# Batteries: Now and Future

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# Mobile Phone Evolution

Battery in iphone 6 plus

Drone

Electrical Vehicles

Stationary Storage

~10 Wh
1 billion pieces/yr

~70Wh

~85,000Wh

CA, ~60 GWh
World ~10 TWh


# How far can battery technology go?

- Energy density (Wh/kg, Wh/L)
- Cost ($/kWh)
- Safety
- Cycle life
- Charge rate

# Lithium Ion Battery Cells: Now and Future Goals

| | Cell level (goal) | System level (goal) |
|---|---|---|
| **Energy (Wh/kg)** | ~200 (600) | ~100 (300) |
| **Cost ($/kWh)** | 150-200 (70) | 300-500 (150) |
| **Cycle life** | 3000 (10,000 for grid) | |

## Safety

**High energy density (weight/volume)**

**-Range increase**

**-Lower cost**

**Revolution in**

**Transportation, Grid, Renewable**

# How do We Store Electrons?

$$e^- + M^+ \longleftrightarrow M$$

$$e^- + M^+ + Host \longleftrightarrow MHost$$

M atomic weight

- $Pb^{2+/4+}$ (207)
- $Zn^{2+}$ (65)
- $Al^{3+}$ (27)
- $Mg^{2+}$ (25)
- $Na^+$ (23)
- $Li^+$ (7)
- $H^+$ (1)

M maximum voltage

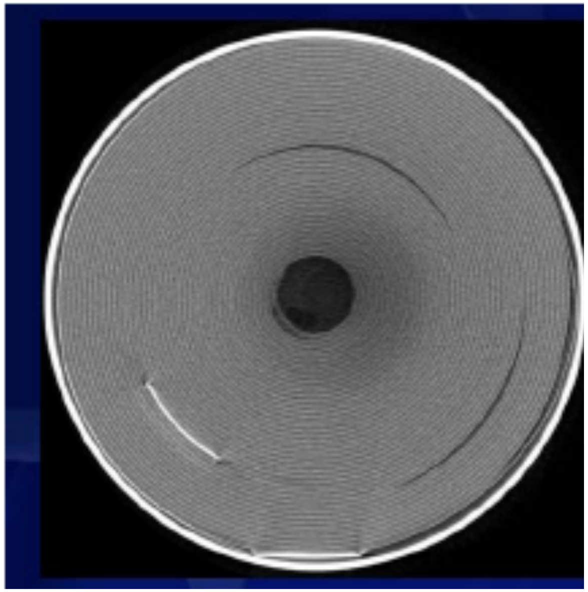
- $Li^+$ (<4.5V)
- $Na^+$ (<4.2V)
- $Mg^{2+}$ (<~3.8V)
- $Al^{3+}$ (<~3.1V)
- $Zn^{2+}$ (<~2.2V)
- $Pb^{2+/4+}$ (<2.1V)
- $H^+$ (<~1.5V)

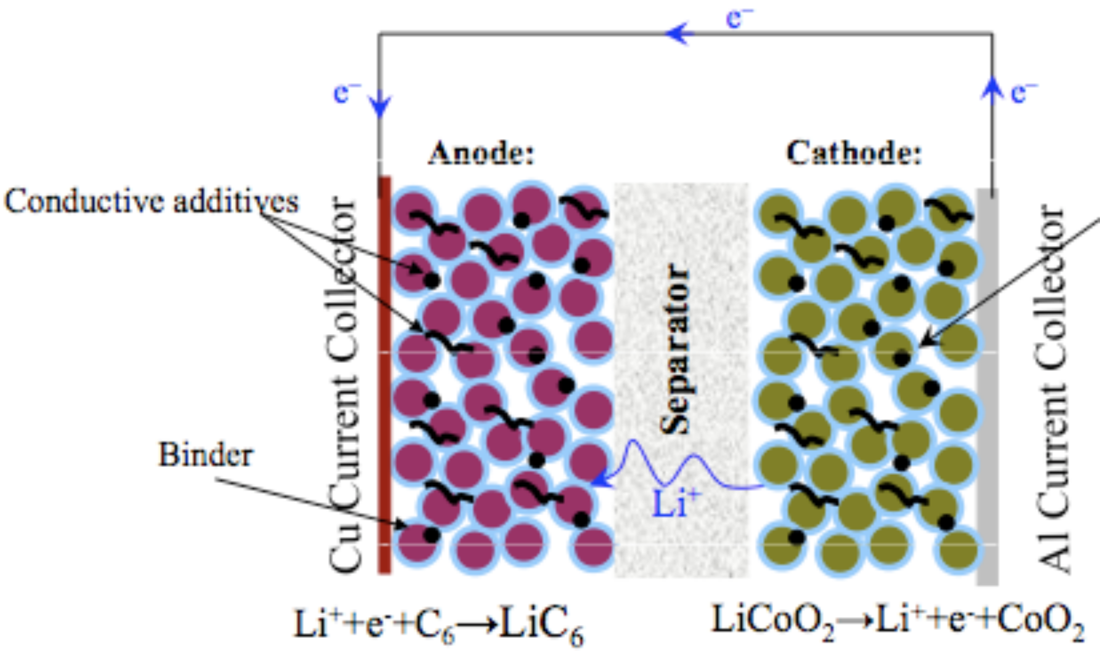
M cost ($/kg)

- Li (40)*
- Na (1)
- Mg (2)
- Al (2)
- Zn (2)
- Pb (2)
- H (nearly free)

*The cost of Li in Li ion batteries is only ~3%.

# Battery Operation: Li Ion Batteries

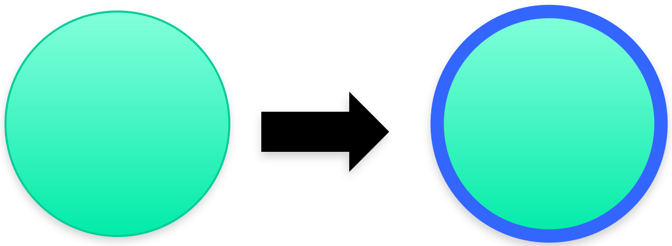





(Courtesy of Venkat Srinivasan)

**Materials issues of batteries**

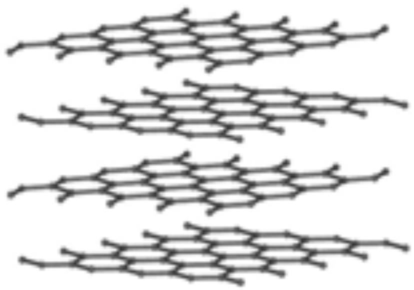
- Electron transport in solid
- Ionic diffusion in liquid and solid
- Structure/volume change: strain
- Solid electrolyte intephase (SEI)



# High Energy Lithium Batteries

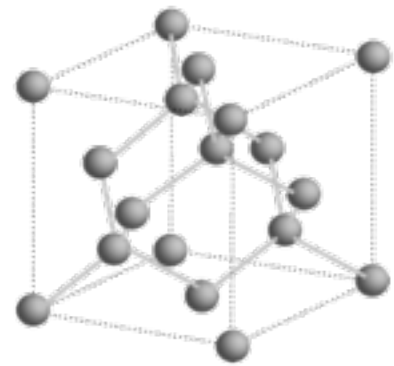
**Negative electrodes**

**Graphite (2D): 370 mAh/g**



10X

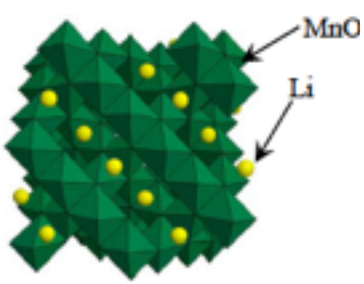
**Silicon: 4200 mAh/g**



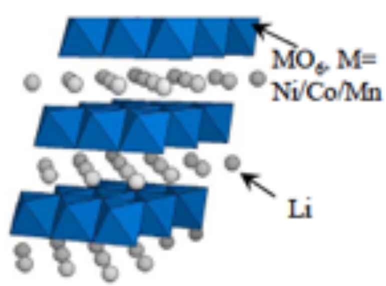
**Li (3860 mAh/g)**
**P (2600 mAh/g)**

**Positive electrodes**

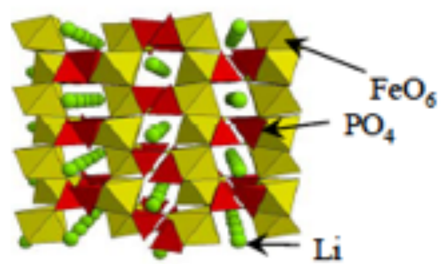
**$LiMn_2O_4$ (3D): 150 mAh/g**




**$LiCoO_2$(2D) 150mAh/g**

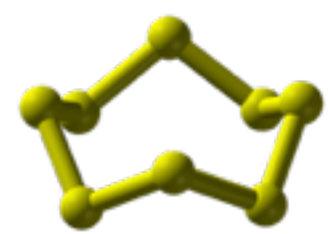



**$LiFePO_4$ (1D) 170mAh/g**

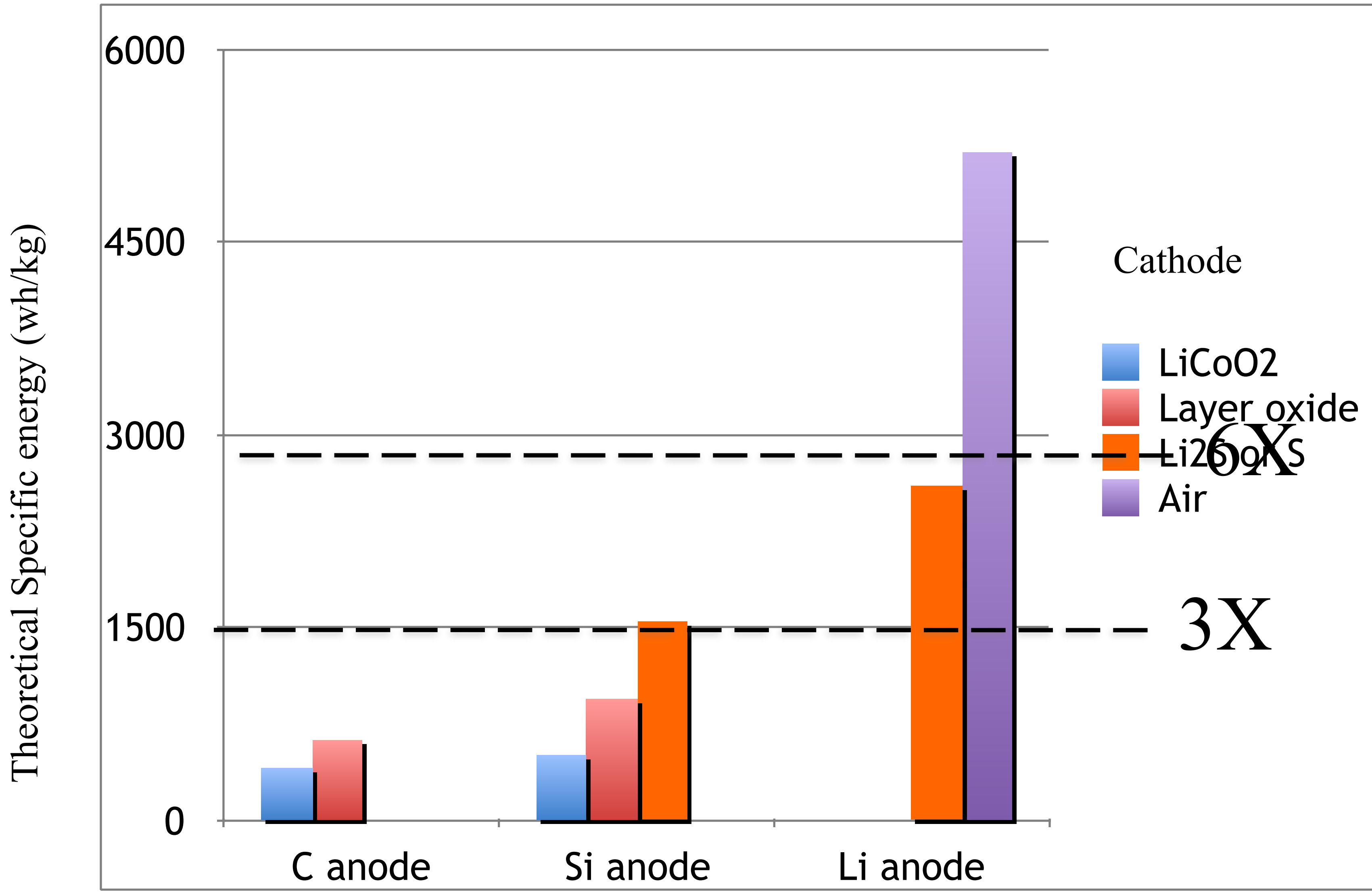



10X

**Sulfur ~1670 mAh/g**

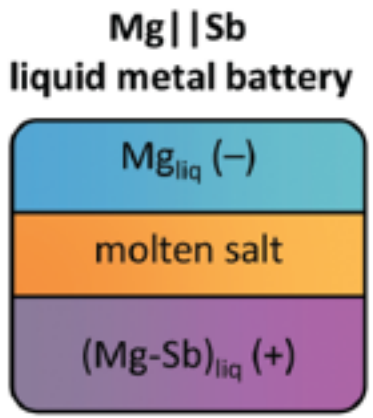


# Theoretical Specific Energy

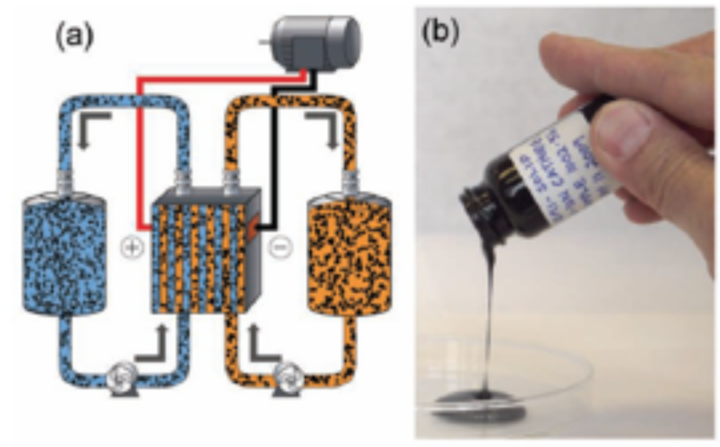


# Grid-Scale Storage Technology

**Liquid metal batteries**
D. Sadoway, *JACS* 134, 1895 (2012)

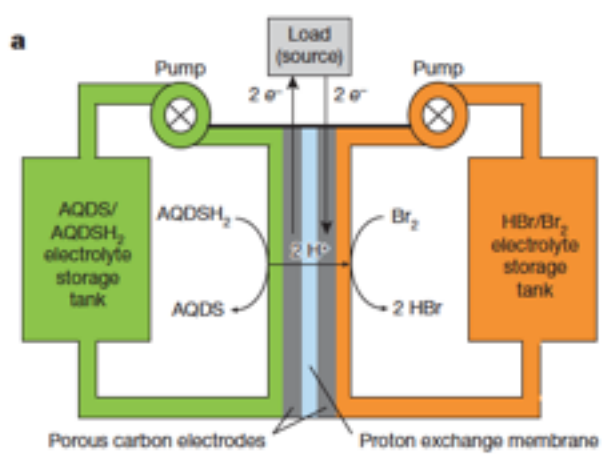



**Semi-solid flow batteries**
Y.M Chiang, C. Carter *Adv. Eng. Mater.* 2011, 1, 511



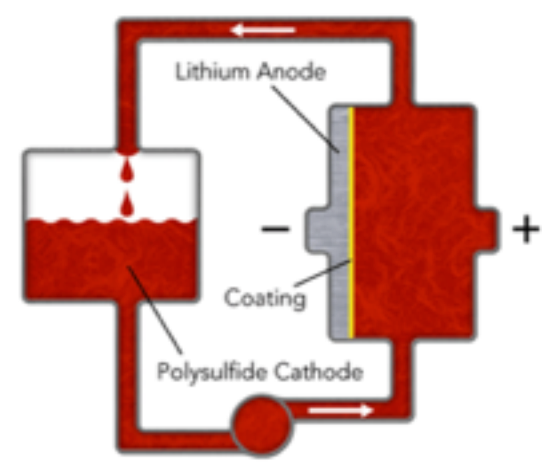

**Quinone-based flow batteries**

(M. Aziz, R. Gordon, A. Aspuru-Guzik Nature 505, 195 2014)




**Li-polysulfide semiflow batteries**

Y. Yang, G. Zheng, Y. Cui
*Energy Environ. Sci* 2013,6, 1552-1558.



# High Energy Batteries: Paradigm Shift

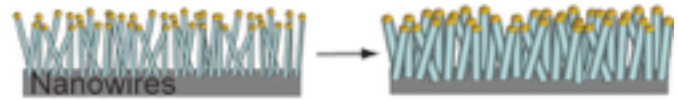
| Stable Host: past 20 years | Unstable Host: Now<br>3-10x specific charge capacity |
| --- | --- |
| No bond breaking | Significant bonding breaking |
| Host atoms do not move | Host atoms move |
| Little structure change | Complete structure change |
| Volume change <10% | Volume change ~100% |

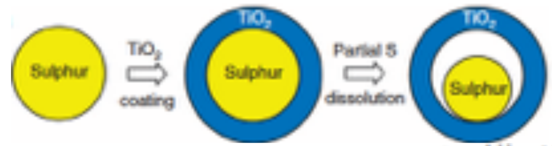
**New challenges:**
- Atomic bonding level: reversibility
- Individual material particle level: breaking, SEI, phases
- The whole electrode level: expansion, breaking

# Outline

**High Energy:**
**- Si, P, Li metal anodes**
**- S cathodes**

*Nature Nanotechnology* 3, 31 (2008).
*Nature Nanotechnology* 7, 310 (2012).
*Nature Communication* 4: 1331 (2013).
*Nature Communication* 4:1943 (2013).
*Nature Chemistry* 5, 1042 (2013).
*Nature Nanotechnology* 9, 187 (2014).
*Nature Nanotechnology* 9, 618 (2014).

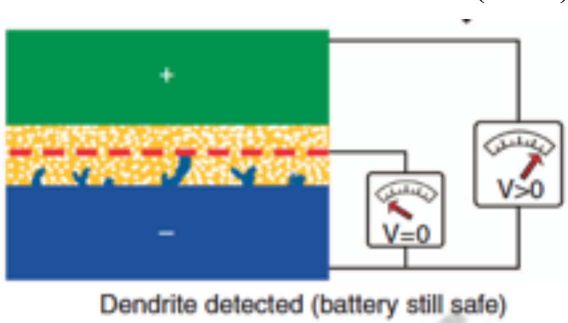


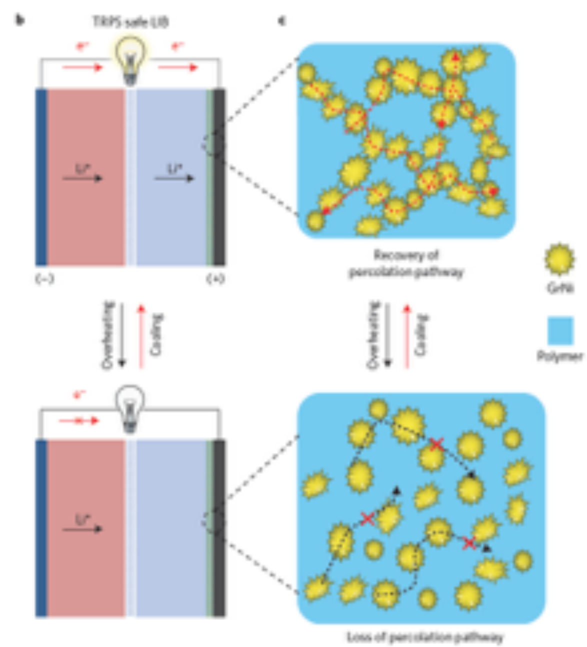





**Battery Safety**

*Nature Communications* 5: 5193 (2014).



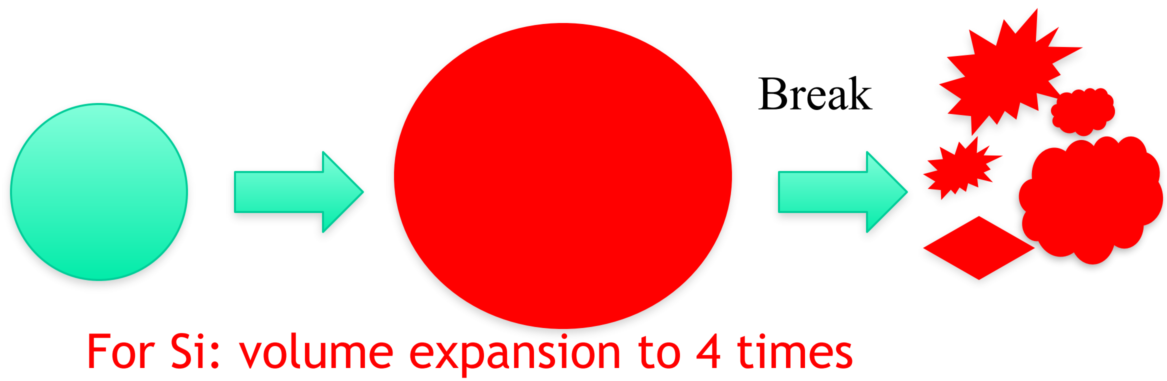



# Silicon Anodes With 11X Specific Capacity

$$Si \longleftrightarrow Li_{4.4}Si \quad \text{4200 mAh/g}$$

$$C_6 \longleftrightarrow LiC_6 \quad \text{370 mAh/g}$$

**Individual particle:**

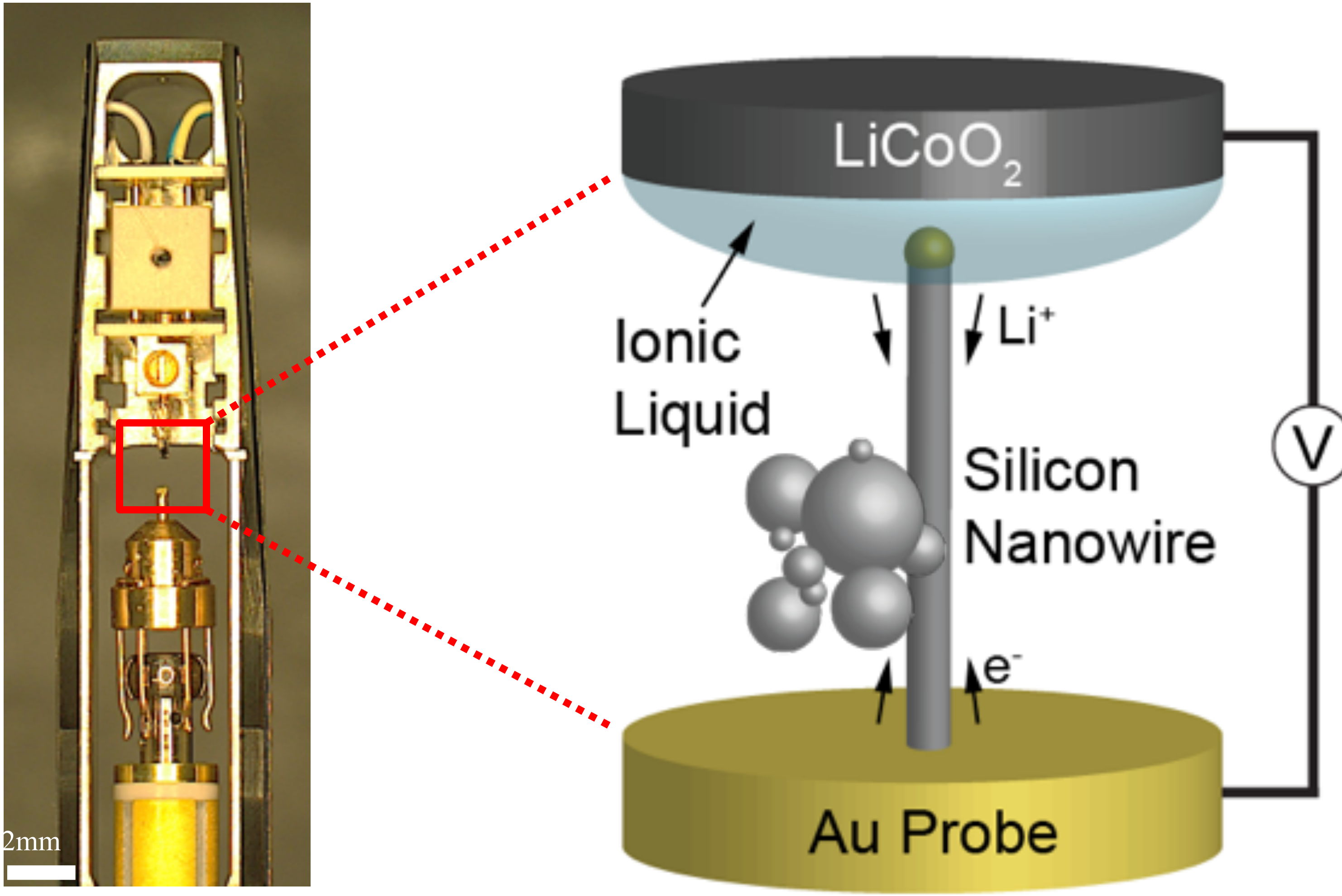



**Problems:**

**1) How to avoid breaking?**

**2) How to build stable solid-electrolyte-interphase (SEI)?**

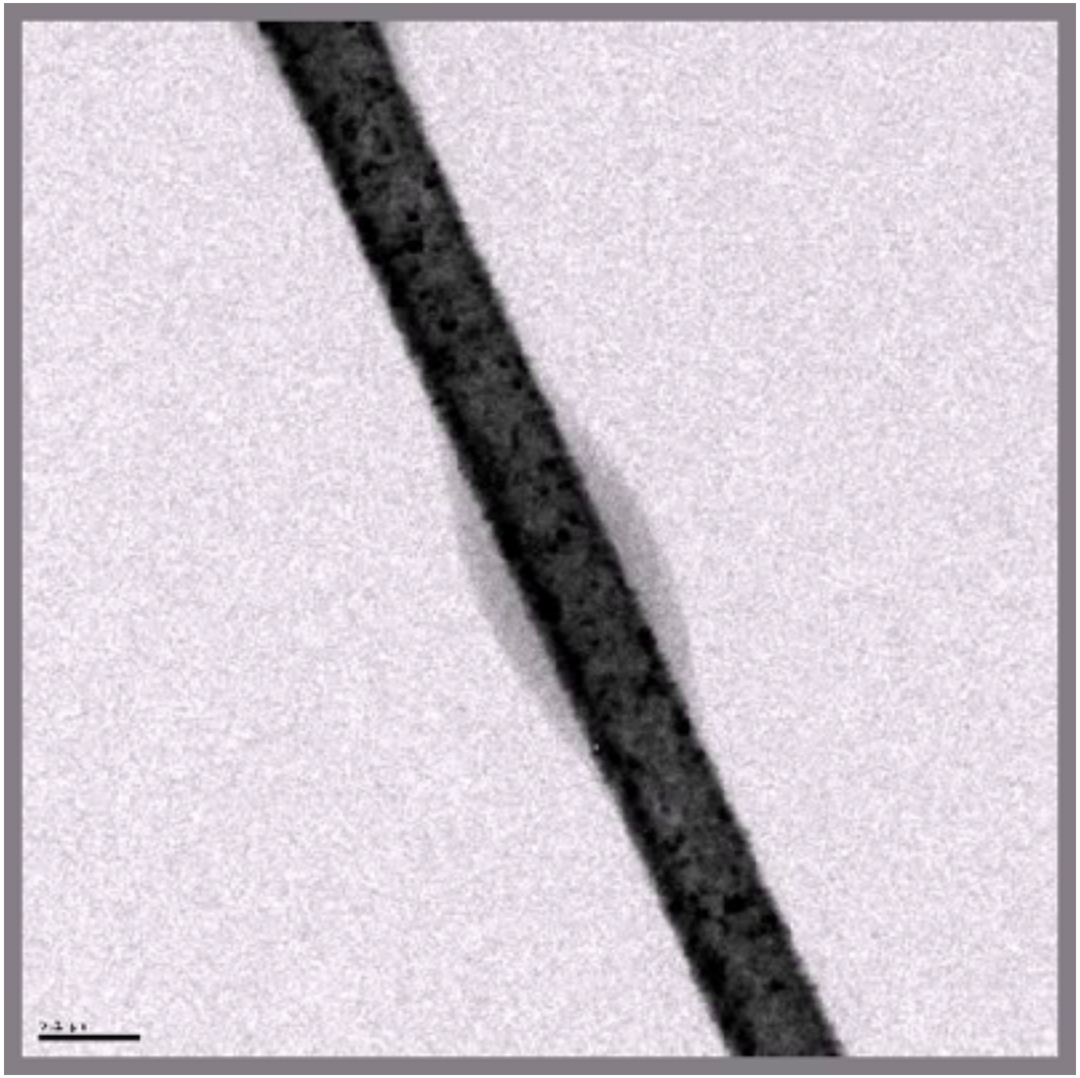
# *In-situ* Transmission Electron Microscopy (TEM)




Nanofactory TEM-STM holder

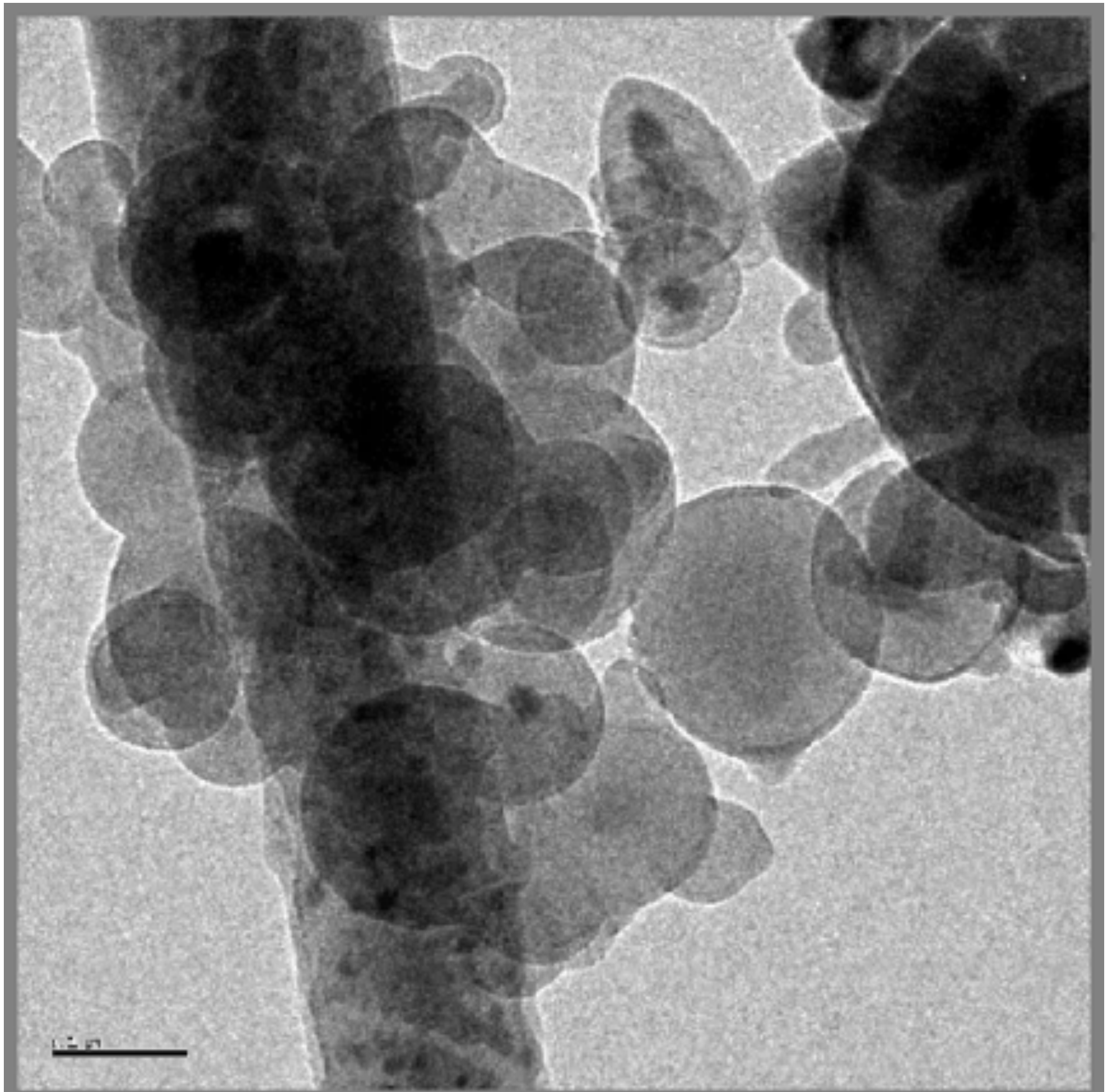
(M. McDowell, C. Wang, Yi Cui, *Nano Energy* 1, 401, 2012)

# Fracture of Surface Cu Coatings



5x actual speed

Nanoparticle critical breaking size: ~150nm
Nanowire critical breaking size: ~300nm

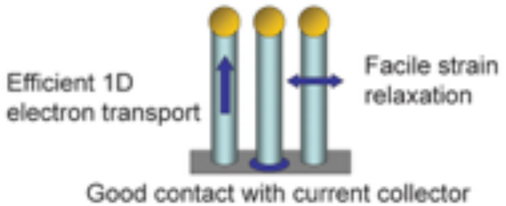


(M. McDowell, I. Ryu, S.W. Lee,  W. Nix, Y. Cui *Adv. Materials* 24, 6034 (2012))

# 11 Generations of Si Anode Design from Cui Group

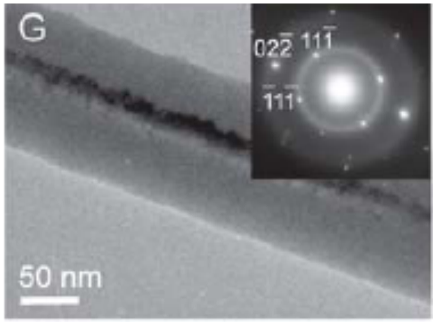
## Gen 1: Nanowire

*Nature Nanotechnology* 3, 31 (2008).



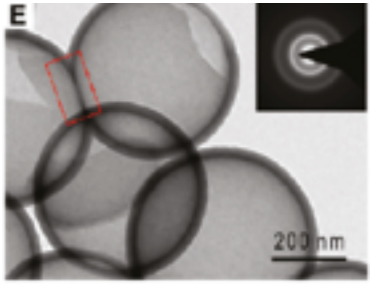

## Gen 2: Core-Shell Nanowire

*Nano Letters* 9, 491 (2009).




## Gen 3: Hollow

*Nano Letters* 11, 2949 (2011).

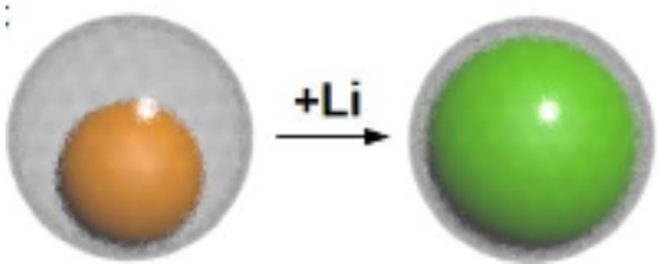



## Gen 4: Double-walled hollow

*Nature Nanotechnology* 7, 310 (2012).

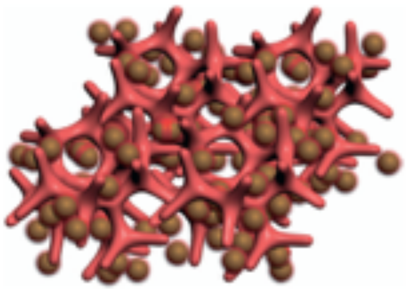

## Gen 5: Yolk-shell

*Nano Letters* 12, 3315 (2012).




## Gen 6: Si-hydrogel

*Nature Communication* 4:1943 (2013)
with Zhenan Bao



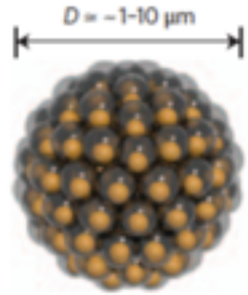
# 11 Generations of Si Anode Design from Cui Group

## Gen 7: Self-Healing

*Nature Chemistry* 5, 1042 (2013).
with Zhenan Bao

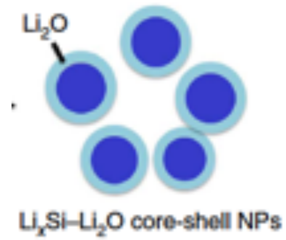

## Gen 8: Pomegranate-Like

*Nature Nanotechnology* 9, 187 (2014).



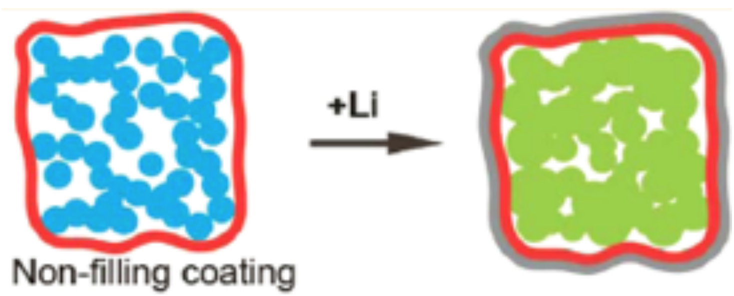

## Gen 10: Prelithiation of Si anodes

*Nature Communications* 5, 5088, 2014



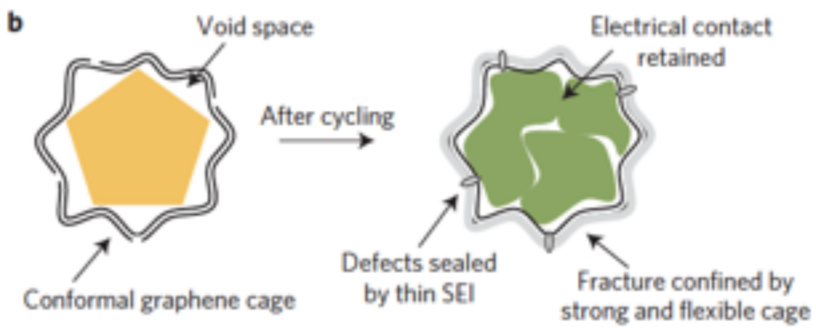

## Gen 9: Non-filling carbon coating or porous Si

*ACS Nano* 9, 2540 (2015).

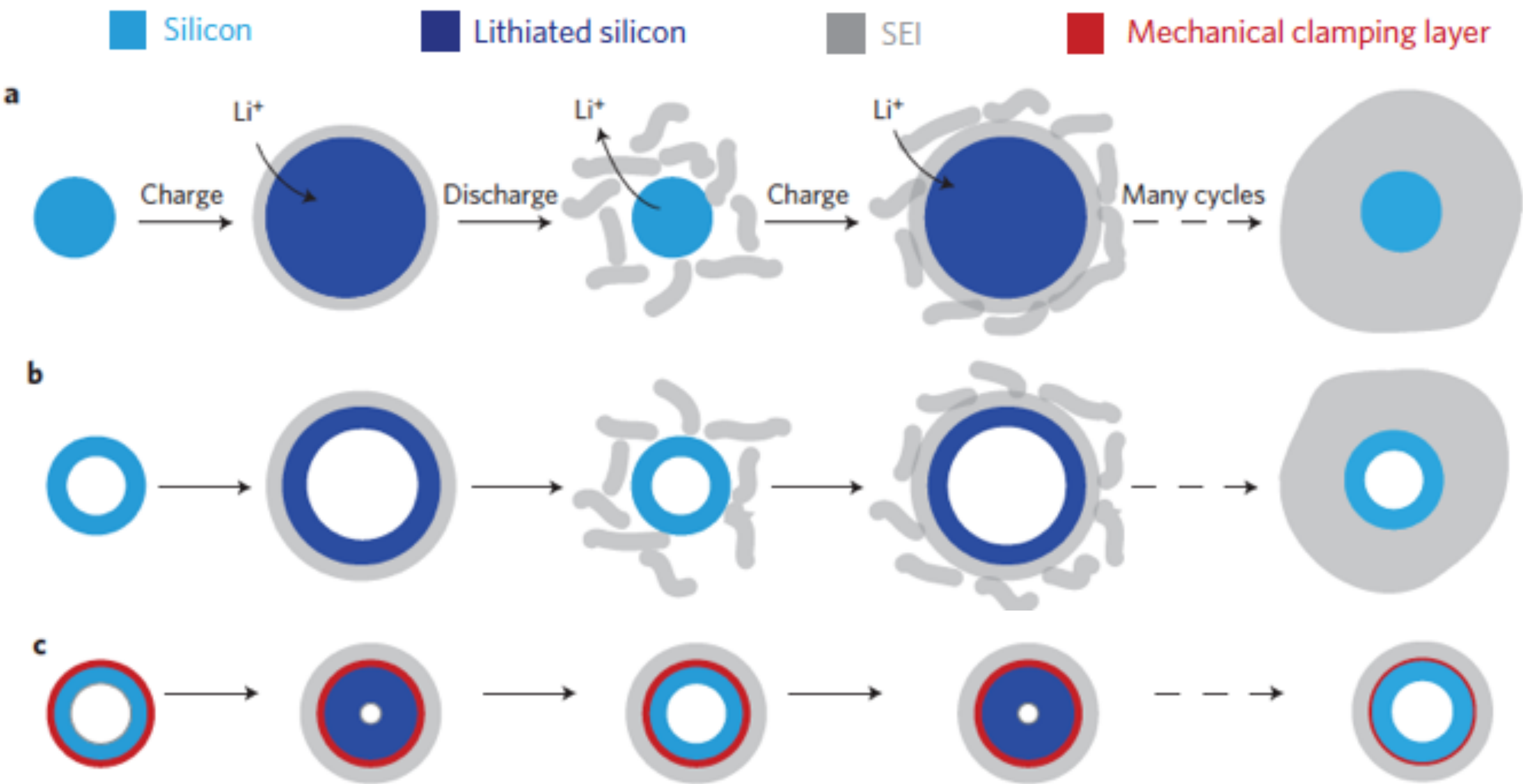



## Gen 11: Micro-Si gaphene cage

*Nature Energy* 15029, 2016

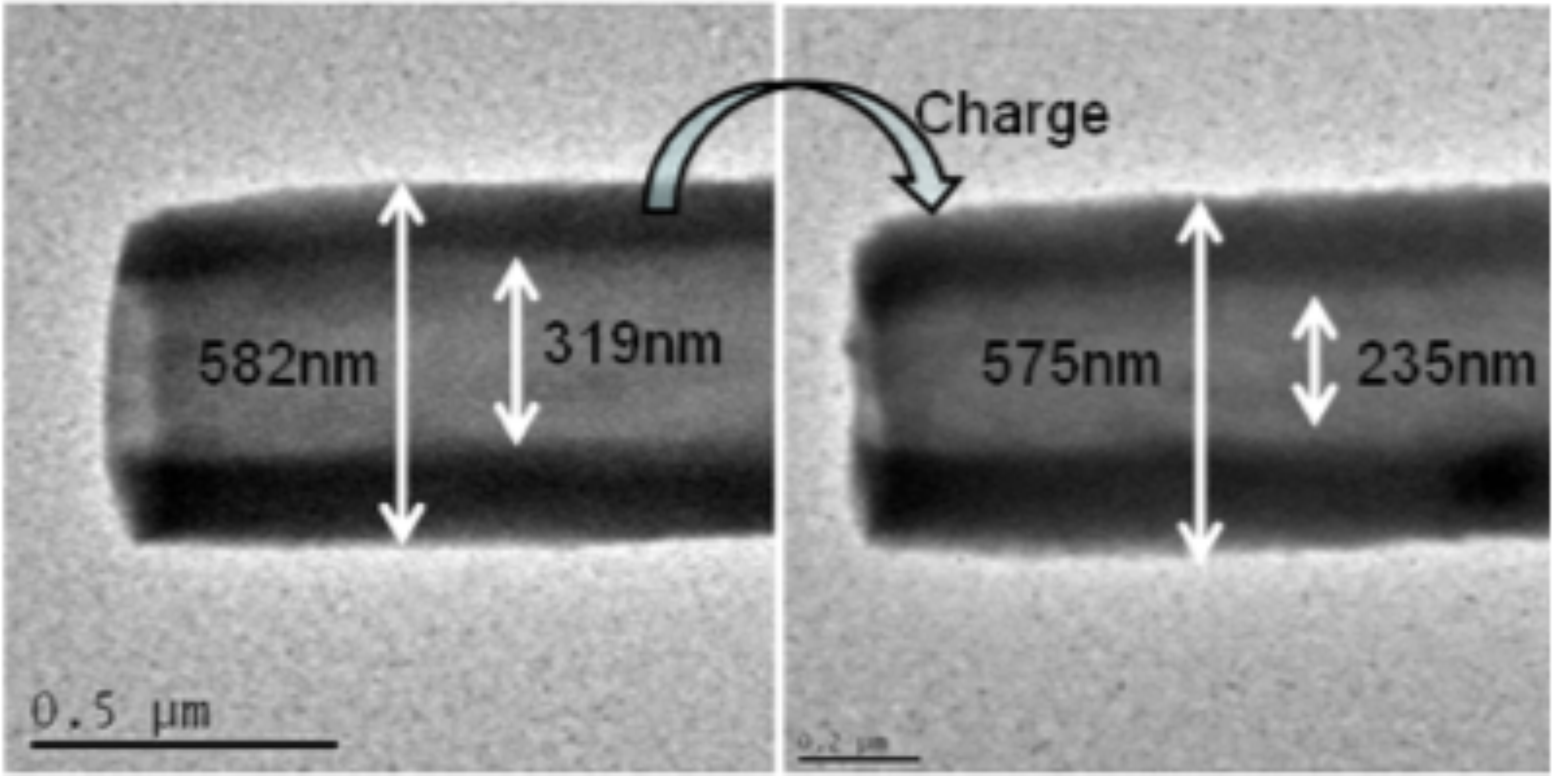


# Gen 4: Double Walled Hollow Structure: Stable Solid Electrolyte Interphase (SEI)



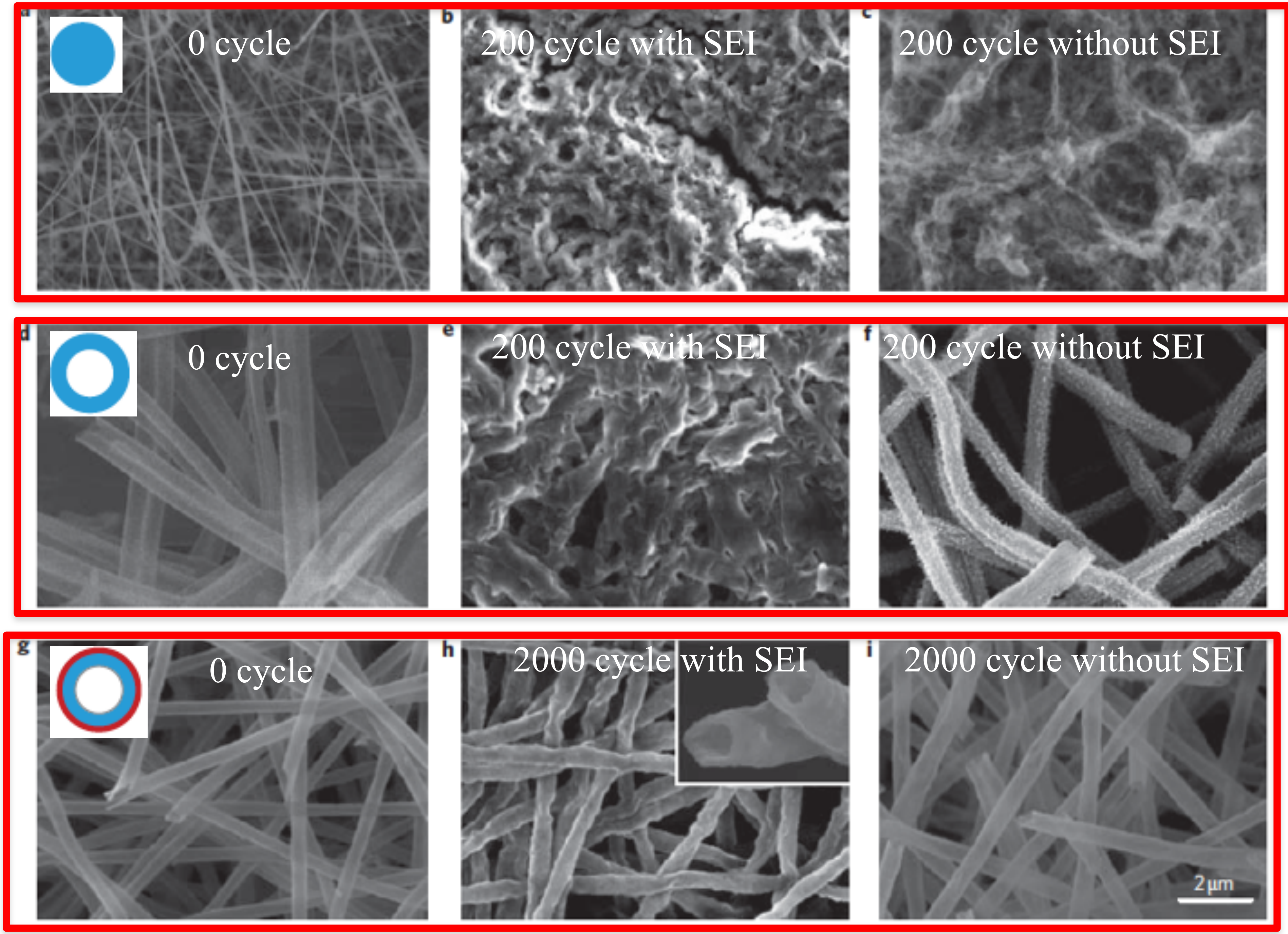

(Hui Wu, Yi Cui *Nature Nanotech* 7, 310 (2012))

# Double-Walled Si Nanotubes

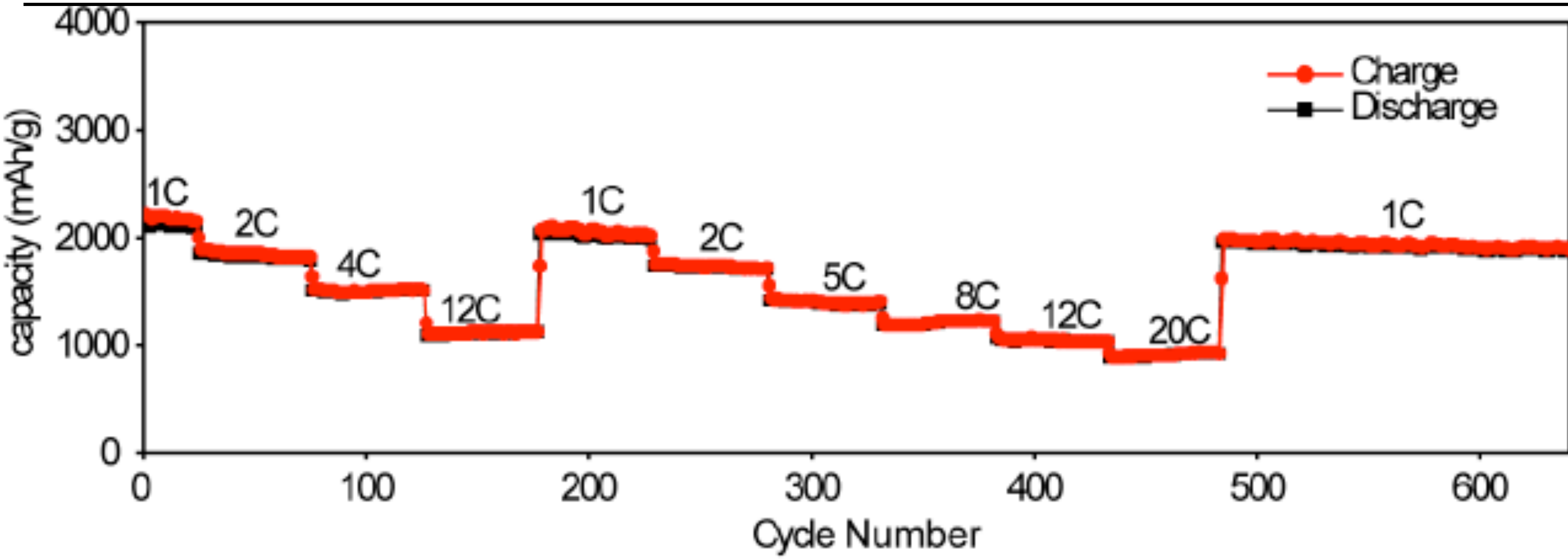


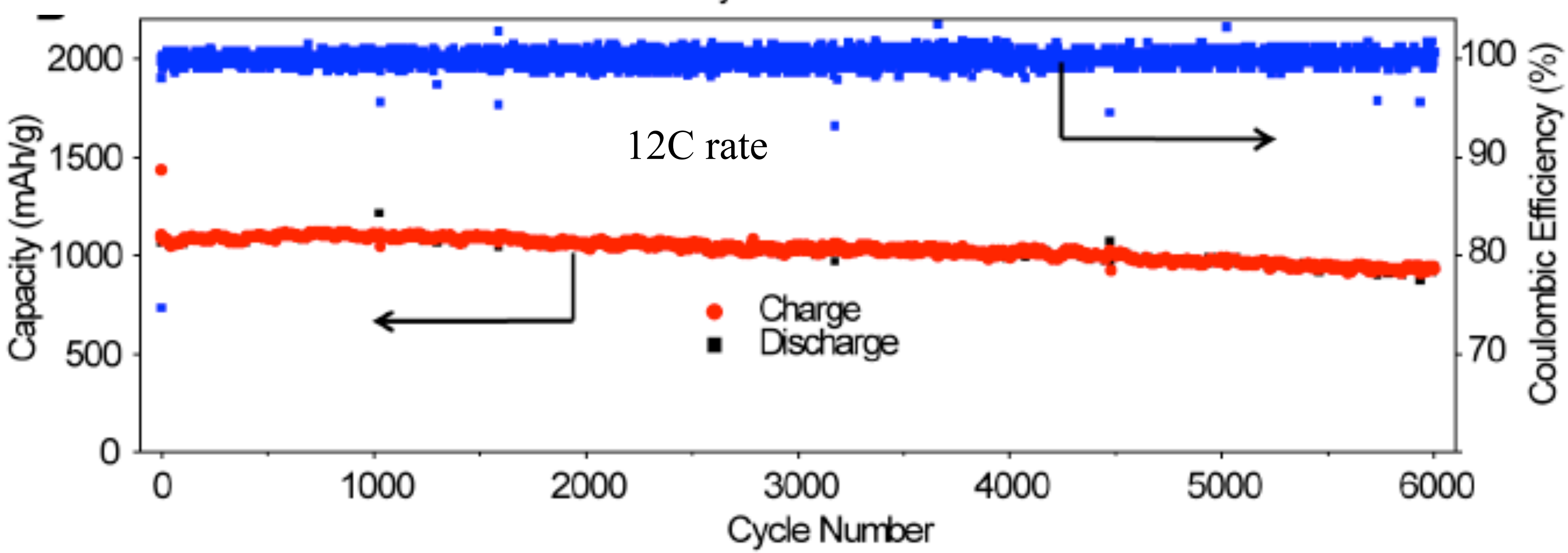

- Outer diameter has no change.
- Inner diameter changes.

(Hui Wu, Yi Cui *Nature Nanotech* 7, 310 (2012))


a
0 cycle
b
200 cycle with SEI
c
200 cycle without SEI
d
0 cycle
e
200 cycle with SEI
f
200 cycle without SEI
g
0 cycle
h
2000 cycle with SEI
i
2000 cycle without SEI
2 µm

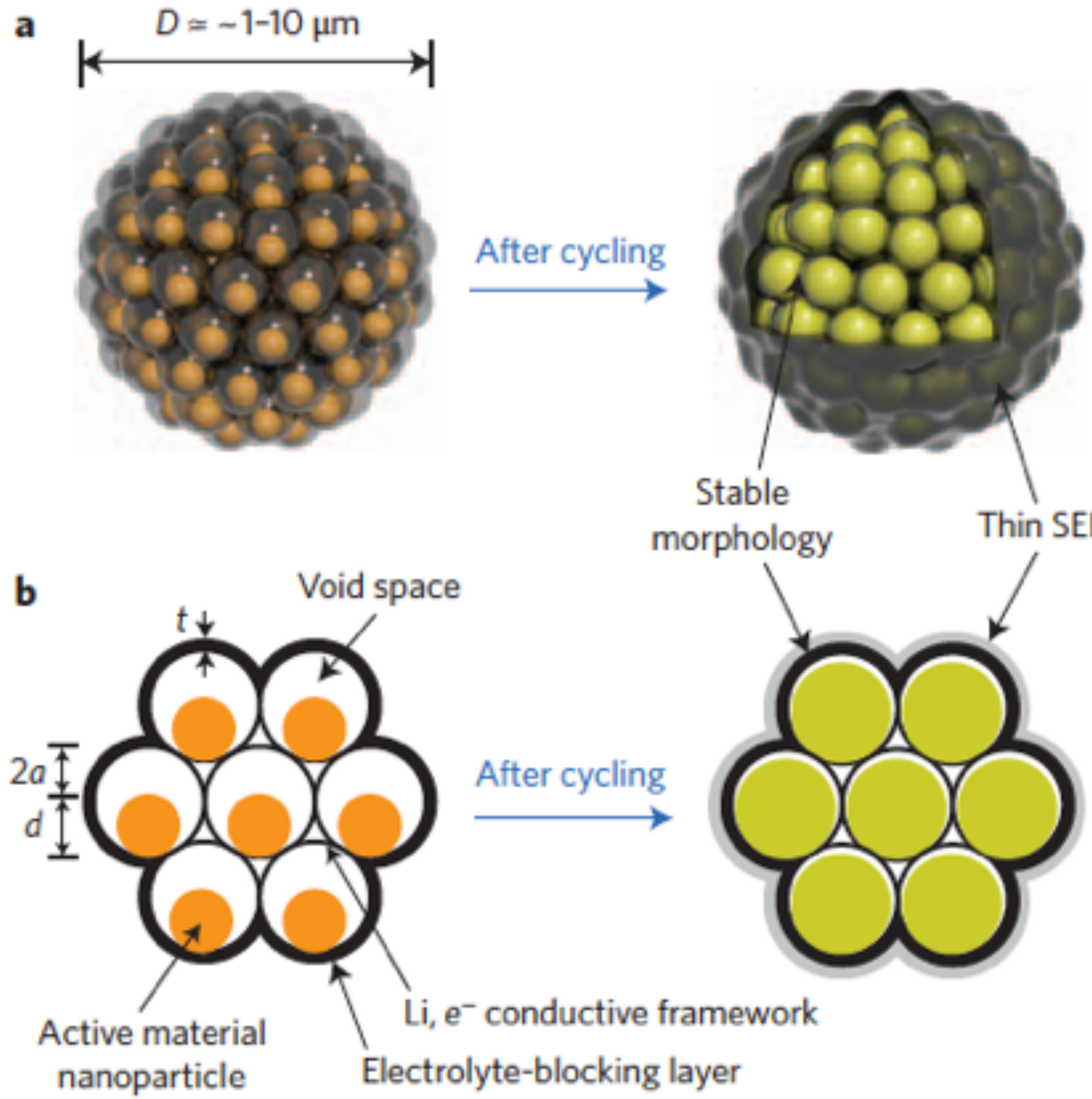
# Ultralong Cycle Life of Si Nanotubes



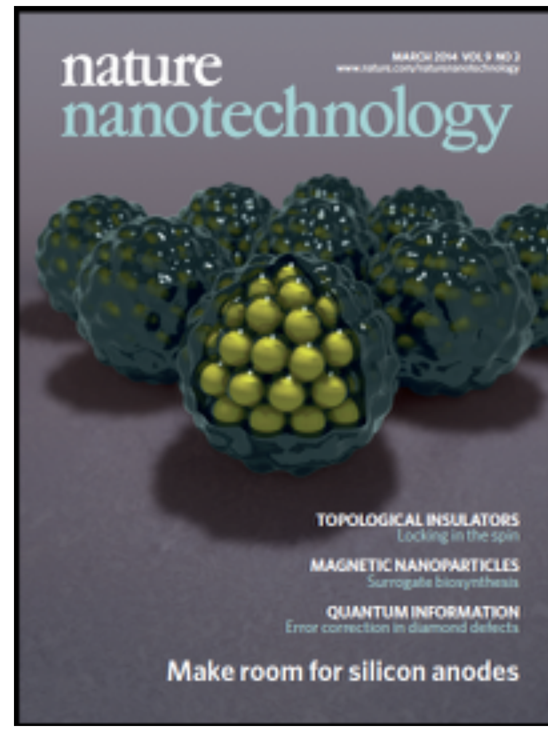




(Yi Cui Group *Nature Nanotech* 7, 310 (2012))

# Gen 8: Pomegranate-Like Si Batteries

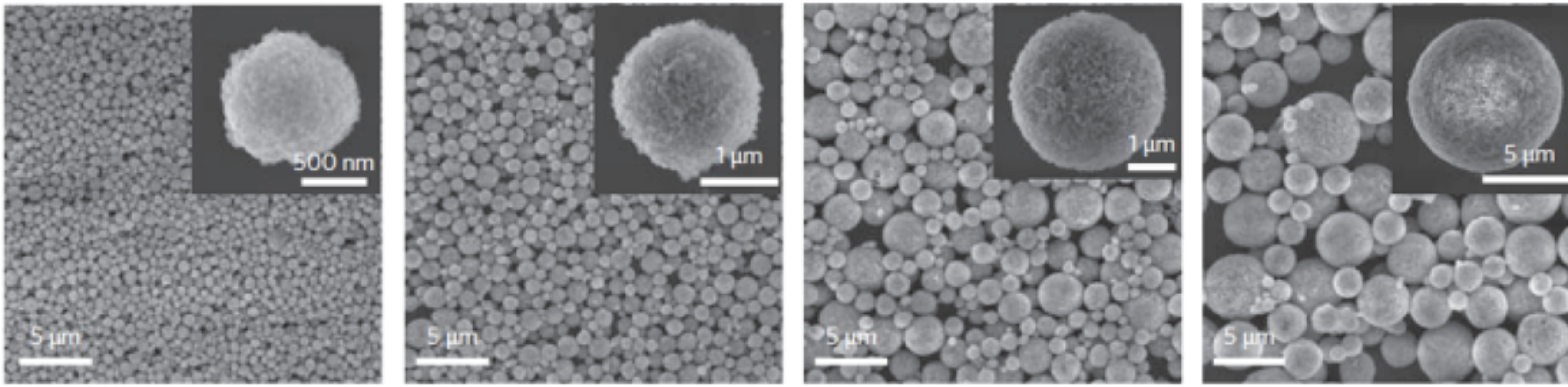


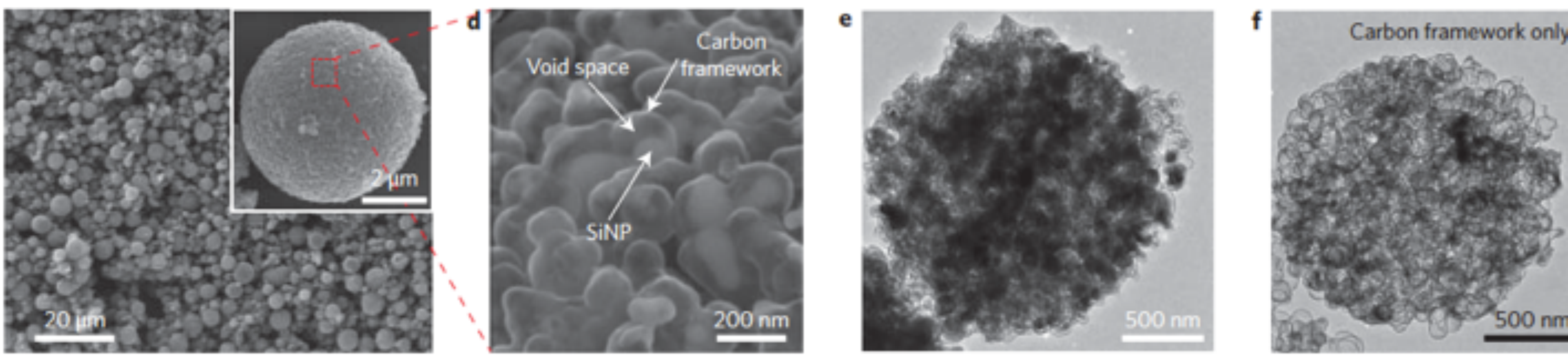

- **Reduce surface area**
- **Increase mass loading**
- **Dense packing**




N. Liu, Z. Lu, Y. Cui *Nature Nanotech* 9, 187 (2014).

# Gen 8: Pomegranate-Like Si Batteries




N. Liu, Z. Lu, Y. Cui *Nature Nanotech* 9, 187 (2014).

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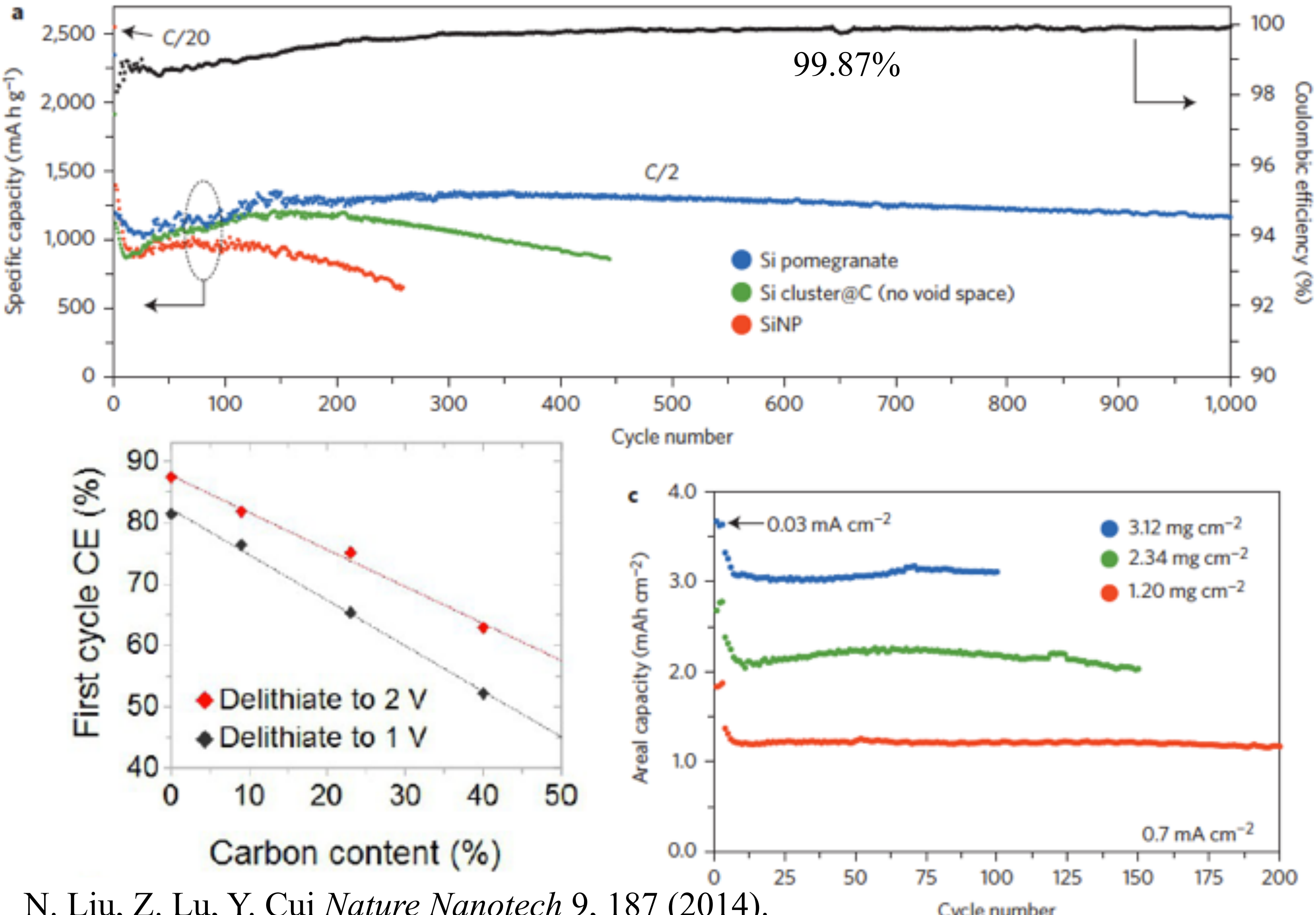
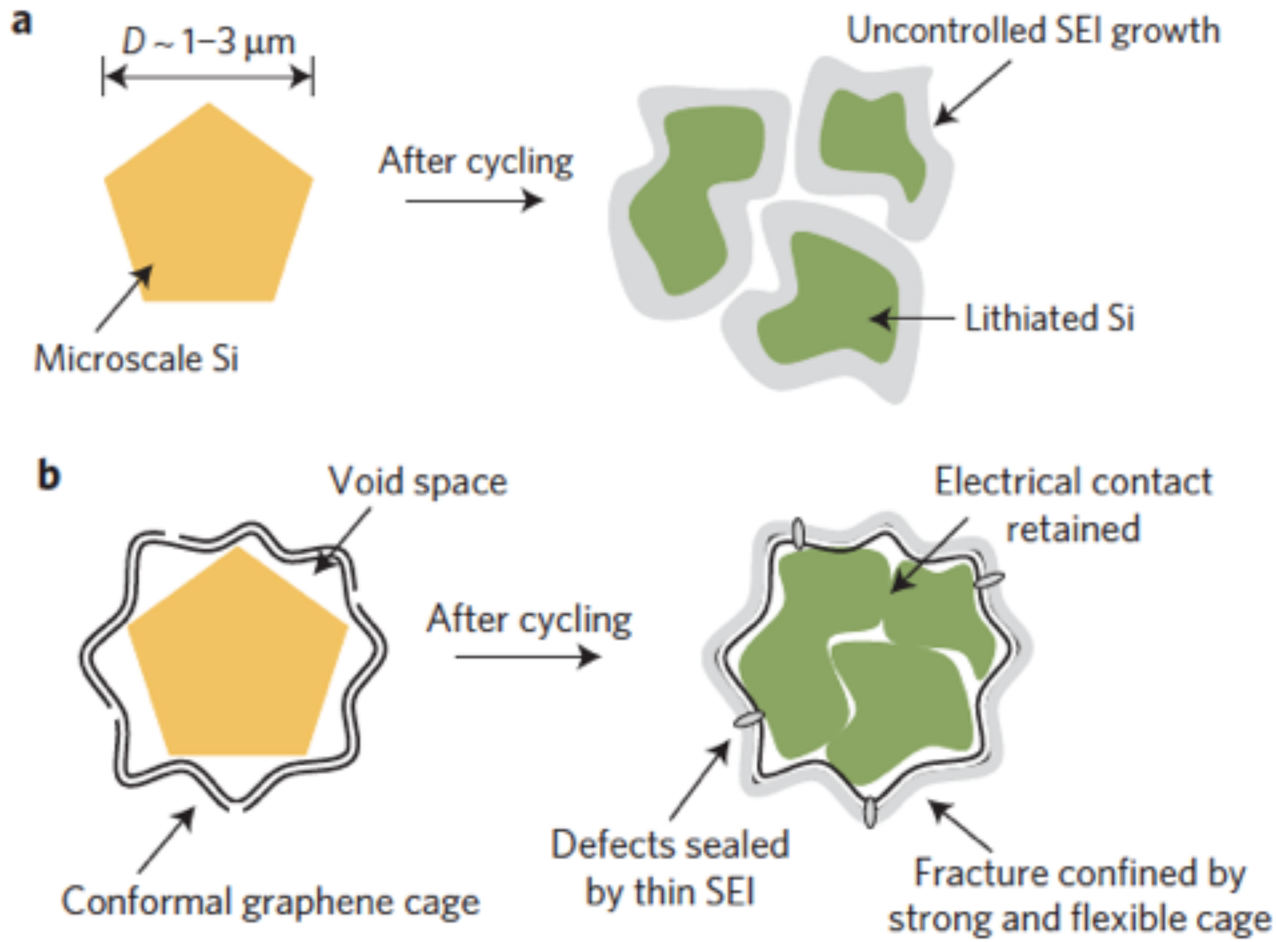
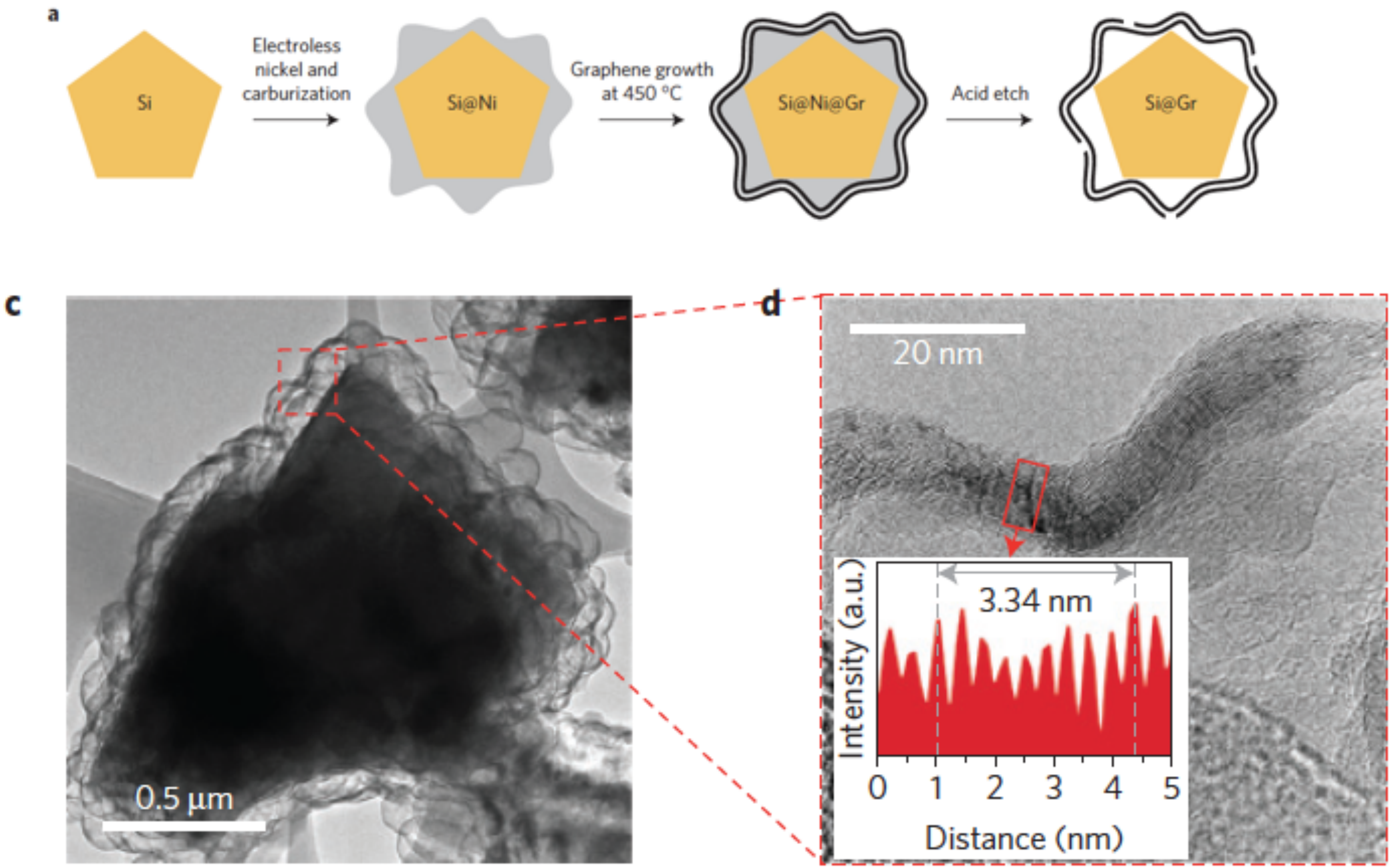



N. Liu, Z. Lu, Y. Cui *Nature Nanotech* 9, 187 (2014).

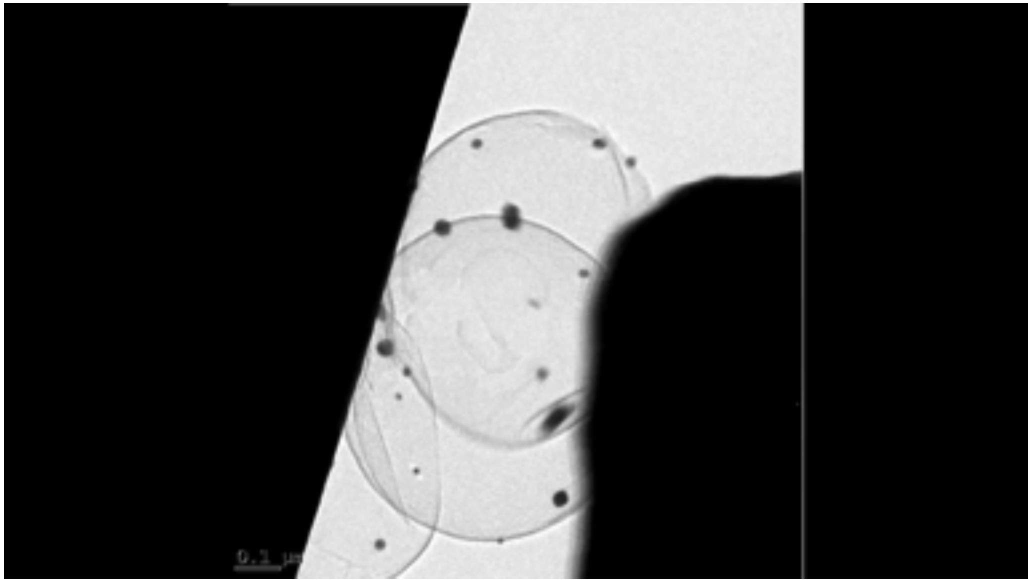
# Micron Si Particles as Anodes



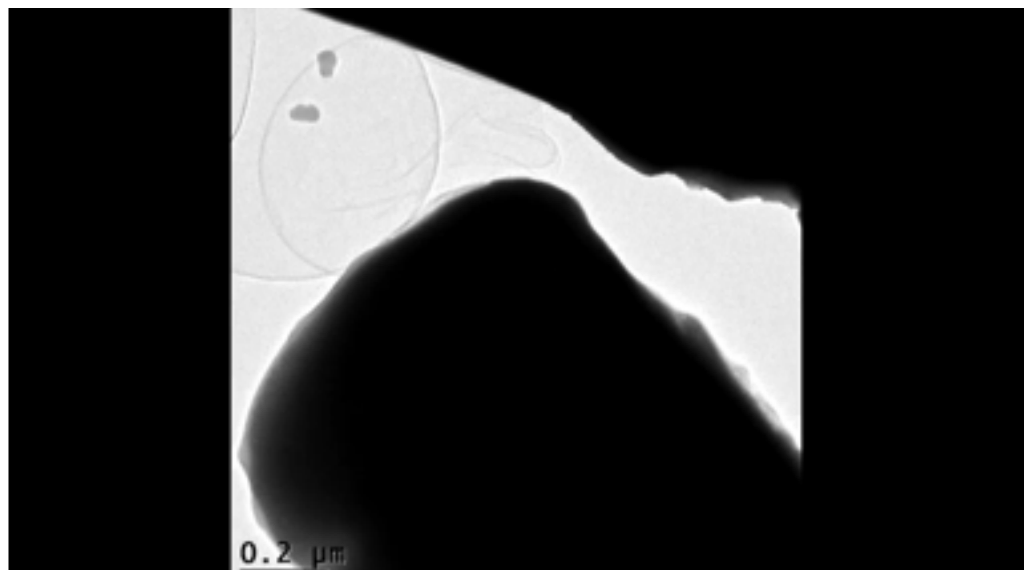

(Y. Li, K. Yan, Y. Cui *Nature Energy* 15029, 2016)



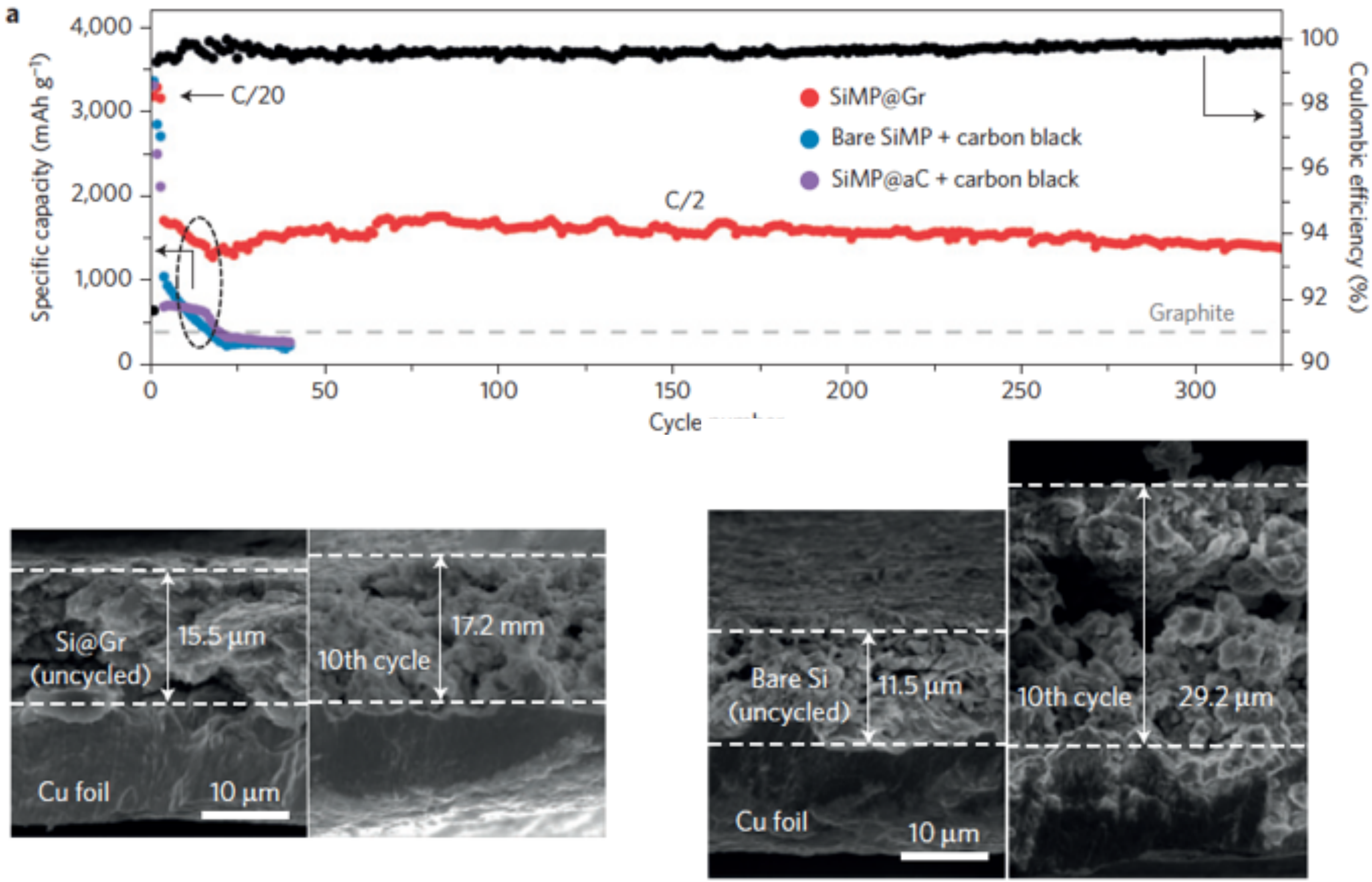

(Y. Li, K. Yan, Y. Cui *Nature Energy* 15029, 2016)




Amorphous carbon cage



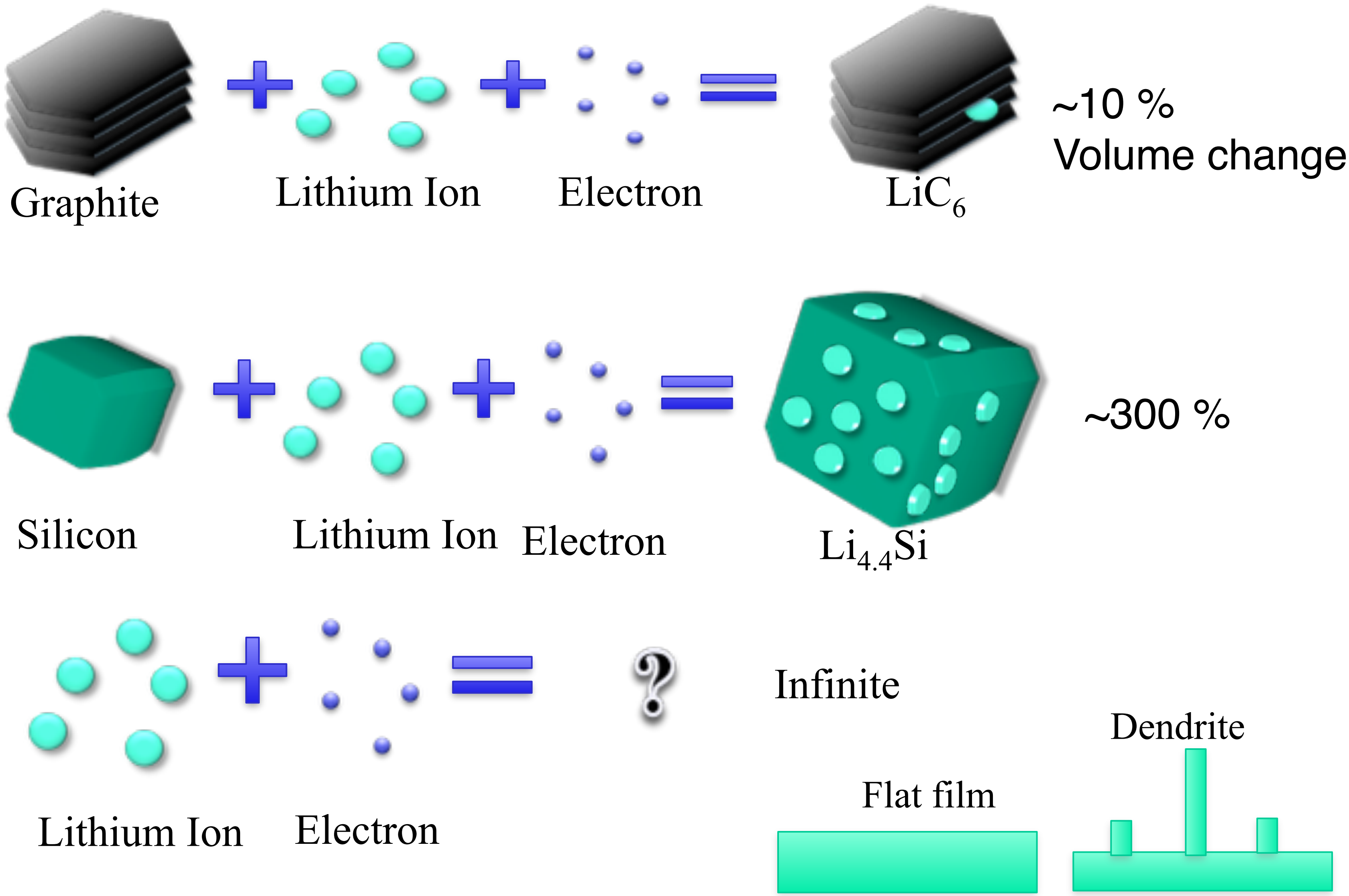

Graphene cage



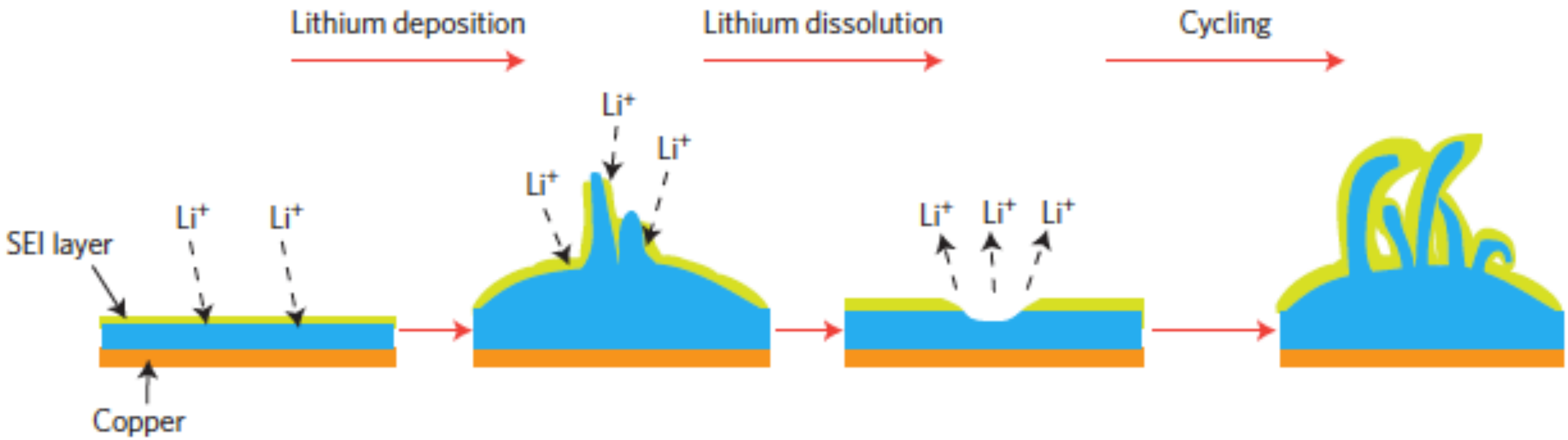

(Y. Li, K. Yan, Y. Cui *Nature Energy* 15029, 2016)

# Host: Graphite, Si

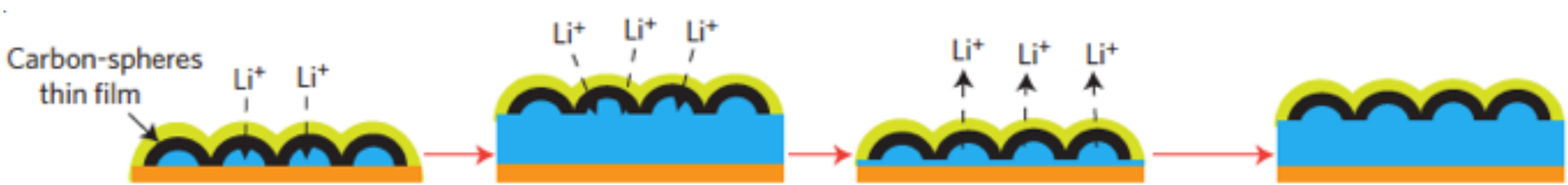
# No Host: Li metal, electroplating



# Nanoscale Interfacial Materials Design

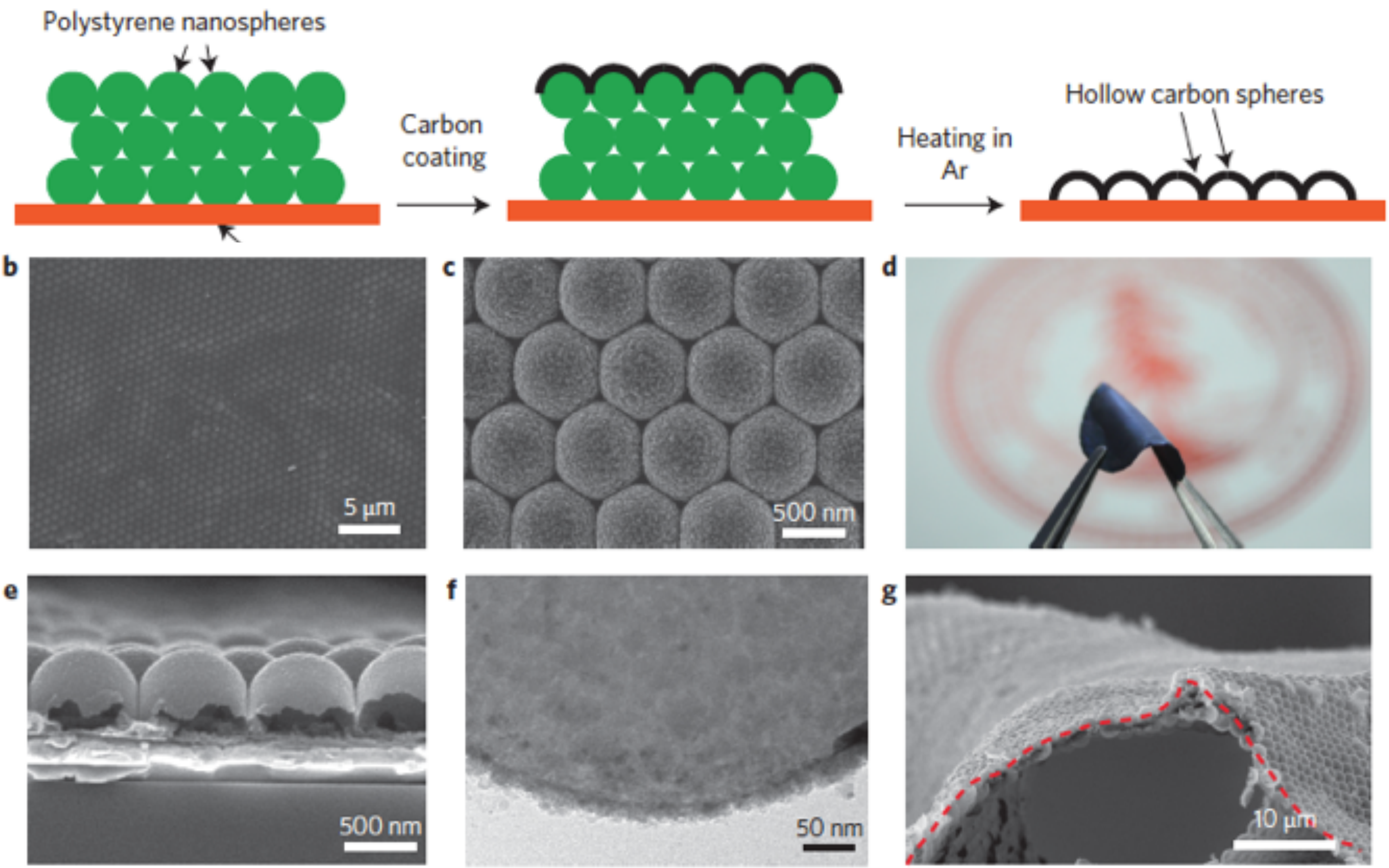



**Stable interfacial design using nanomaterials: chemically and mechanically stable**



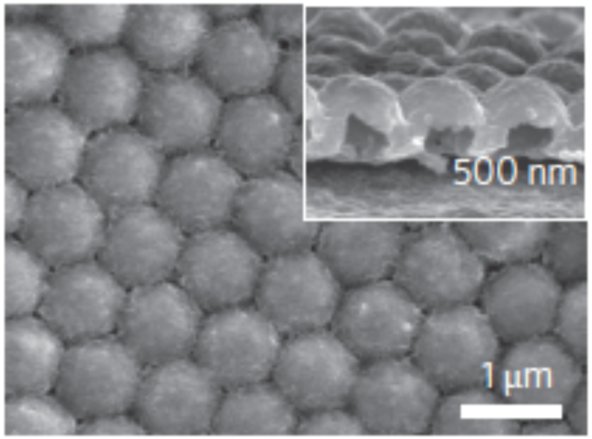

Guangyuan Zheng, Steven Chu, Yi Cui . *Nature Nanotechnology* 9, 618 (2014).

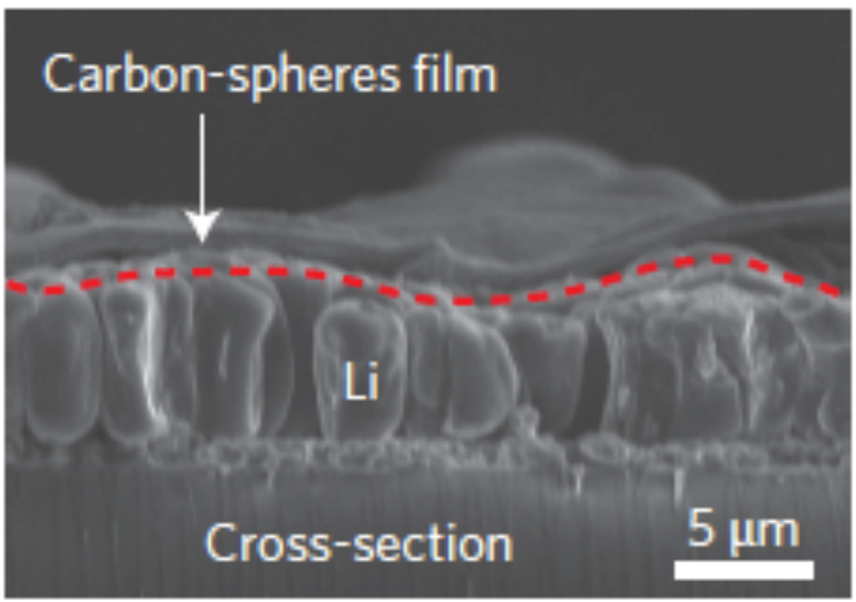
# Interconnected Hollow Carbon Sphere Fabrication

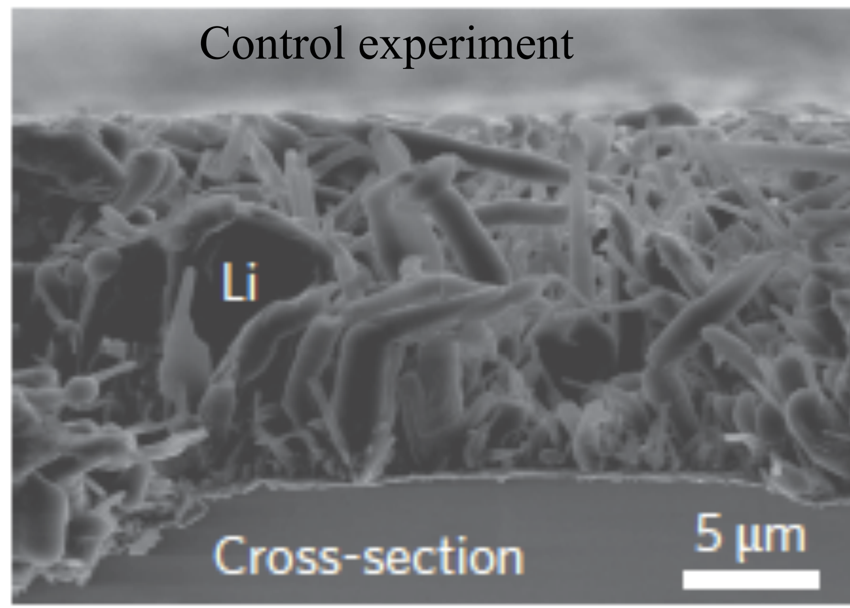



Guangyuan Zheng, Steven Chu, Yi Cui . *Nature Nanotechnology* 9, 618 (2014).

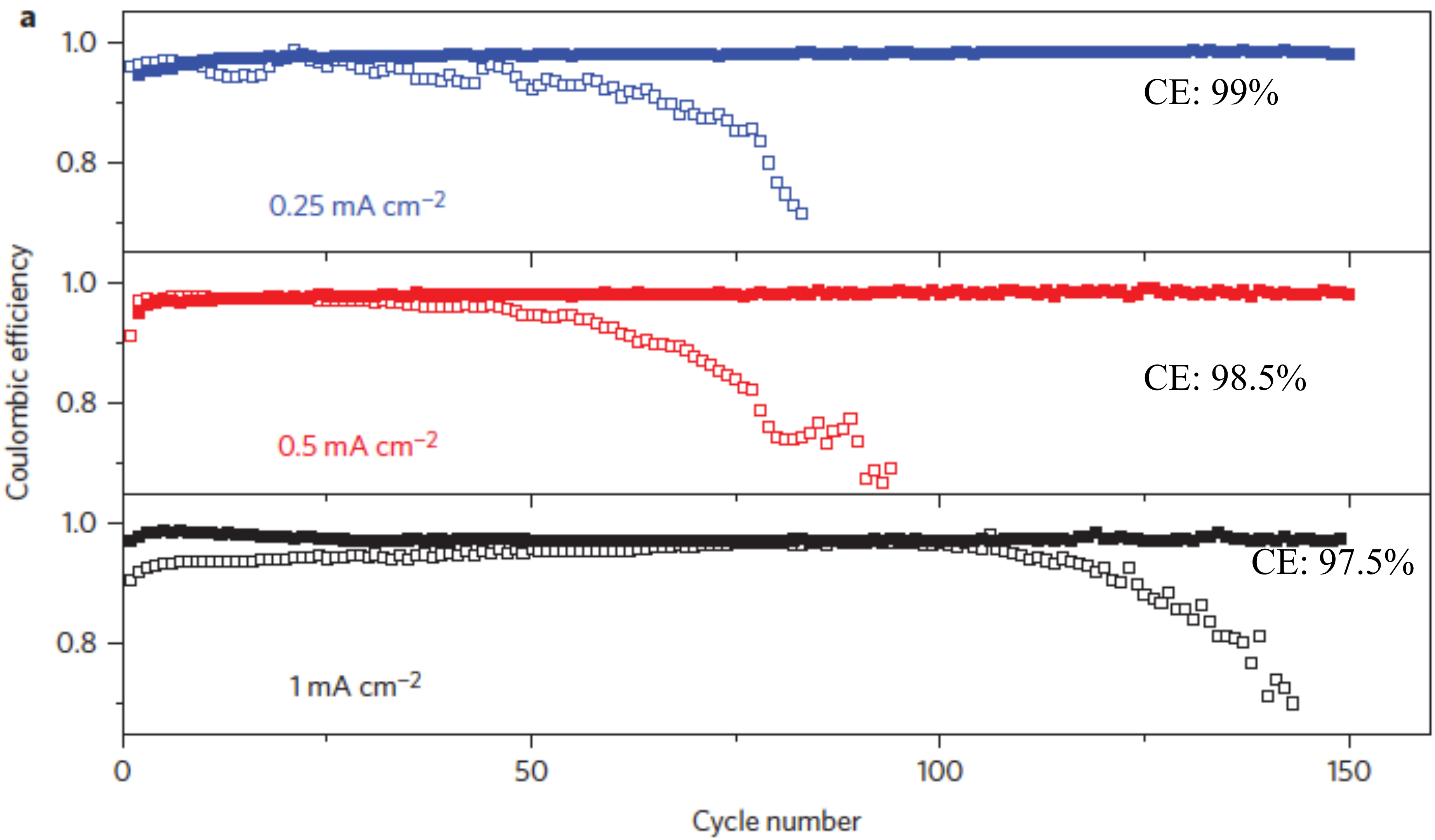
# After Li metal electrodeposition



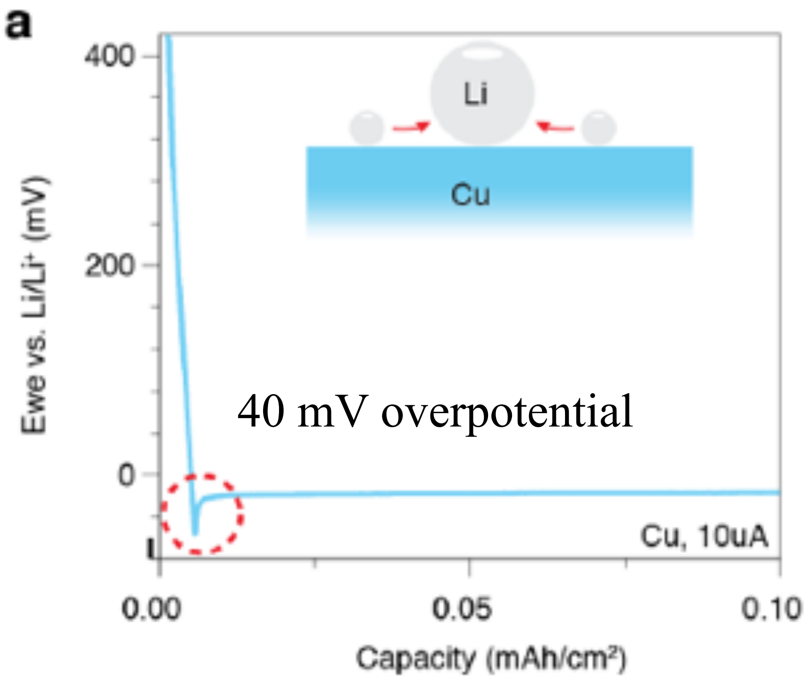

Guangyuan Zheng, Steven Chu, Yi Cui . *Nature Nanotechnology* 9, 618 (2014).



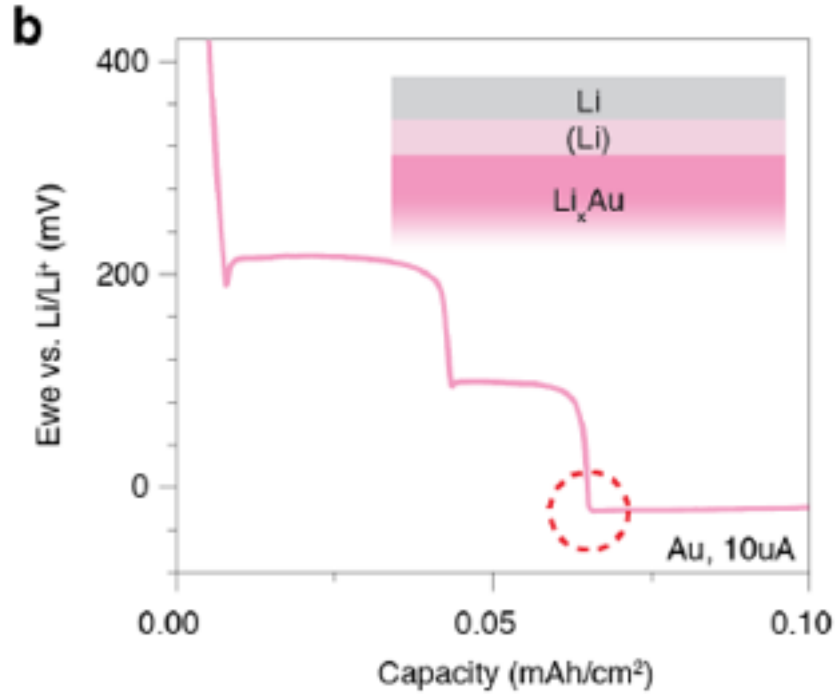

1 M LiTFSI in DOL:DME w/ 2% $LiNO_3$

Guangyuan Zheng, Steven Chu, Yi Cui . *Nature Nanotechnology* 9, 618 (2014).

**Do we understand how Li metal nucleates on different substrate?**



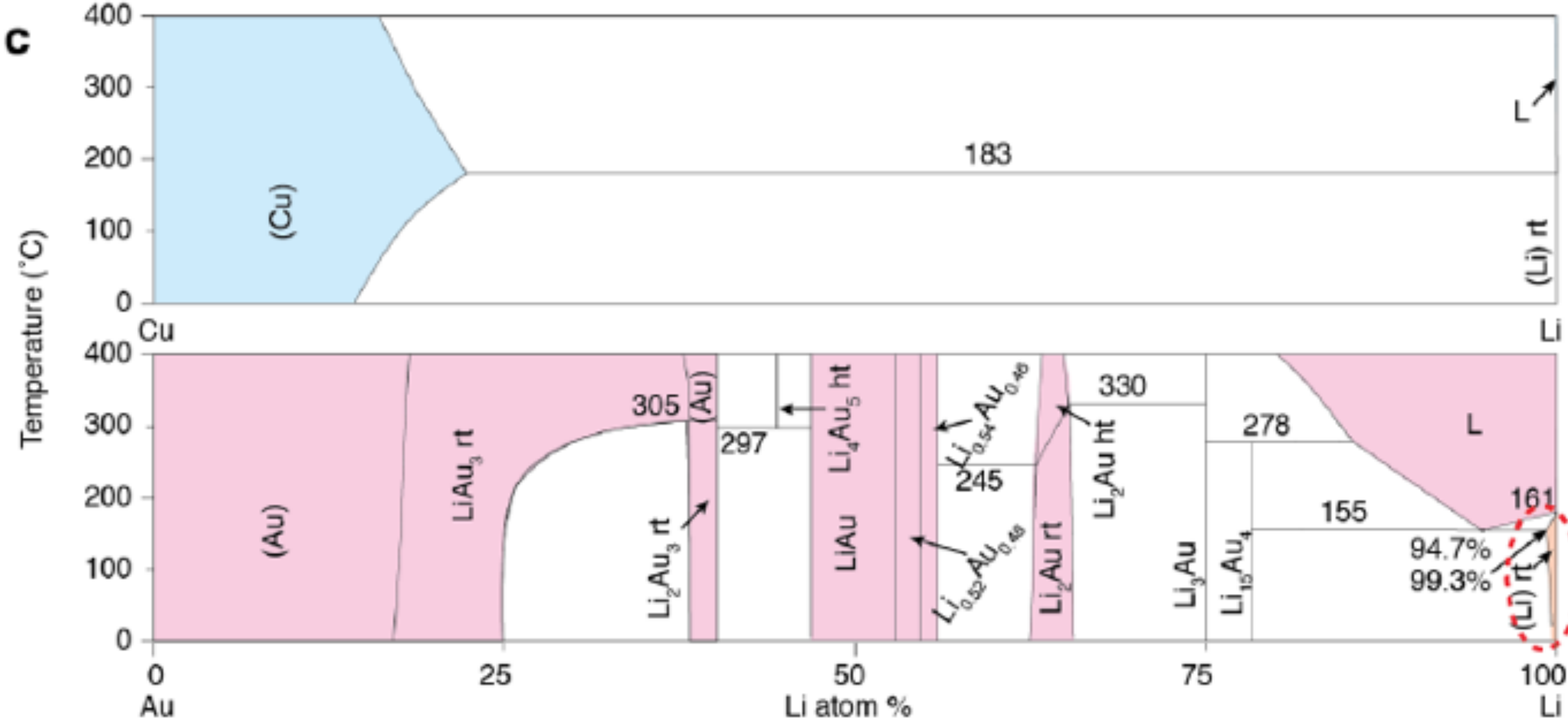

40 mV overpotential




1 M $LiPF_6$ in EC:DEC

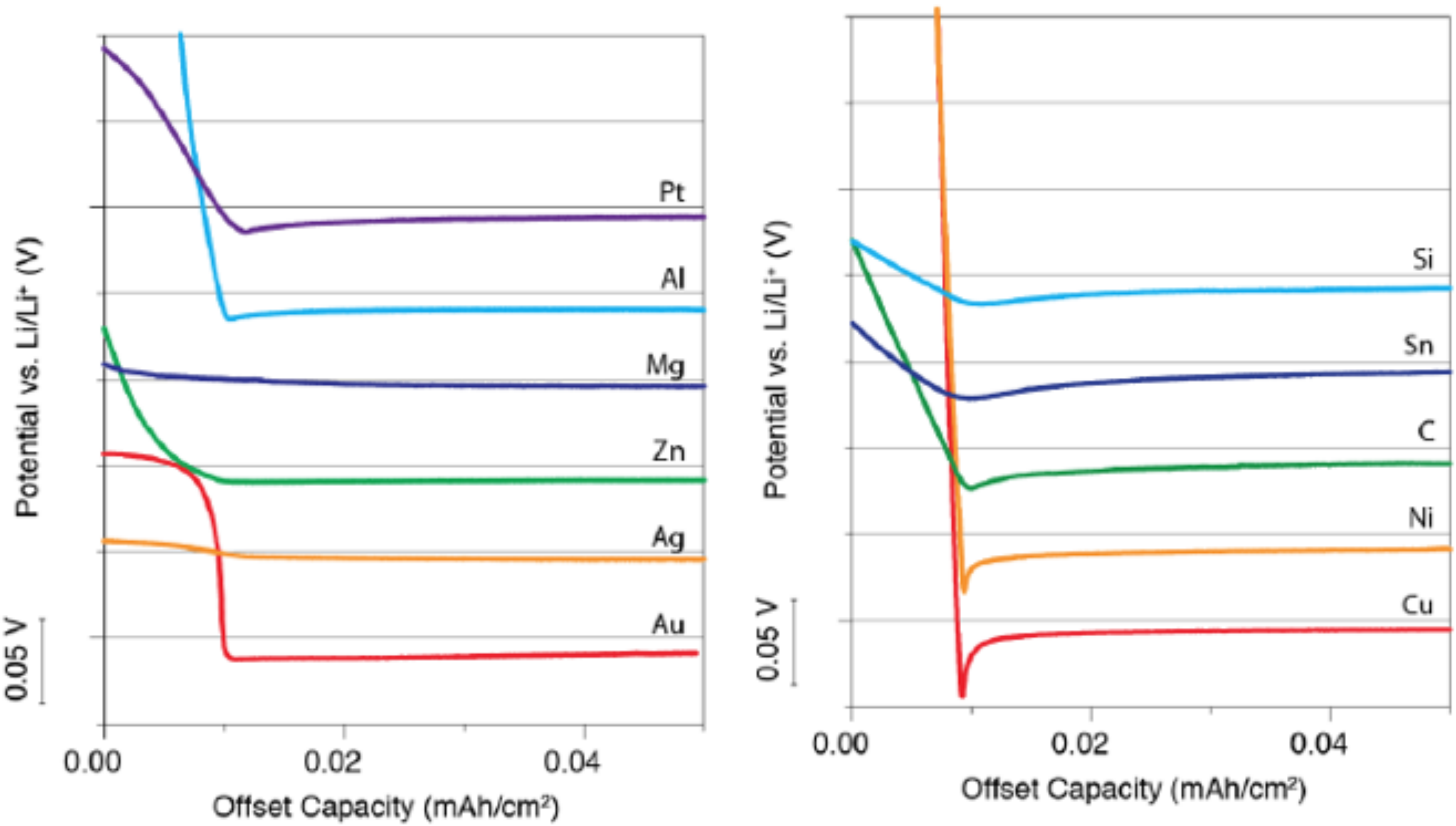
K Yan, S. Chu, Y. Cui *Nature Energy* (March, 2016)

# Phase Diagrams of Li-Cu and Li-Au



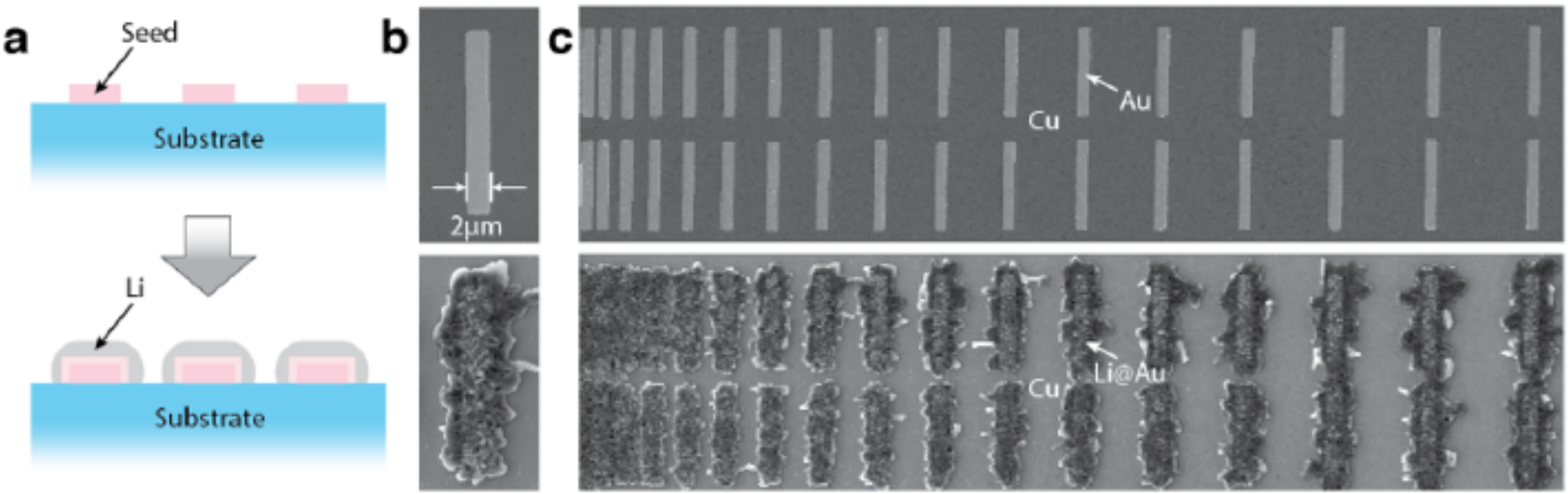

**Cu has negligible solubility in Li.**
**Au has some solubility in Li.**

K Yan, S. Chu, Y. Cui *Nature Energy* (March, 2016)



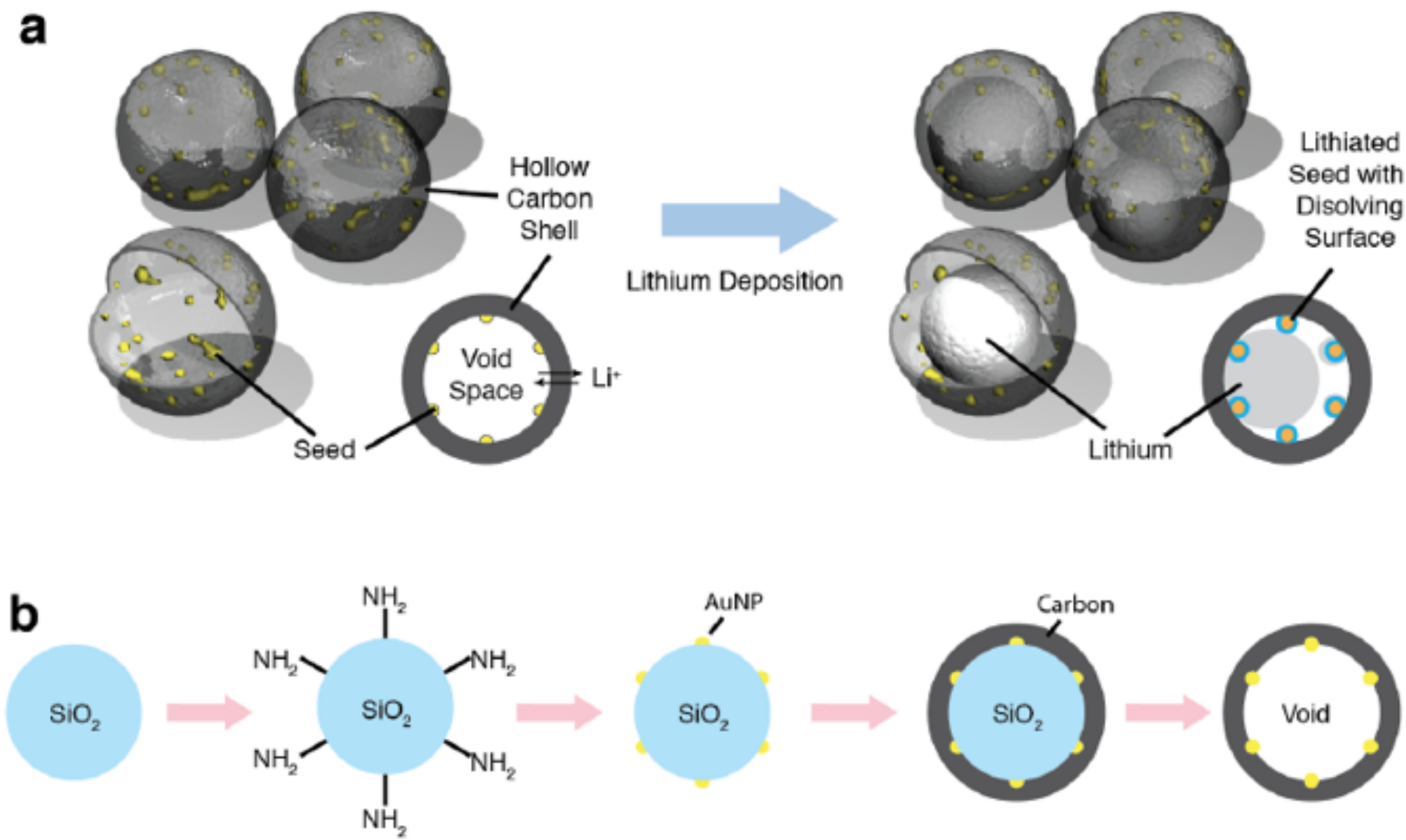

K Yan, S. Chu, Y. Cui *Nature Energy* (March, 2016)

# Seeded Li Metal Deposition fro Spatial Control

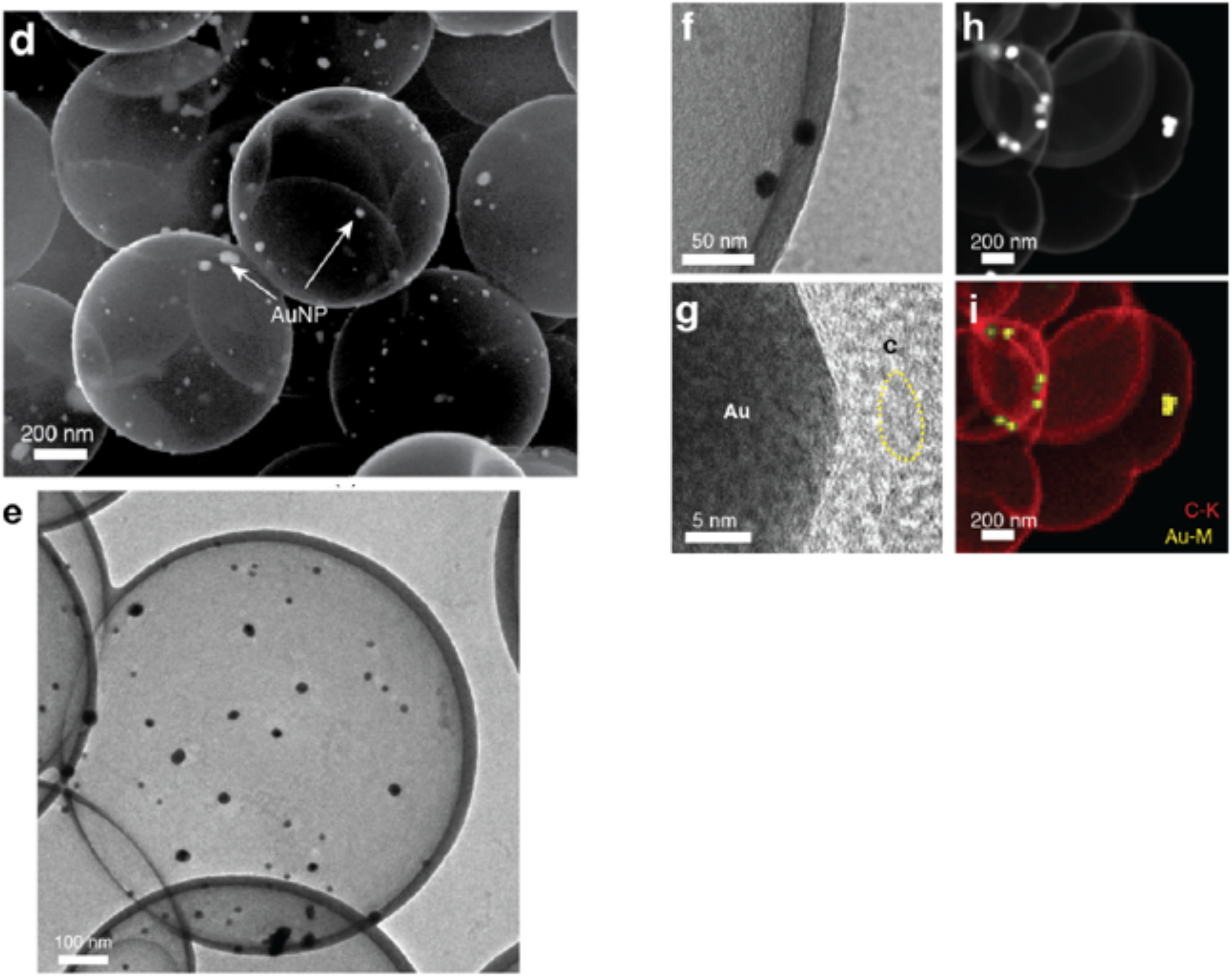


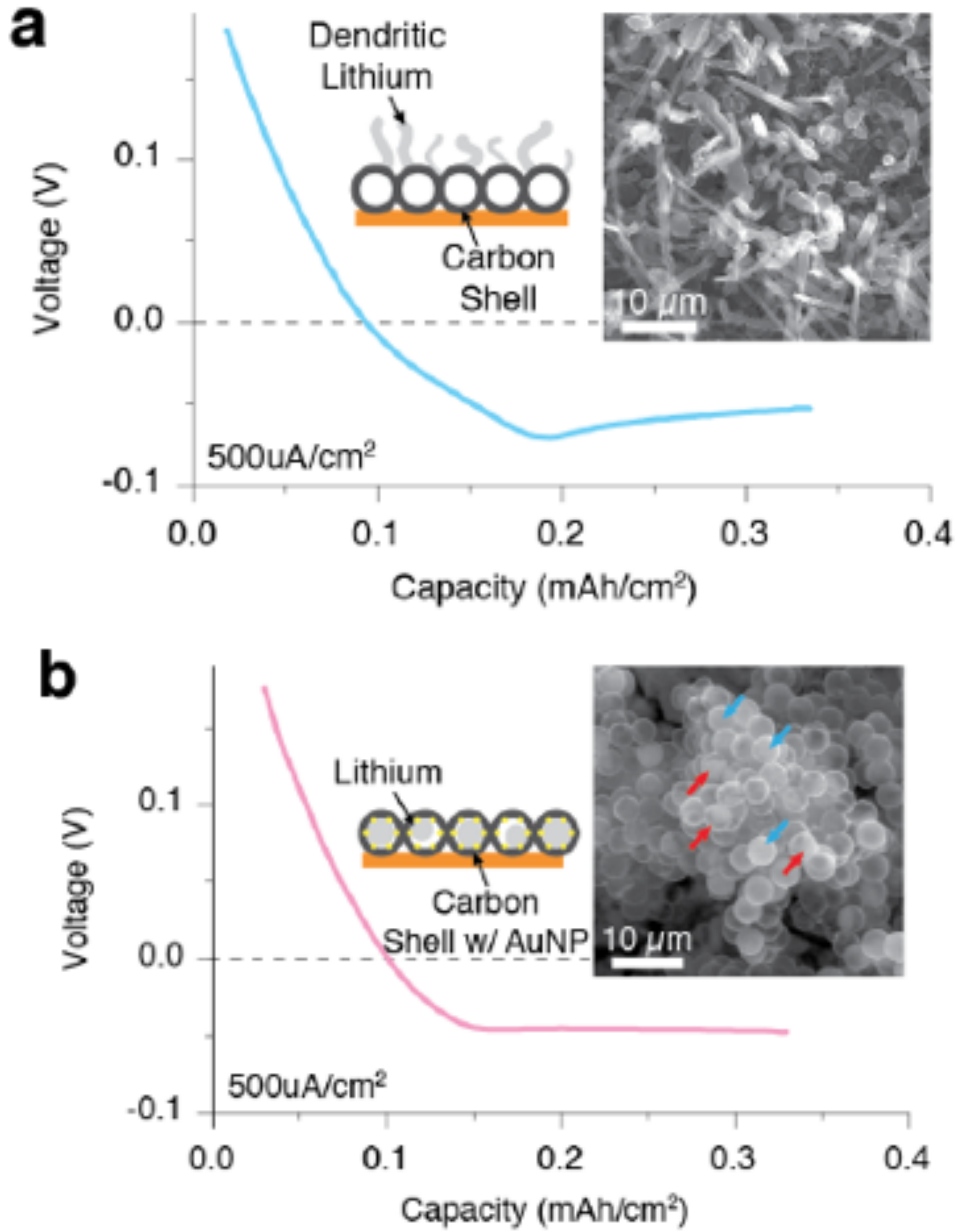

K Yan, S. Chu, Y. Cui *Nature Energy* (March, 2016)

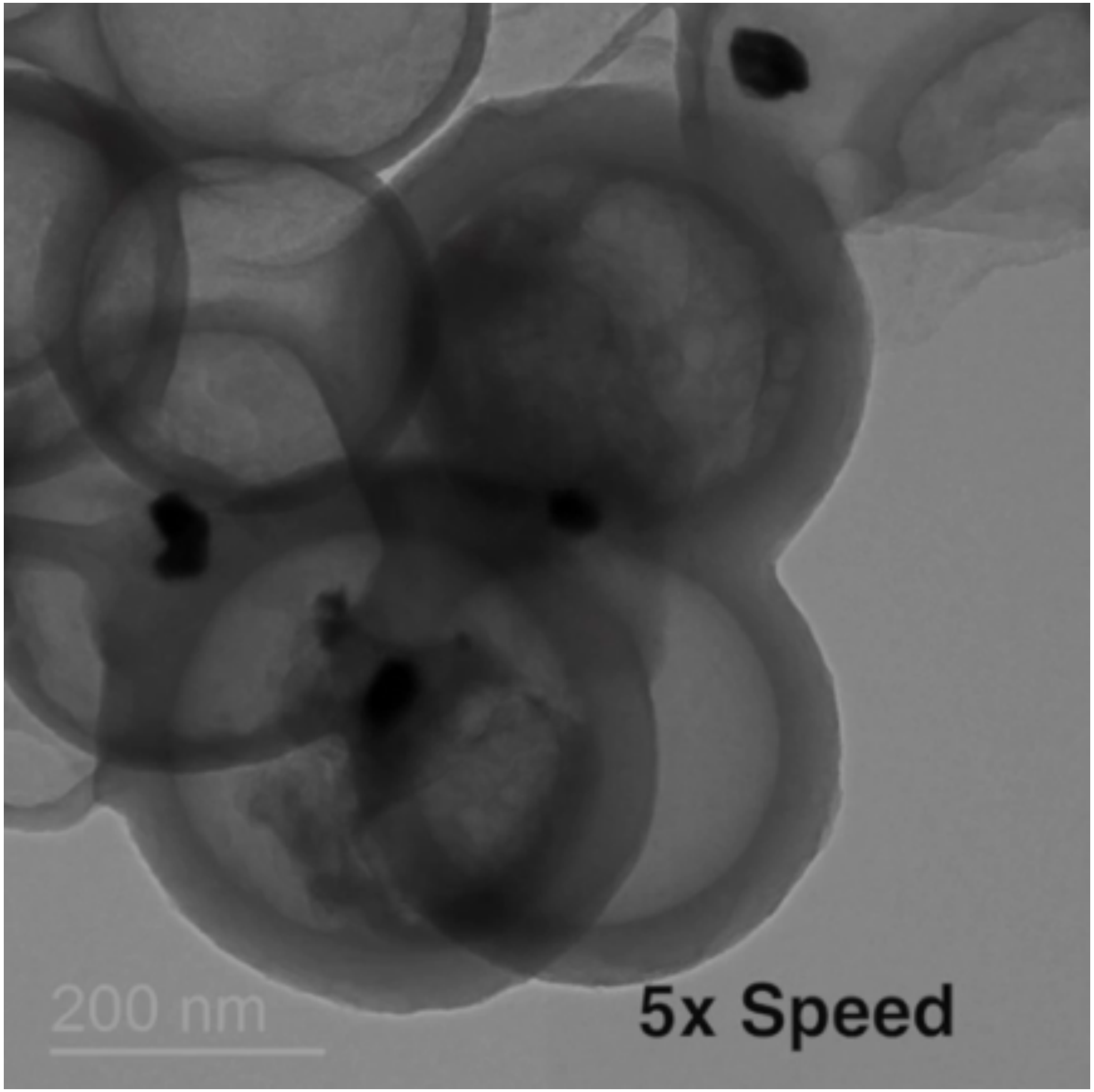
# Nanocapsule as a "Host" for Lithium Metal




K Yan, S. Chu, Y. Cui *Nature Energy* (March, 2016)

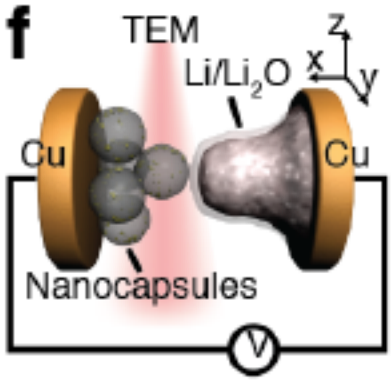

d
AuNP
200 nm
e
100 nm
f
50 nm
g
Au
C
5 nm
h
200 nm
i
200 nm
C-K
Au-M

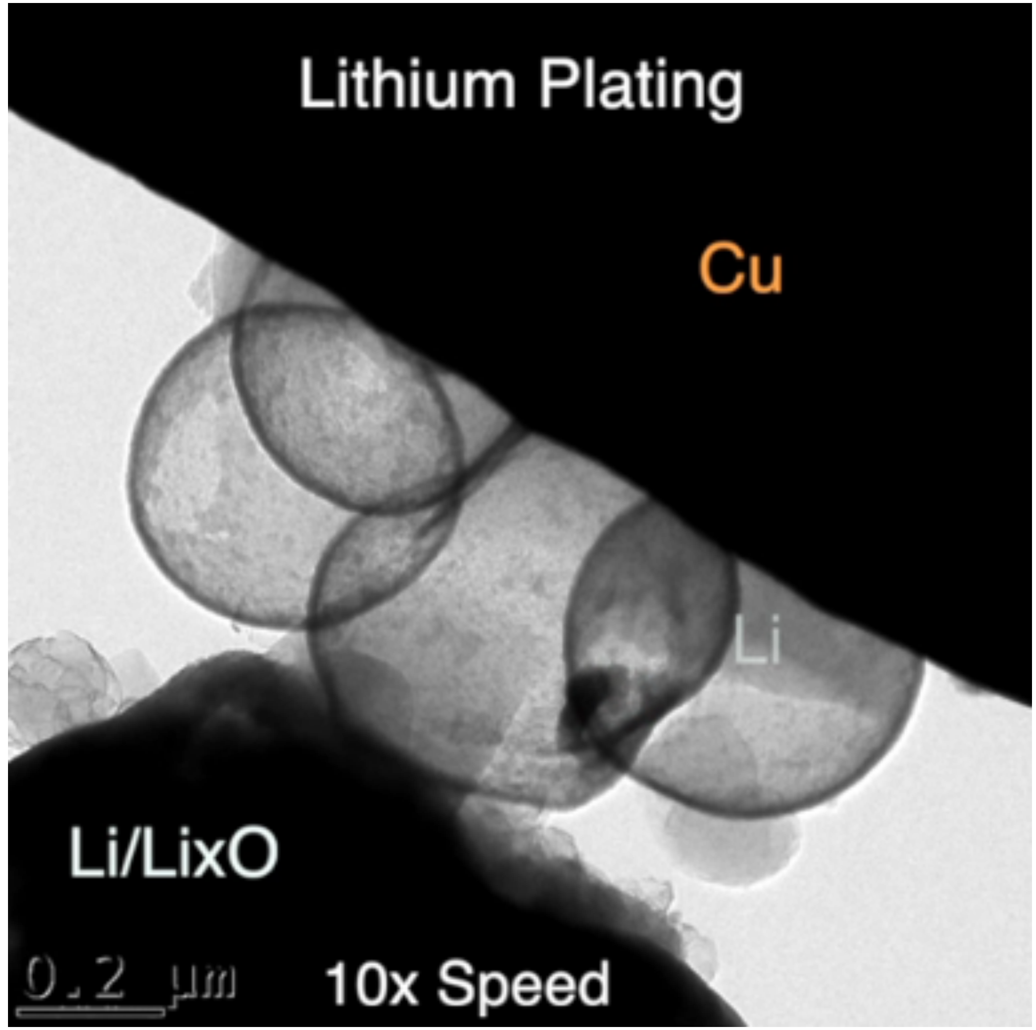

a
Dendritic
Lithium
Carbon
Shell
10 μm
500uA/cm²
Voltage (V)
0.1
0.0
-0.1
0.0
0.1
0.2
0.3
0.4
Capacity (mAh/cm²)
b
Lithium
Carbon
Shell w/ AuNP
10 μm
500uA/cm²
Voltage (V)
0.1
0.0
-0.1
0.0
0.1
0.2
0.3
0.4
Capacity (mAh/cm²)

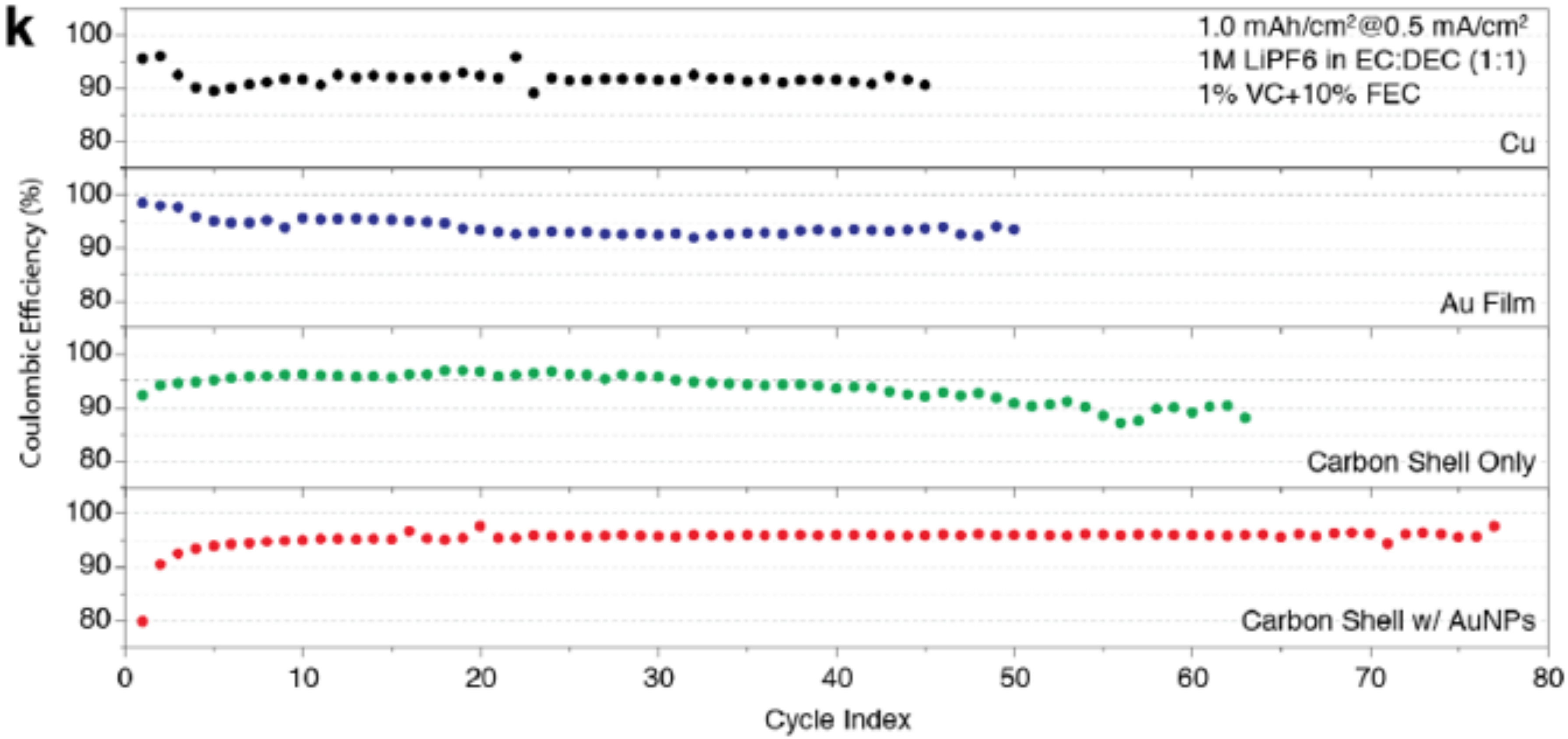



K Yan, S. Chu, Y. Cui *Nature Energy* (March, 2016)

# In-situ TEM


f
TEM
Li/Li2O
z
x
y
Cu
Cu
Nanocapsules
V


Lithium Plating
Cu
Li
Li/LixO
0.2 µm
10x Speed


k
1.0 mAh/cm²@0.5 mA/cm²
1M LiPF6 in EC:DEC (1:1)
1% VC+10% FEC
Cu
Au Film
Carbon Shell Only
Carbon Shell w/ AuNPs
Coulombic Efficiency (%)
Cycle Index
100
90
80
0
10
20
30
40
50
60
70
80

# Global reserve of lithium: 40 million ton

**Nissan Leaf, 24 kWh, 84 miles**
**4 kg Lithium**

## 10 Billion Leaf

**Tesla S model, 85 kWh, 265 miles**
**14 kg Lithium**

## 3 Billion Tesla


## There are ~1 billion cars in the world.

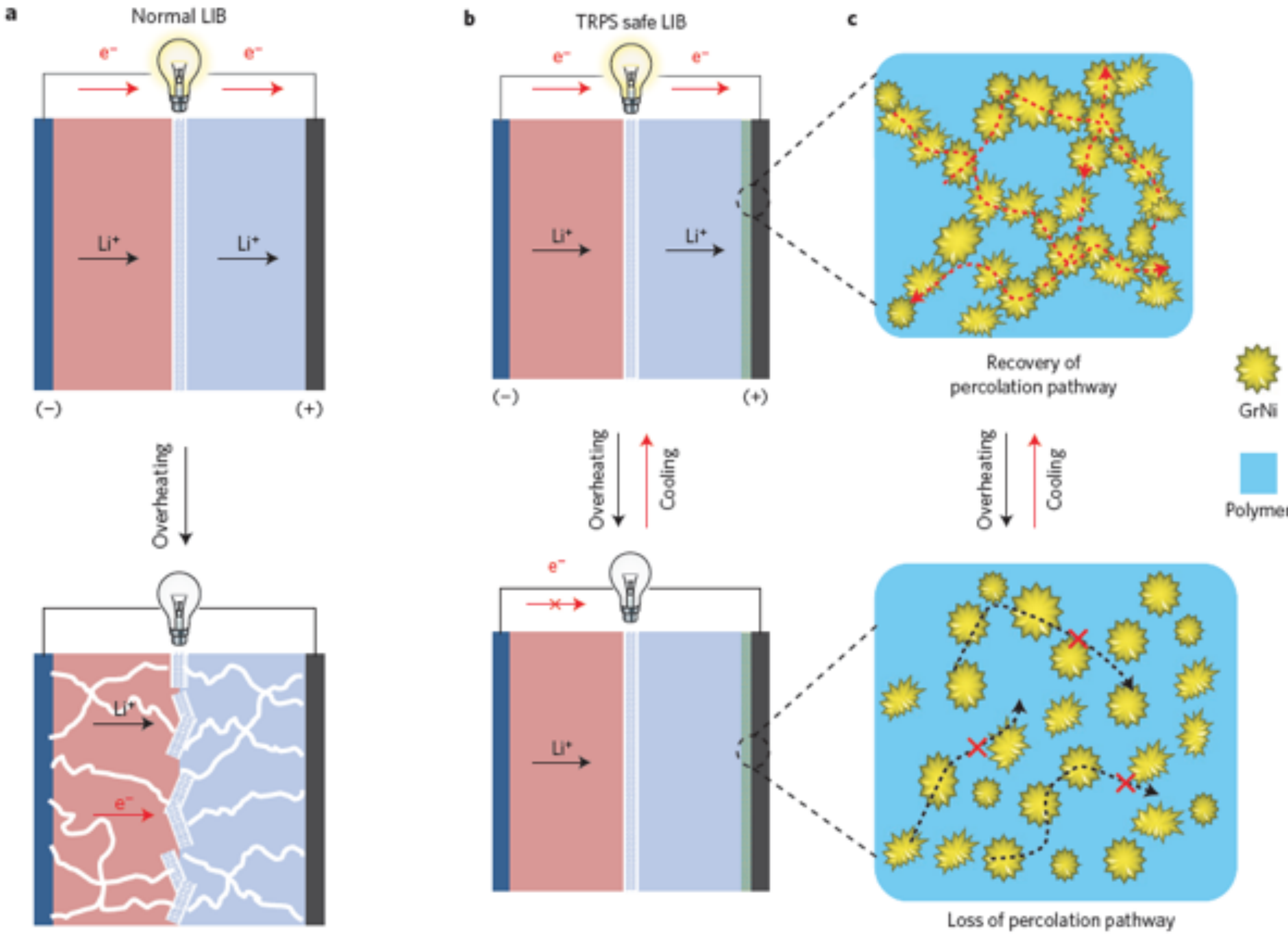
**In 2009, Li production: 92,000 ton, which is 23,000,000 Nissan Leaf.**

# Ocean: 230,000 million ton (0.1778ppm)

**World Electricity Consumption: ~4 TW**
**Need TeraBattery for 6 hours: ~24 TWh**

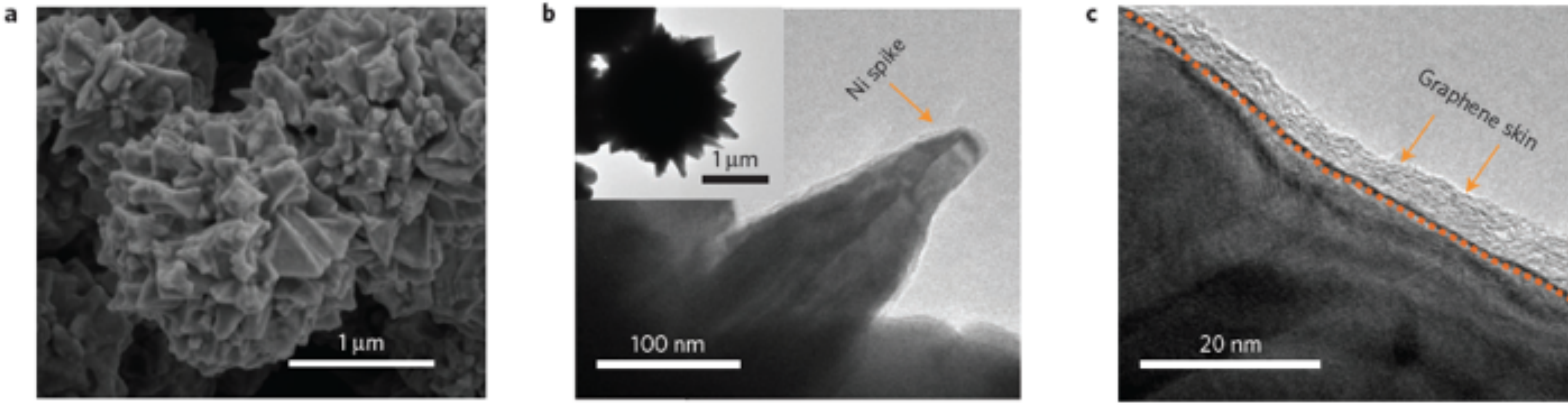
**Global reserve of lithium: 40 million ton**
**Battery 240TWh**

# Battery Safety: Reversible Thermal Fuse

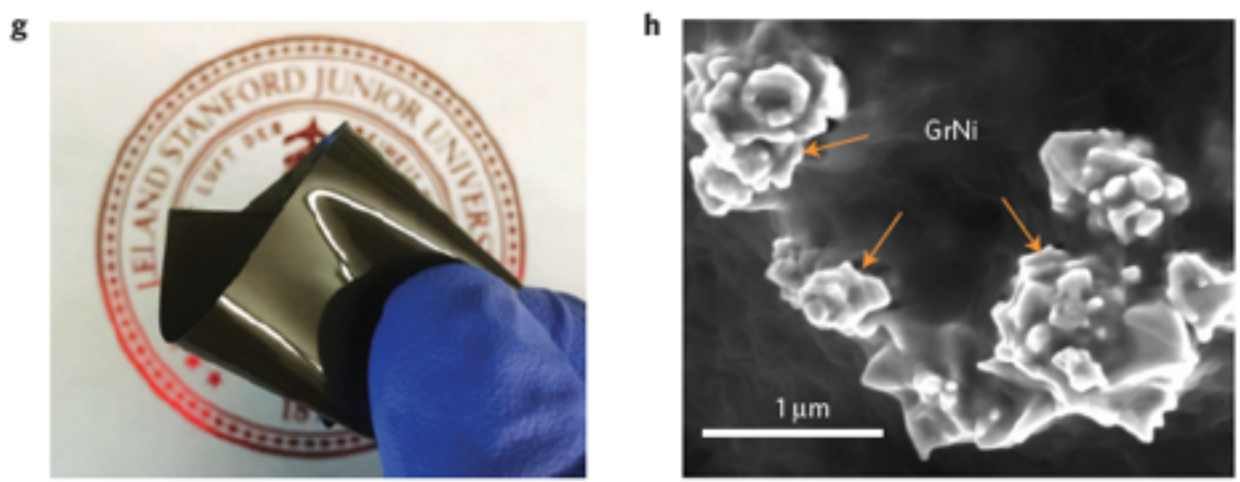



Z. Chen, Y. Cui, Z. Bao Nature Energy (2016)

## Ni Nanospikes coated with graphene

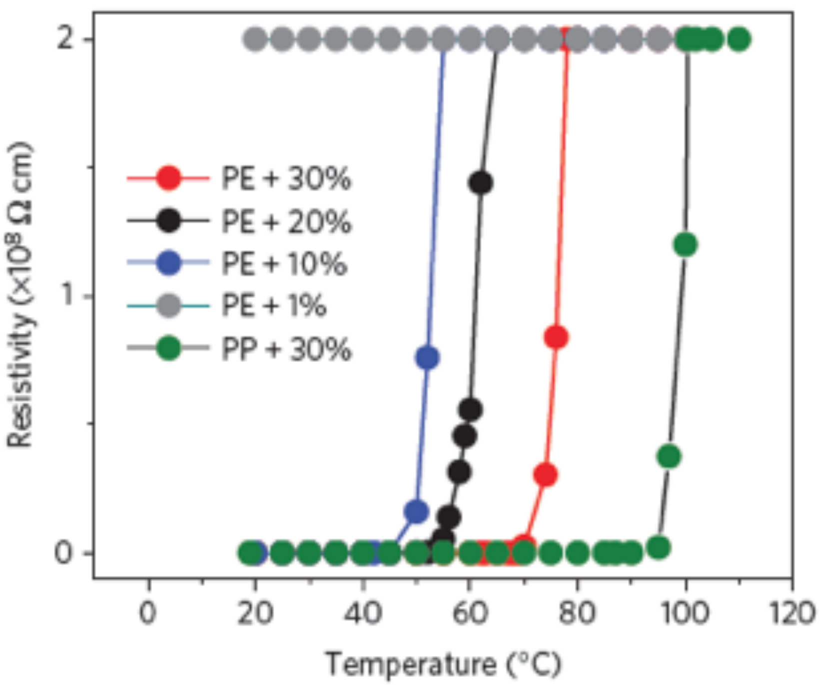


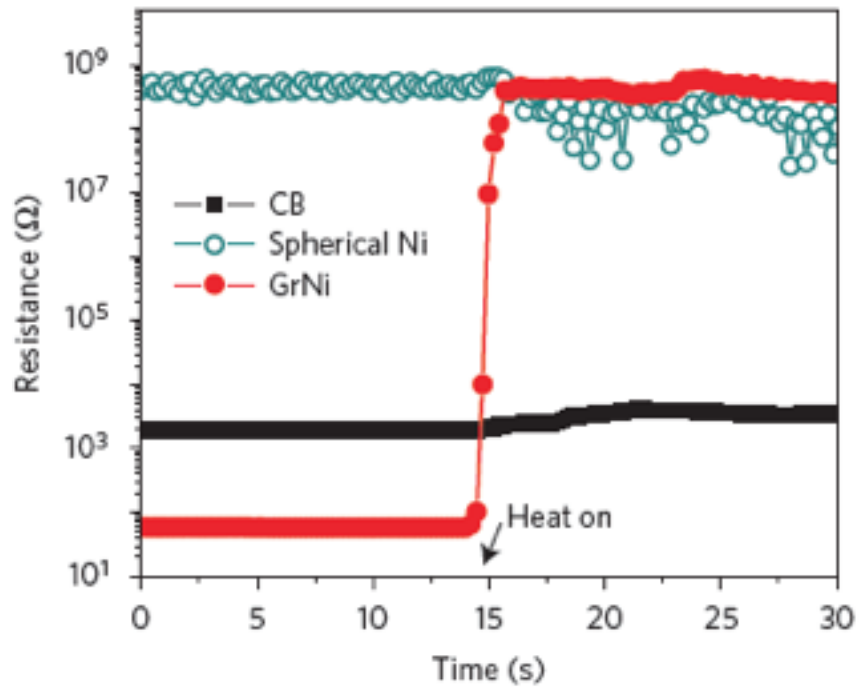

## Ni nanospikes mixed with polyethylene polymer

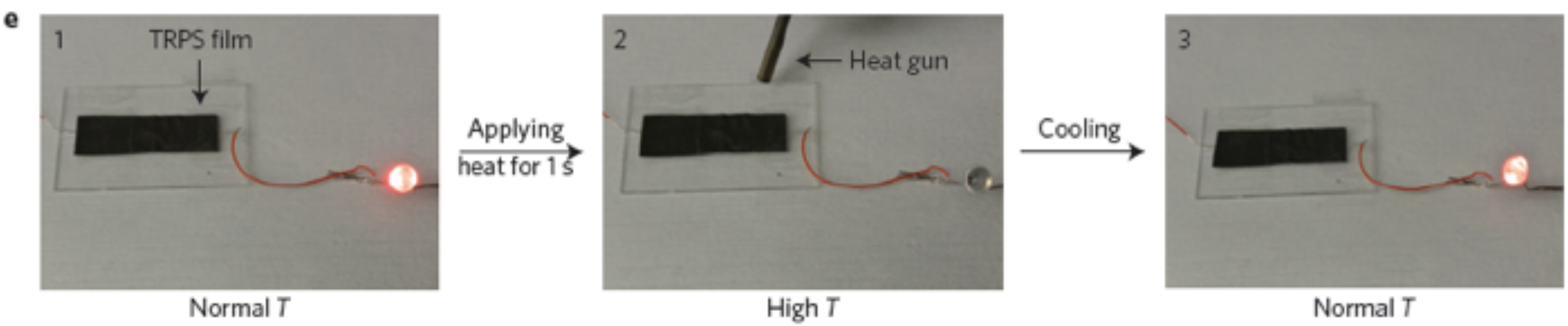



Z. Chen, Y. Cui, Z. Bao Nature Energy (2016)

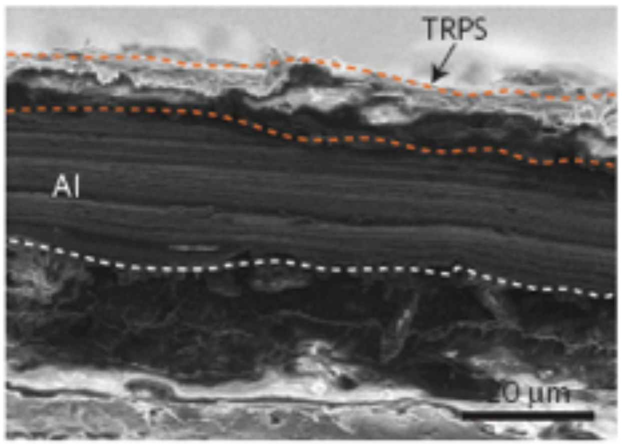
# Reversible Thermal Fuse

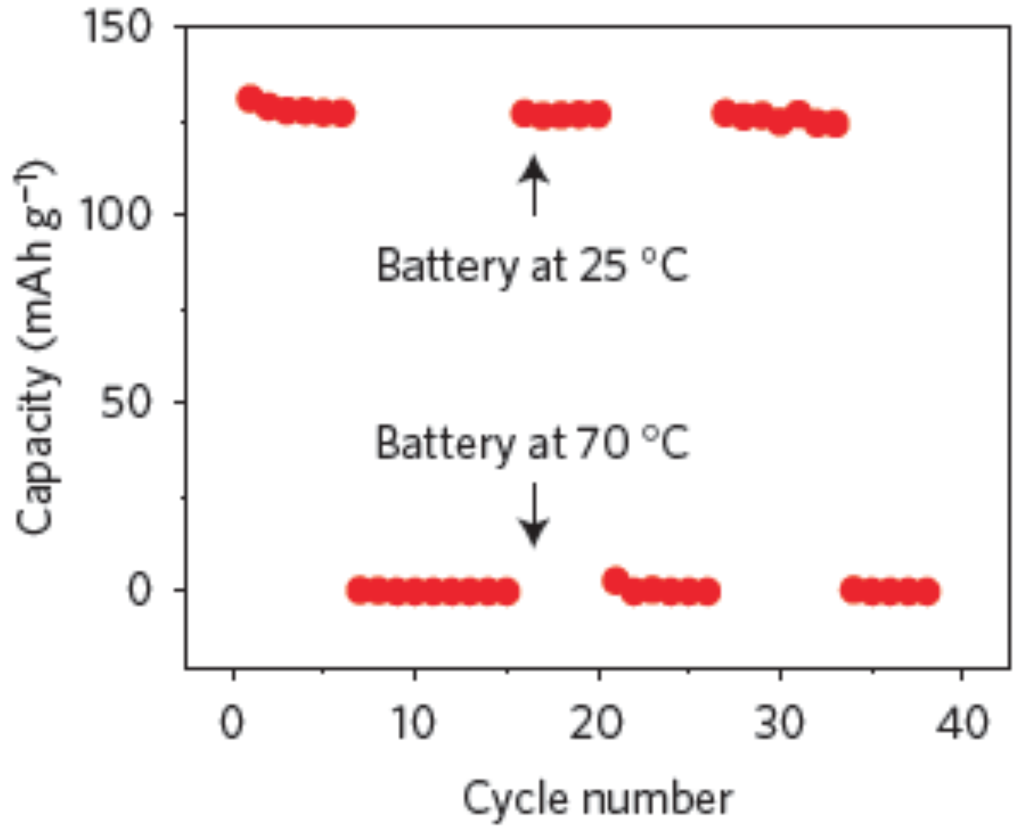


# Reversible Thermal Fuse

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# Lithium Ion Battery Cells: Now and Future Goals

| | Cell level (goal) | System level (goal) |
|---|---|---|
| Energy (Wh/kg) | ~200 (600) | ~100 (300) |
| Cost ($/kWh) | 150-200 (70) | 300-500 (150) |
| Cycle life | 3000 (10,000 for grid) | |

## Safety

# Acknowledgement

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- Mike Toney (SLAC)
- Zhenan Bao
- Robert Huggins
- Steven Chu

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- Global Climate & Energy Projects (Stanford)
- Precourt Institute for Energy (Stanford)
- ONR Young Investigator