be fabricated into free-standing electrodes: current collector, active material support, and anode – lithium ion storage





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Laser Vaporization Synthesis of SWCNTs



Control of SWCNT Properties Quality of raw soot for purification

B.J. Landi, et al. J. Phys. Chem. B 2004, 108, 17089.

B.J. Landi, et al. J. Phys. Chem. B 2005, 109, 9952.

- B.J. Landi, et al. Chem. Mater. 2006, 17, 6819.
- B.J. Landi, et al. J. Nanosci. & Nanotechnol., 2007, 7, 883-890.



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CNT Conductive Additives in Li⁺ Batteries



Typical Conductive Carbon Additive



- Can achieve equivalent conductivity to conventional additives with <1% CNTs
- Comparable capacity for LiNiCoO₂ cathode and MCMB anode, but more active material is present.
- The SWCNT additive electrode shows a significantly higher retention of capacity at higher discharge rate and can lead to enhanced cyclability



Anodes



SWCNT Additive Replacement



Carbon Nanotubes for Li⁺ Batteries
RIT Approach

RESEARCH LABS

RIT Approach to High Energy Density Anode



Cathode Capacity (mAh/g) 200 400 1000 800 0 600 5 Li_xMn₂O₄ Li_xCoO₂ LixNivCo1-vO2 Positive Electrode 4 -Li_xFePO₄ Cathode Voltage (V vs. Li/Li⁺) 3 LixV205 LixV6013 Li_xMnO₂ **Battery Potential** 2 **Negative Electrode** Carbons Anode Silicon Graphite Tin 1 Germanium LICE Lithium 0 1000 2000 3000 4000 5000 0 Anode Capacity (mAh/g)

Silicon vs. Germanium

- Silicon has higher capacity
- Germanium has a higher density (5.35 vs. 2.33 g/cm³) volumetric capacity nearly equal
- Germanium has higher electronic conductivity (217 S/m vs. 1.2 E-3 S/m)



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Battery Metric	Proposed Advantage
Energy Density	Physical support for high capacity lithium alloys (Si, Ge) Elimination of heavy inactive copper current collector High lithium ion storage capacity in CNTs
Power Density	Nanoscale electrical percolation network Potential for ballistic conduction with metallic CNTs Nanostructures offer higher electrolyte wetting
Performance	Flexible electrode design Elimination of copper promotes zero volt storage Enhanced cyclability due to particle entanglement

Landi, B.J.; et al. "Carbon Nanotubes for Lithium Ion Batteries." *Energy* & *Environ Sci.* **2009**, *2*, 549.



Thin Film Ge-SWCNT Anodes





- » Paired with LiCoO₂
- » Increased energy density by ~3x over MCMB anode and >>CNT electrode

R.A. DiLeo, et al. J. Mater. Res. 2010, 25, 1441.





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Modeling of High Energy Density Anodes



Significant improvement over SOA with conventional cathode designs
Improvements in high voltage cathodes can increase approach further

B.J. Landi, et al. J. Mater. Res. 2010, 25, 1636.



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Ti-enhanced SWCNT electrodes



•Both Nickel and Titanium "wet" the surface of SWCNT electrodes through e-beam evaporation

The use of a Ti layer with Ge-SWCNT anodes shows the ability to have a higher capacity for both the Ge and SWCNT contributions over a range of constant currents
No evidence of reversible lithium ion capacity from TiOx compounds which occur at 1.5 V vs. Li/Li+

R.A. DiLeo, et al. ACS Nano. 2010, ASAP.



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Conclusions and Impact



R.A. DiLeo, et al. ACS Nano. 2010, ASAP.

Carbon Nanotubes offer the potential to create a unique lithium ion battery with both <u>high energy and power density</u>

Incorporation of high purity SWCNTs as a direct replacement of the conductive carbon in a typical cathode has maintained equivalent capacity with an improved rate capability

Advancement in titanium contacting of high capacity Ge-SWCNT anodes has shown the ability to maintain both high energy and power (>1C) capability; promising candidate to pair with LiFePO₄ for a balanced cell design.



Energy & Environmental Science

