Carbon Nanotubes based Electrode Architectures for Enhanced Lithium Ion Battery Performance

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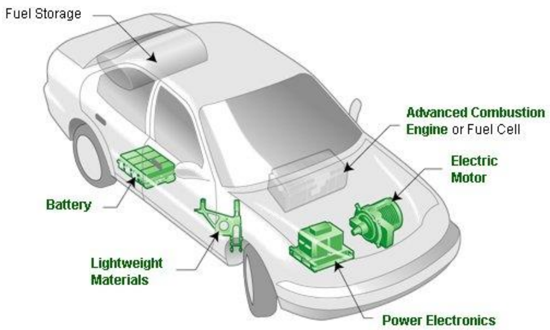
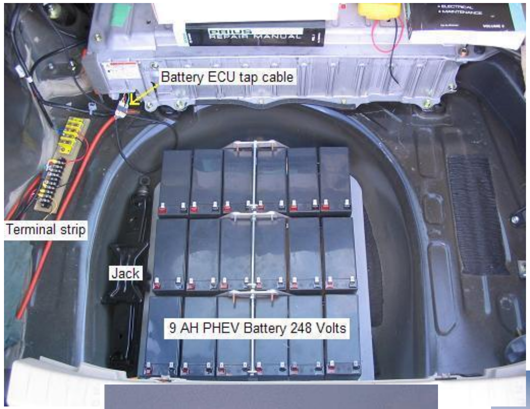
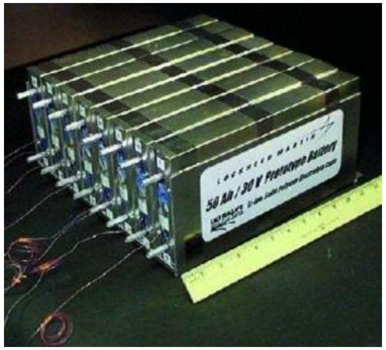
Introduction

1. Introduction
2. Background
3. Layer-by-Layer Electrode Architecture
4. Conclusions

Next generation battery –Requirements







- Charge rate of 1C or greater; i.e. 1 hour or less.
- Energy density of > 300 Wh/kg.
- Cycle life of > 20,000 cycles.
- Thermal cycle survivability of -40ºC to +75ºC.
- Storage life of 5 years.
- Significant reduction or elimination of thermal runaway.

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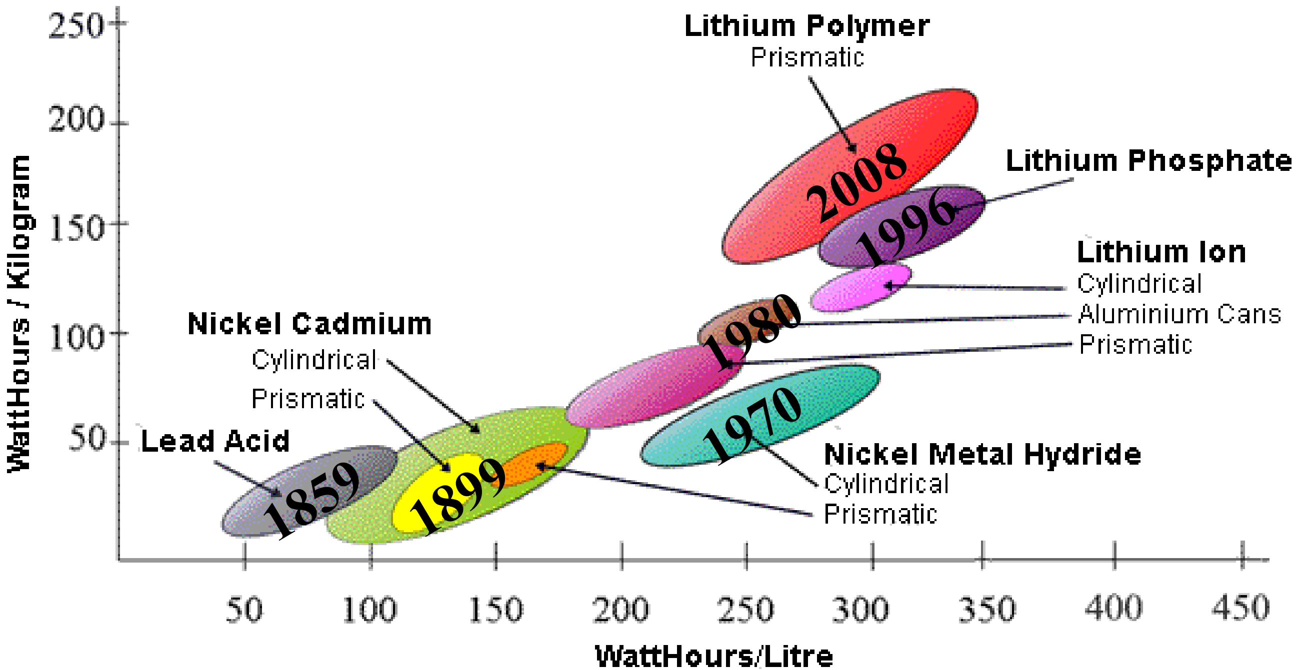
What is the State of the Art



➔ **Limited improvement has been achieved over 2 centuries**

- **40-60% of a typical battery's weight is its enclosures and protective covers. (Dead weight)**
- **To have high power output several cells need to work in tandem (connected parallel).**

For high power applications dead weight has to be reduce to achieve goals.

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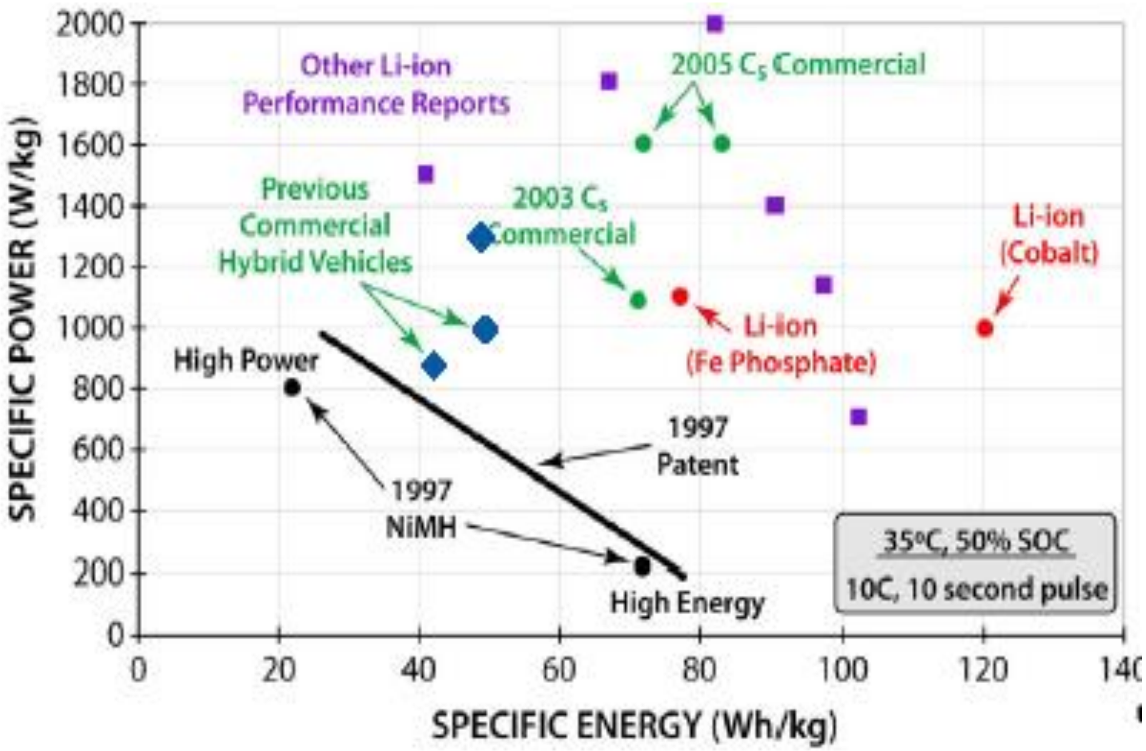
Current Li-ion Drawback- Cannot be used for high power / high energy applications



Current State of the Art Li-ion Technology

- Cycle Life typically 300 deep discharge cycles (1 Year)
- Mostly small (5W)
- Safety Issues with Large Packs

- In typical lithium ion battery Anode and cathodes are sheets -- If prepared by conventional methods their performance degrades with increase in thickness. i.e. long charging times and low power output.
- Faster charging can lead to thermal runaway ➔ Batteries bursting
- Performance degrades after ~1000 cycles

High power requirements IMPEDES high energy.

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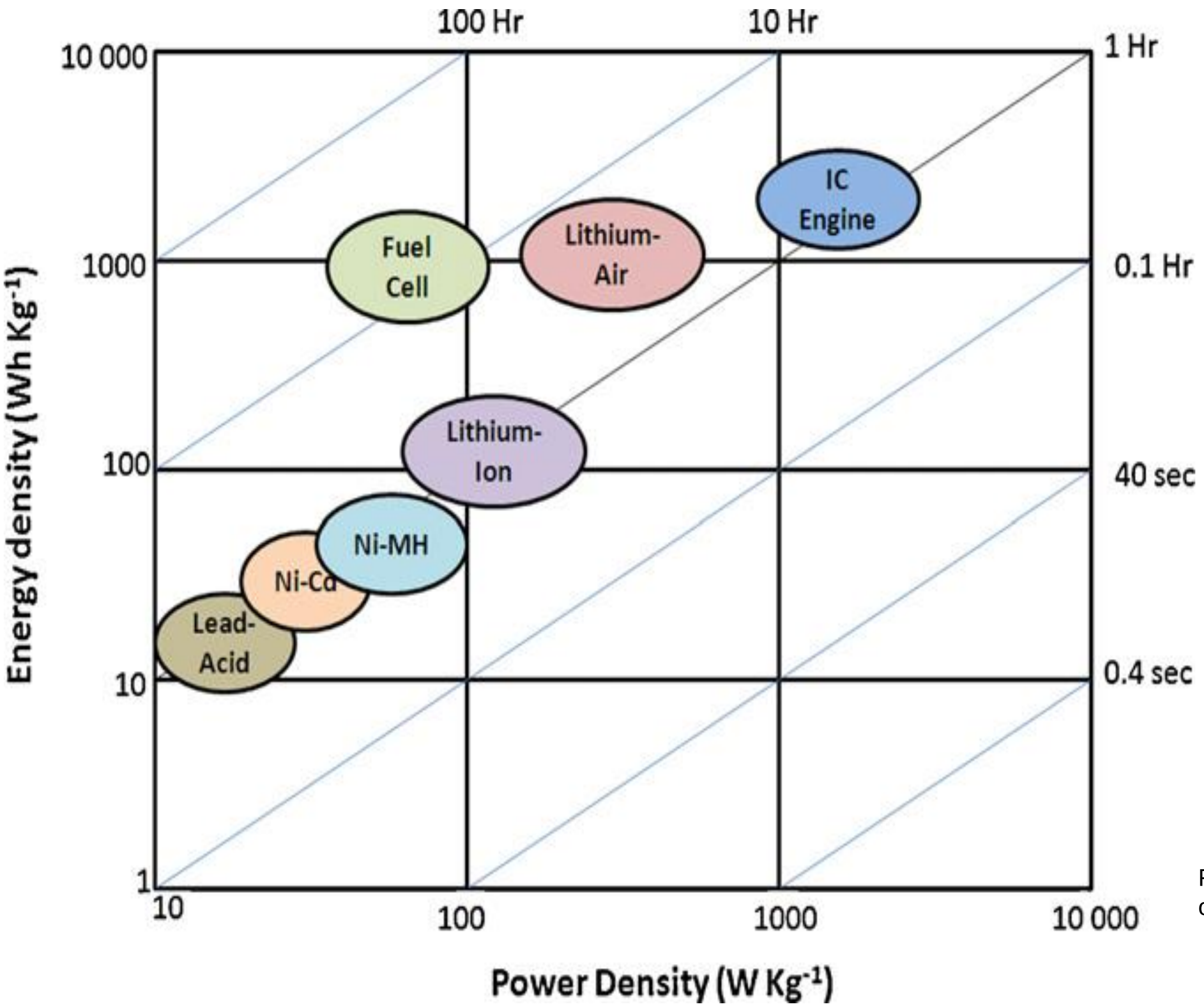
Battery Performance



- Capacity
- Cycle Life
- Power Density
- Energy Density

Figure Source: Padbury and Zhang, Journal of Power Sources, 2011

Factors influencing commercial viability of batteries

- **Performance**
- **Cost**
- **Size/Weight**
- **Safety**
- **Sustainability**

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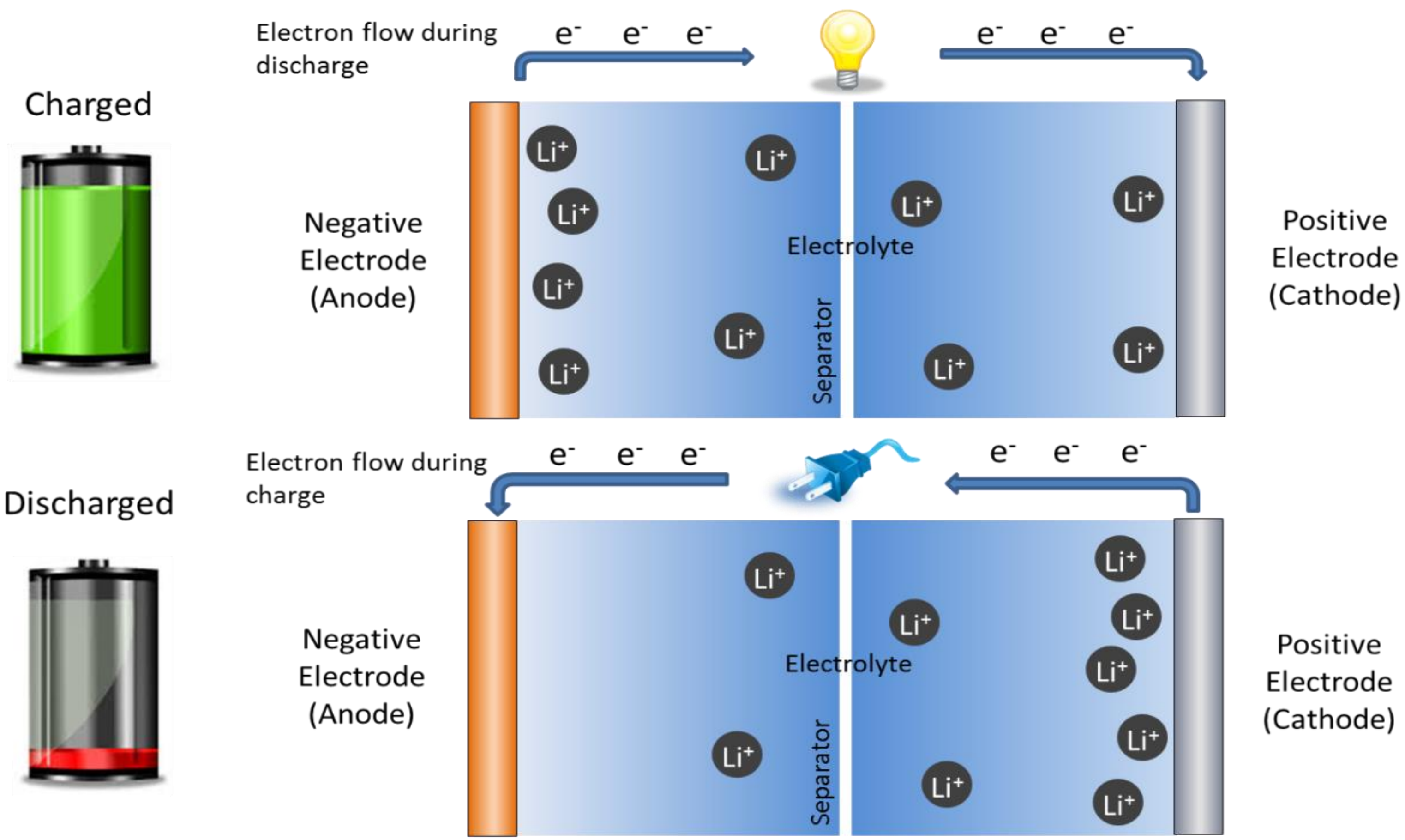
Working Principle



Governing Equations

Power Output of a Battery:

Ohm's Law ⟶

$$P = \frac{V^2}{R_i}$$

To maximize power, minimize internal resistance

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Internal Resistance

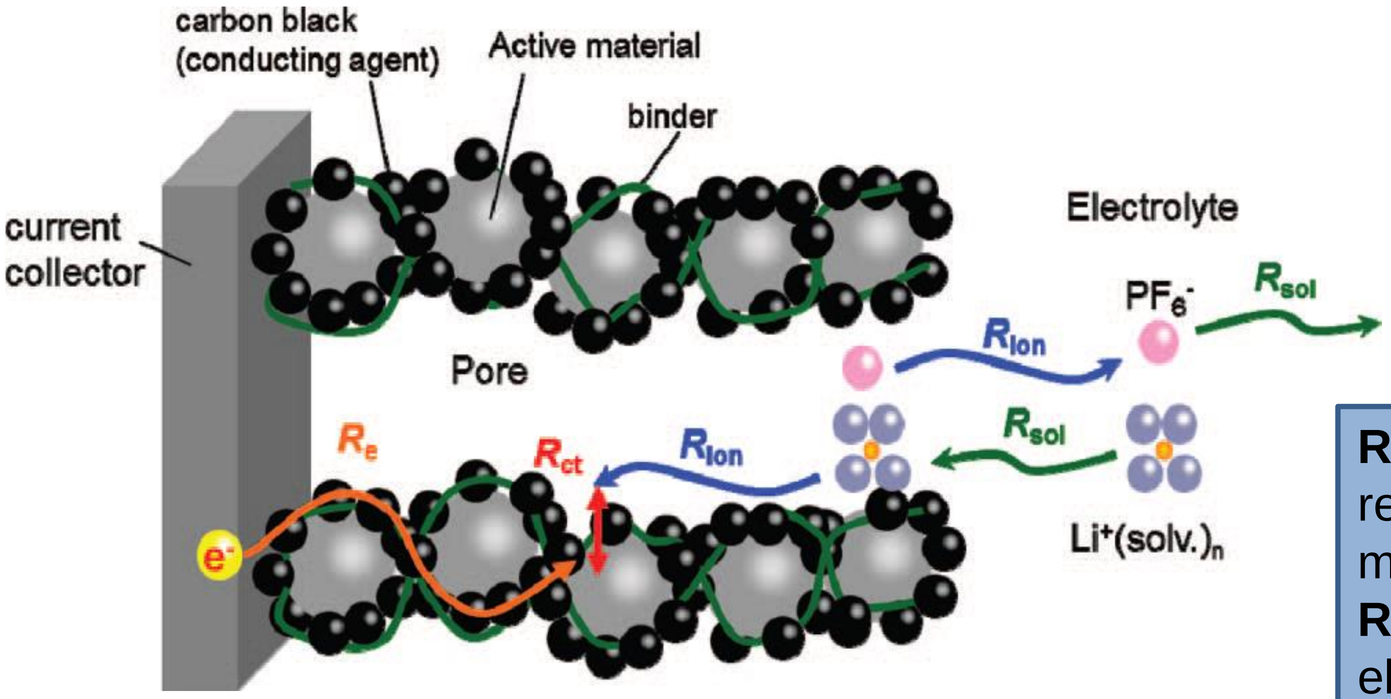


Figure Source: Ogihara et al. J. Electrochem. Soc., 2012

$$R_i = R_e + R_{sol} + R_{ion} + R_{ct}$$

R_e: Electrical resistance of bulk material
R_{sol}: Resistance in electrolyte
R_{ion}: Ionic resistance of active material
R_{ct}: Charge transfer resistance

Internal Resistance

$$R_e = \frac{\rho t}{A}$$

$$R_{sol} = \frac{L}{\kappa A}$$

$$R_{ion} = \frac{t}{\kappa_{eff} A}$$

$$R_{ct} = \frac{RT}{nFi_0}$$

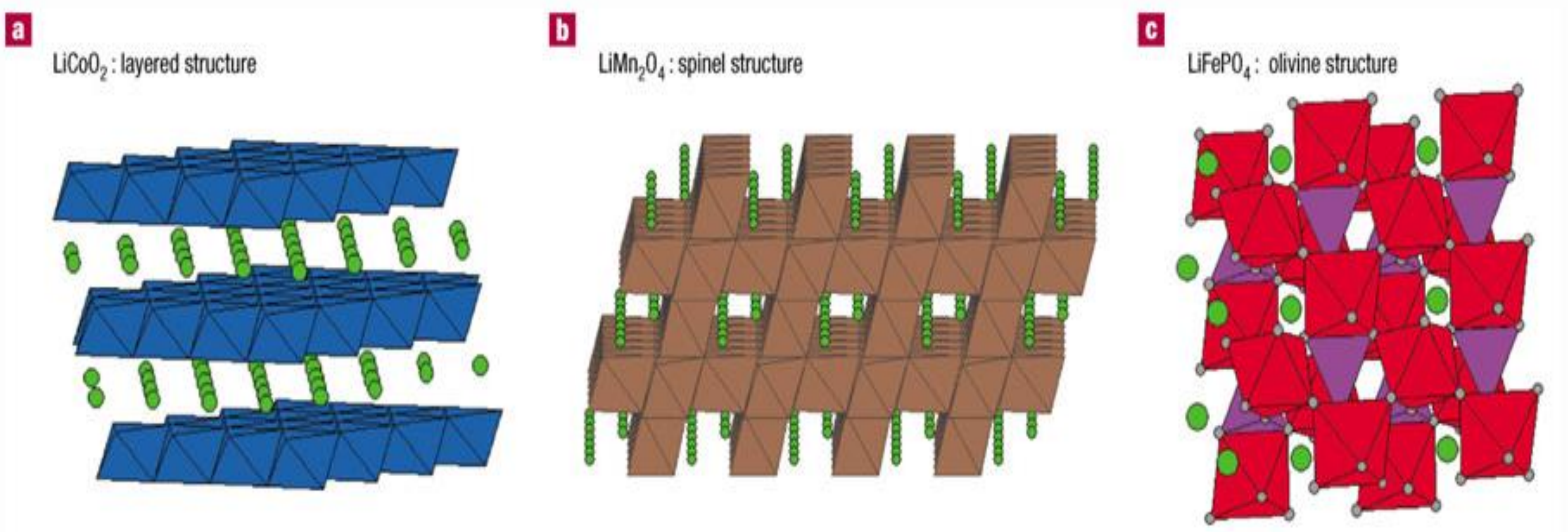
ρ: resistivity
t: thickness
A: area
L: distance between electrodes
κ: ionic conductivity of electrolyte
κ_{eff}: effective ionic conductivity of electrode
R: gas constant
T: temperature
n: number of electrons
F: Faraday constant
i_0: exchange current

Internal resistance depends on both material used and geometry of the battery

Cathode Materials

- Typically transition metal oxides

Lithium metal oxide crvstal structures:



Increasing rate capability and safety

Increasing energy density

Figure source: Thackeray, Nature Materials, 2002

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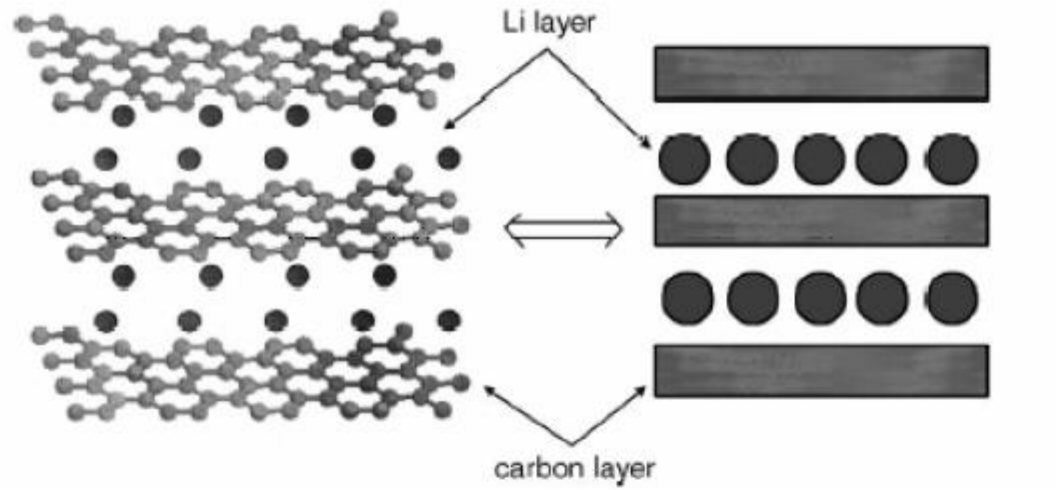
Anode Materials

- Graphitic carbon

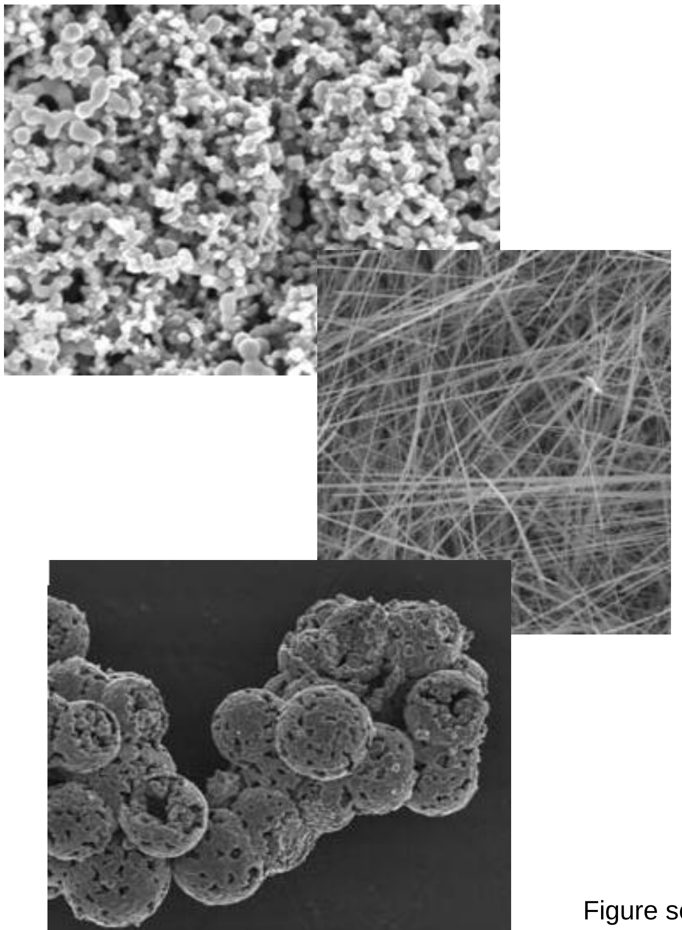


- Silicon

One of a number of high-capacity anode materials, silicon has the highest known theoretical capacity.

Figure source: Bianco, ed. 2011

Nanomaterials



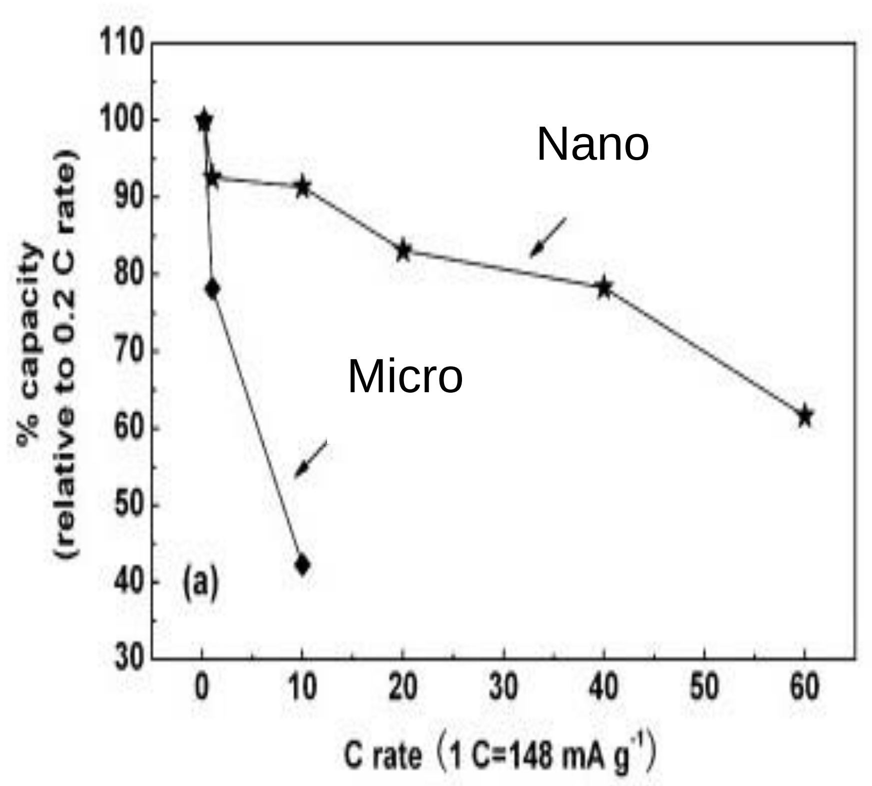


Figure sources: (nanowires) Bourzac, MIT Tech. Rev., 2009, (hollow nanospheres) Ding et al. J. Mat. Chem., 2011, (graph) Chen et al. J. of Power Sources, 2011

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Nanomaterials

Advantages:

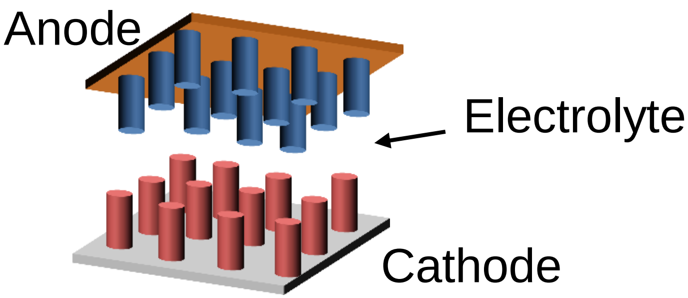
- Shorter ion diffusion lengths lead to faster ion insertion and extraction
- Novel lithium ion storage mechanisms
- More ion storage sites accessible within charging time due to decreased diffusion length
- High surface area increases electrolyte wetting, making more surface storage sites accessible
- Structural integrity

Disadvantages:

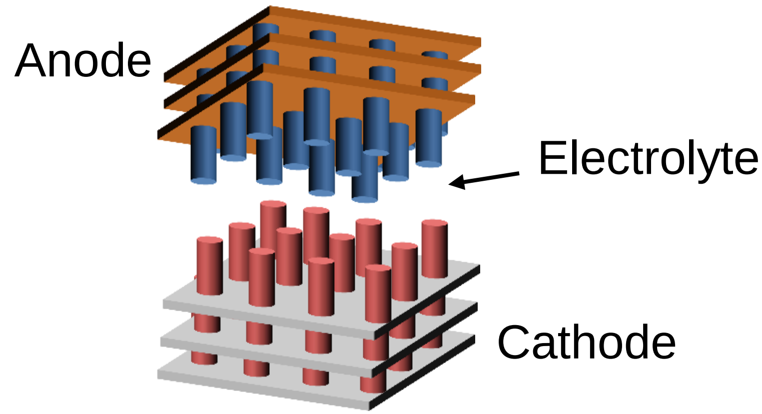
- Low packing density
- High surface area increases unwanted reactions with electrolyte
- Consumption of lithium ions
- Complicated and/or costly synthesis
- Nanomaterials often hazardous

Electrode Architectures

1D: parallel plate design (can incorporate “3D” elements)



2D: parallel plate design but using a layered scaffolding; allows for more active material per footprint area



3D: Cathode and anode materials integrated together within the cell to keep transport time small while maximizing amount of active material present

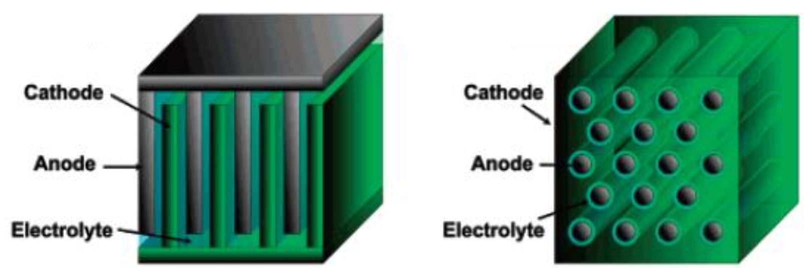
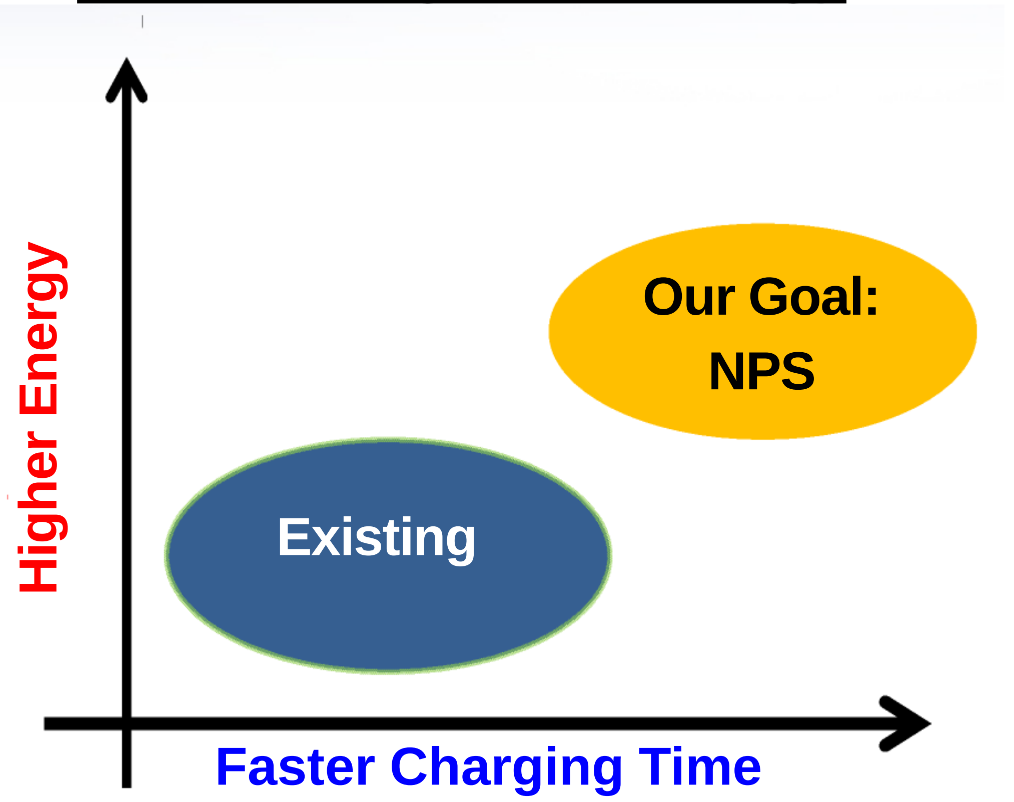


Figure source: Long et al. Chem Rev., 2004

Our Approach

- CNT based scaffolding electrode architecture.
- Enhanced electronic & ion transport.
- Reduced footprint & battery dead weight.
- Reduced thermal runaway.
- Unique manufacturing process.

Breakthrough Technology



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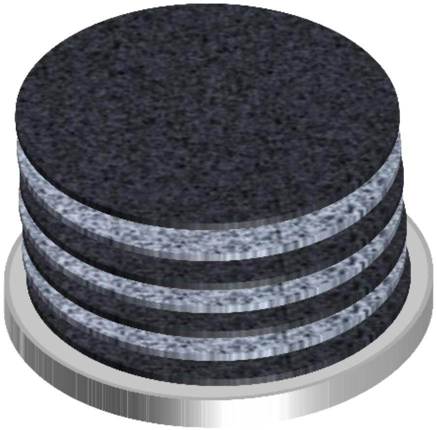
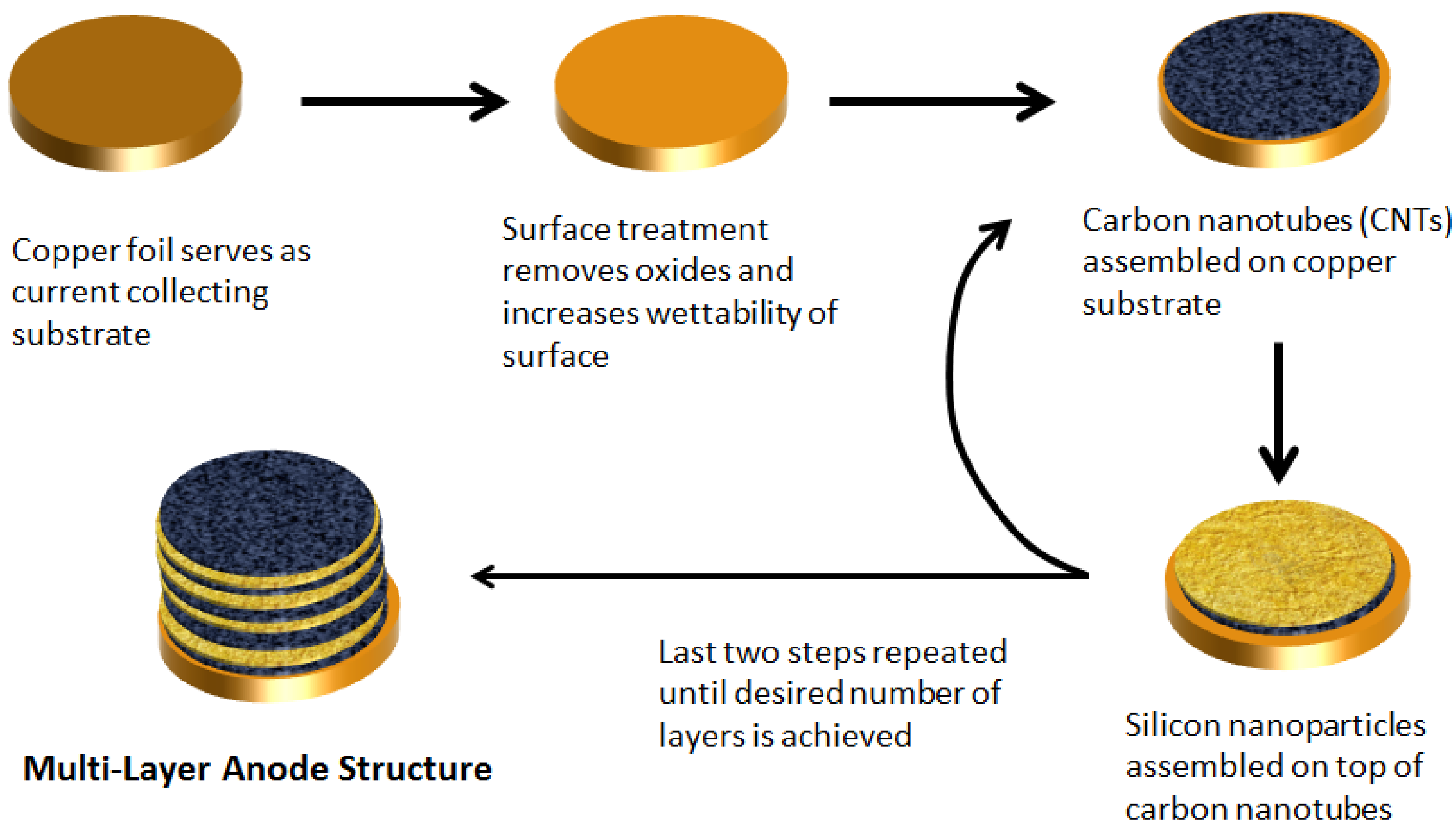
Specific Project Tasks



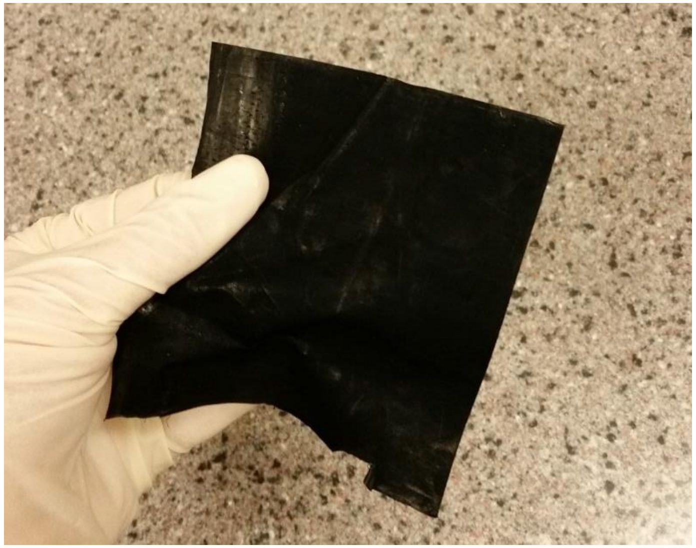
Layer-by-Layer CNT/nanoparticle architecture for lithium ion battery performance enhancement using a high-rate scalable fabrication procedure

1. Develop the layered architecture in order to enhance the ionic and electronic conductivities of the electrode.
2. Compare the electrodes with those made using standard fabrication methods.
3. Investigate the effects of electrode thickness and composition, number of layers, and fabrication methods on cell performance.
4. Examine physical properties of electrodes before and after cycling to enhance understanding of internal changes within the cell due to cycling and assess durability of electrode architecture.
5. Explore various fabrication techniques and develop a process which is low-cost, high-rate, and scalable.

Fabrication Procedure



CNT Paper

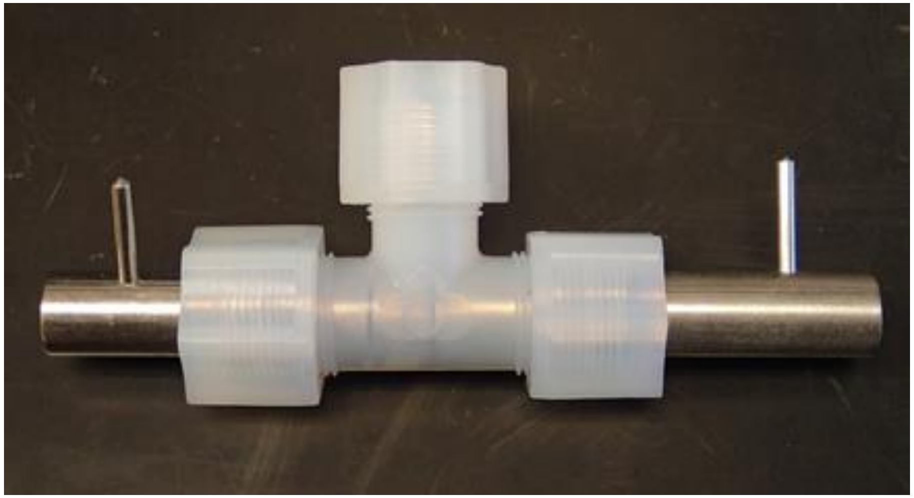


Advantages:
- CNT paper is very strong and flexible—can be used to make flexible or even foldable batteries
- No substrate needed—reduces weight and thickness of battery
- Can be used to make any shape

Disadvantages:
- CNT layers are thicker than sprayed CNT layers—increased amount of inactive material
- Not compatible with spraying method
- Possible problems with doctor blade approach

Half-Cell Approach

T-cell



Coin cell

- Lithium foil counter electrode
- Polypropylene separator
- $LiPF_6$ in ethylene carbonate/dimethyl carbonate electrolyte

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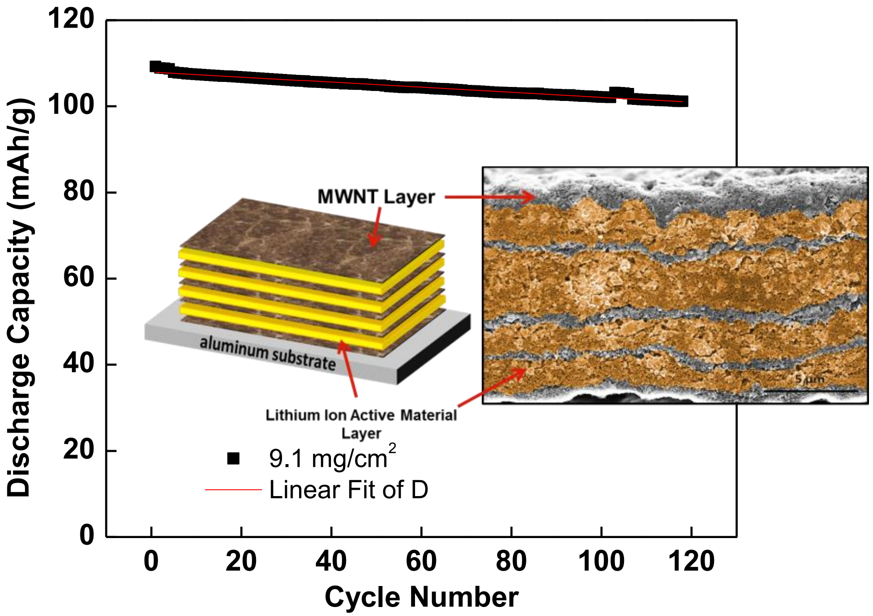
Preliminary Results: CNT Li-ion Battery

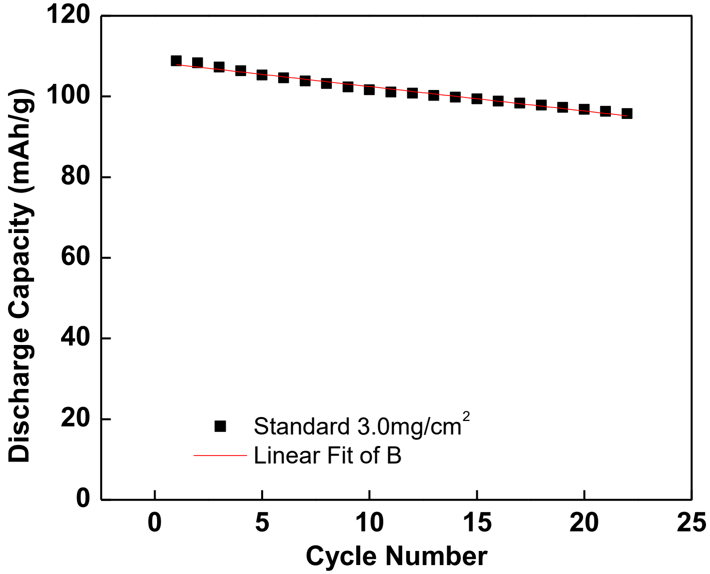
Our CNT scaffolding Architecture

- **At 1C, LMO exhibits 5.4% capacity fade after 100 cycles**



Standard architecture

- **At C/10, LMO exhibits 11% capacity fade after 20 cycles**



- **Layered architecture improve the Arial power density, energy density.**
- **At full charge in 5 min (10C), it shows 25 times more capacity compared to standard battery.**
- **Longer life (less fading) and 40% lighter**
- **Low manufacturing cost, compatible with any Li-ion Battery chemistry.**
- **Dead weight of the battery is reduced by 40%.**

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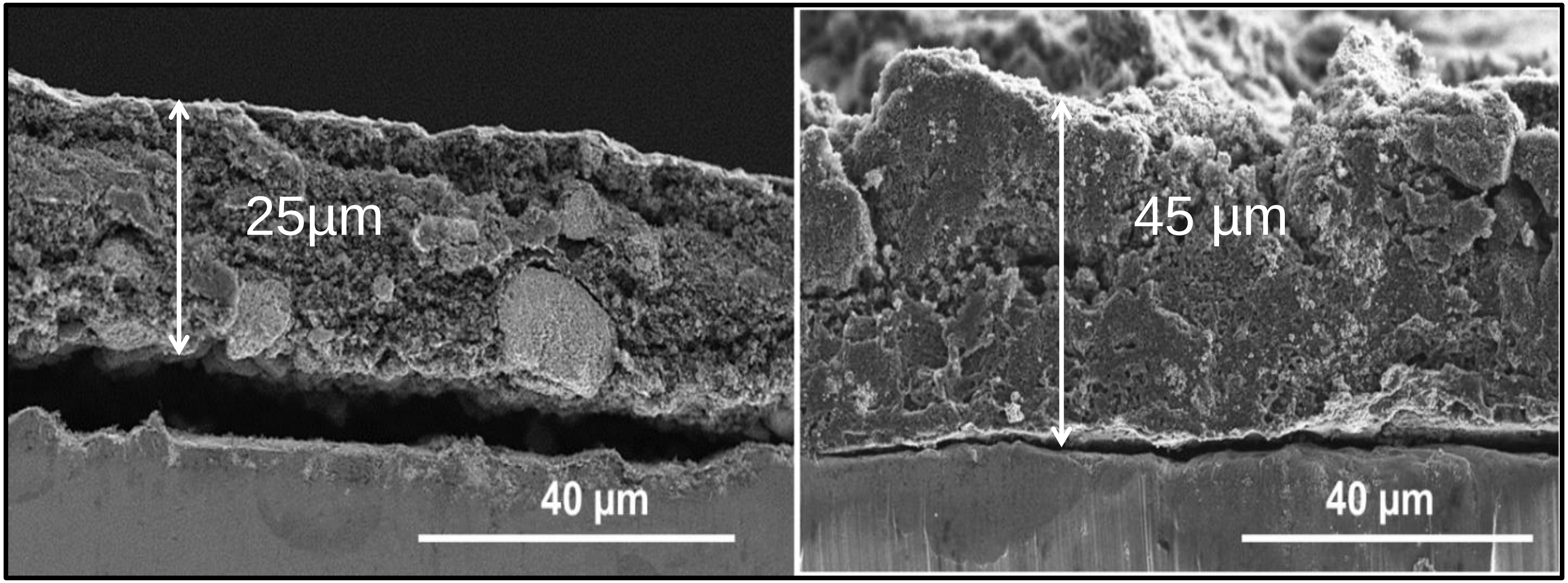
Increased Volumetric Energy Density



Our electrodes: 9.1mg/cm^2

Density: 3.64mg/cm^3

Standard: 5.6 mg/cm^2

Density: 1.27mg/cm^3

- **Our technology exhibits higher volumetric energy density**

Optimization can further improve the volumetric energy density

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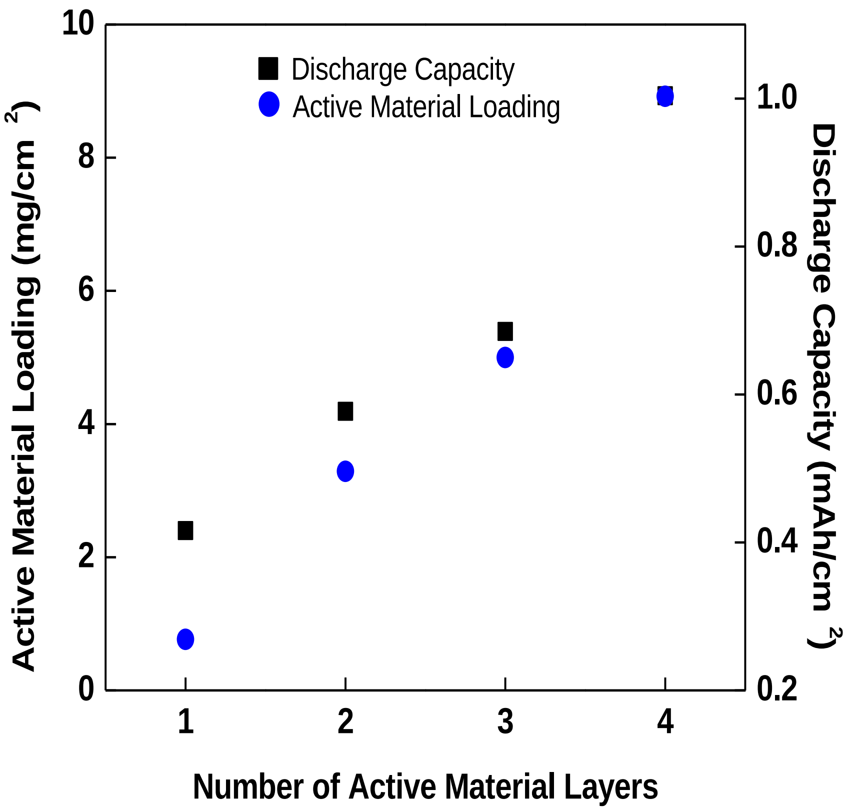
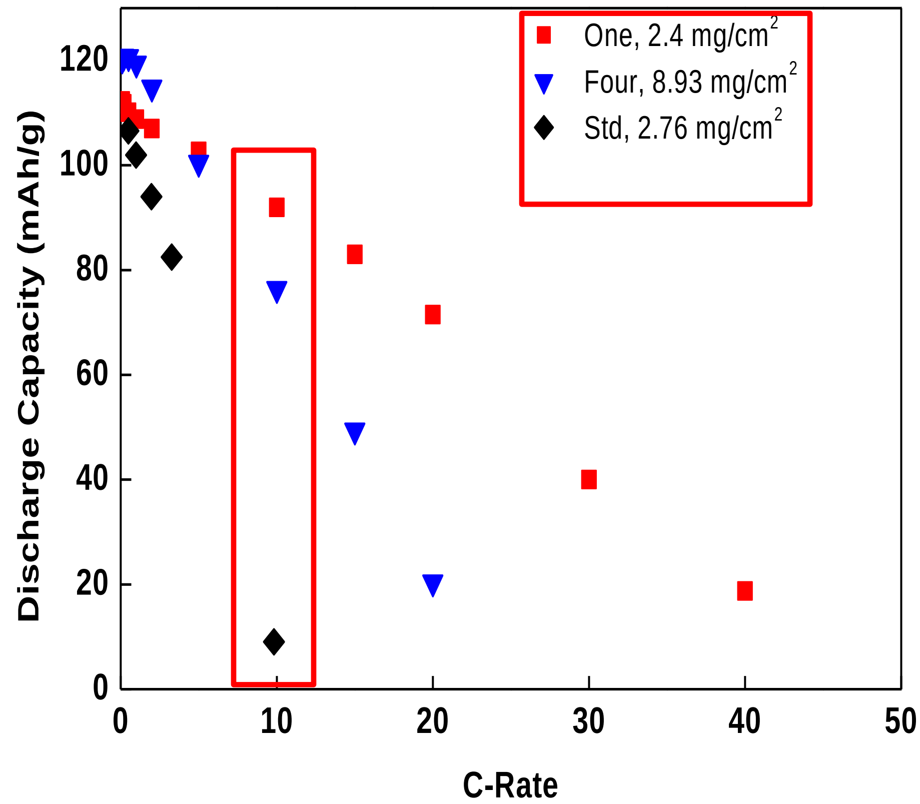
Increased Power density





- Our electrode electrode = 1.0m Ah/cm^2; Standard electrode is $0.328 Ah/cm^2$
- At 10C our electrode exhibits 25x more capacity per unit area than the standard electrode
- At 2C and 4C they exhibit 4X increment

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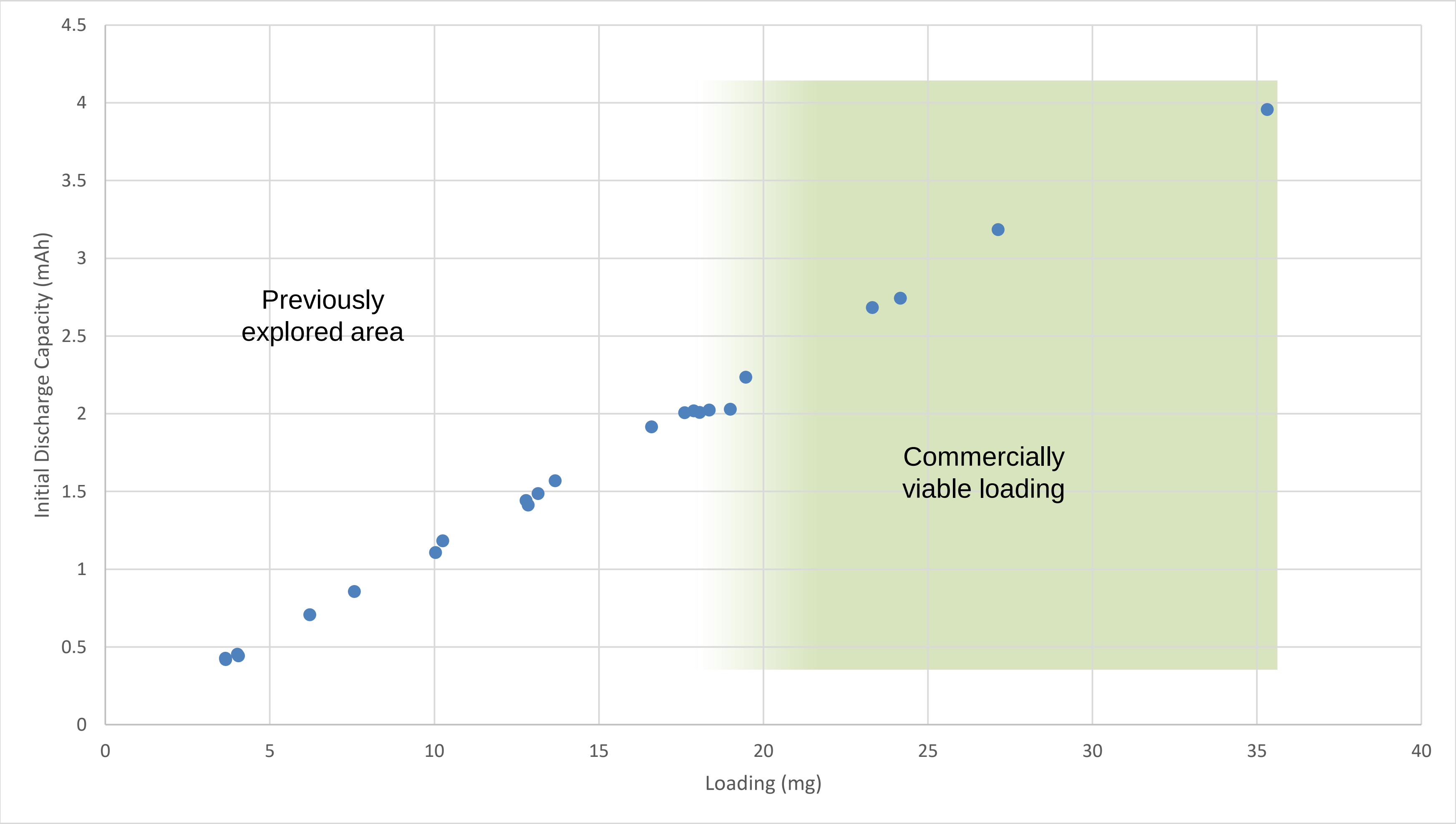
LMO Cathode: Increased Loading



- **Capacity increases linearly with loading: upper limit on loading has not been reached**

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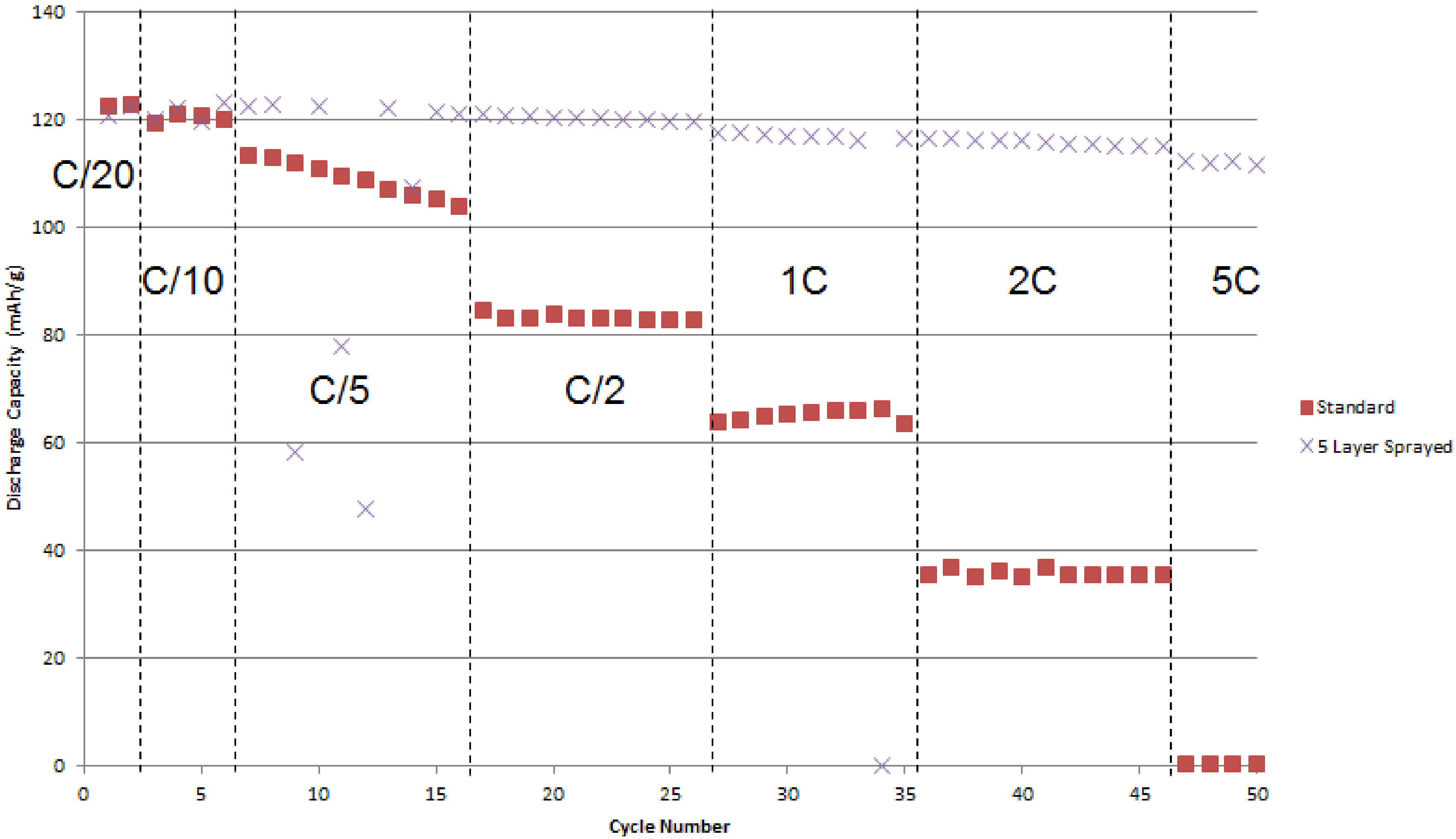
LMO Cathode High-Power Applications: Cycling Performance



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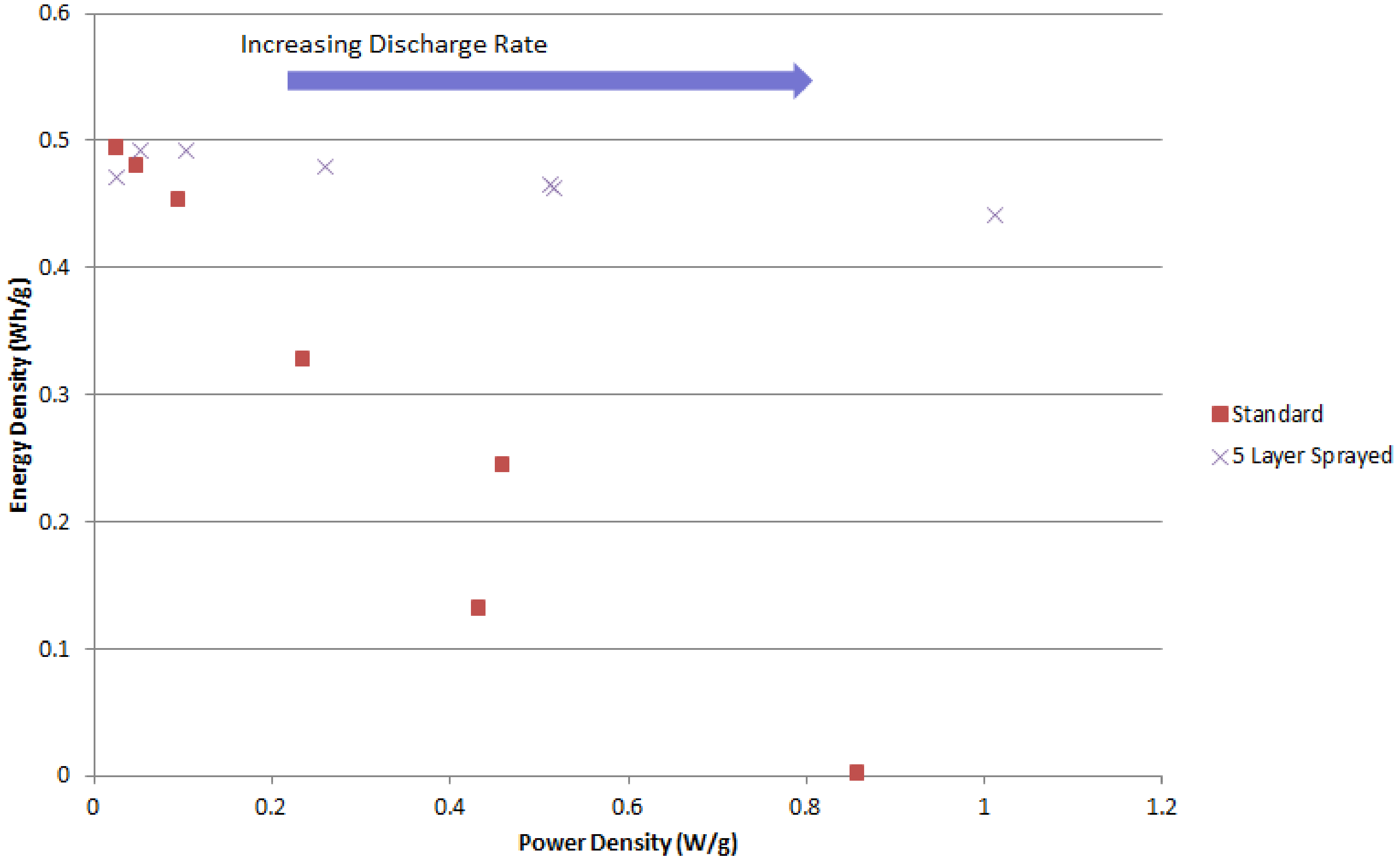
High-Power Applications: Cycling Performance



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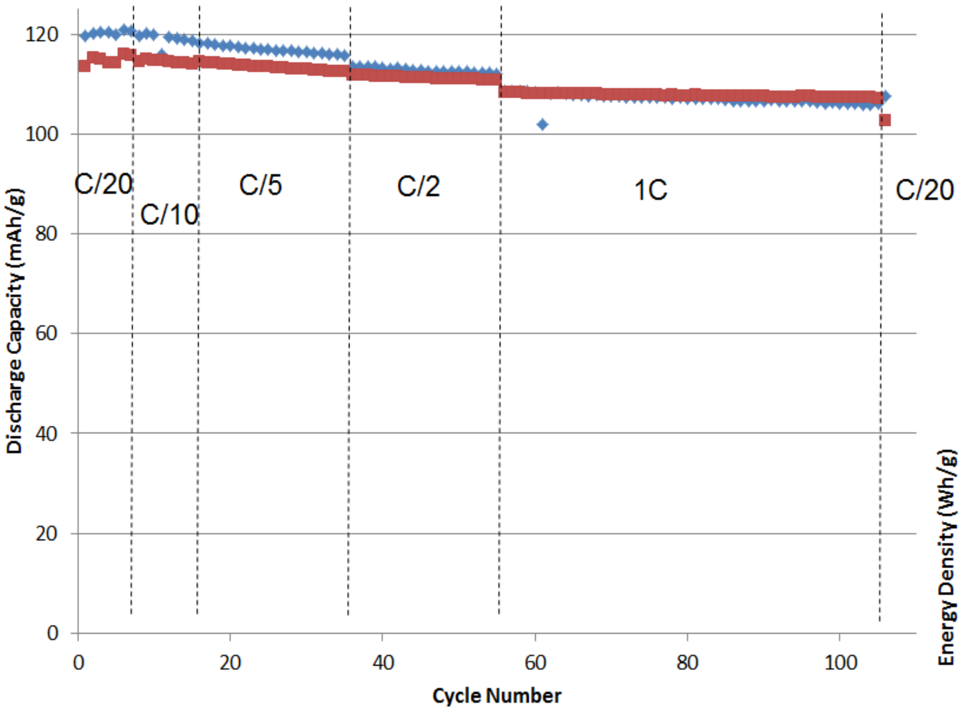
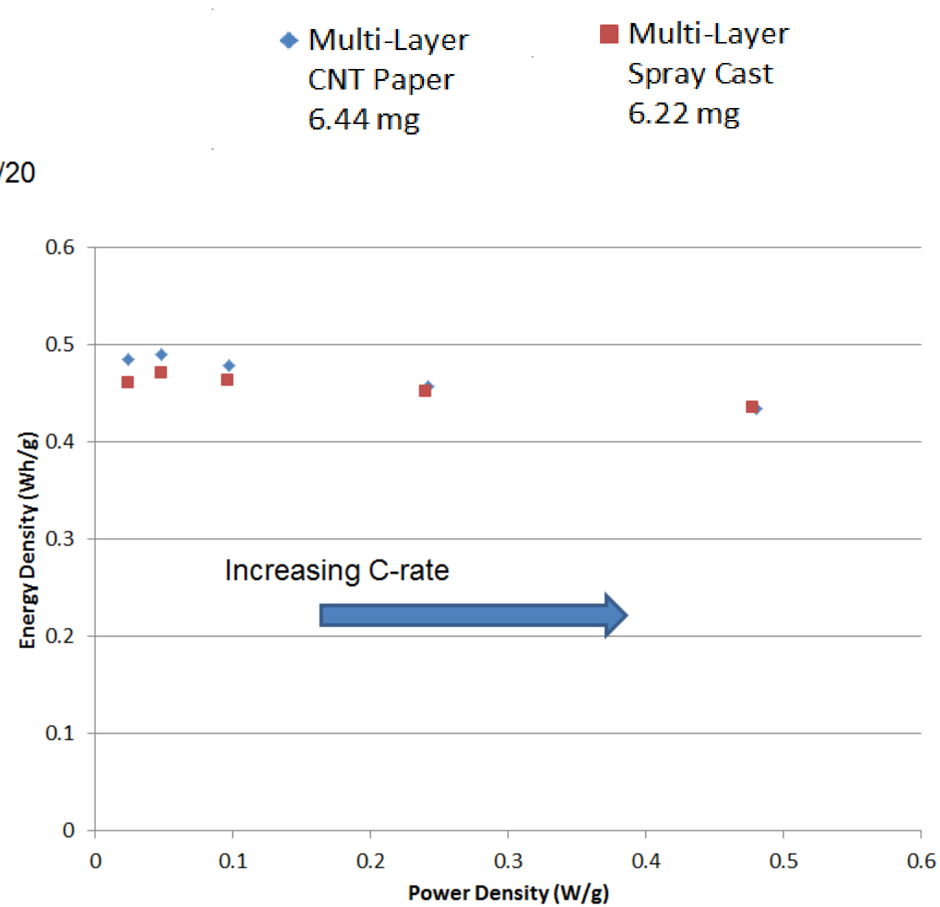
CNT Paper Cathodes: Comparison to Deposited CNT





- Extremely similar cycling performance

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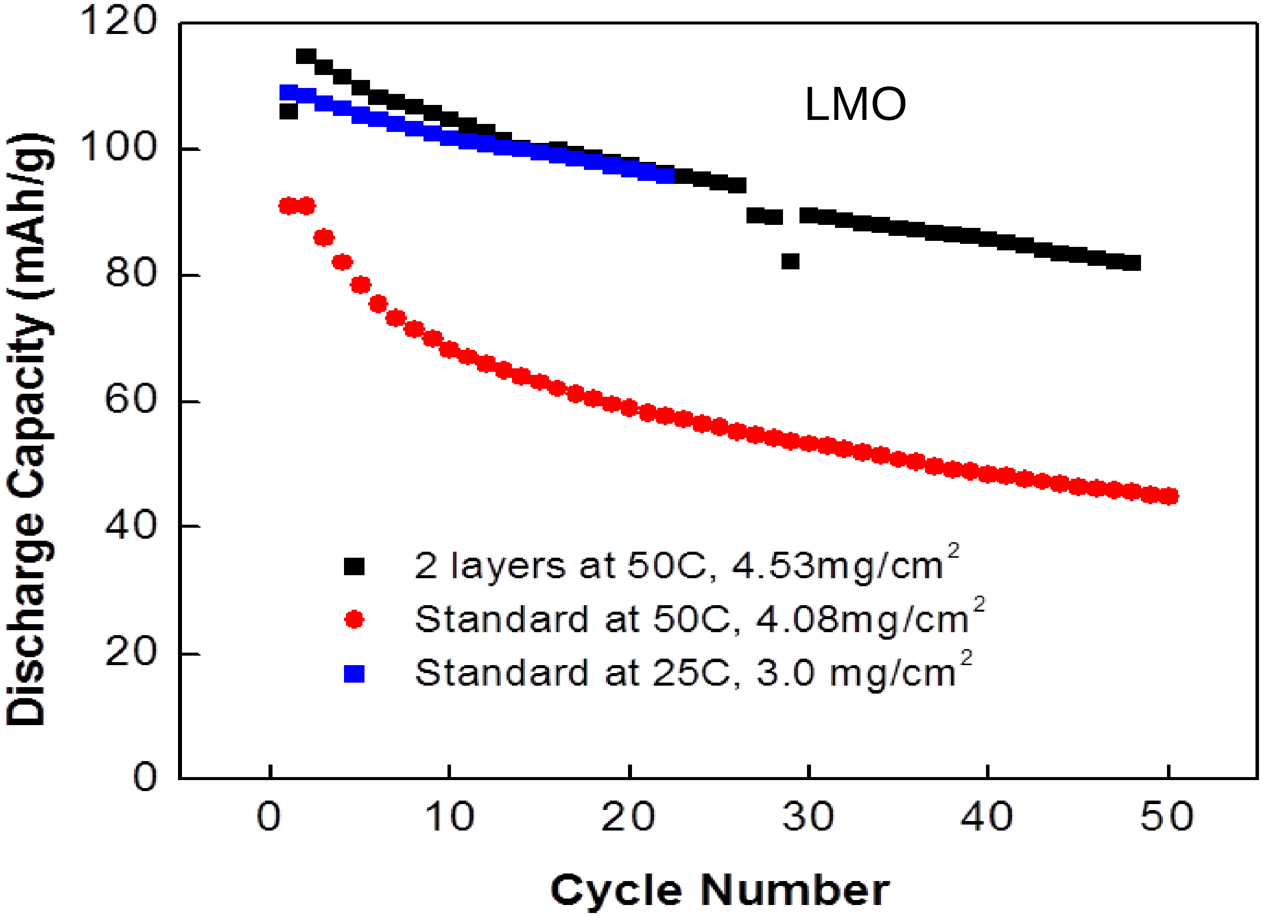
Minimizing Thermal Runaway
High Temperatures Cycling at 1C Rate



➔ Battery architecture at 50^0C has similar performance as that of standard electrode at 25^0C.

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Comparison with Our Layered CNT Battery

	1. Specific energy (mWh/cm^2)	2. Specific power (mW/cm^2)	3. Inactive Components (%)	4. Cycle Life (Fading)	5. Volumetric energy density (mWh/cm^3)	6. Fabrication Cost
1. *J. Electrochem. Soc.* 2000.	1.92	28.8	22	No long term study	High	Low
2. *Nano Letters* .2010.	0.432	8.64	25	78 mAh/g for 100 cycles	Low	Very high
3. *J. Mater. Chem.* 2011.	1.92	4.8	30	4.8% loss after 80 cycles	Low	Moderate
4. *J. Power Sources.* 2011.	1.44*	40.8*	20	No long term study	Low	Low
5. *J. Mater. Chem.* 2013	2.02	14.3	20	8% loss after 100 cycles	High	High
6. *J. Mater. Chem.* 2011.	0.96*	80*	44	4% loss after 100 cycles	Low	Moderate
7. Our Work	***4.32***	***21.6***	***13-23***	***5% loss after 100 cycles***	***Very high***	***Low***

Yellow highlights indicate necessary values for commercialization

* Low energy density and high power density (similar to a capacitor)

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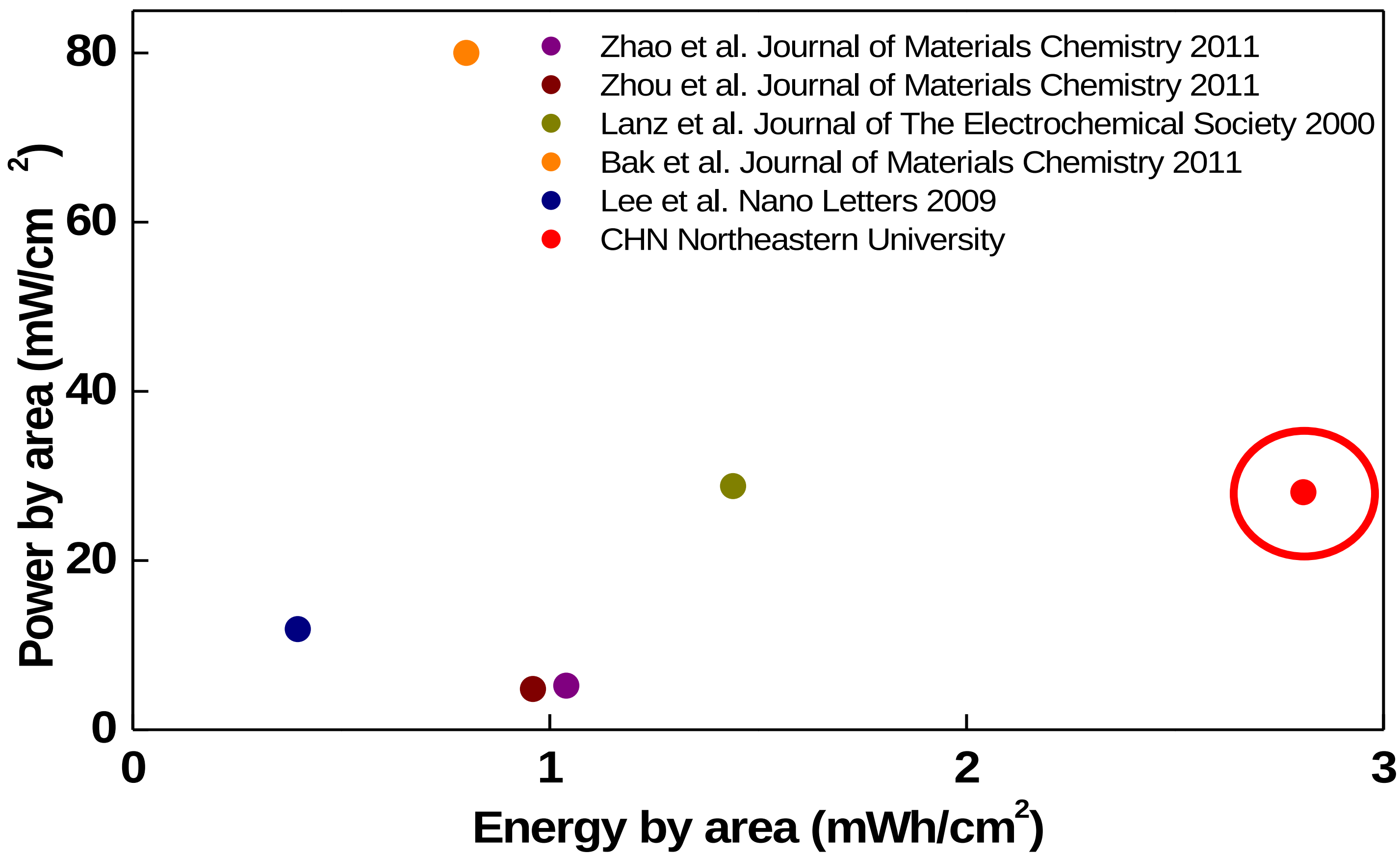
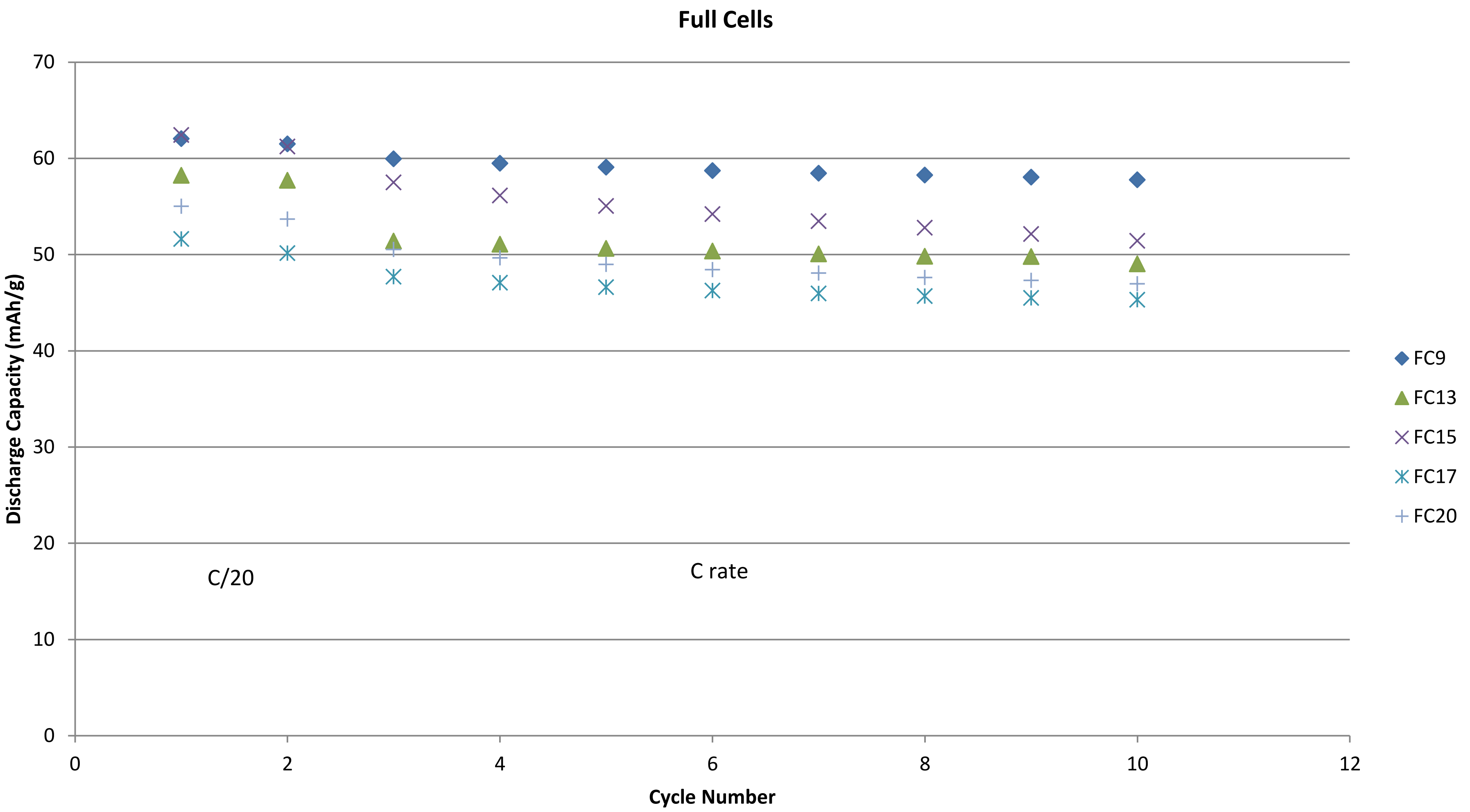
Comparison- Ragone Plot



- ➢ **Multi-layer enhance power density while maintaining energy density**

Full Cell Initial Results



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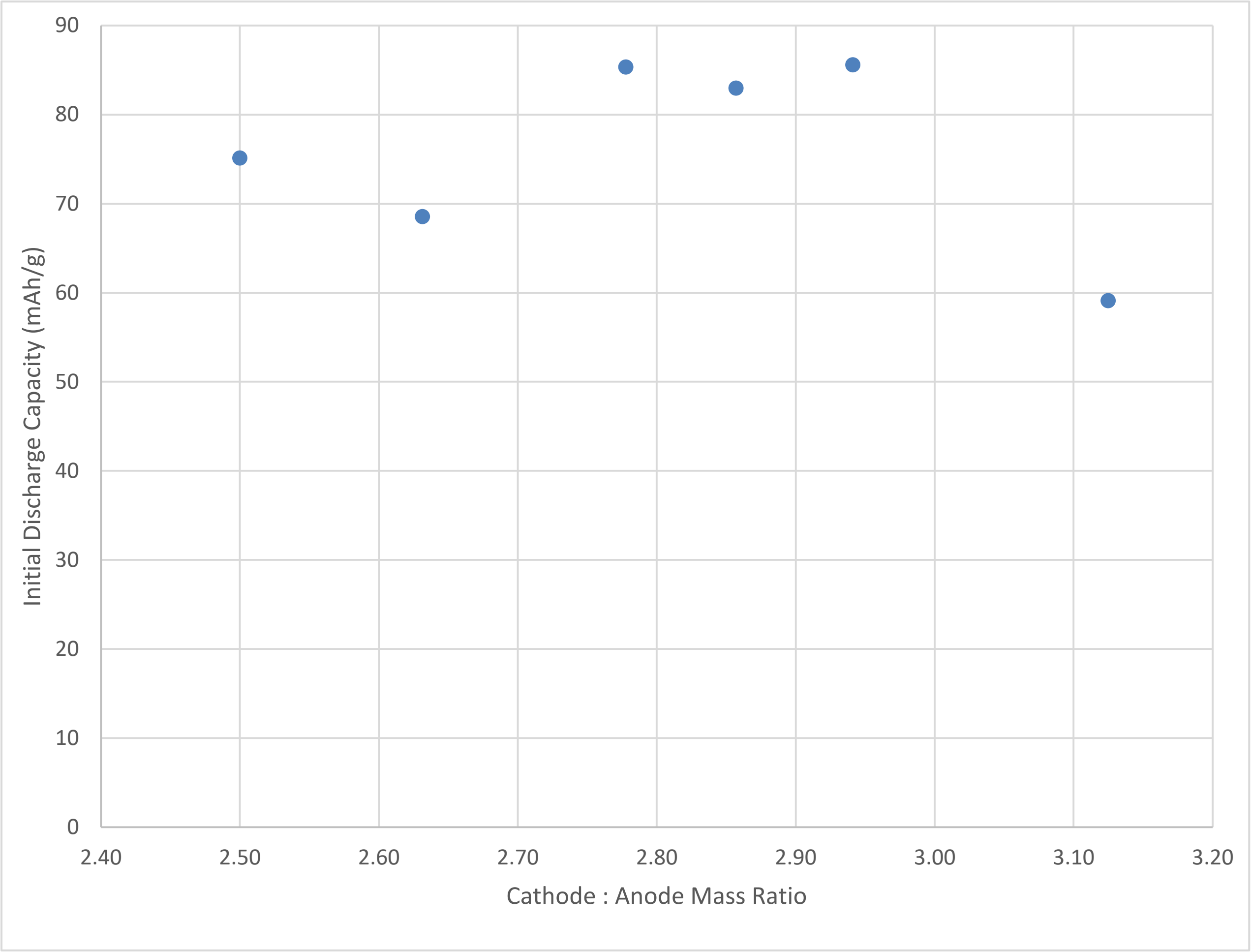
Full Cells: Determination of Matching Ratio



- Ideal ratio between 2.75 and 3.00

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Conclusions and Future Directions

- **LMO cathodes with high loading successfully fabricated**
- **Compared to standard fabrication cathodes of similar loading, multi-layer cathodes show much higher rates**
- **Established good connectivity between layers**
- **Density of CNT layers investigated; little impact on performance**
- **When charged at a lower rate than discharged, a multi-layer cathode of higher loading shows much higher rates compared to a standard fabrication cathode.**
- **Alternative to sprayed CNT layers investigated; showed that nearly identical performance can be achieved**
- **Future work may include flexible or very large, thin batteries.**

Conclusions and Future Directions

- **Determined ideal matching ratio to be between 2.75 and 3.00**
- **Capacity retention for full cells still needs improvements. Reasons may include:**
  - **Uncertainty in the mass of hand-made electrodes**
  - **Ratio is based on first cycle data; ideal ratio may shift as cycling continues**
  - **Side reactions consuming lithium ions that are currently unaccounted for**
- **Future work will need to address capacity fade**

Acknowledgements

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Questions and Discussion?

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