Engineering Inorganic-Organic Composites for Lithium-Ion Batteries

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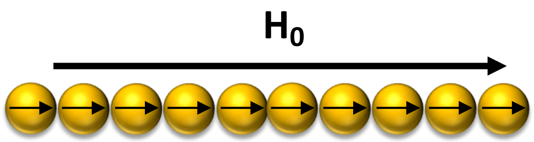
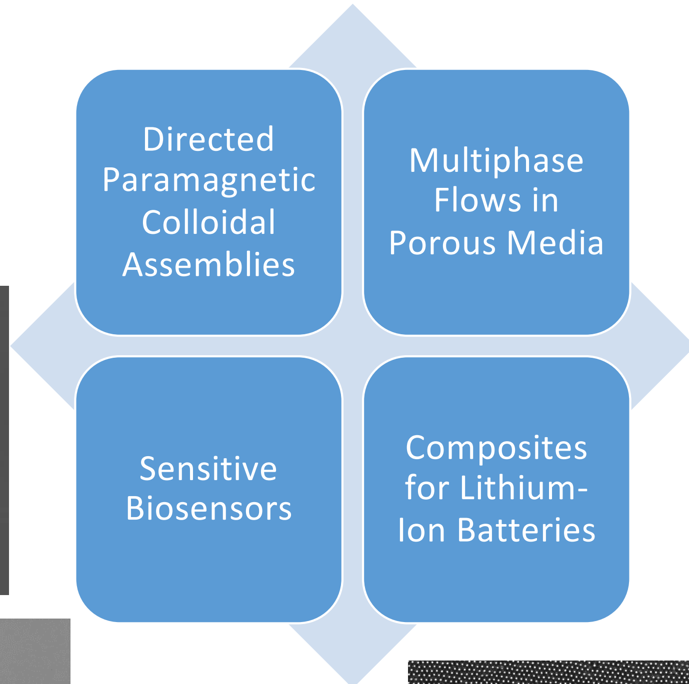
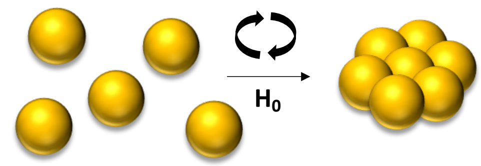
September 7, 2023
STS AICHE

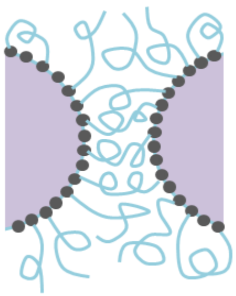
RICE ENGINEERING

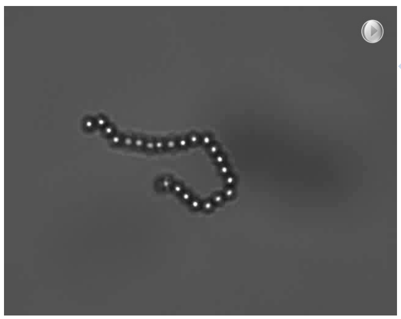
Biswal Group: Engineering Soft Matter

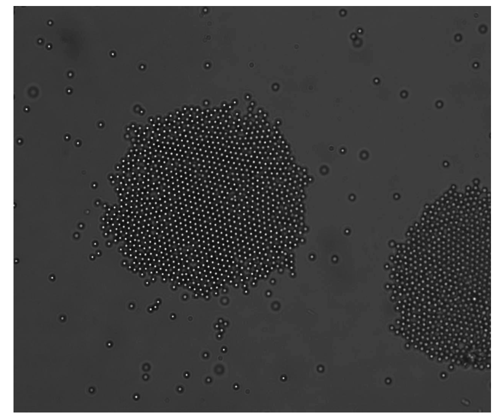


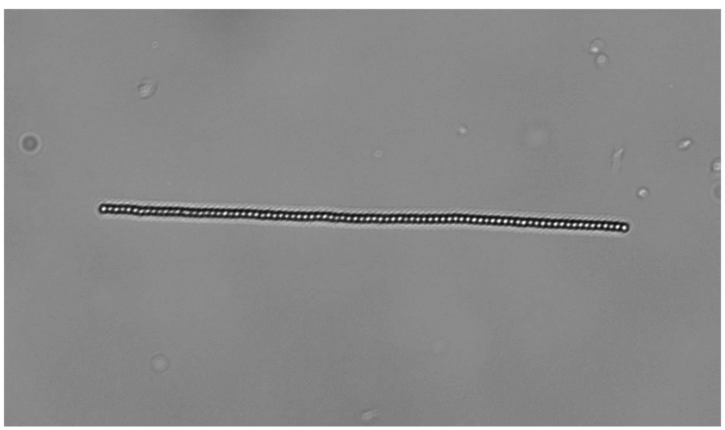


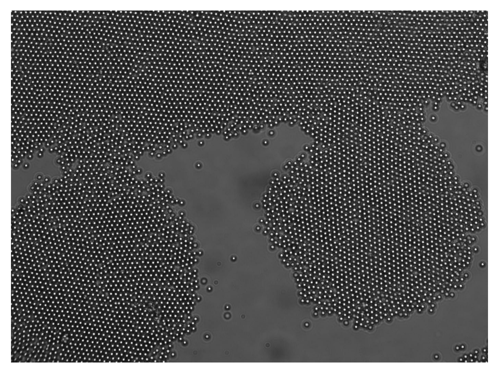


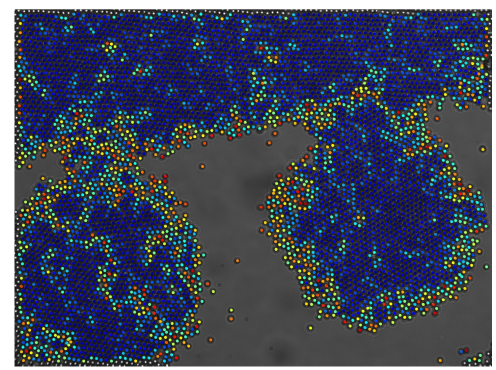












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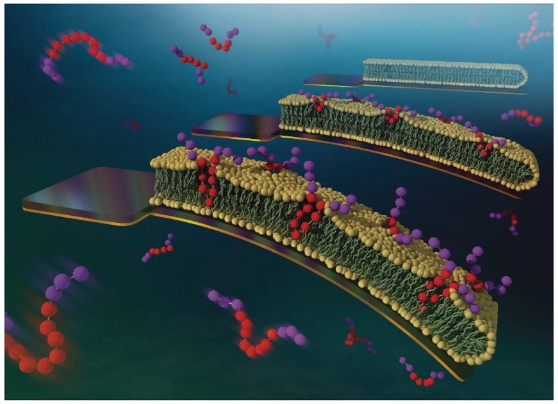
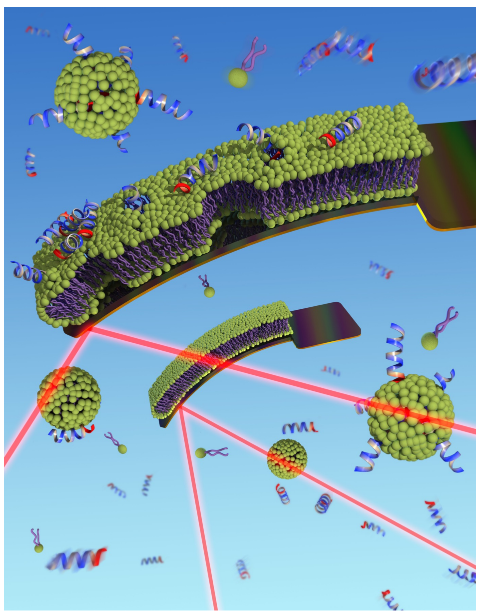


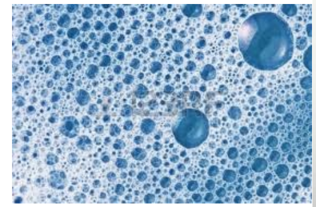


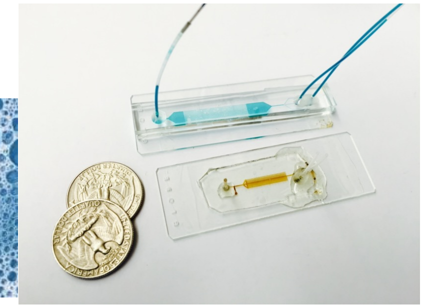
Directed Paramagnetic Colloidal Assemblies

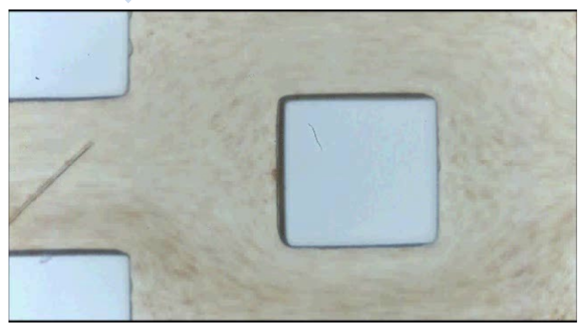
Multiphase Flows in Porous Media

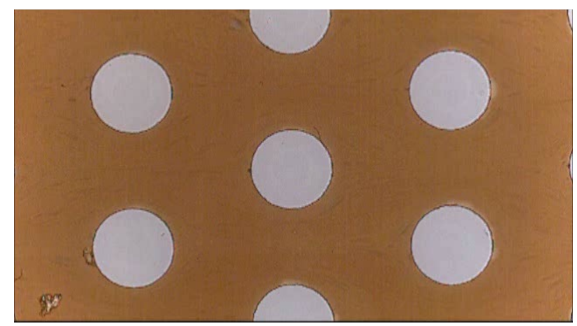
Sensitive Biosensors

Composites for Lithium-Ion Batteries

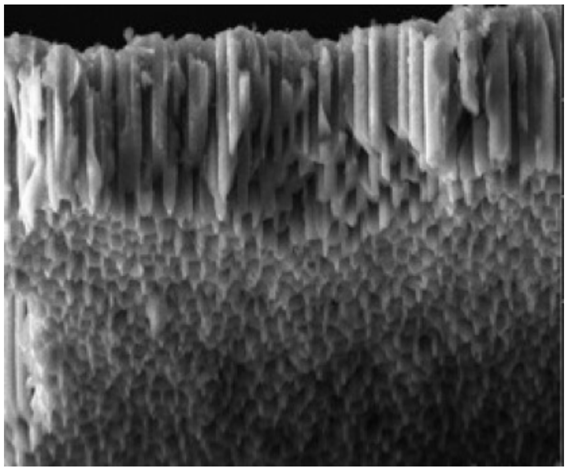


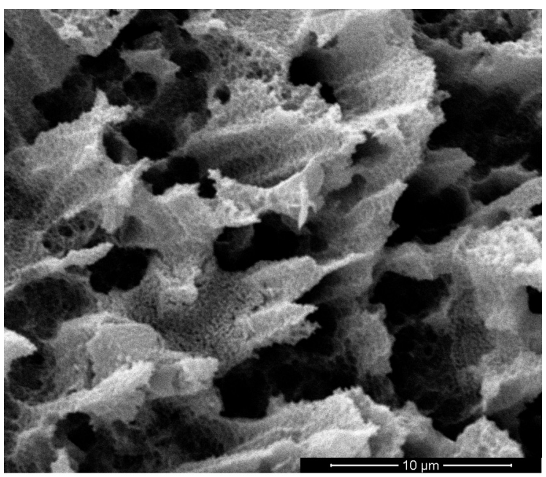






Biswal Group: Engineering Soft Matter



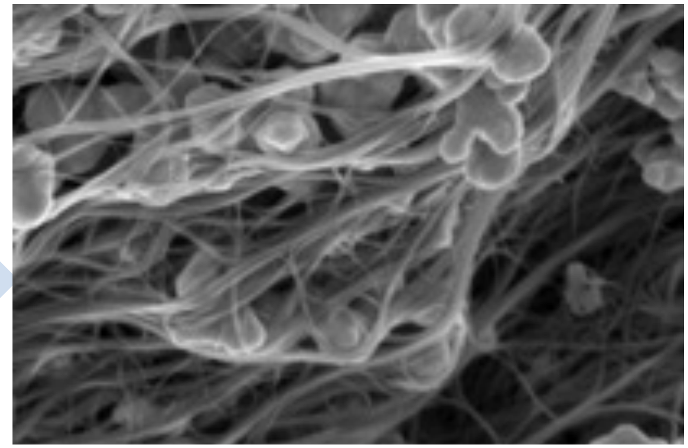


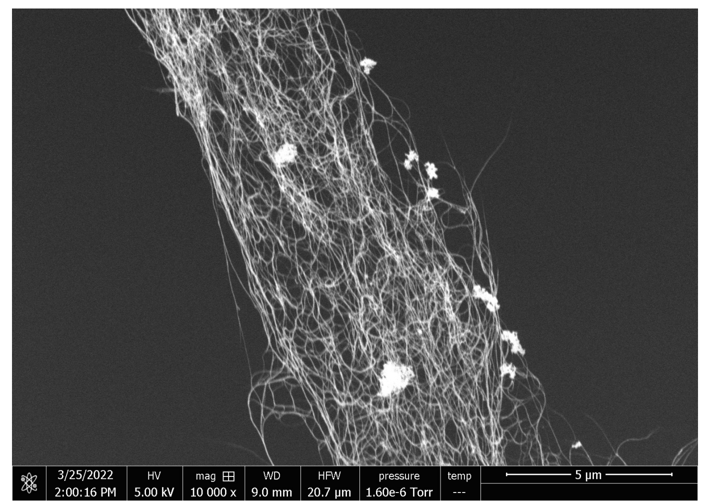
Directed Paramagnetic Colloidal Assemblies

Multiphase Flows in Porous Media

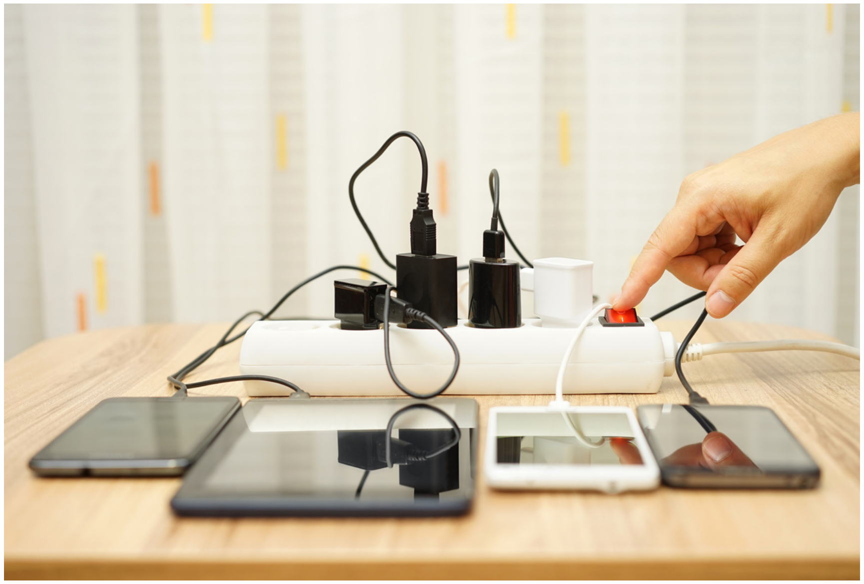
Lipid and Protein-Based Biosensors

Composites for Lithium-Ion Batteries



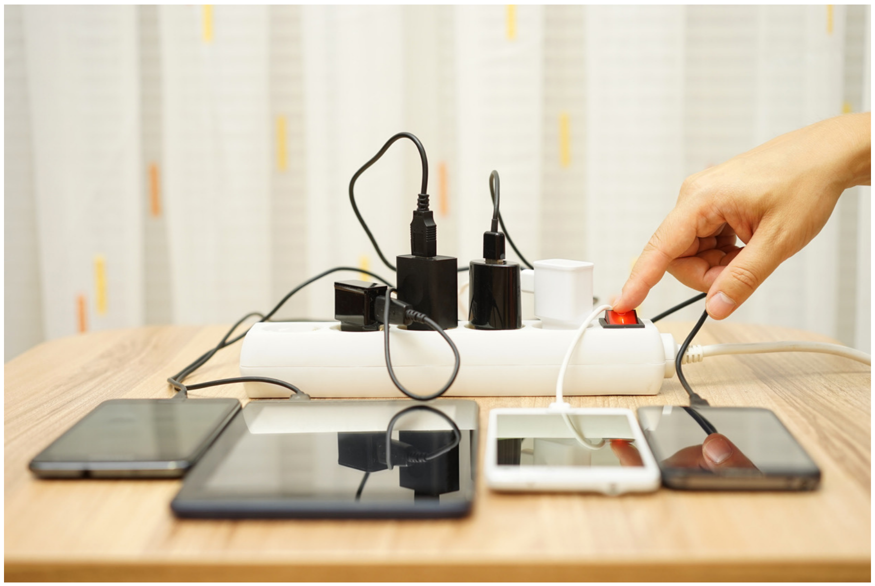


Lithium-Ion Batteries

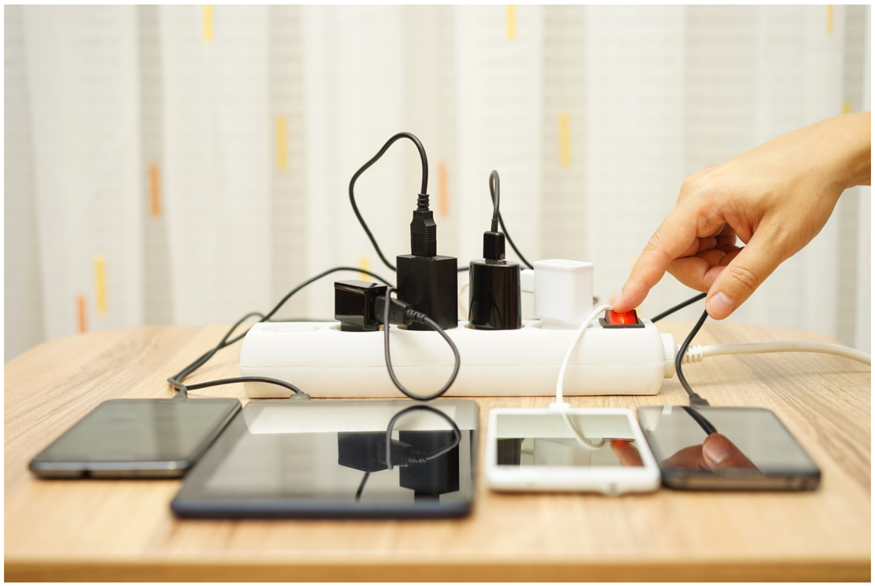


Lithium-ion batteries have become the energy storage of choice for our consumer electronics

Lithium-Ion Batteries



Lithium-Ion Batteries



iWatch 8:
1.19 W-h

iPad Pro:
36.71 W-h

iPhone 13:
12.41 W-h

16" Macbook Pro:
100 W-h

Lithium-Ion Batteries: Electric Vehicles

2023 Nisson Leaf: 200 miles
62,000 Wh

2023 Chevy Bolt: 260 miles
66,000 Wh

2023 BMW iX: 324 miles
110,000 Wh

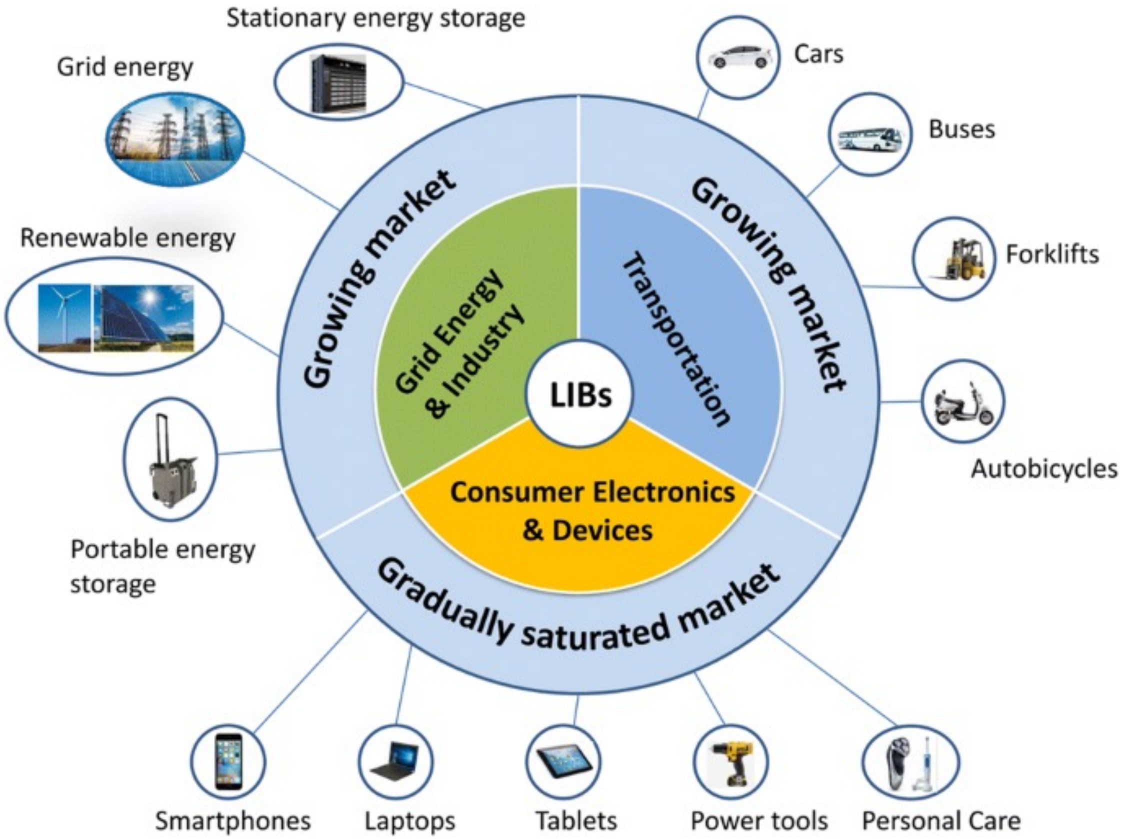
Tesla Powerwall:
13,500 Wh

2023 Tesla Model 3: 350 miles
82,000 Wh

Compared to consumer electronics, automotive applications have more stringent technical requirements:

- Life: 10 years
- Cycle life: 1000 cycles
- Temperature range: −30 to 52 °C
- Cost: $100/kWh

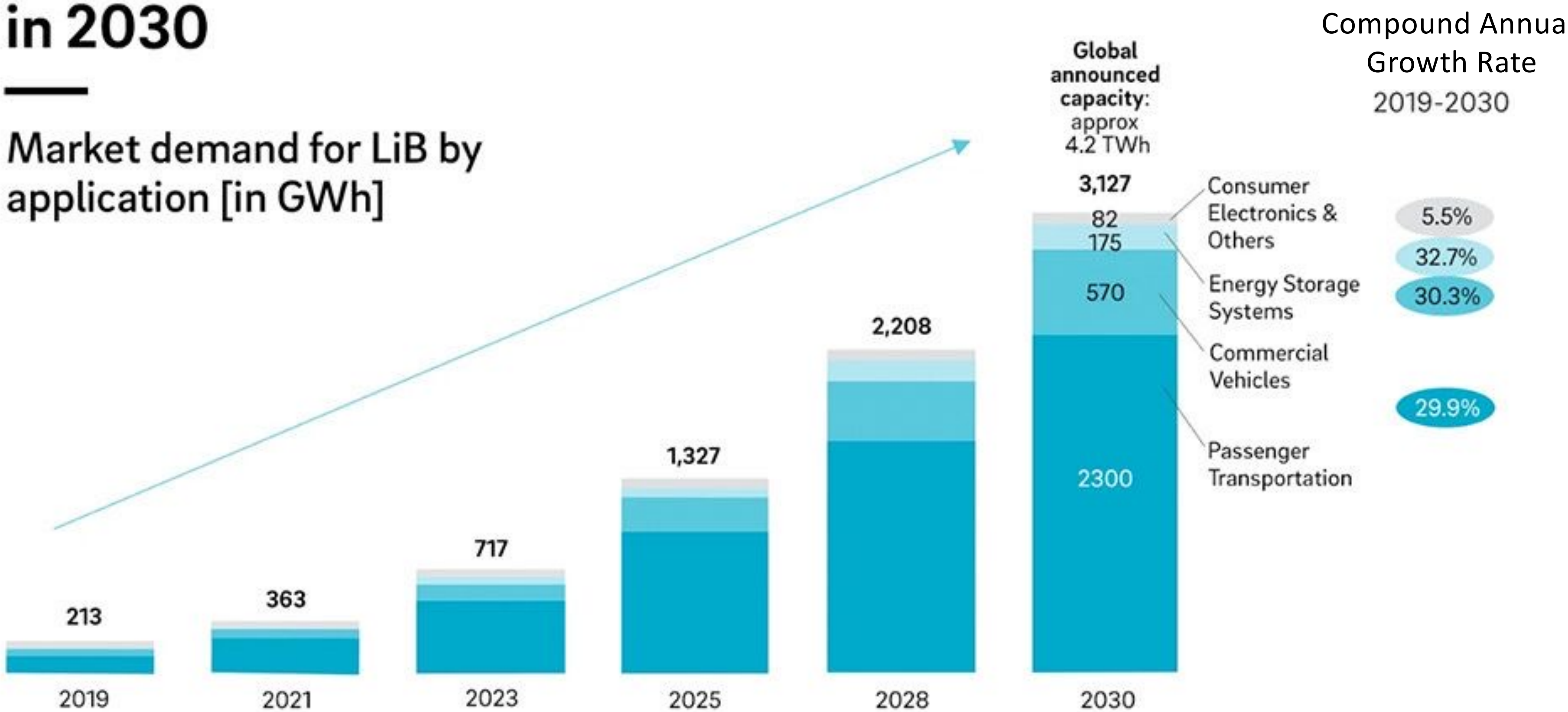
We are electrifying everything …



Ding, Y., Cano, Z.P., Yu, A. *et al.* Automotive Li-Ion Batteries: Current Status and Future Perspectives. *Electrochem. Energ. Rev.* **2**, 1–28 (2019). https://doi.org/10.1007/s41918-018-0022-z

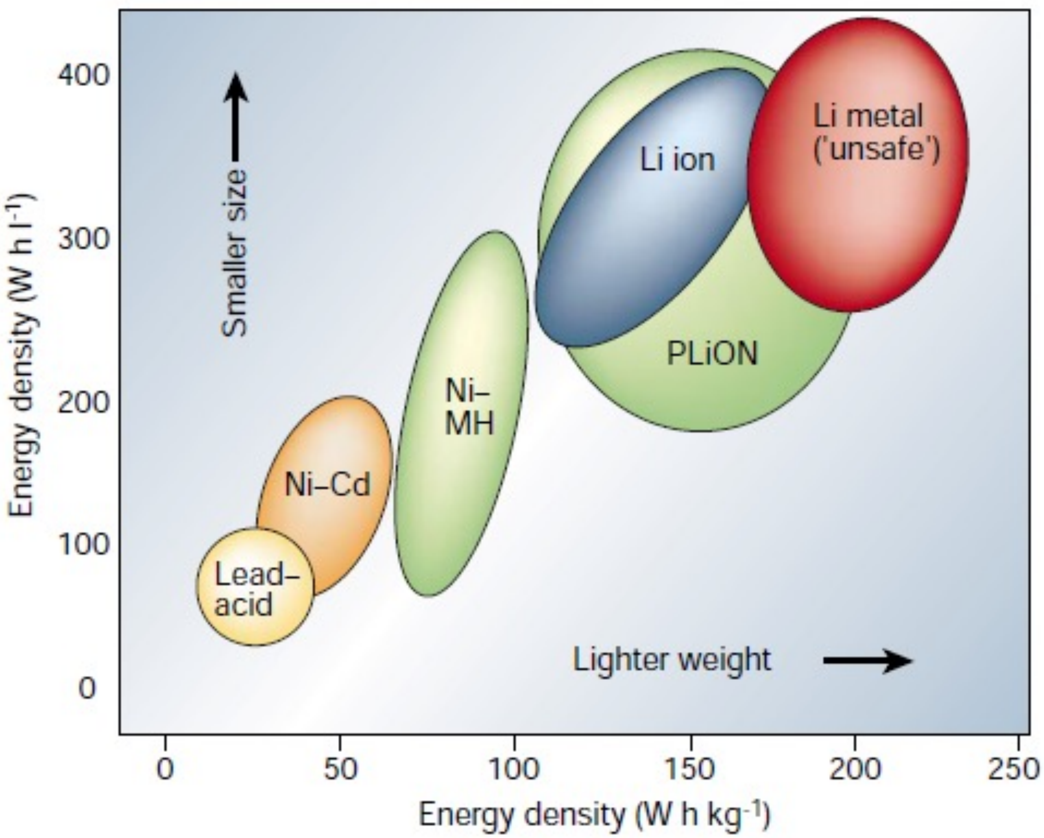
Global demand for lithium-ion batteries will be over 3,100 GWh in 2030

Market demand for LiB by application [in GWh]



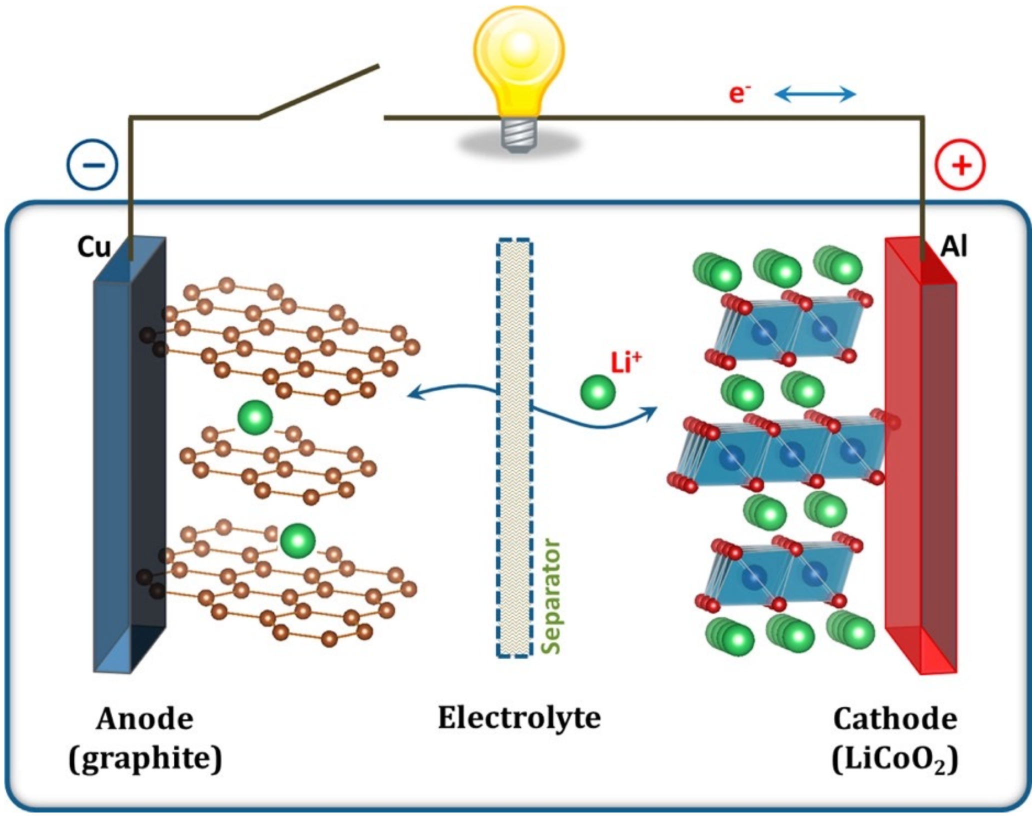
Sources: Avicenne, Fraunhofer, IHS Markit, Interviews with market participants, Roland Berger

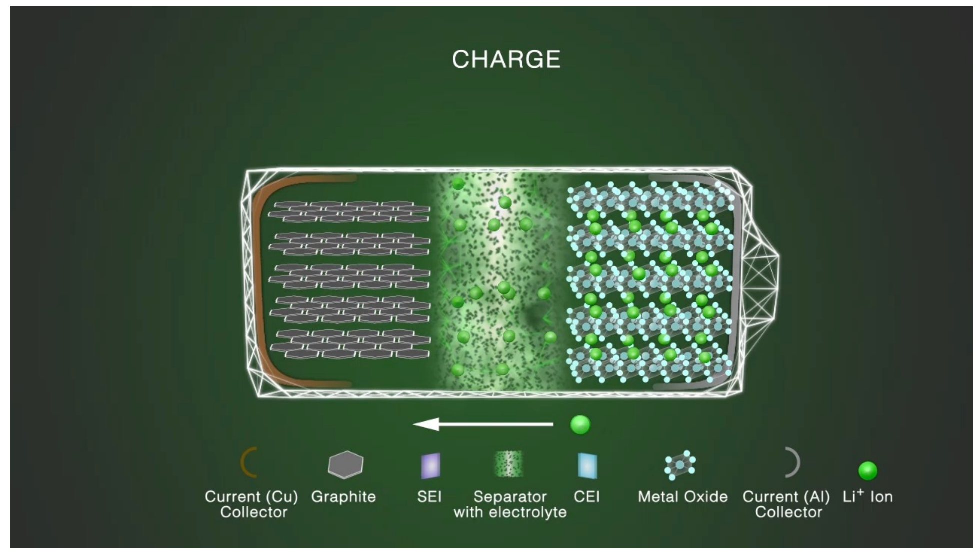
Why Lithium-Ion Batteries?



J.-M. Tarascon et al., Nature, 2001

Working Principle of Lithium-Ion Batteries

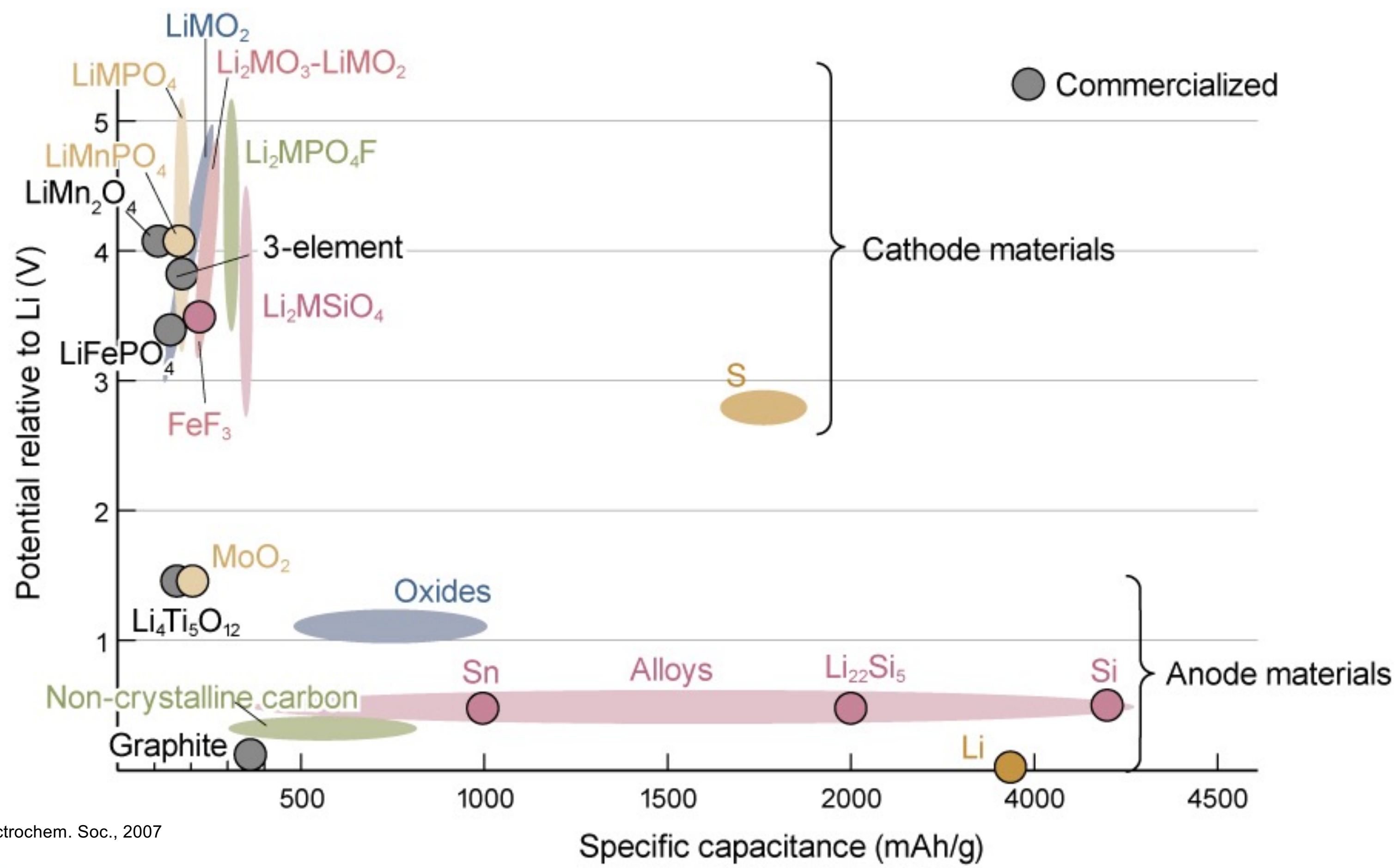




Goodenough, J. B., & Park, K. S. (2013). The Li-ion rechargeable battery: a perspective. *Journal of the American Chemical Society*, *135*(4), 1167-1176.

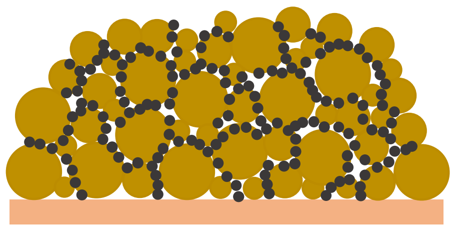
https://e-lyte-innovations.de/

Active Materials for Lithium Ion Batteries



M. N. Obrovac et al., J. Electrochem. Soc., 2007

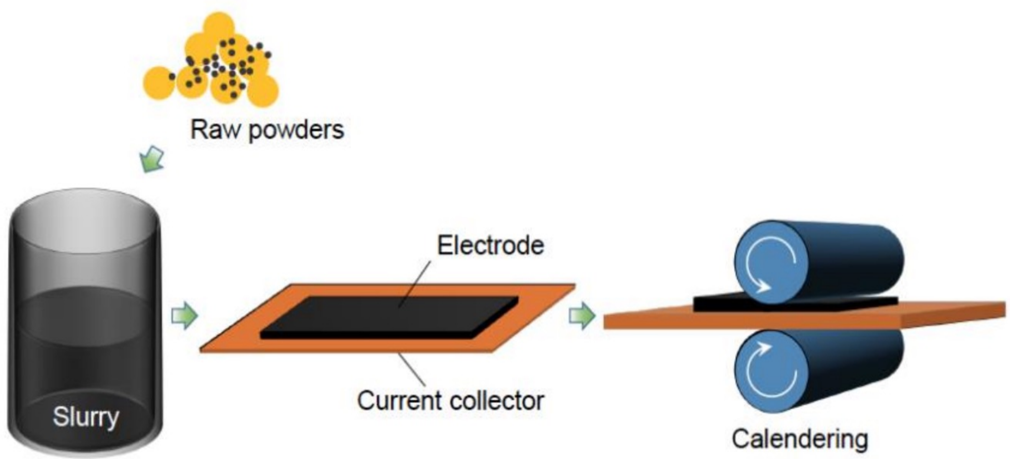
Standard Graphite Anodes



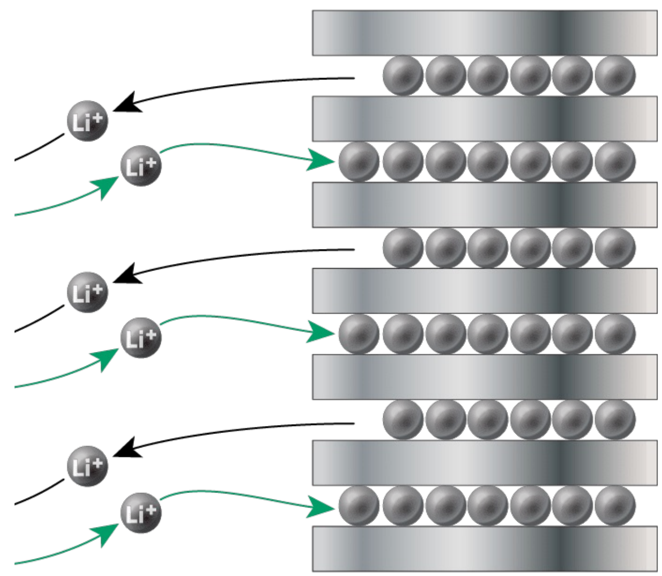
Graphite Anode:
90% SFG 6L carbon; 5% C45; 5% HSV900 PVDF

Conductive Additive:
Carbon black

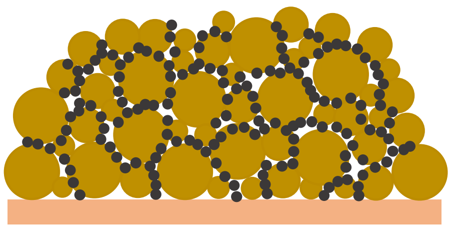
Binder:
Polyvinylidene fluoride



(Hu, Uni. of Kentucky, 2019)



Does not work for Silicon



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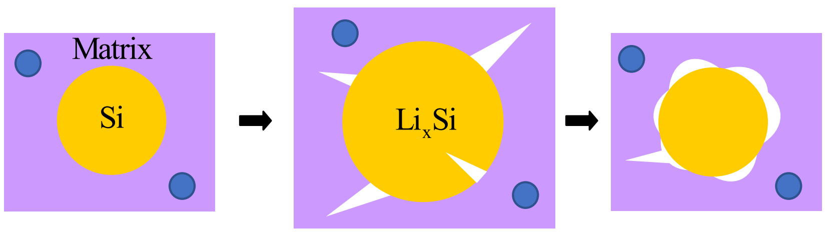
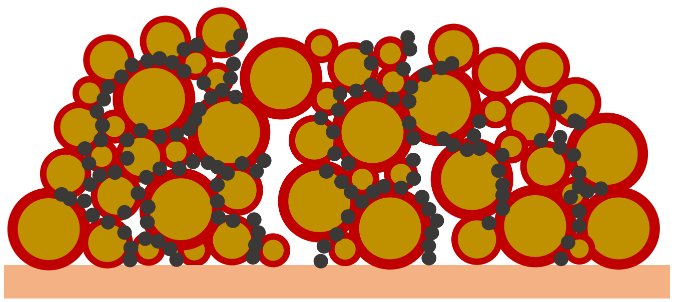


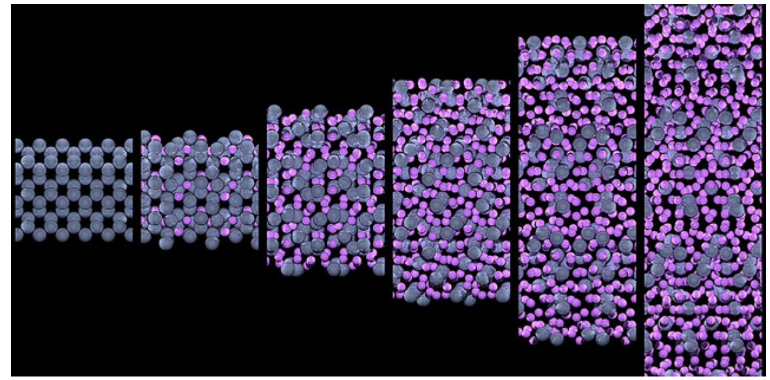


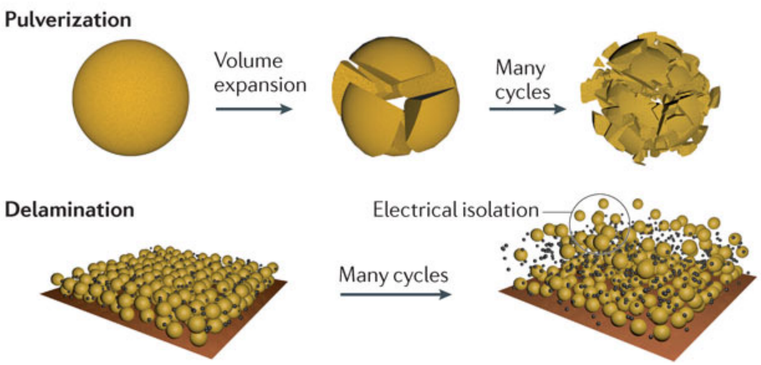
Challenges of Silicon-based Anodes

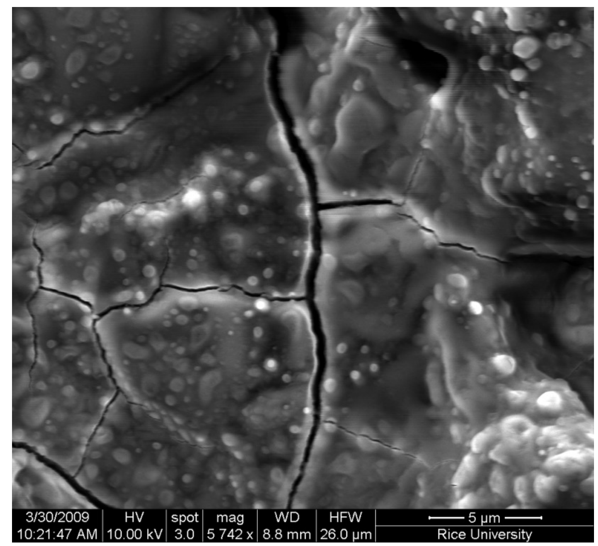
Graphite: $6C + Li^+ + e^- \longleftrightarrow LiC_6$

Compound and crystal structure	Unit cell volume (Å^3)	Volume per silicon atom (Å^3)
Silicon cubic	160.2	20.0
$Li_{12}Si_7$, ($Li_{1.71}Si$) orthorhombic	243.6	58.0
$Li_{14}Si_6$, ($Li_{1.71}Si$) rhombohedral	308.9	51.5
$Li_{13}Si_4$, ($Li_{3.25}Si$) orthorhombic	538.4	67.3
$Li_{22}Si_5$, ($Li_{4.4}Si$) cubic	659.2	82.4

Volume change:
120% for $Li_{1.7}Si$
160% for $Li_{2.3}Si$
240% for $Li_{3.25}Si$
400% for $Li_{4.4}Si$





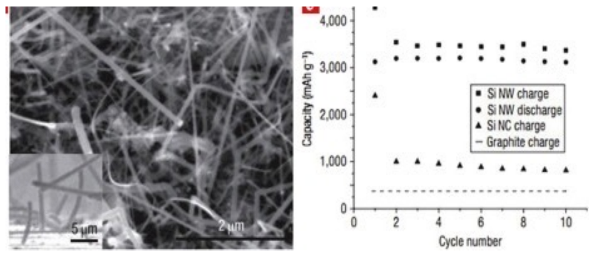


U. Kasavajjula et al., J. of Power Sources, 2007 Image: Argonne National Laboratory
Choi, J. W. & Aurbach, D. (2016) *Nat. Rev. Mater.*

Strategies

- Expensive Synthesis methods
- Not amenable for large scale production
- Low cycle life/ poor rate capability
- Large capacity fade

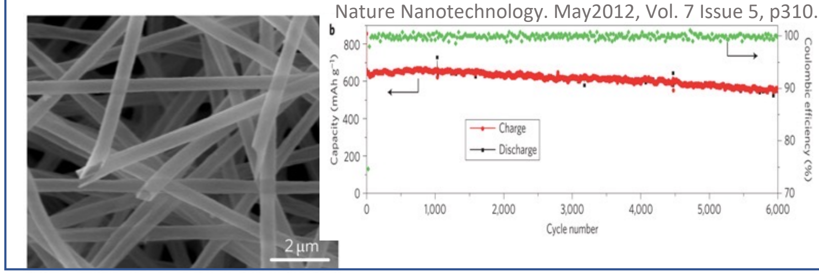
Silicon Nanowires



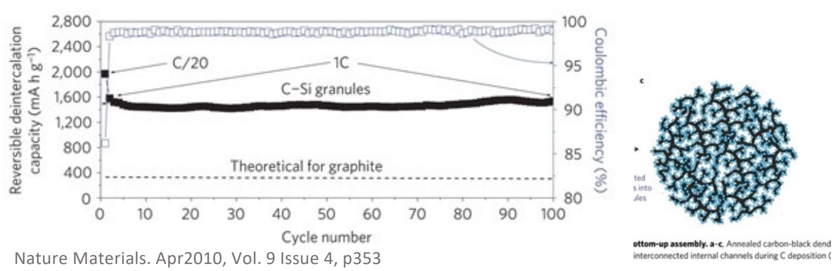
Nature Nanotechnology 3, 31 - 35 (2008)

Silicon Nanotube

Nature Nanotechnology. May2012, Vol. 7 Issue 5, p310.

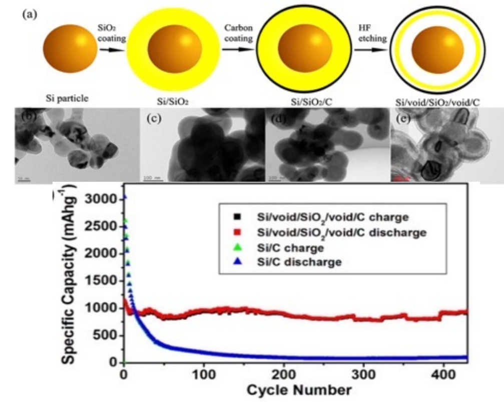


Bottom-up Approach of Porous Silicon



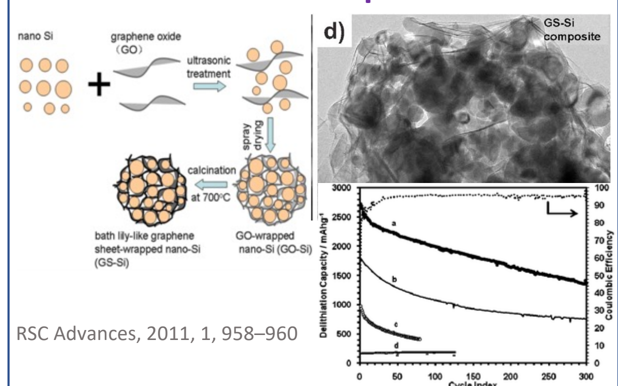
Nature Materials. Apr2010, Vol. 9 Issue 4, p353

Core/shell



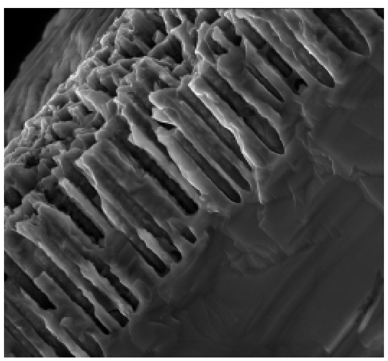
Scientific Reports **5**, Article number: 10908 (2015)

Nanocomposites



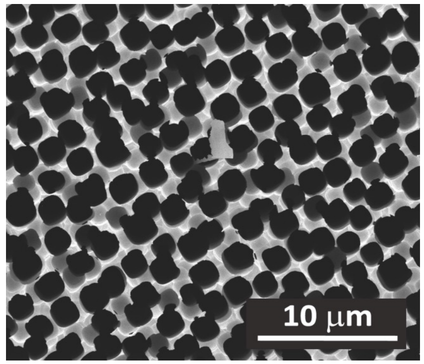
RSC Advances, 2011, 1, 958–960

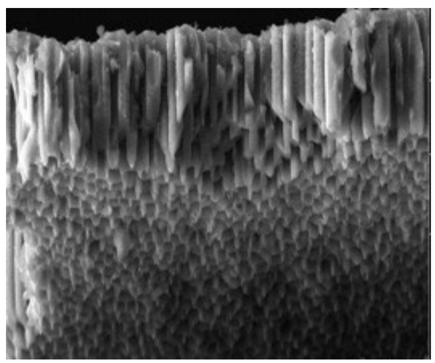
Our approach: Nanostructured Silicon



Gold-Coated
Porous Silicon Film

Journal of Power Sources, 205 pp 426-432 (2012).

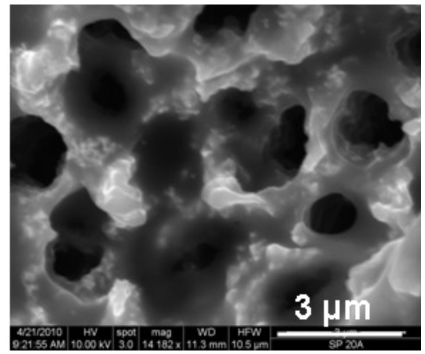


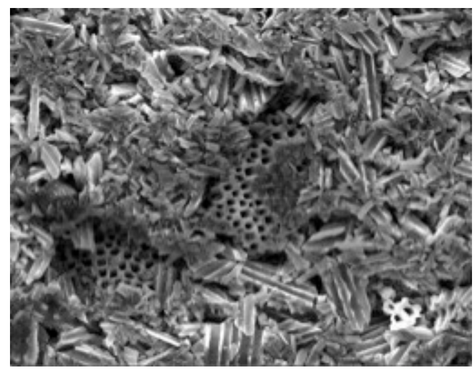


Lift-off Porous Silicon
Films

Chemistry of Materials (2012), 24(15) pp 2998-3003 (2012).

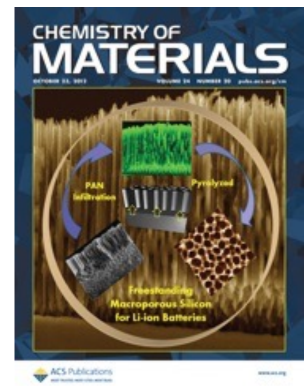
100 µm





Macroporous Silicon
Particulates

Scientific Reports, 2:795 (2012). DOI:10.1038/srep00795



Polymer Binder Characteristics

Mechanical

1. Strong interfacial adhesion

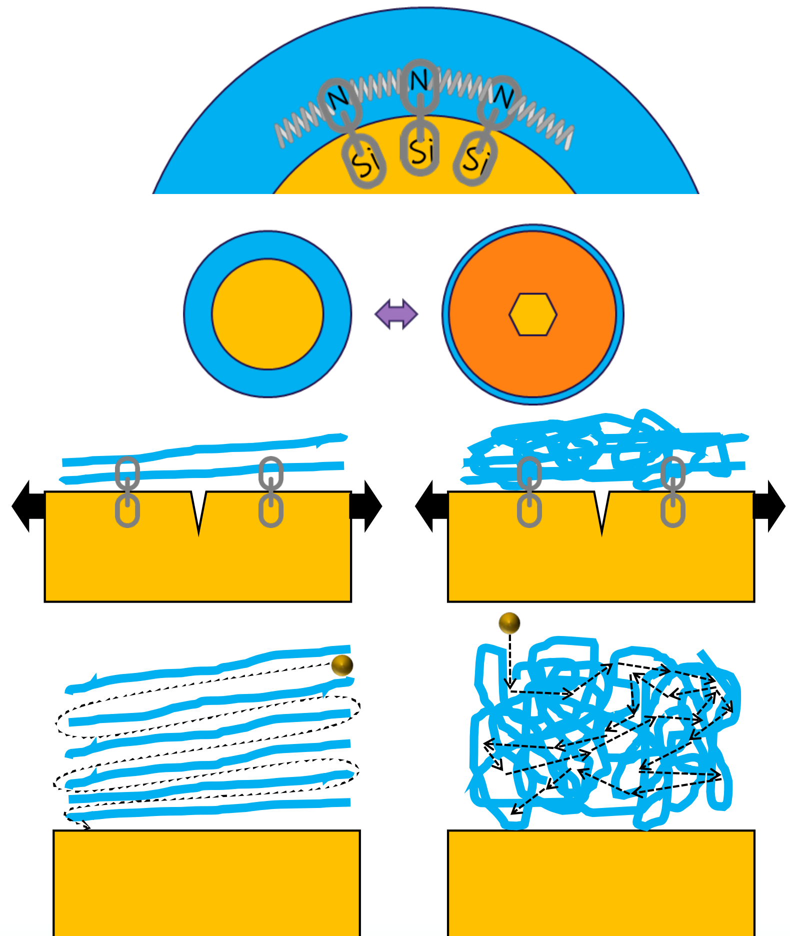
2A. High binder elastic property
2B. Reducing lithiation stress

3. Prevents crack propagation

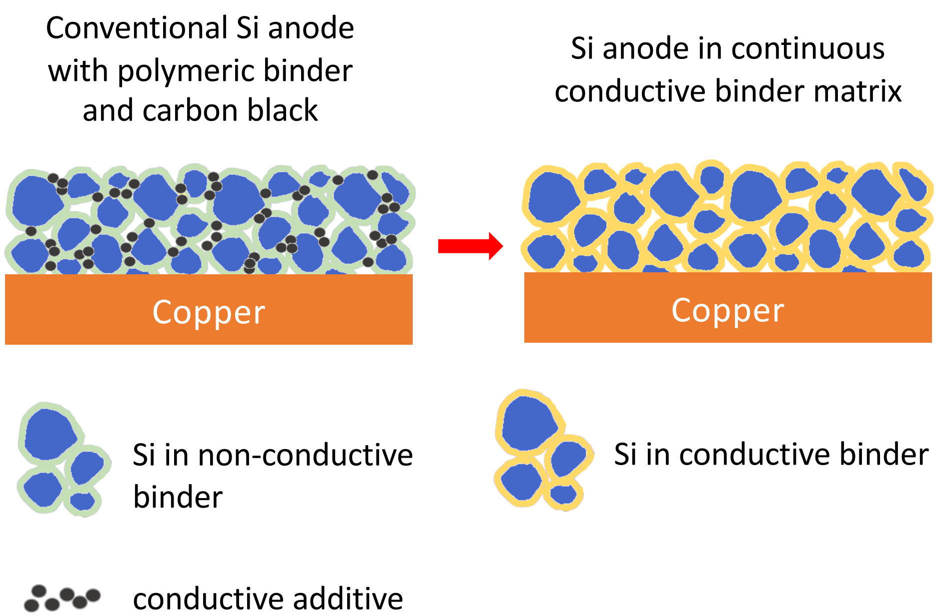
Conductivity

4. Facile ion conduction

5. Electron conduction

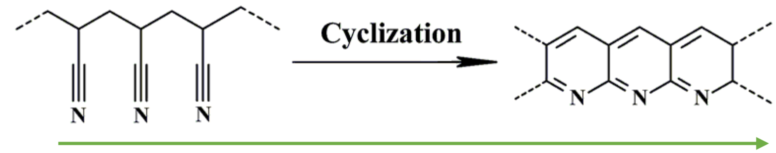


Silicon Anodes with PAN

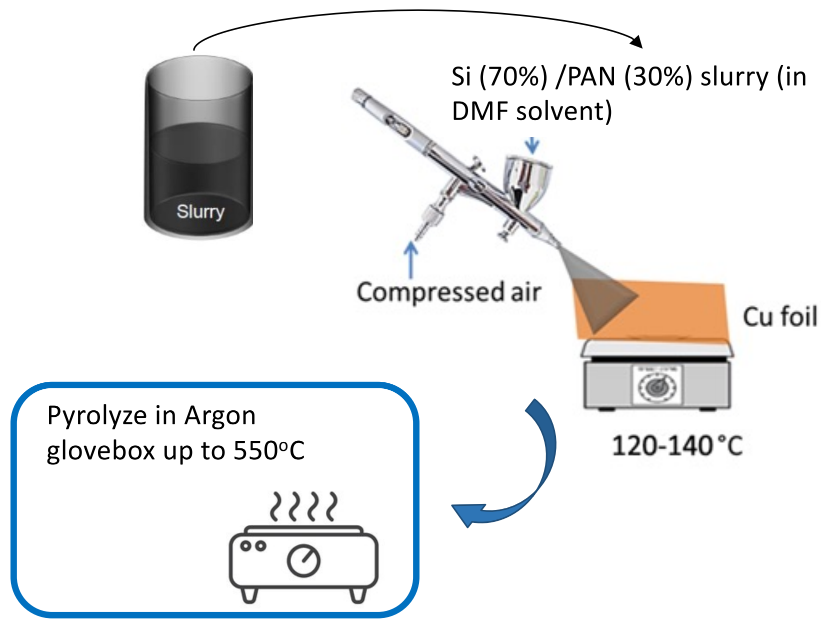


Promises of conductive binder:

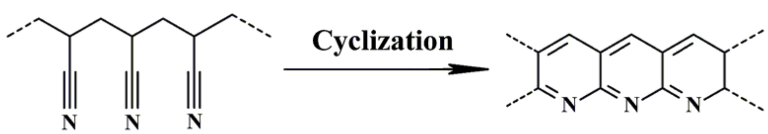
- Continuous electronic conductive matrix
- Maintains good interface with silicon particles even as they expand
- More scalable electrode fabrication



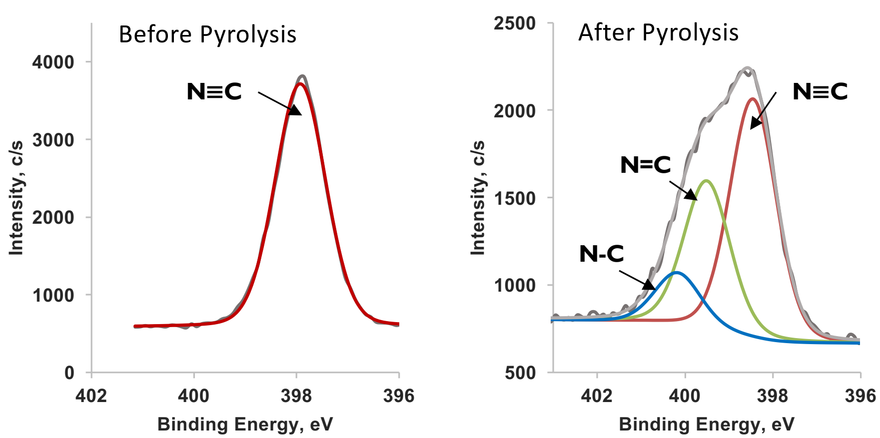
Converting polyacrylonitrile (PAN) into a conductive binder through pyrolysis



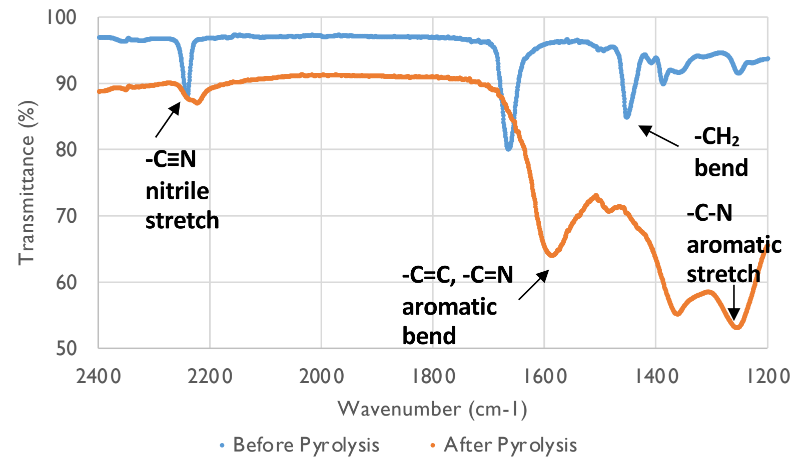
Silicon Anodes with PAN



XPS spectrum of N1s

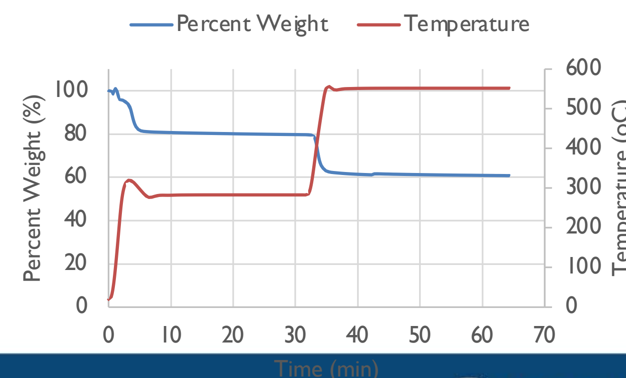


Heating Temperature Pyrolysis of PAN (^{o}C)	Average Sheet Resistance (kilo-ohm-square)
350	32.26
450	15.39
550	2.19

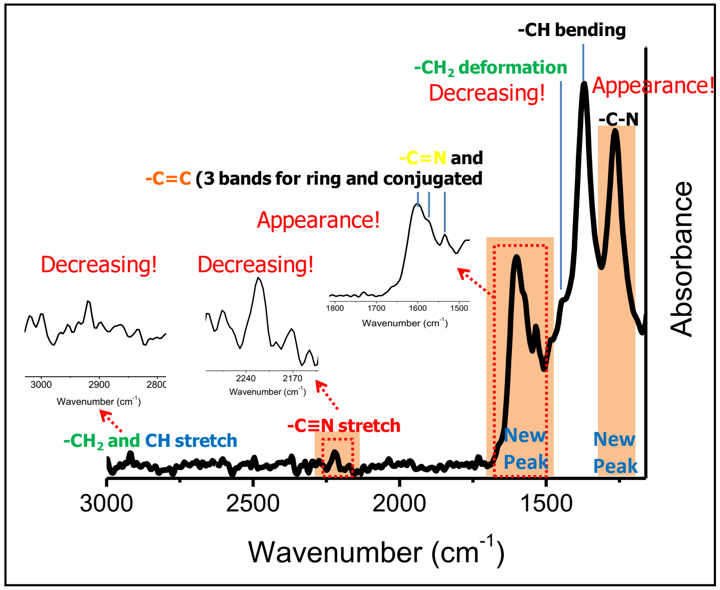


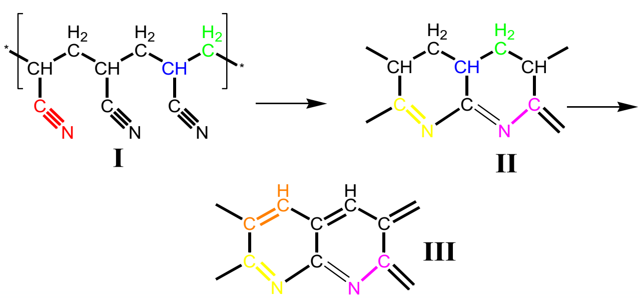
Attenuated Total Reflectance (ATR) FTIR for PAN

TGA Experiment on PAN



Polyacrylonitrile: PAN





The Journal of Chemical Physics

Electronicstructure evolution upon thermal treatment of polyacrylonitrile: A theoretical investigation

J. L. Brédas and W. R. Salaneck

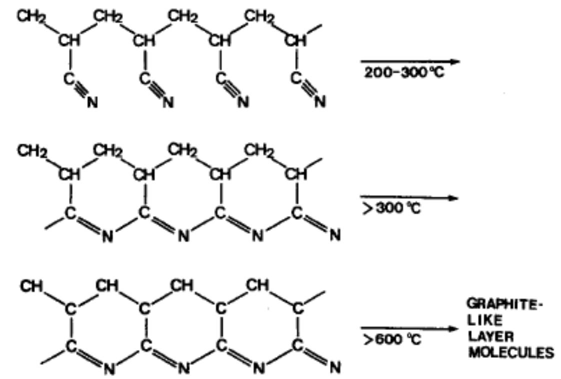
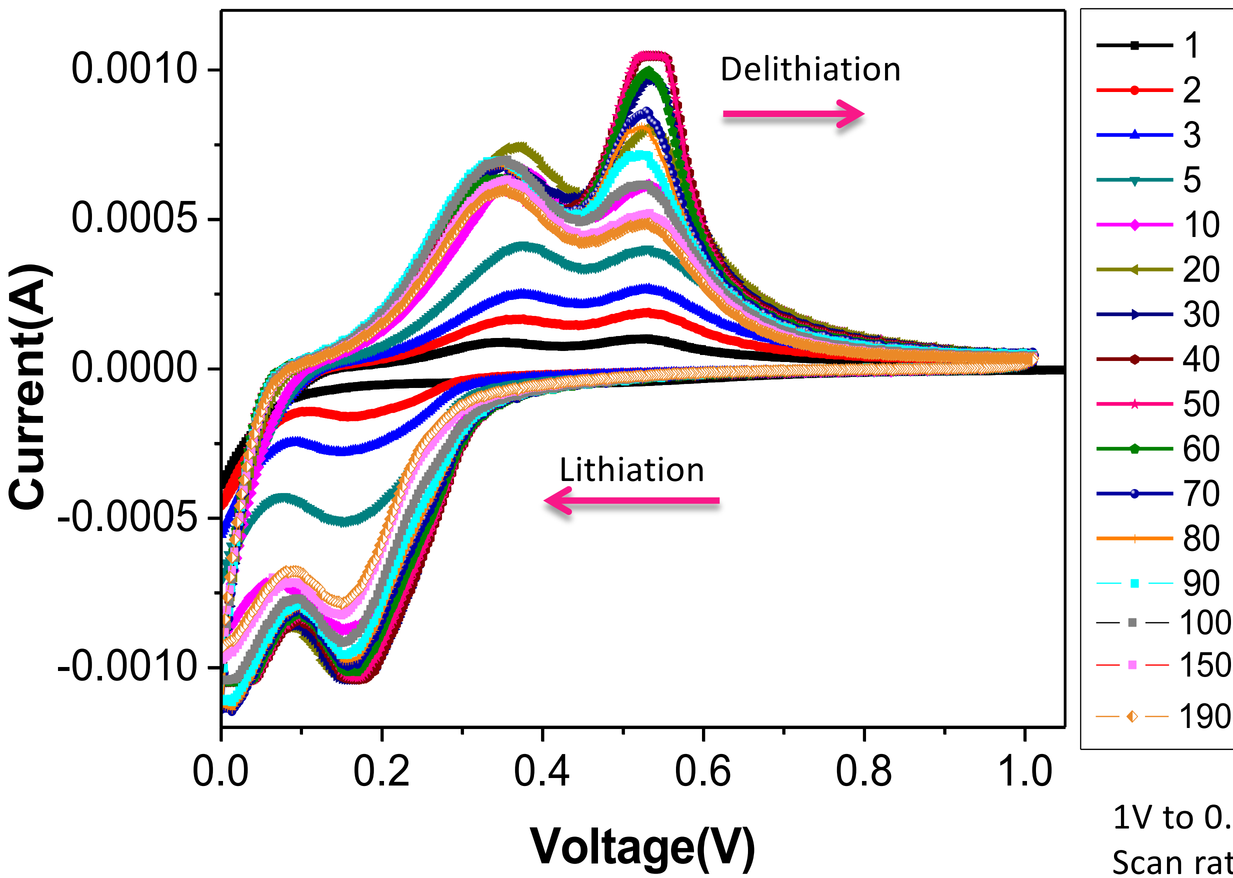


FIG. 1. Suggested molecular structure evolution of polyacrylonitrile under pyrolysis. From top to bottom: structure of polyacrylonitrile (PAN); structure of polyethyleno-methineimine (PEMI); structure of polypyridinopyridine (PPyPy).

The conductivity of the prepared PAN was determined to be 9.08 × 10^{-1} S/m, which augmented to 2.36 S/m after pyrolysis at 550 °C.

Cyclic Voltammetry



- Peaks at 0.2V: Lithium-Si alloy formation
- Peaks between 0.3V-0.7 V: Delithiation of Lithium-Silicon alloy
- Increase in the peak intensity is due to the formation of amorphous Si.

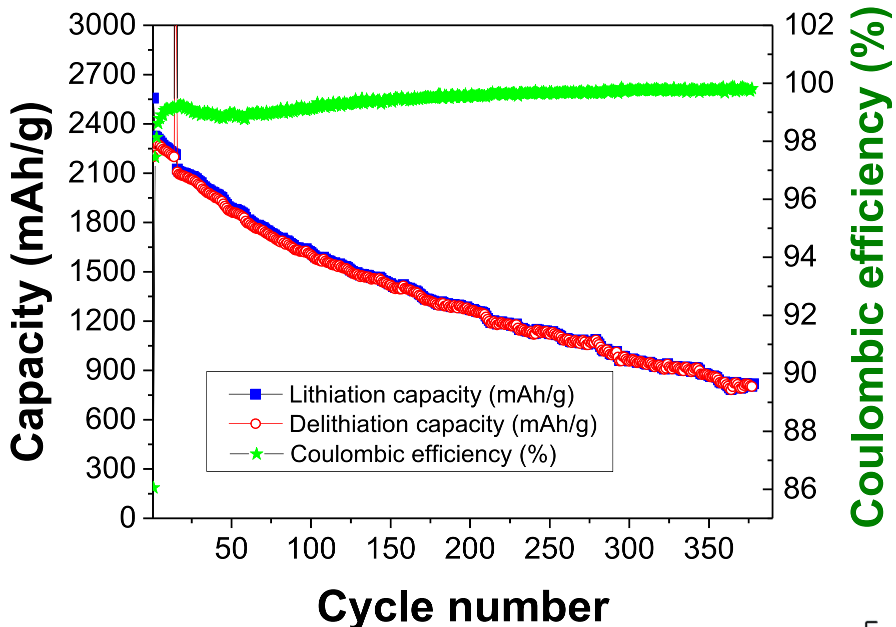
1V to 0.001V
Scan rate: 0.1mV/sec

Galvanostatic Cycling

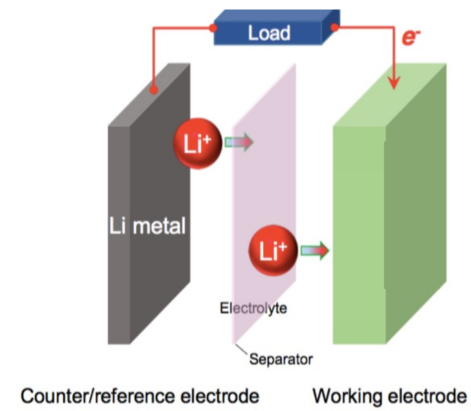
Lithiation:
1^{st} cycle: 2557 mAh/g
377^{th} cycle: 803 mAh/g
Capacity fade: 69%

Delithiation:
1^{st} cycle: 2200 mAh/g
377^{th} cycle: 801 mAh/g
Capacity fade: 64%

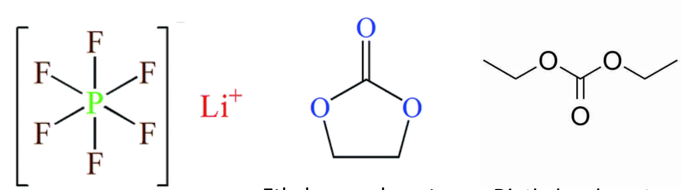
Galvanostatic cycling between 1 V and 0.01V



C/5 rate: Efficiency at 377^{th} cycle = 99.8%

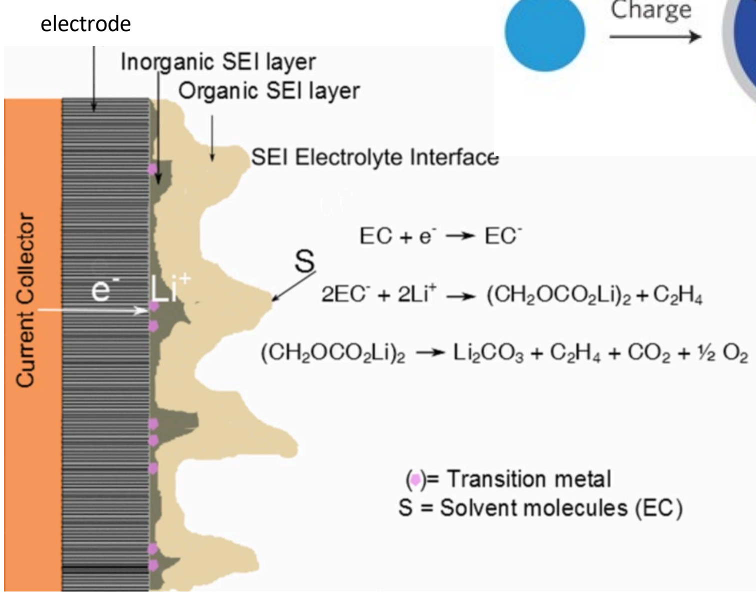


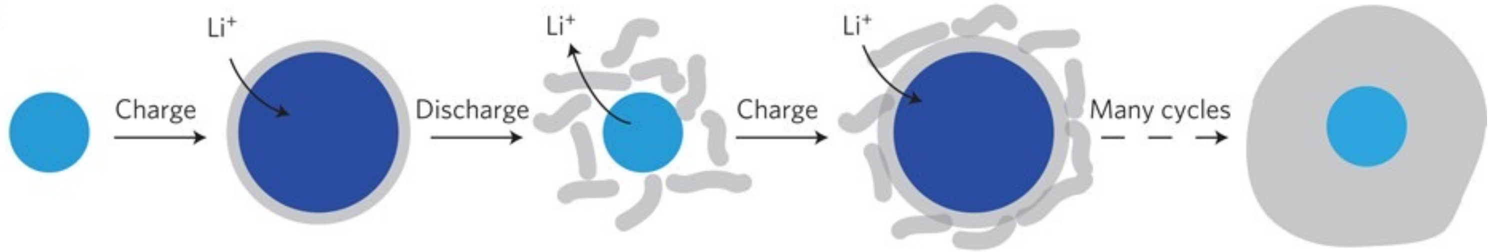
1.0 M $LiPF_6$
in EC/DC



$LiPF_6$ EC DC

Solid-Electrolyte Interface (SEI)





Solid-Electrolyte Interface (SEI):

-Liquid organic electrolyte undergoes decomposition that precipitate into the SEI layer

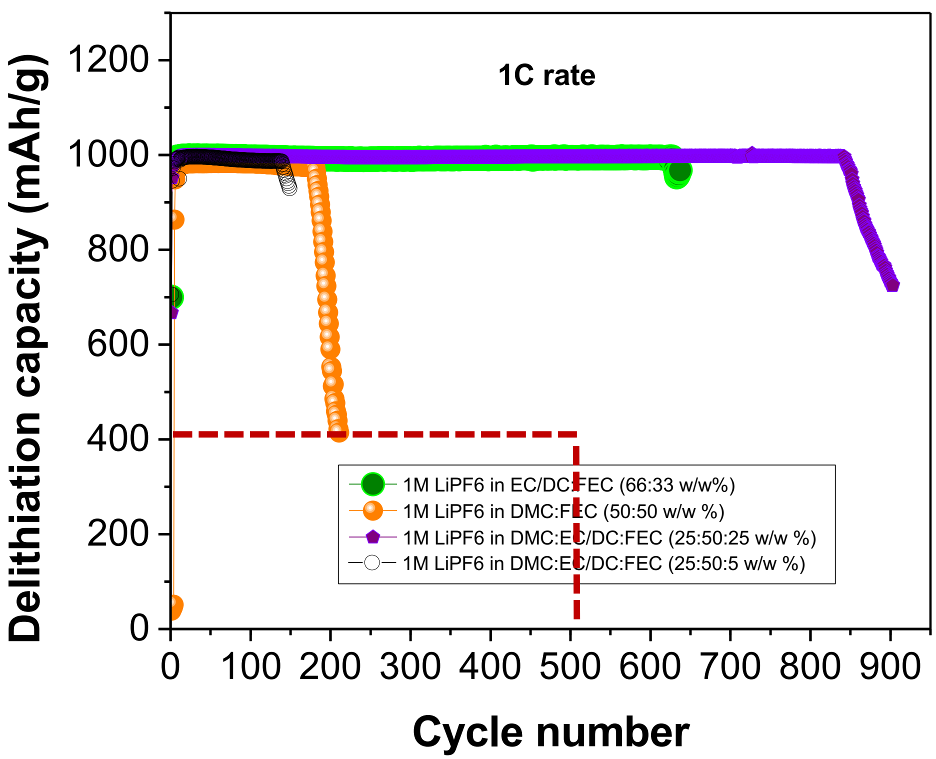
-Precipitate is insulating

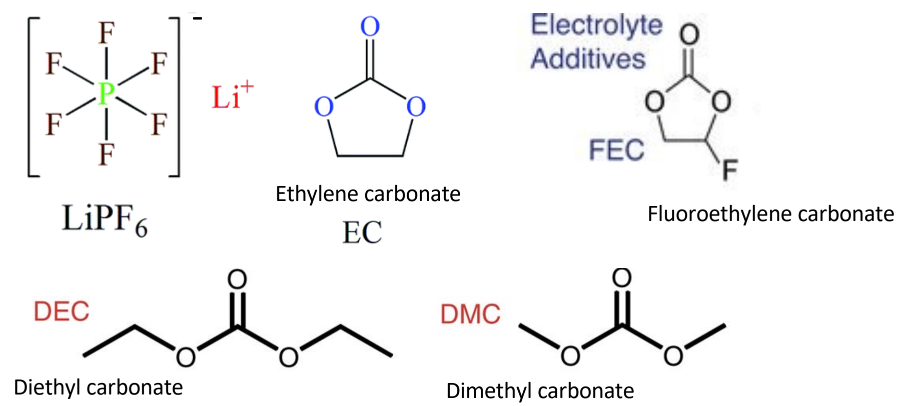
Tapesh Joshi et al. J. Electrochem. Soc. 2014;161:A1915-A1921

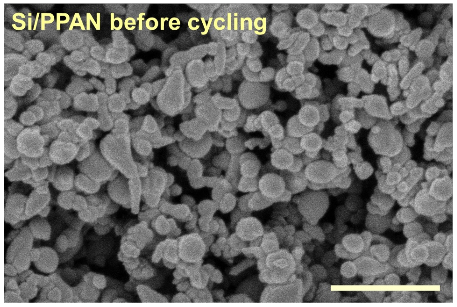
Hui Wu et. al. Nature Nanotechnology, 2012, **7**, 310–315

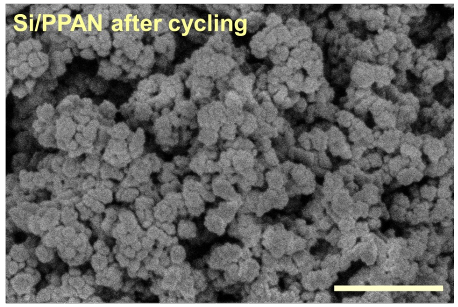
Capacity Controlled Cycling + Additives

Capacity is limited to control the amount of lithium that intercalates into silicon





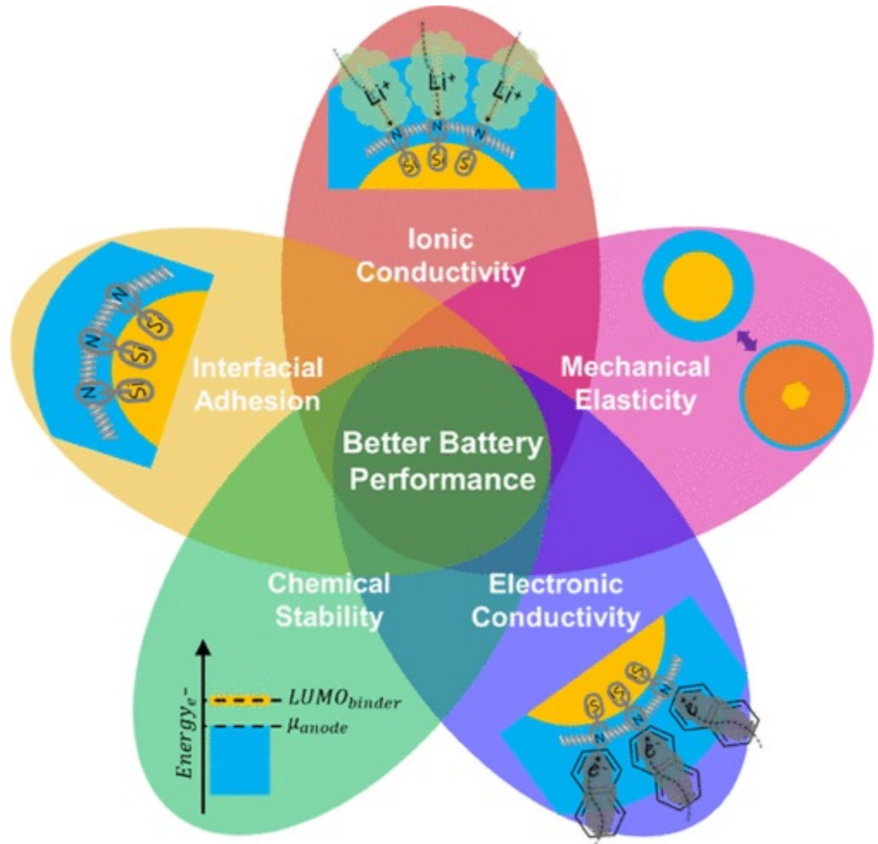




(Scale bar: 500 nm)

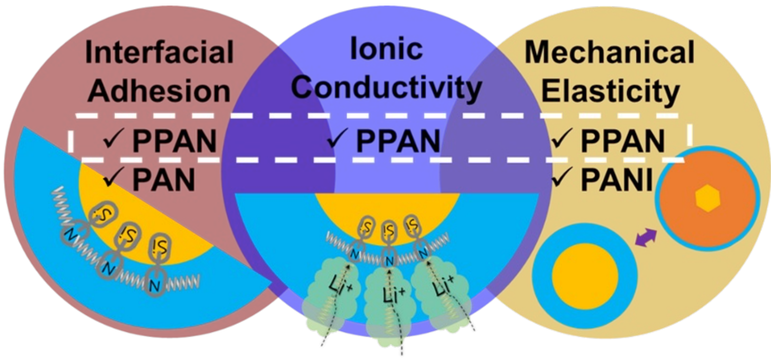
Advantage of PAN - ReaxFF

“ReaxFF casts the empirical interatomic potential within a bond-order formalism, thus implicitly describing chemical bonding without expensive QM calculations.” - Tom Senftle

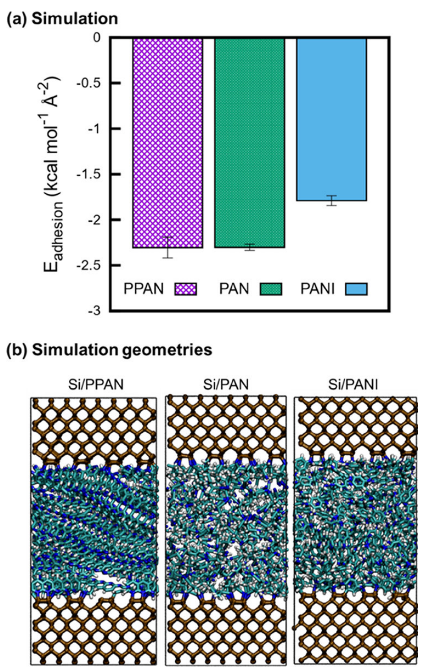


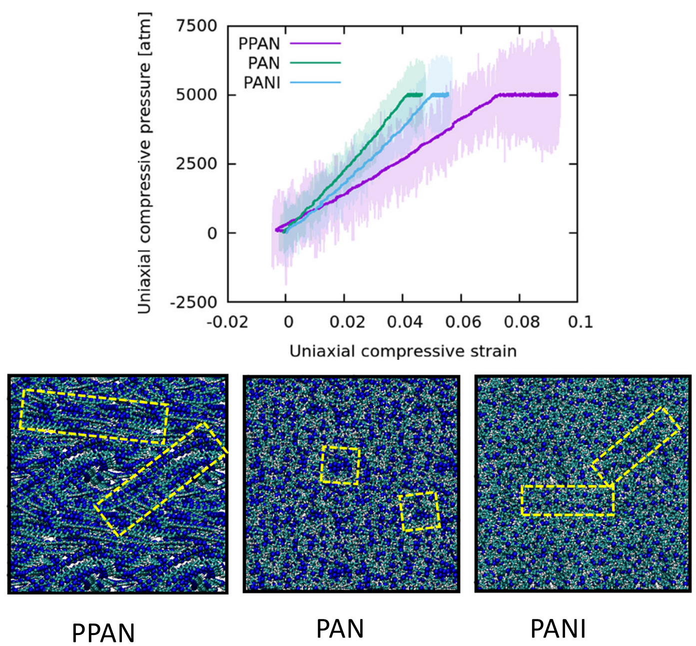
Bhati, M., Nguyen, Q. A., Biswal, S. L., & Senftle, T. P. (2021). Combining ReaxFF Simulations and Experiments to Evaluate the Structure–Property Characteristics of Polymeric Binders in Si-Based Li-Ion Batteries. *ACS Applied Materials & Interfaces*, *13*(35), 41956-41967.

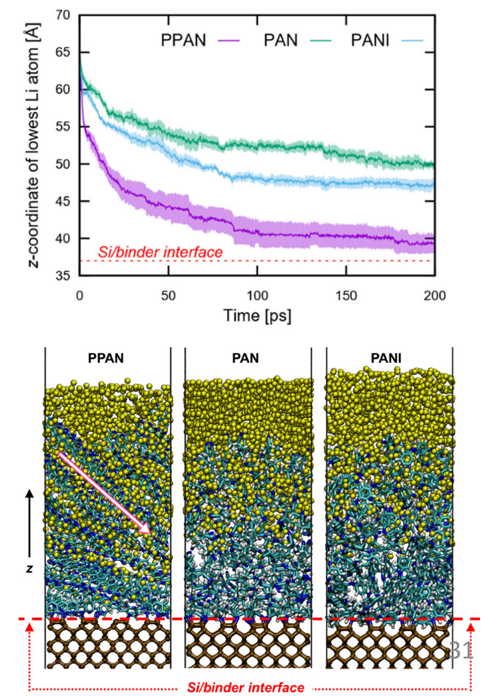
ReaxFF Simulations Elucidate the Si/PPAN Interface



	PPAN	PAN	PANI
Interfacial Adhesion	✅ Strong	✅ Strong	❌ Weak
Mechanical Elasticity	✅ High	❌ Low	✅ High
Ionic Conductivity	✅ High	❌ Low	❌ Low

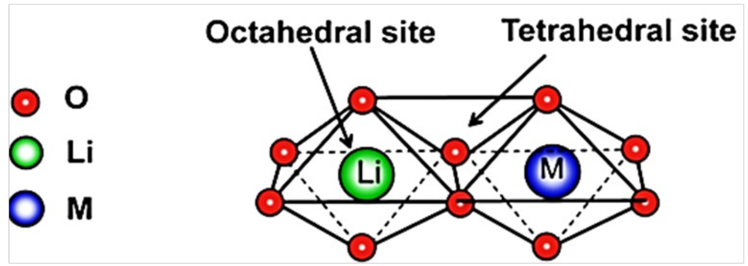






Layered oxide cathodes

- Both $LiCoO_2$ and $LiNiMnCoO_2$ falls in the hexagonal crystal structure

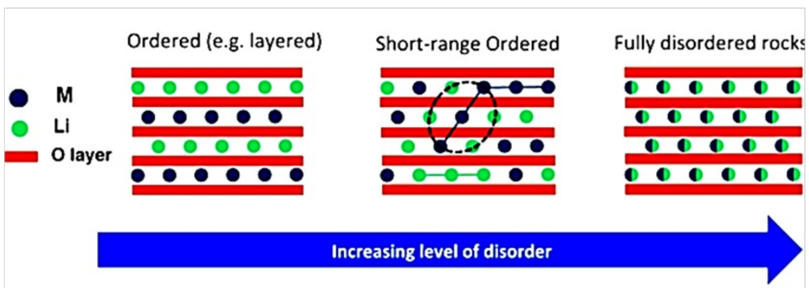


$LiCoO_2$ (LCO)

- High Cobalt content- Costly
- Thermally unstable

$LiNiCoMnO_2$ (NMC)

- The current commercial NMC uses nickel, manganese and cobalt in equal proportions ($LiNi_{0.33}Mn_{0.33}Co_{0.33}O_2$)
- **Co** limits the *anti-site mixing*, ***Mn*** *inactive* ***Ni*** *redox reactions (*Ni: +4 ↔ +3), during the beginning of cycling, then followed by ***Co*** at higher voltages.



(Aziz Abdellahi et al, Chem. Mater. 2016, 28, 5373−5383)

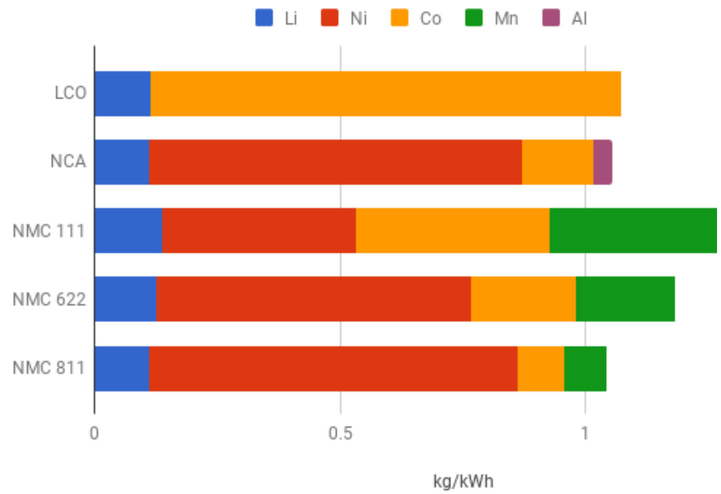
- A little **cation disorder** and insignificant volume change are observed in $LiNi_{1/3}Mn_{1/3}Co_{1/3}O_2$ from the insertion and extraction of Li ions

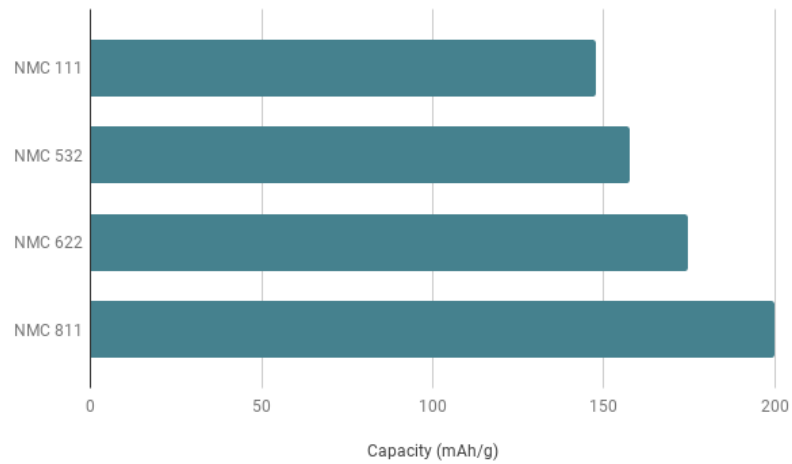
- As the level of **disorders increases** accessibility of Li from the octahedral site becomes difficult. this leads to **lower material capacity.**

- For better electrochemical performance **level of orderings** in the NMC system **should be >1.2**

NMC Cathodes

NMC Cathodes have become mainstream

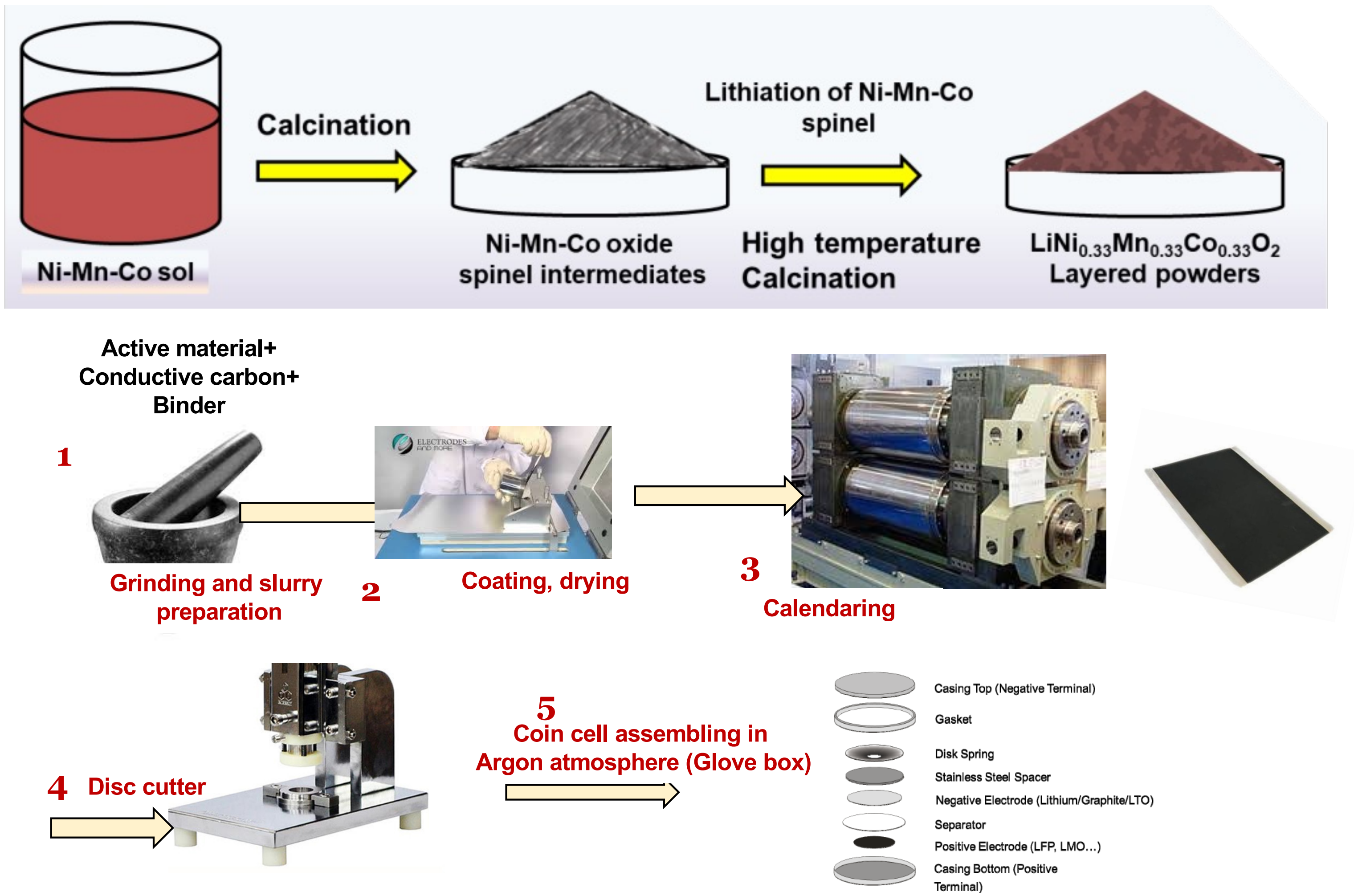




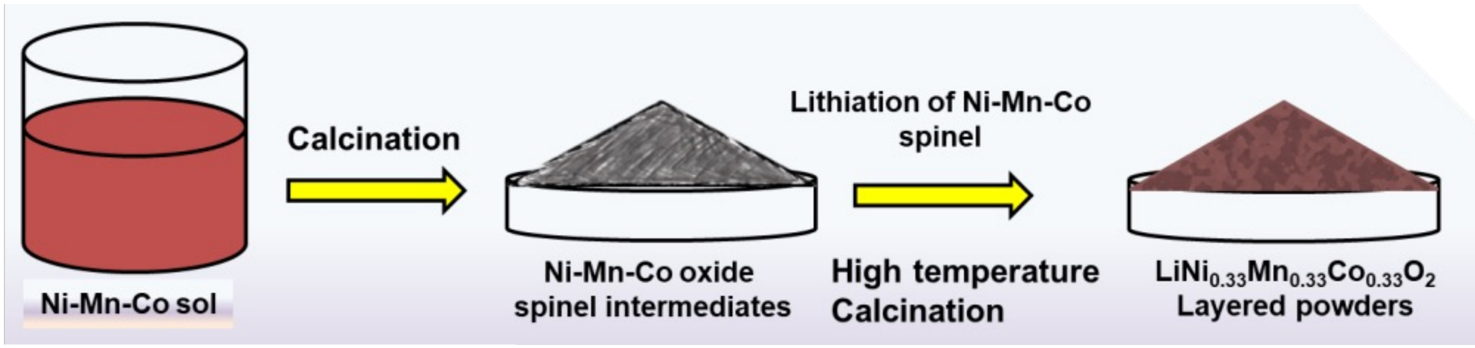
NMC cathodes are being used in the BMW i3, Chevy Bolt, and Nissan Leaf (on the grid side, it's the Tesla Powerwall).

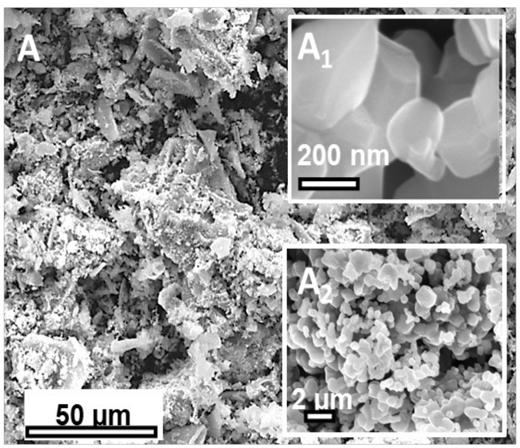
Fu et al., Lithium-Ion Battery Supply Chain Considerations: Analysis of Potential Bottlenecks in Critical Metals (DOI: 10.1016/j.joule.2017.08.019)

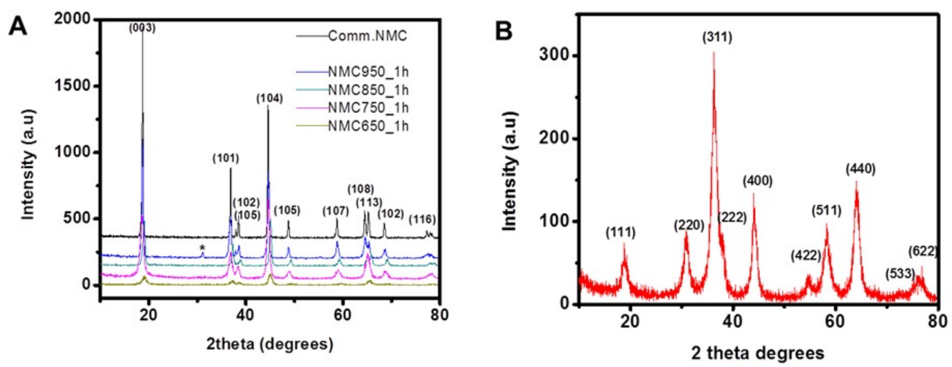
NMC 111 Preparation



NMC 111 Preparation



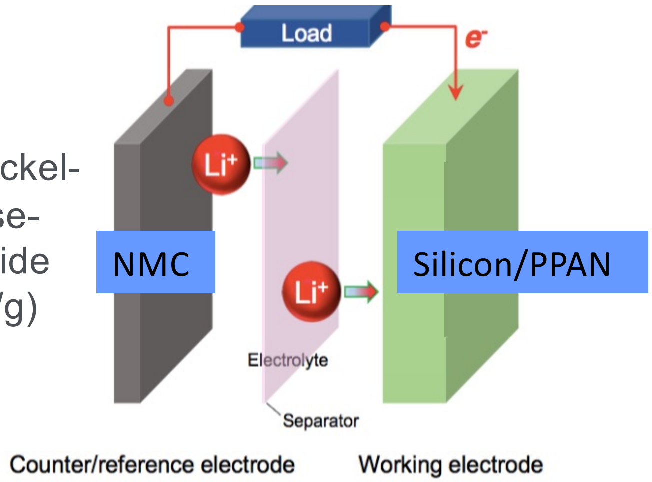


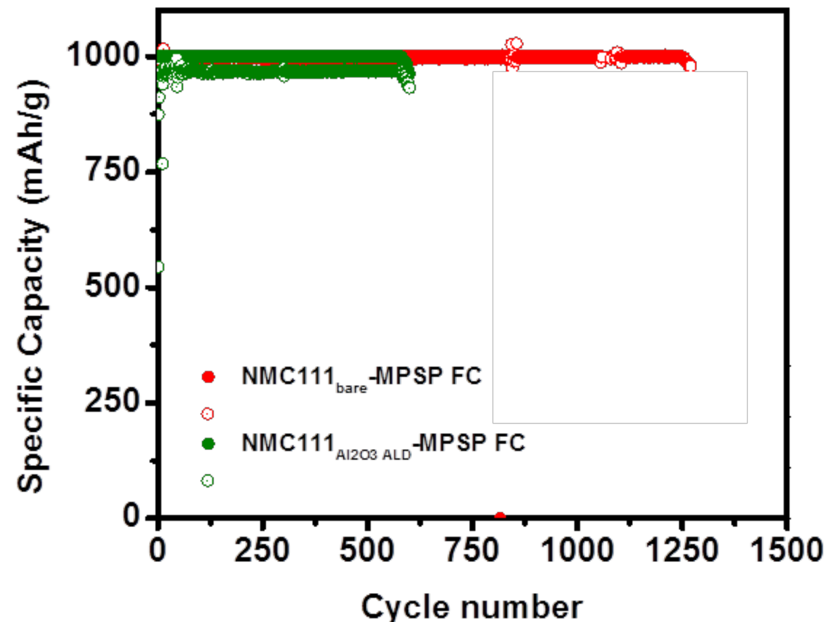


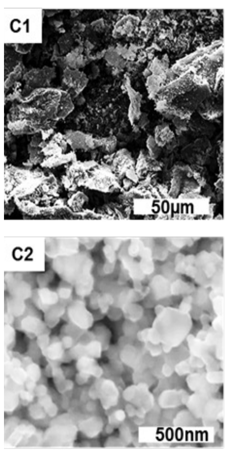
Intermediate spinel phase obtained in the two-step sol-combustion synthesis method

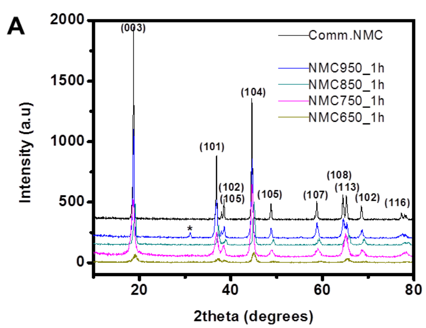
Full cell (Si anode vs NMC cathode)

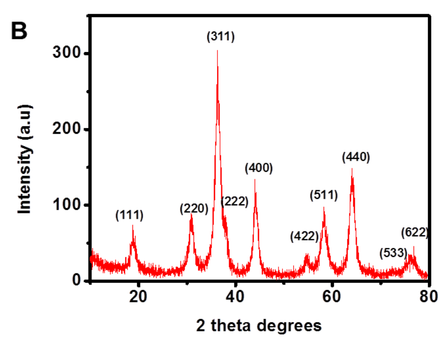
Lithium-Nickel-Manganese-Cobalt-Oxide (160 mAh/g)





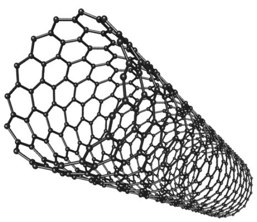


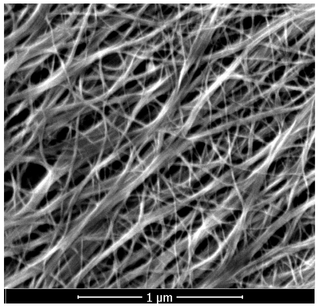


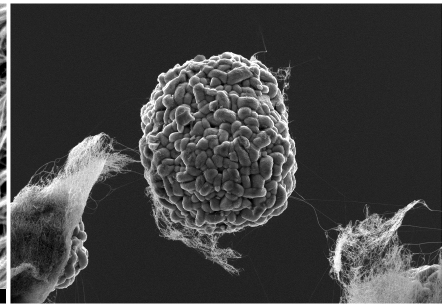


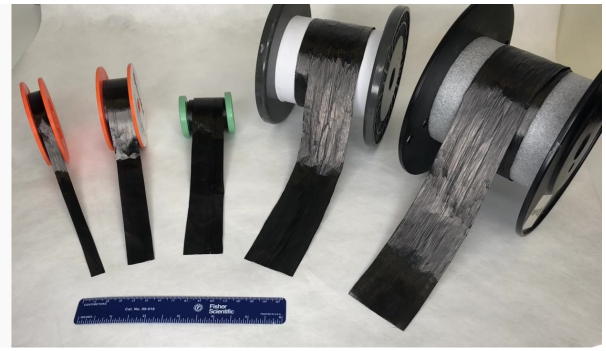
Haridas, A. K.; Nguyen, Q.A. et al; ACS Applied Energy Materials, 2020
Haridas, A. K.; Nguyen, Q.A. et al; ACS Applied Materials & Interfaces, 2021

Silicon Anodes with CNTs





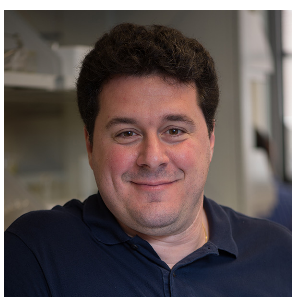




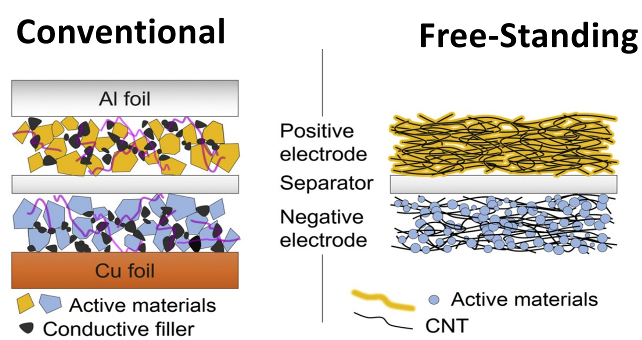
Carbon Nanotubes (CNTs):

- Electronically conductive
- Mechanically strong

→ Can replace conductive agent, polymer binder, current collector



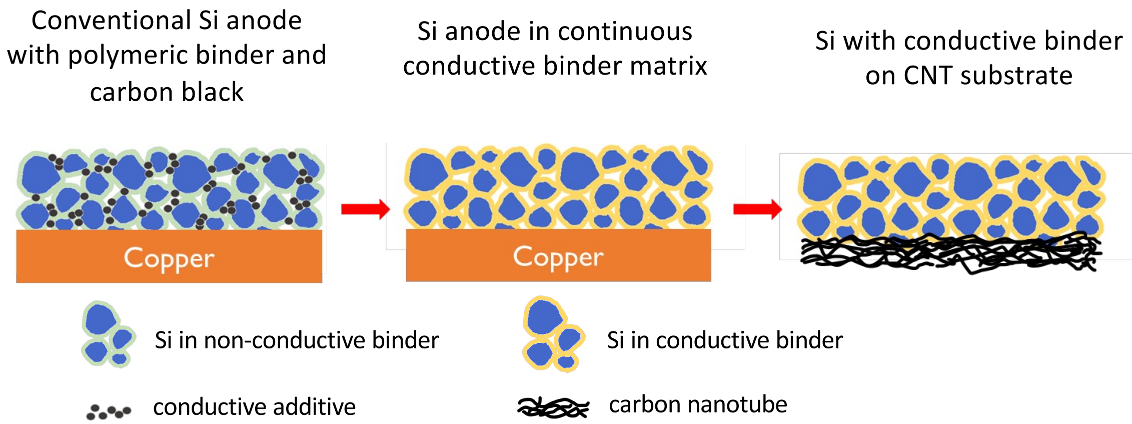
Matteo Pasquali

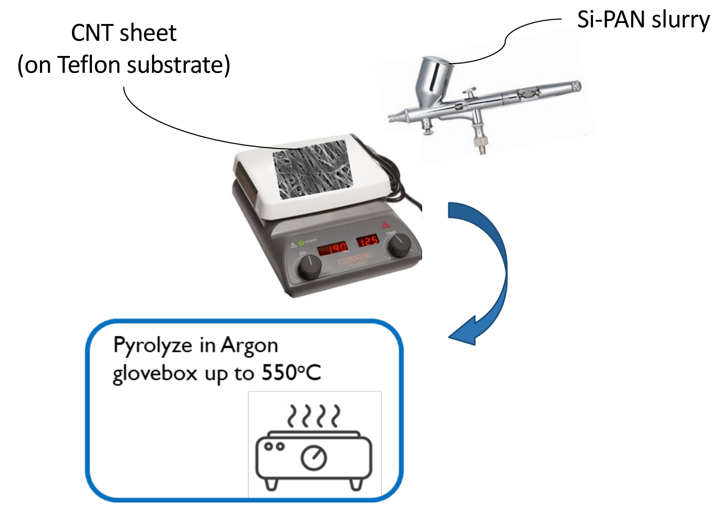


(Hori et al, Carbon, 2020)

- Increase capacity by eliminating inactive components (dead weight, no capacity contribution)
- Potentially enable flexible, stretchable batteries

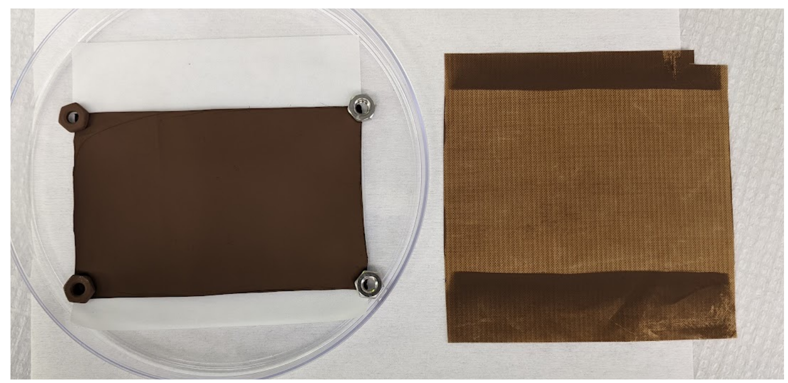
Silicon Anodes with PPAN on CNT fabrics





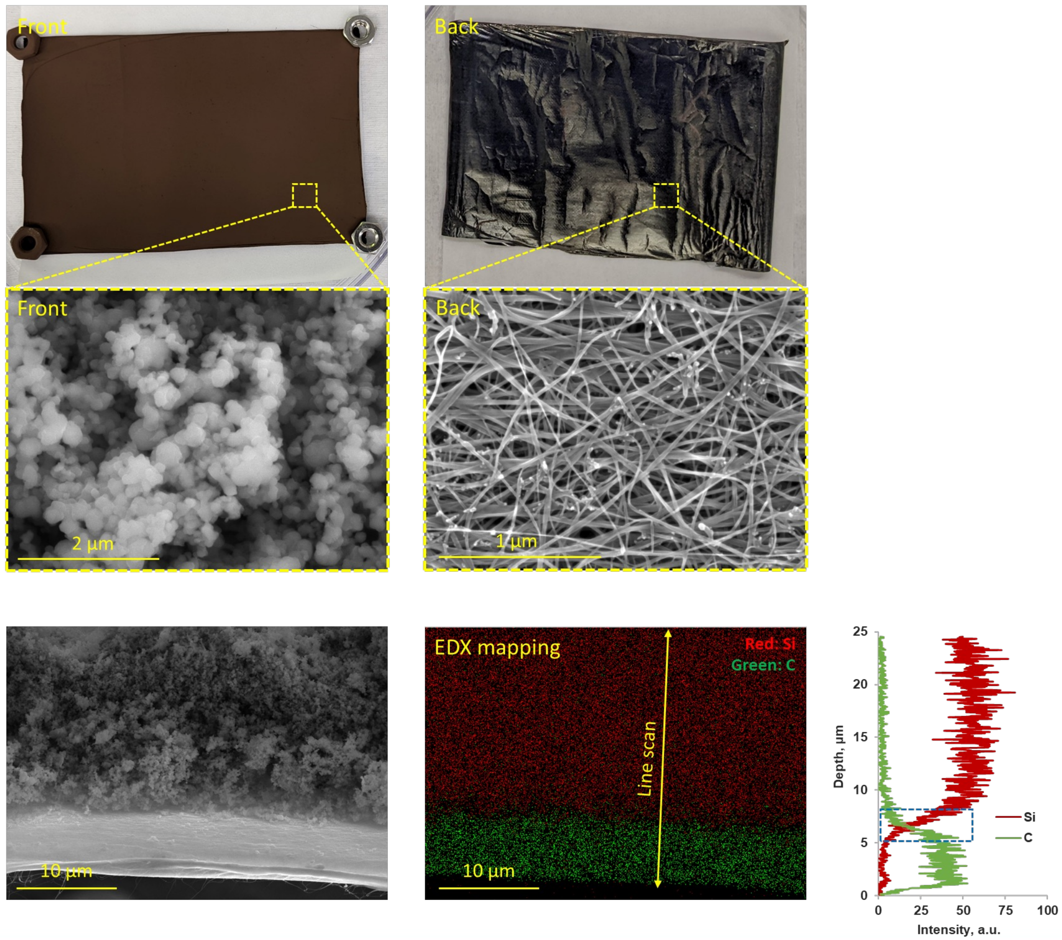
Material	Thickness (μm)	Mass loading (mg cm^{-2})
Si/PPAN	15	1.00
Copper foil	9	8.60
CNT fabric*	5	0.14

Significant dead weight from metallic current collectors in battery electrodes can be reduced!

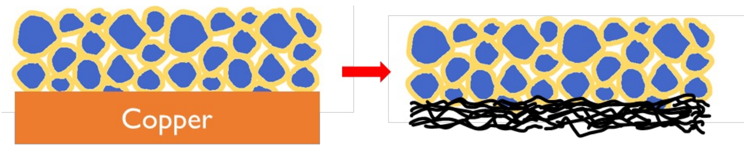


*(*CNT fabric produced by collaborators using FC-CVD method)*

Silicon Anodes with Conductive Binder on CNT

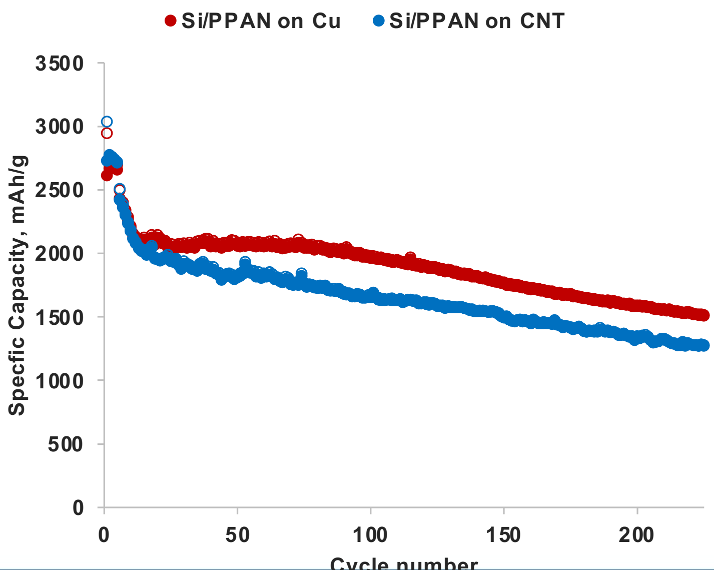


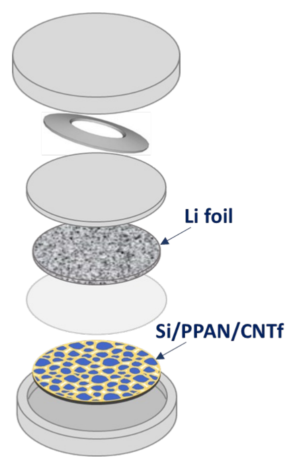
Silicon Anodes with PPAN on CNT fabrics



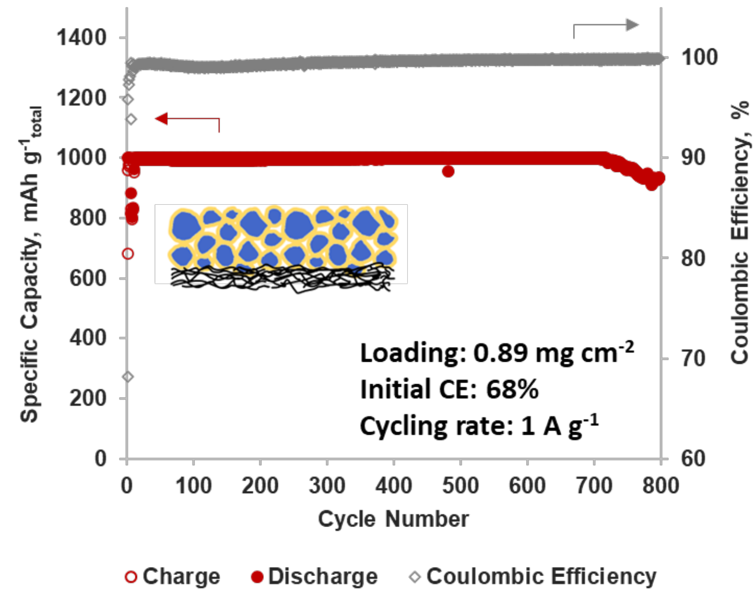
Material	Thickness (μm)	Mass loading (mg cm^{-2})
Copper foil	9	8.60
CNT fabric	5	0.14

In half-cell with Li, Si/PPAN on Cu has better capacity retention than Si/PPAN on CNT





When state of charge is controlled to 1000 mAh g^{-1}, Si/PPAN/CNT shows significant cycle life



How much Copper is in Batteries?

International Copper Association
Copper Alliance

Copper and Energy Storage

The greatest concentration of copper in electric vehicles is contained within the battery.

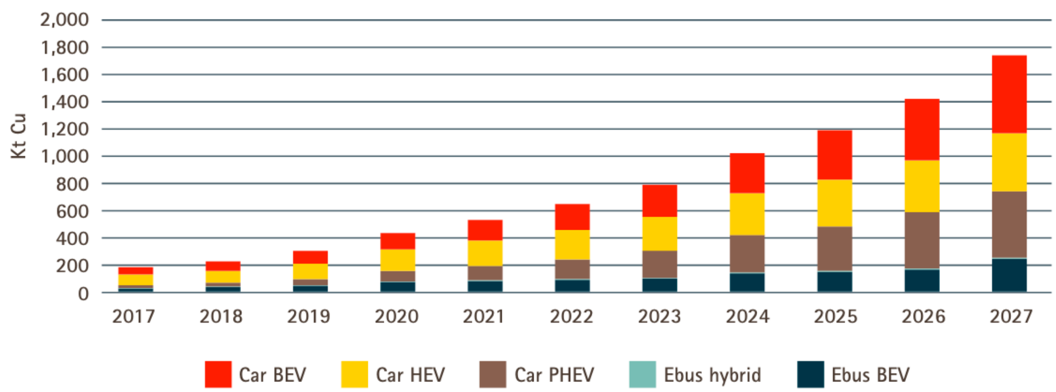
- Estimates show that for every kilowatt-hour of a lithium ion battery, 1.1 to 1.2 kilograms (kg) of copper is used.
  - As a result, projections show the potential for up to 600 kilotonnes of additional copper use by 2027.

Copper Content by Electric Vehicle Type

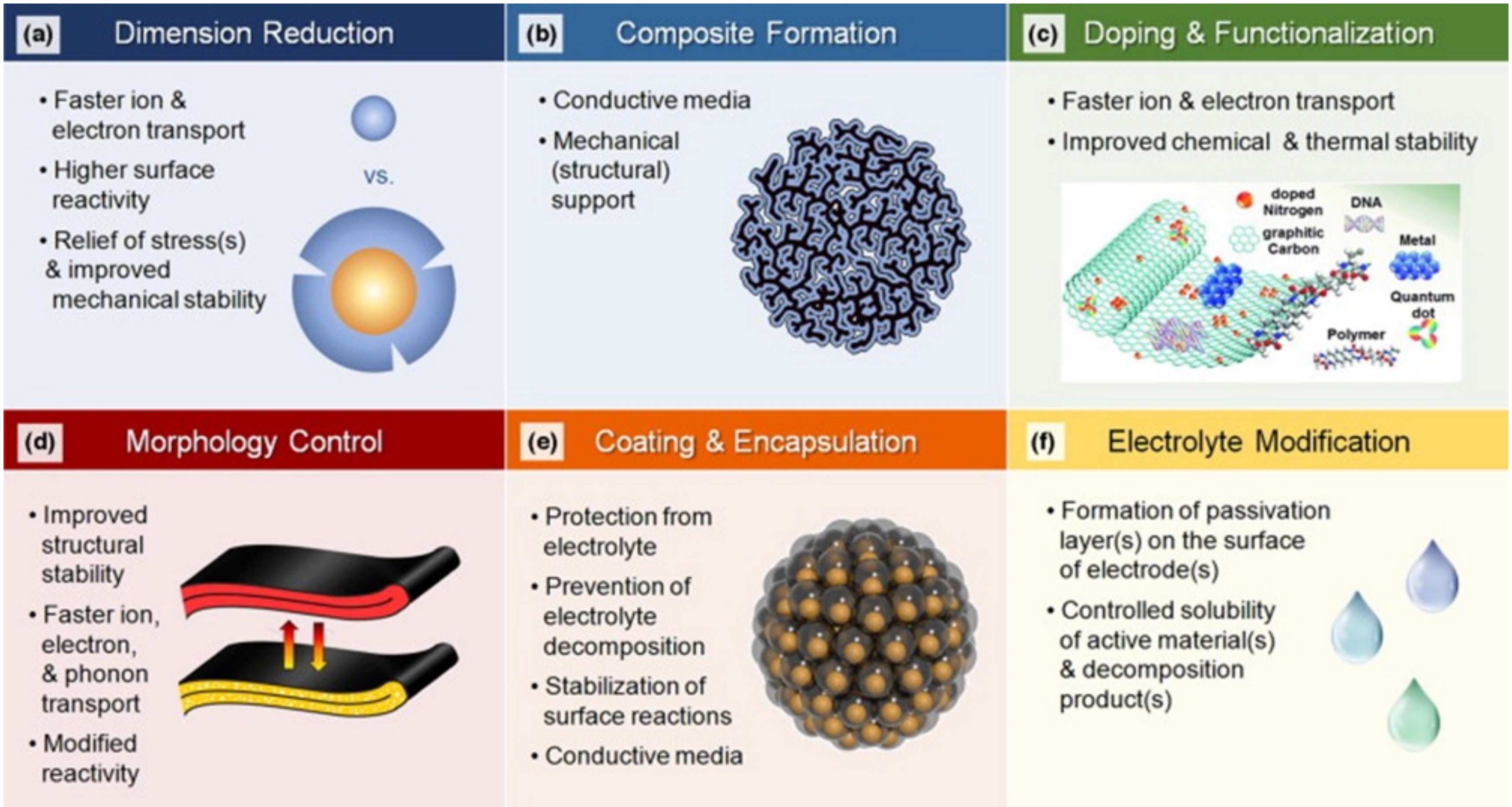
The total copper content among the spectrum of electric vehicles includes the following:

- Electric bus – 224-369 kg of copper per vehicle.
- Electric vehicle – 83 kg of copper per vehicle.
- Plug-in hybrid electric vehicle – 60 kg of copper per vehicle.
- Hybrid electric vehicle – 39 kg of copper per vehicle.

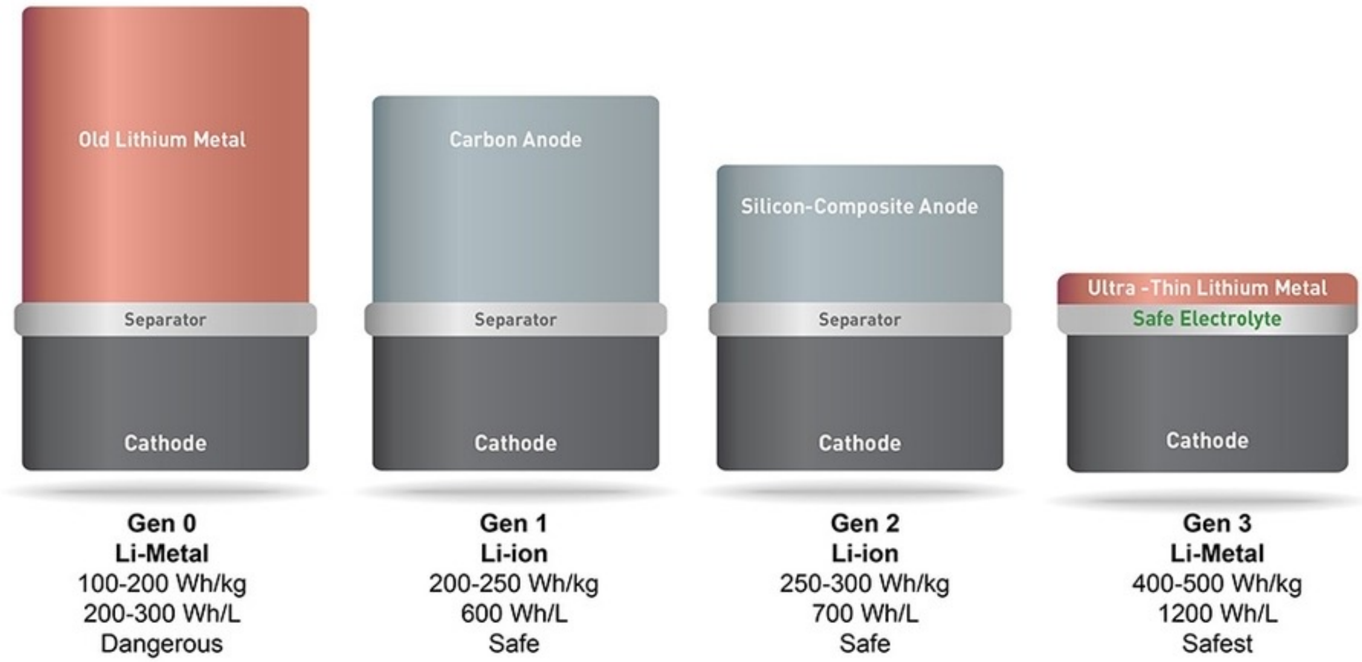
Electric vehicle Cu demand



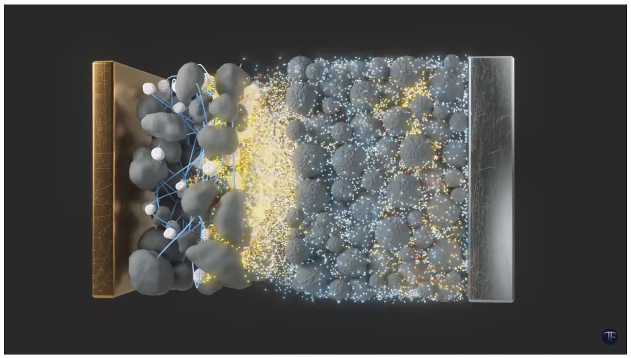
What have we learned?

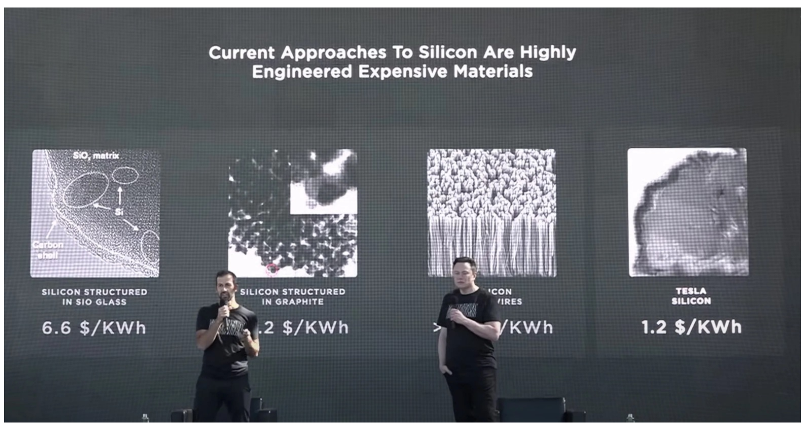


How close are we?



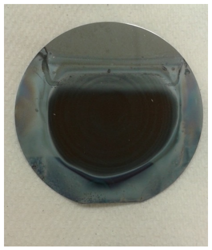
How close are we to Si based anodes?



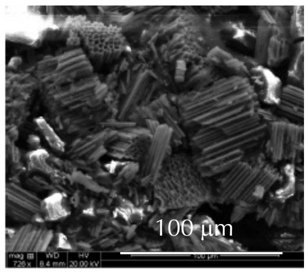


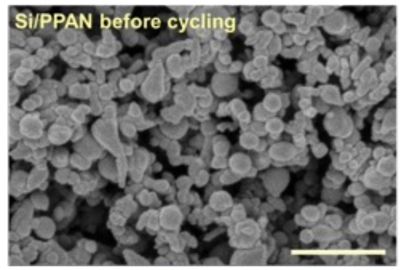
Tesla Silicon Anode – 30% Silicon + 70% graphite – 20% increase in range

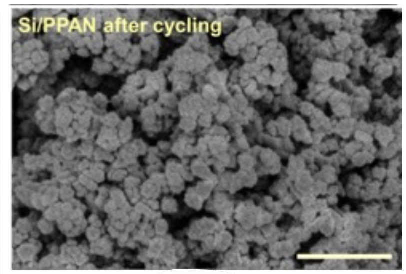
Continuing to Push the Limits



Material Synthesis:

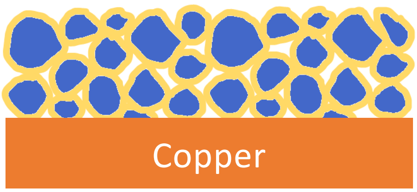




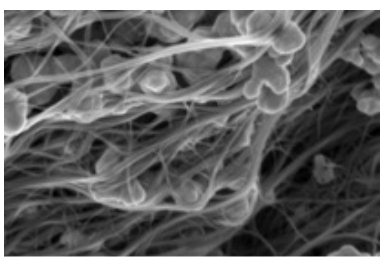


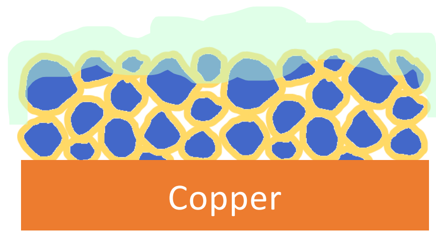
Nanostructured silicon mitigates stresses and provides improved mechanical stability

Material Processing & Testing

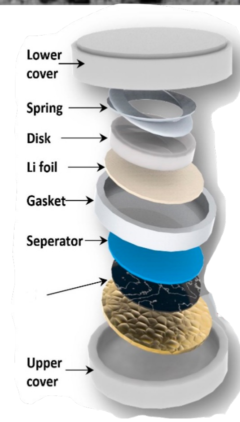


PPAN Binder: Relives stress, improved mechanical properties

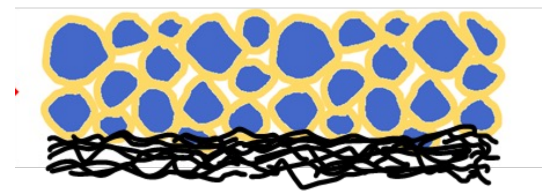




FEC: Protects anode from electrolyte degradation



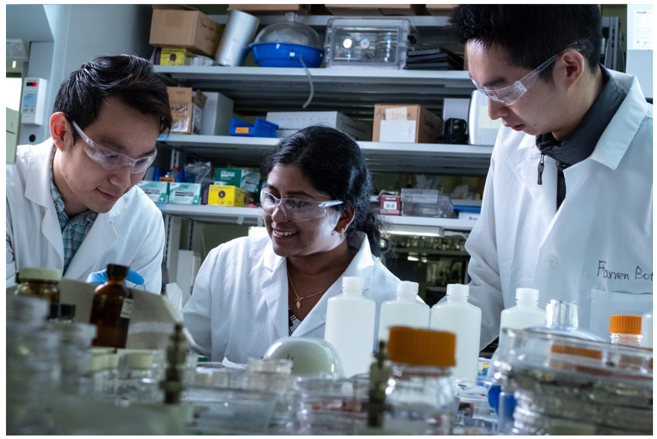
Pairing with NMC Cathodes: Engineer the ratio and additives to match capacity differences



Reducing weight with CNT current collectors

Acknowledgments

Engineering Soft Matter – Colloidal and Interfacial Phenomena



LOCKHEED MARTIN

Ford

Carbon Hub

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