Energy Tutorial:
Battery Storage 101

GCEP RESEARCH SYMPOSIUM 2010 | STANFORD, CA

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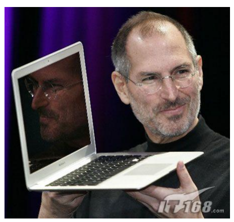
SEPTEMBER 29, 2010

GLOBAL CHALLENGES – GLOBAL SOLUTIONS – GLOBAL OPPORTUNITIES

Importance of Batteries

Portable Electronics

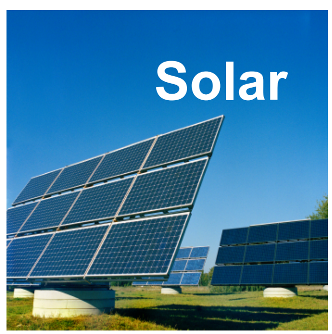


Cars: lead acid

Electrical Vehicles

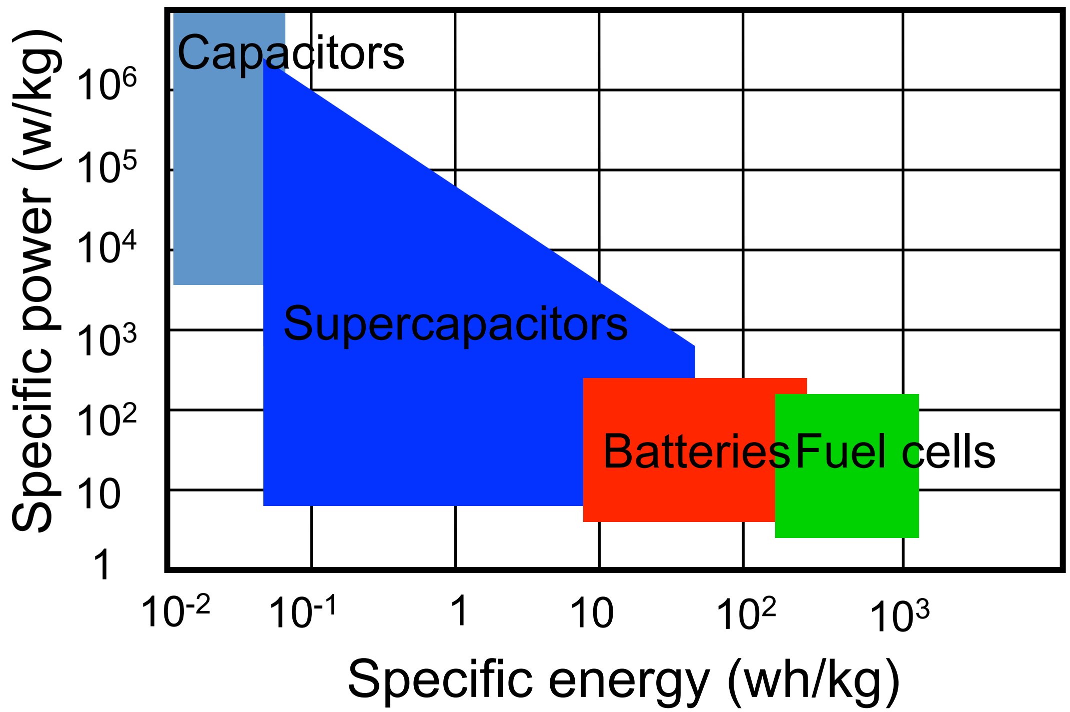
25-30% CO_2 emission

Renewable Energy and Electric Grid



Toys

Comparison of Energy Storage Technologies



Important parameters:

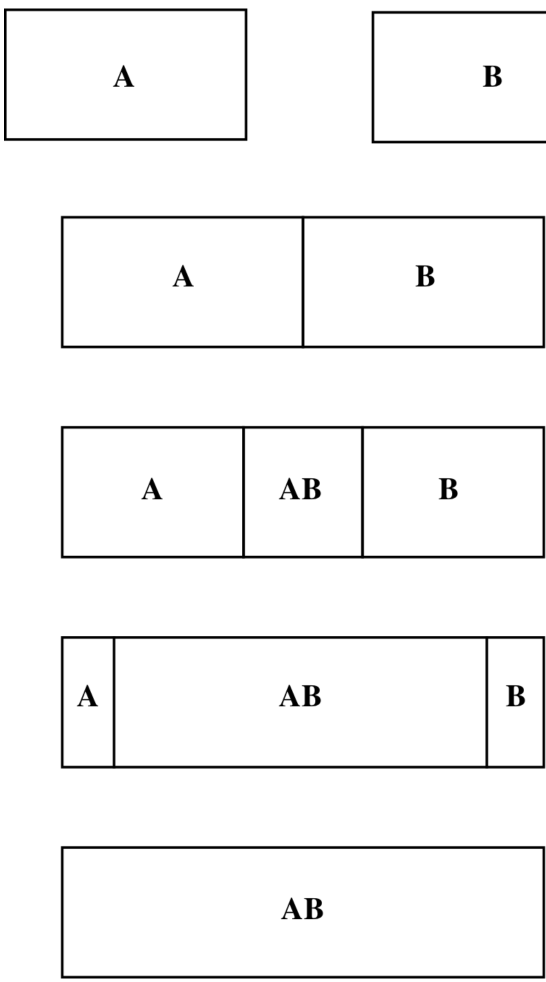
- Energy density (volume); Specific Energy (weight)
- Power density; Specific power
- Cycle life, calendar life
- Safety
- Cost

Chemical Reaction to Electrochemical Cell

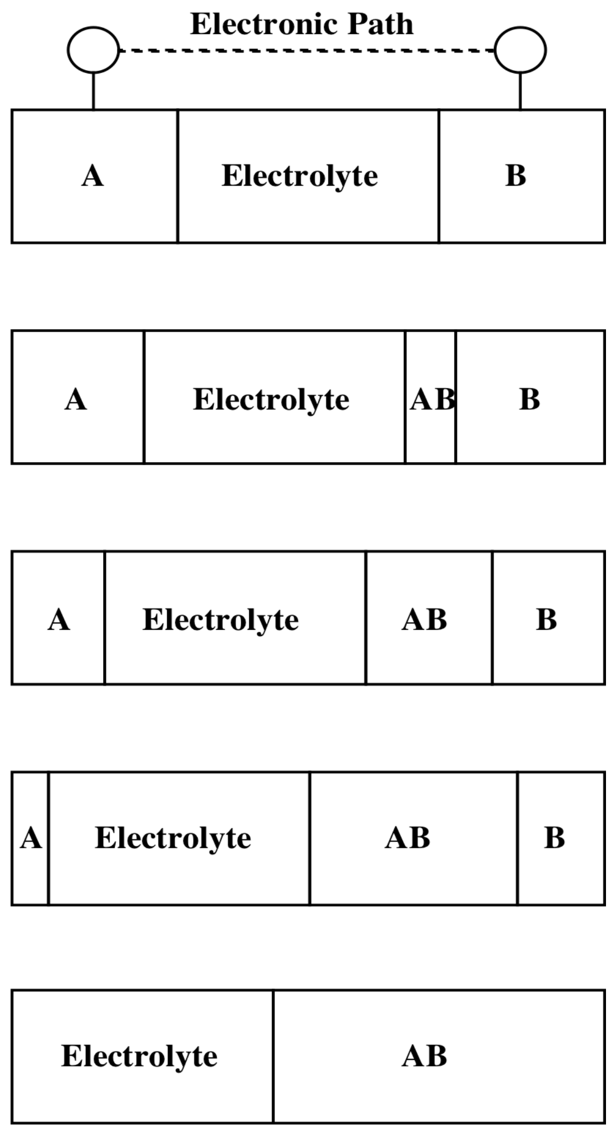
Chemical Reaction

$$A + B \xrightarrow{\Delta G} AB$$

Free energy becomes heat



Electrochemical Cell



$$A + B \xrightarrow{\Delta G} AB$$

$$1) A \longrightarrow A^{+} + e^{-}$$

$$2) B + A^{+} + e^{-} \longrightarrow AB$$

$$\Delta G = -nFE$$

E Voltage

F Faraday constant

n moles of electrons

(Advanced Batteries" R.A. Huggins)

High Energy Efficiency of Batteries

Batteries

$$w_{electrical} = -\Delta G = -(\Delta H - T\Delta S) = -\Delta H(1 - \frac{T\Delta S}{\Delta H})$$

Heat Engine: Carnot efficiency

$$w_{thermal} = -\Delta H(\frac{T_h - T_c}{T_h})$$

For lead acid battery:

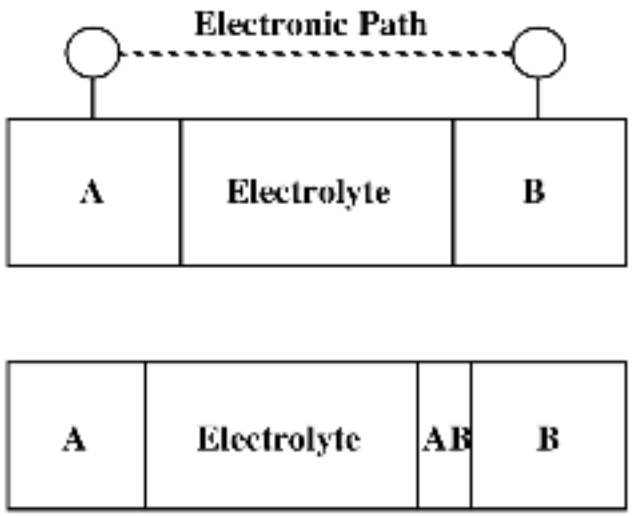
$$\Delta G = -377 kJ/mol, \Delta H = -228 kJ/mol, \Delta S = 502 J/Kmol$$

$$T_h = 600K, T_c = 300K$$

$$\frac{w_{electrical}}{w_{thermal}} = 3$$

Heat engines: ~30% energy efficiency.
Batteries: 90% energy efficiency.

Basic Requirements of Electrochemical Cells



$$A + B \xrightarrow{\Delta G} AB$$

$$1) A \longrightarrow A^{+} + e^{-}$$

$$2) B + A^{+} + e^{-} \longrightarrow AB$$

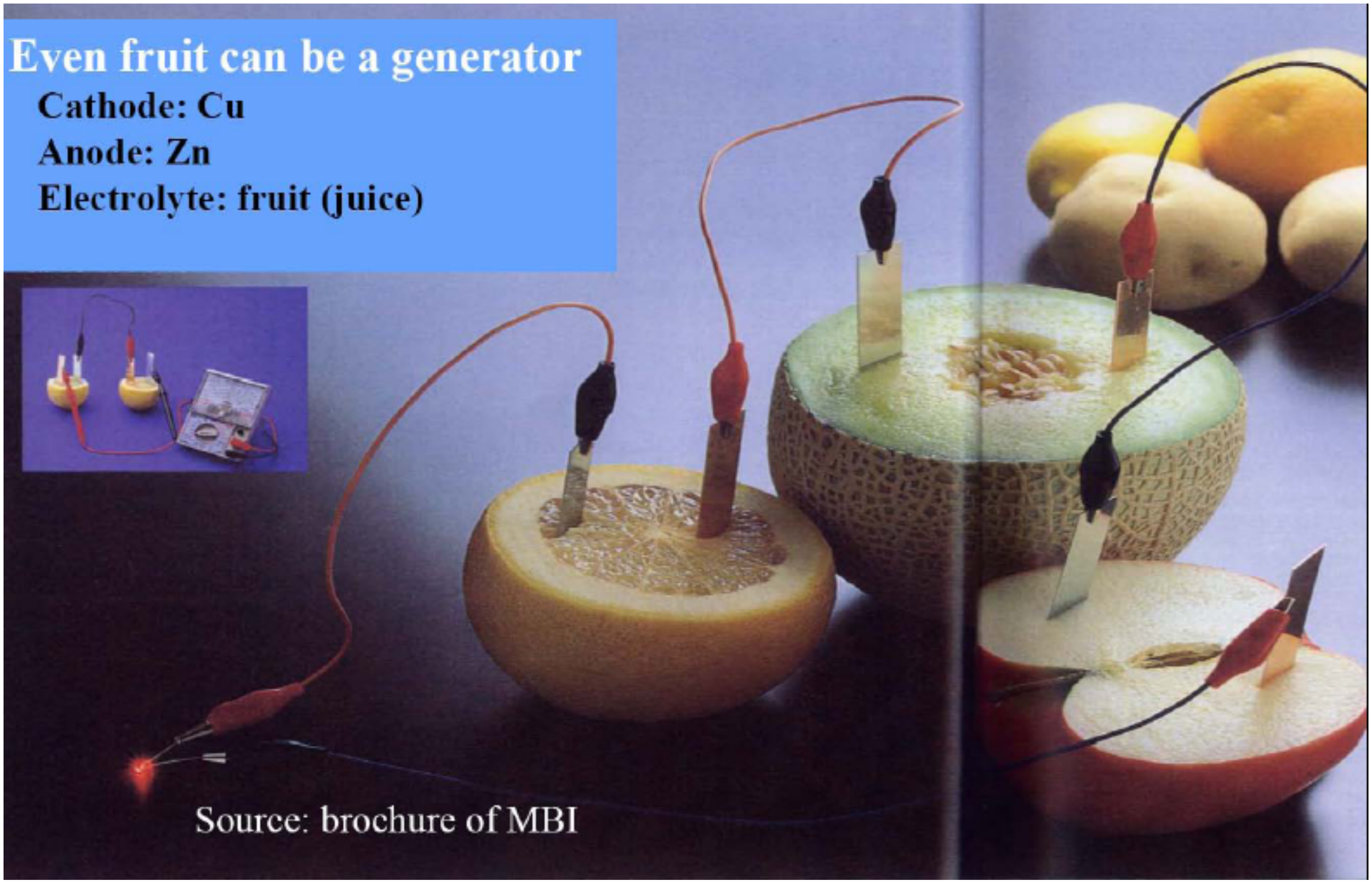
1) A and B have different ability in attracting electrons (electron negativity, electron affinity).

2) A and B is electronically conducting.

3) Electrolyte is electronically insulating and ionically conducting.

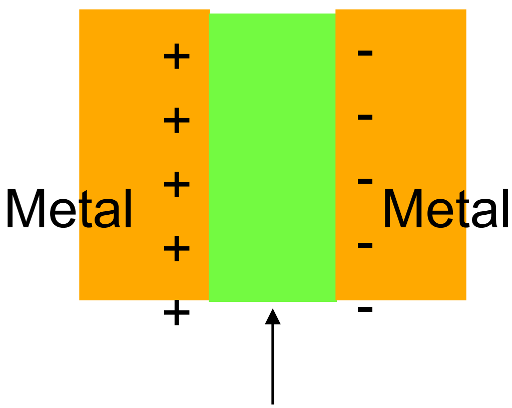
4) For rechargeable batteries, reaction should be reversible.

Fruit Batteries



Energy Storage Mechanisms

Capacitor

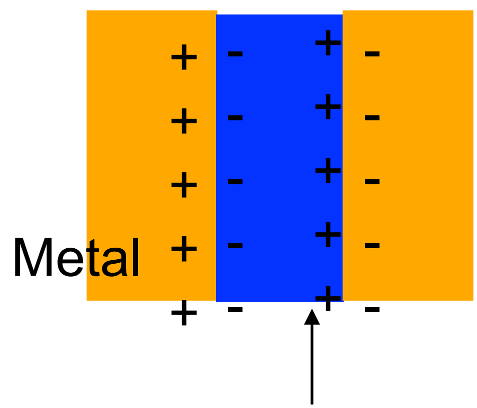


$$E = \frac{1}{2} C V^2$$

$$C \sim \frac{1}{thickness}$$

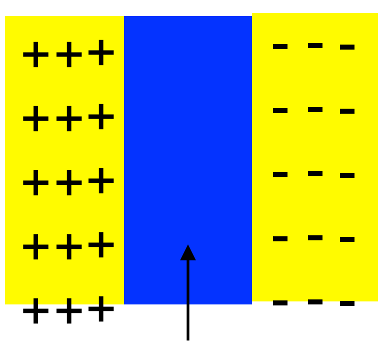
Dielectrics, thickness: >1000nm.

Ultracapacitor



Electrolyte solution
Double layer thickness, <1nm

Battery



Electrolyte solution

Capacitors and supercapacitor: surface storage.
Battery: bulk storage, can store a lot more.

Theoretical Specific Energy of Batteries

Full cell

$$A + B \xrightarrow{\Delta G} AB$$

We can calculate the maximum theoretical specific energy (energy/weight)

$$\frac{\Delta G}{\text{Reactant weights}}$$

$$C_6 + 2LiCoO_2 \xrightarrow{\Delta G} LiC_6 + 2Li_{0.5}CoO_2$$

$$\Delta G = 357 kJ/mol$$

$$E = 3.7V$$

Weight = molar wt of C_6 plus wt of 2 mole of $LiCoO_2$

= 72 + 195.8 = 267.8 g/mol electron of reaction

(We do not consider the dead weight: electrolyte, metal electrode current collector etc.)

Theoretic specific energy = (357) / (267.8) = 1.333 kJ/g = 370 Watt-hours/kg

The unit "Watt-hours" is often used in discussions of the energy content of batteries.

Theoretical Specific Energy of Batteries

$$\frac{\Delta G}{\text{Reactant weights}} = \frac{-nFE}{\text{Reactant weights}} = \frac{Q}{\text{Reactant weights}} E$$

To look for high specific energy, you need:
- Large free energy
- Light weight materials

To look for high specific energy, you need:
- High voltage
- High specific charge storage capacity (light weight to store much charges).

Usually we define specific charge storage capacity of single materials:
$LiCoO_2$: 0.5 mole electrons per molar weight.

$$\frac{0.5mol \times 96485Coulomb/mol}{97.9g} = 150mAh/g$$

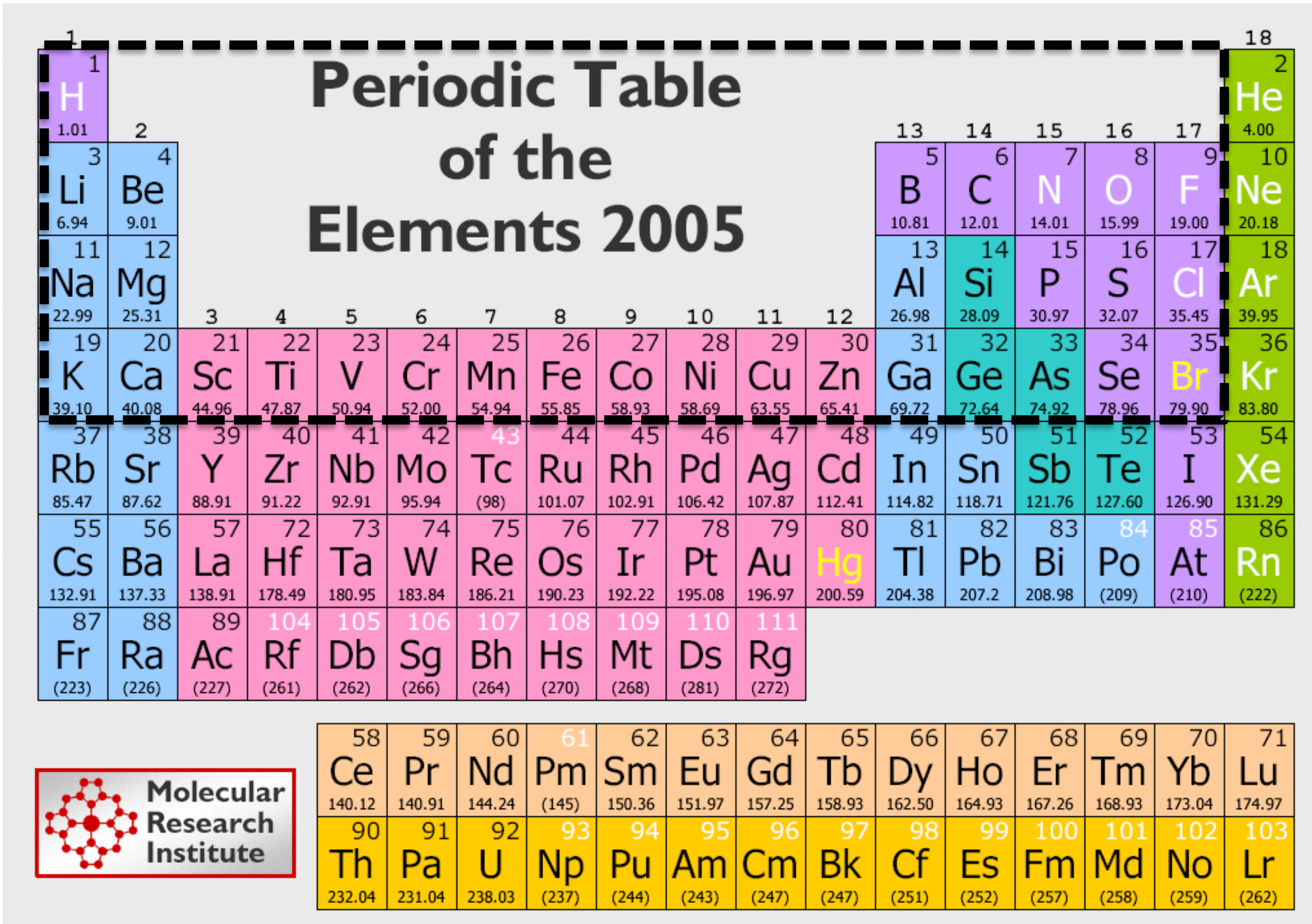
TABLE 18.1 Standard Reduction Potentials at 25°C

Stronger oxidizing agent ↑ — Weaker reducing agent ↓

Reduction Half-Reaction		E° (V)
$F_2(g) + 2e^-$	$\longrightarrow 2F(aq)$	2.87
$H_2O_2(aq) + 2H^+(aq) + 2e^-$	$\longrightarrow 2H_2O(l)$	1.78
$MnO_4^-(aq) + 8H^+(aq) + 5e^-$	$\longrightarrow Mn^{2+}(aq) + 4H_2O(l)$	1.51
$Cl_2(g) + 2e^-$	$\longrightarrow 2Cl^-(aq)$	1.36
$Cr_2O_7^{2-}(aq) + 14H^+(aq) + 6e^-$	$\longrightarrow 2Cr^{3+}(aq) + 7H_2O(l)$	1.33
$O_2(g) + 4H^+(aq) + 4e^-$	$\longrightarrow 2H_2O(l)$	1.23
$Br_2(l) + 2e^-$	$\longrightarrow 2Br^-(aq)$	1.09
$Ag^+(aq) + e^-$	$\longrightarrow Ag(s)$	0.80
$Fe^{3+}(aq) + e^-$	$\longrightarrow Fe^{2+}(aq)$	0.77
$O_2(g) + 2H^+(aq) + 2e^-$	$\longrightarrow H_2O_2(aq)$	0.70
$I_2(s) + 2e^-$	$\longrightarrow 2I^-(aq)$	0.54
$O_2(g) + 2H_2O(l) + 4e^-$	$\longrightarrow 4OH^-(aq)$	0.40
$Cu^{2+}(aq) + 2e^-$	$\longrightarrow Cu(s)$	0.34
$Sn^{4+}(aq) + 2e^-$	$\longrightarrow Sn^{2+}(aq)$	0.15
$2H^+(aq) + 2e^-$	$\longrightarrow H_2(g)$	0
$Pb^{2+}(aq) + 2e^-$	$\longrightarrow Pb(s)$	−0.13
$Ni^{2+}(aq) + 2e^-$	$\longrightarrow Ni(s)$	−0.26
$Cd^{2+}(aq) + 2e^-$	$\longrightarrow Cd(s)$	−0.40
$Fe^{2+}(aq) + 2e^-$	$\longrightarrow Fe(s)$	−0.45
$Zn^{2+}(aq) + 2e^-$	$\longrightarrow Zn(s)$	−0.76
$2H_2O(l) + 2e^-$	$\longrightarrow H_2(g) + 2OH^-(aq)$	−0.83
$Al^{3+}(aq) + 3e^-$	$\longrightarrow Al(s)$	−1.66
$Mg^{2+}(aq) + 2e^-$	$\longrightarrow Mg(s)$	−2.37
$Na^+(aq) + e^-$	$\longrightarrow Na(s)$	−2.71
$Li^+(aq) + e^-$	$\longrightarrow Li(s)$	−3.04

Weaker oxidizing agent — Stronger reducing agent

Light weight

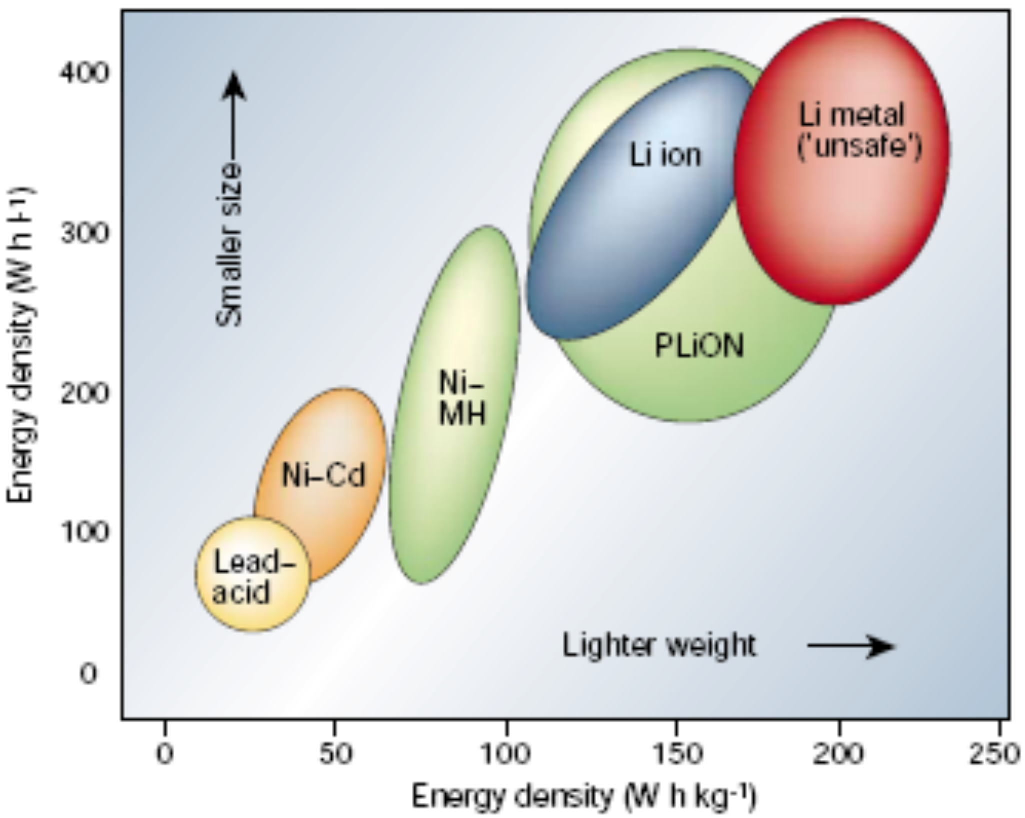


Comparison of Different Types of Batteries

Lead-acid batteries, invented in 1859 by French physicist Gaston Planté

$$PbO_2(s) + Pb(s) + 4H^+(aq) + 2SO_4^{2-}(aq) \leftrightarrow 2PbSO_4(s) + 2H_2O(l), E^0 = +2.04V$$

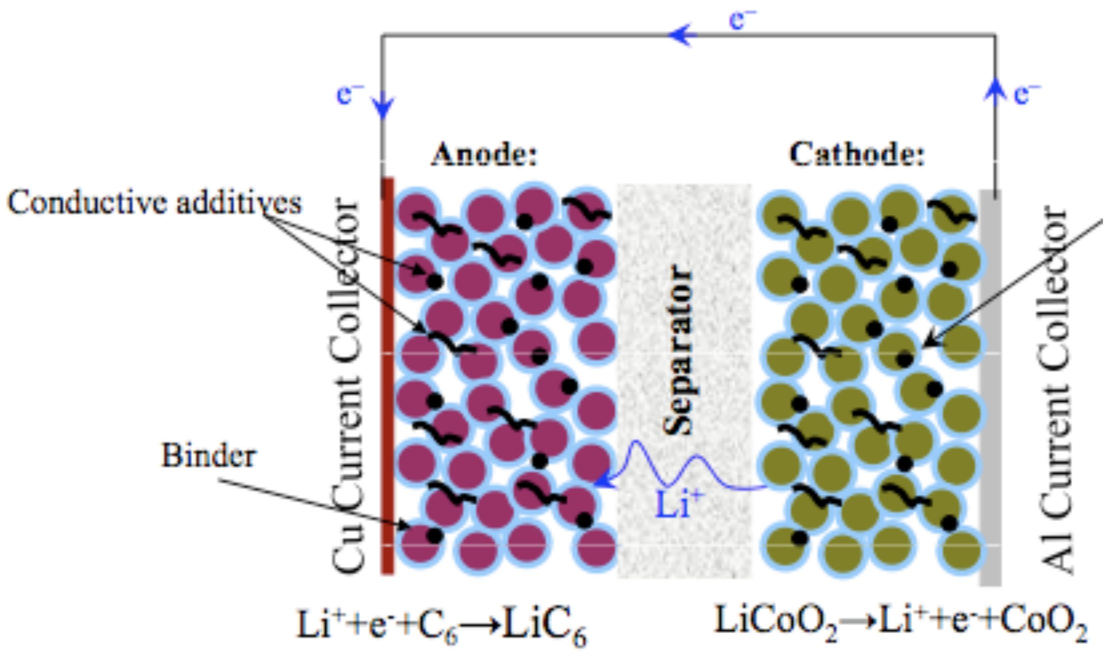
Pb is too heavy (Atomic weight: 207) compared to Co (Atomic weight: 58.9)

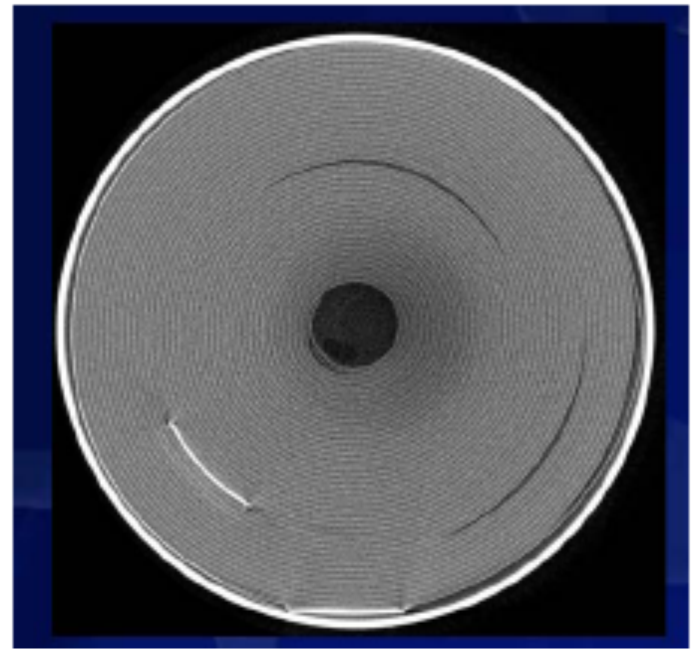


Car Battery

J.-M. Tarascon & M. Armand. Nature. 414, 359 (2001).

Li Ion Batteries

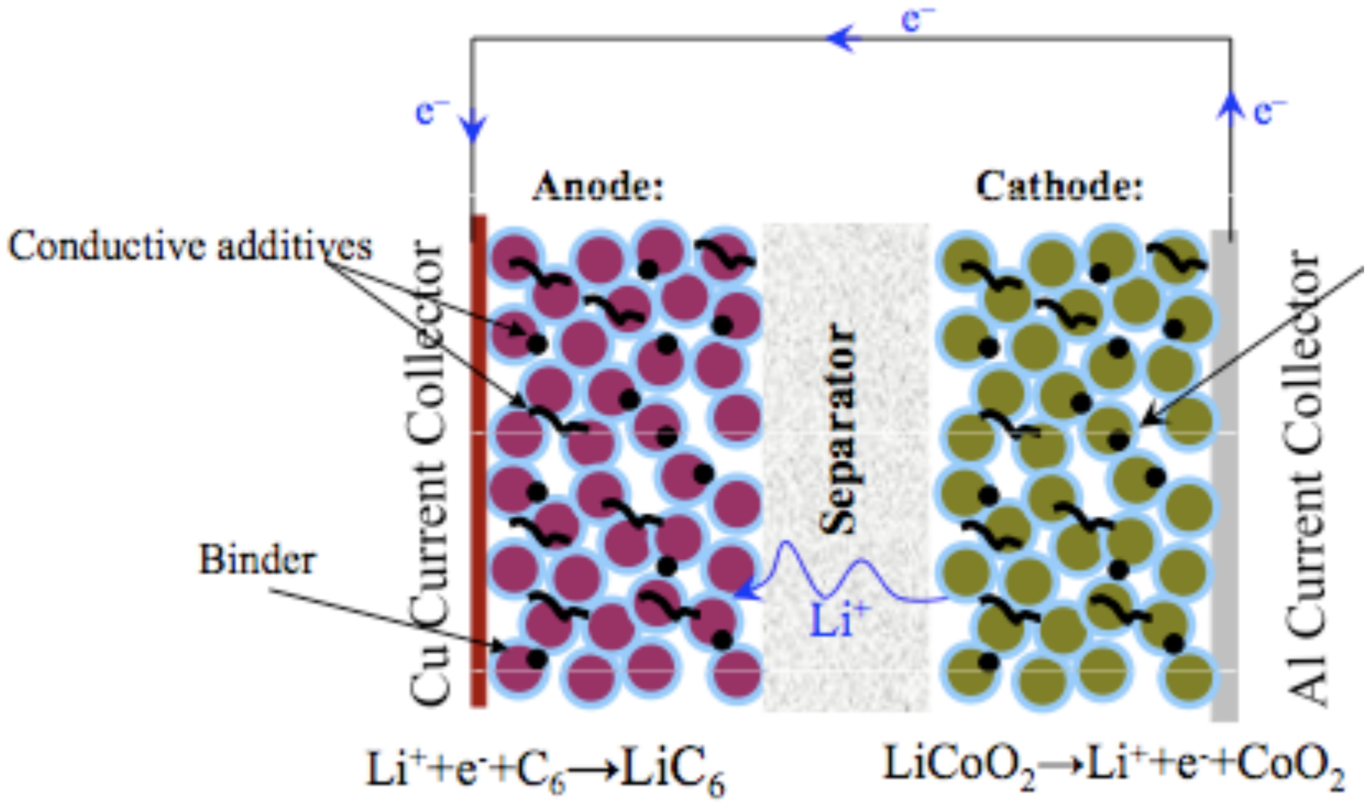




(Courtesy of Venkat Srinivasan)

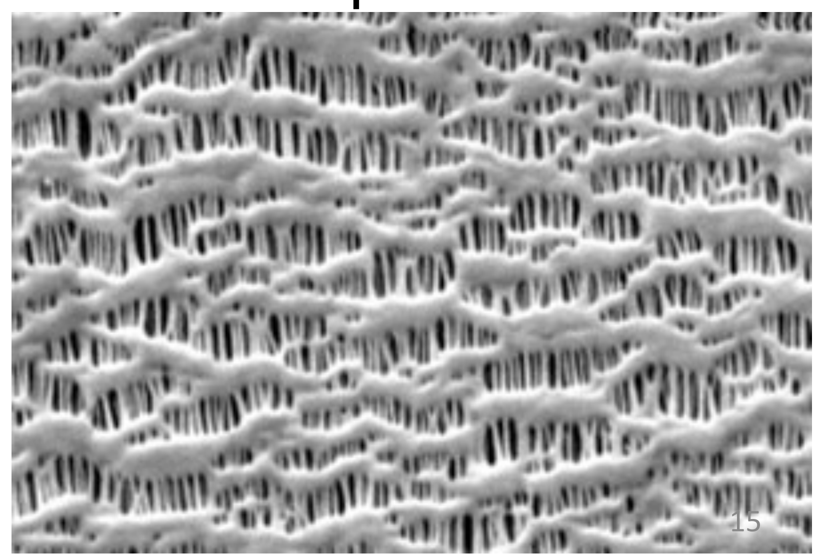
Basic requirements:

- Electron and ion conduction in electrode materials.
- Ionic conduction and electron insulation in electrolyte.

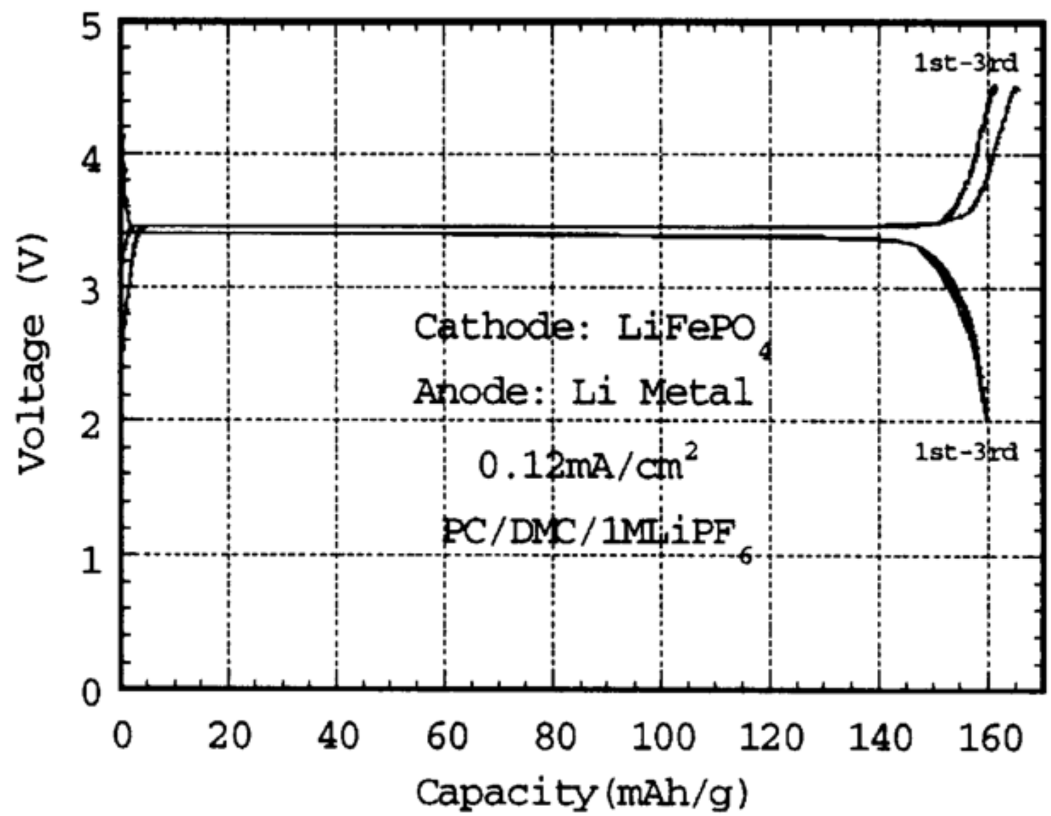


Battery components:
- Metal foil: current collector
- Anode and cathode particles
- Binder: polymer
- Conducting carbon particles
- Separator: polymer
- Electrolyte: organic and salt
- Additives

Separator



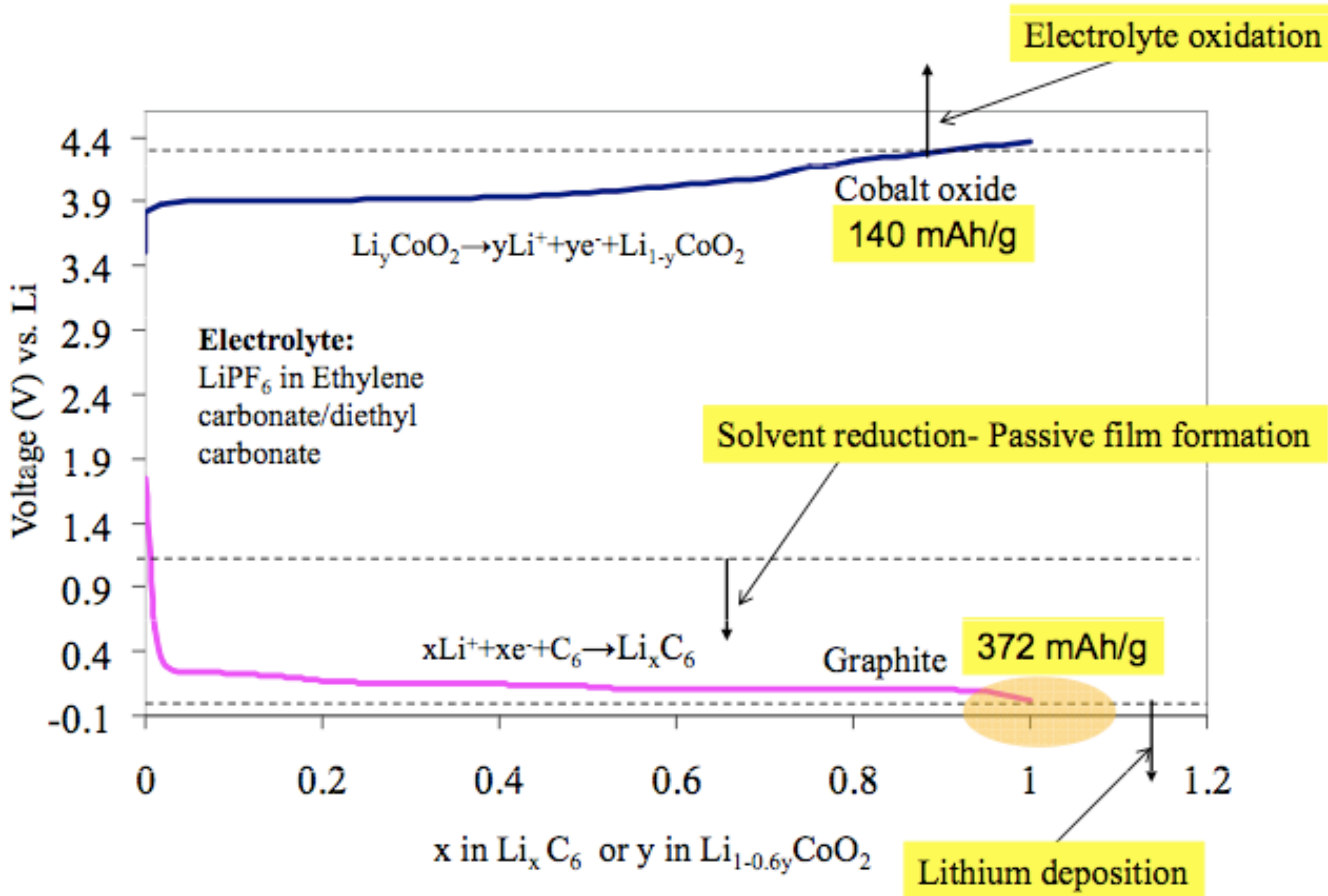
Charge/discharge method:
Constant current charge/discharge and monitor voltage over time.



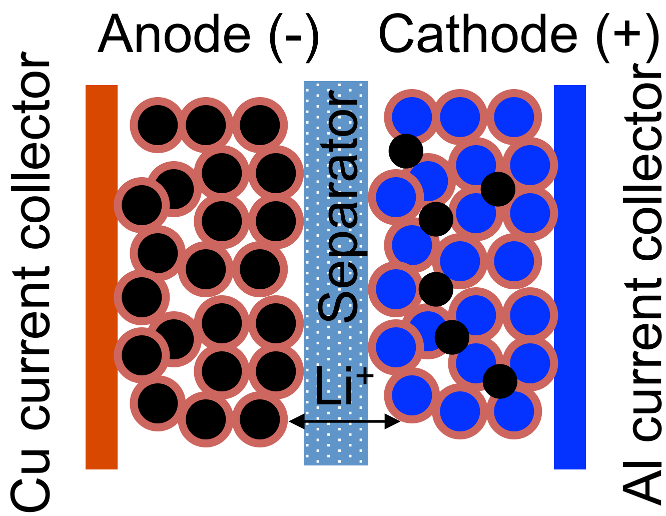
C rate:

1C is one hour charge/discharge.
C/2 is two hour charge/discharge
2C is half an hour charge/discharge.

Chemical Processes in Battery Charging



(Courtesy of Venkat Srinivasan)



Specific Energy (Energy Density): defined by electrode materials chemistry.

Specific Power (Power Density): ions and electrons insertion rate.

Cycle life: 300 cycles for electronics, 3000 cycles for electric cars.

Coulombic efficiency: charge out/charge in.

for example: need 99.99% for 3000 cycles with 74% capacity retention.

Safety: shorting, oxygen release, thermal runaway.

Calendar life: 3 yr for electronics, 10 yr for electric cars.

Cost

Electrode Materials in Existing Li Ion Batteries

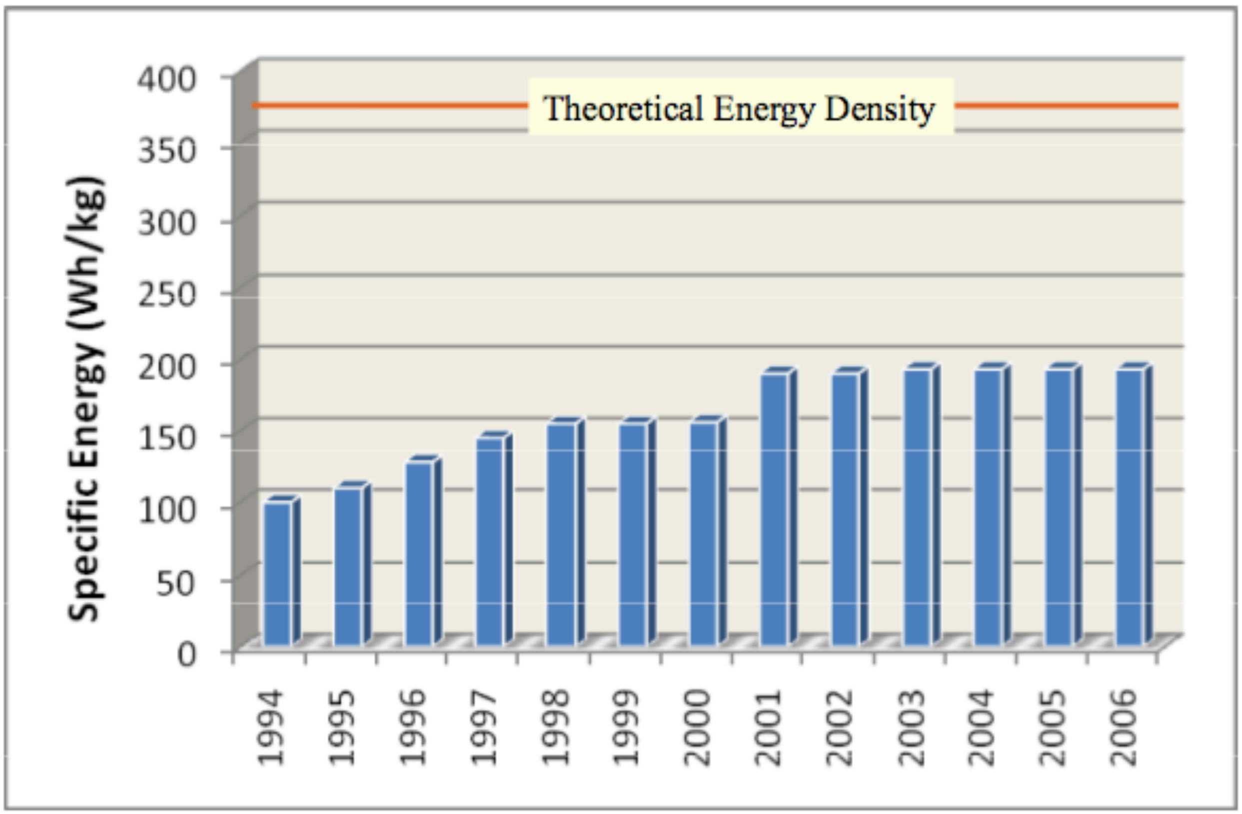
Electrode materials determine the energy density.

Anode materials

Graphite: 370 mAh/g

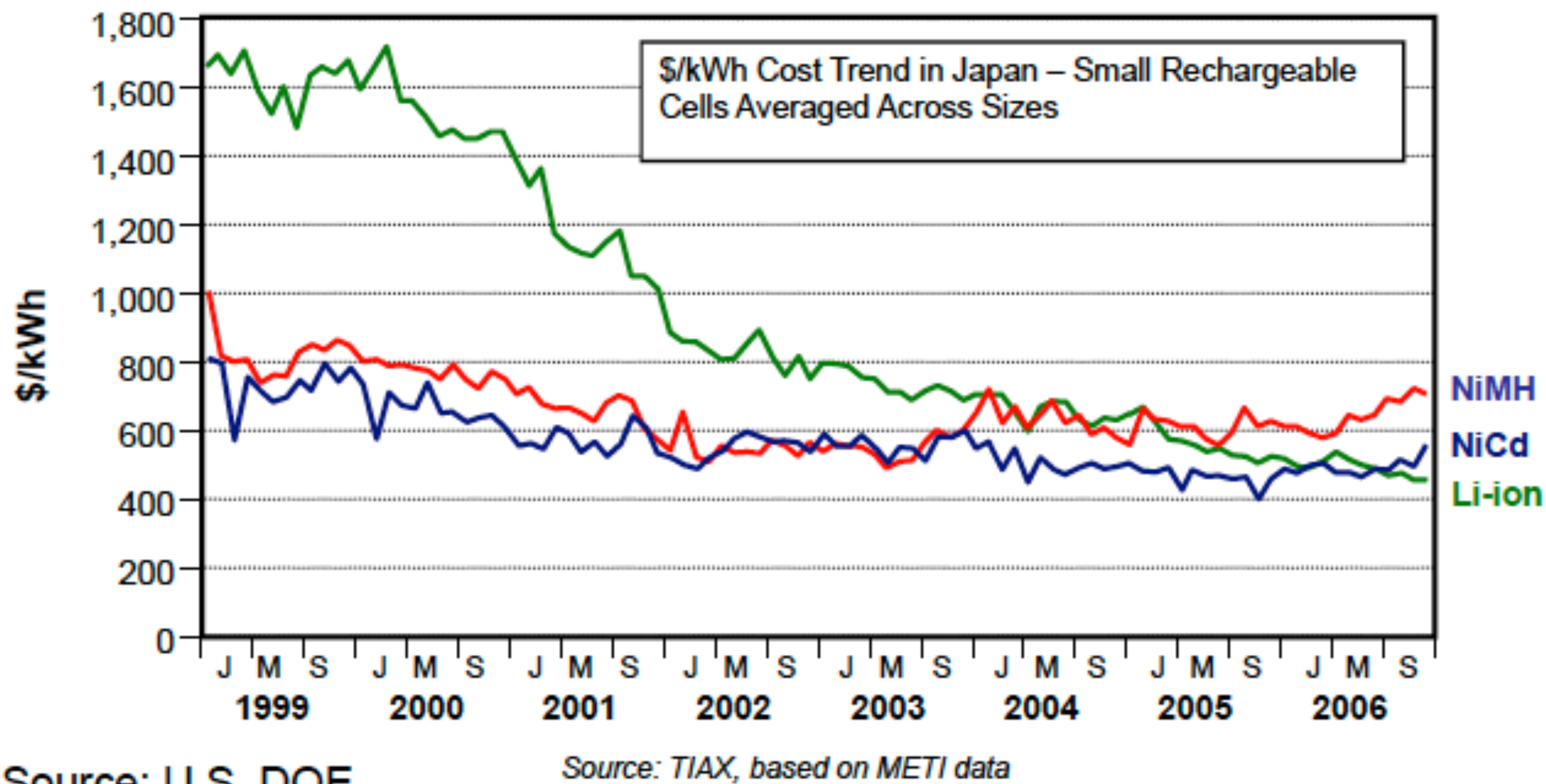
Cathode Materials

$LiCoO_2$	150 mAh/g, 3.7V
$LiMn_2O_4$	140 mAh/g, 3.9V
$LiFePO_4$	170 mAh/g, 3.4V



Source: TIAX, LLC

Price of Li Ion Batteries



Source: U.S. DOE

The price is too high for vehicles and large scale energy storage.

High Energy Batteries

Low-cost and large scale batteries

Electrode Materials in Existing Li Ion Batteries

Electrode materials determine the energy density.

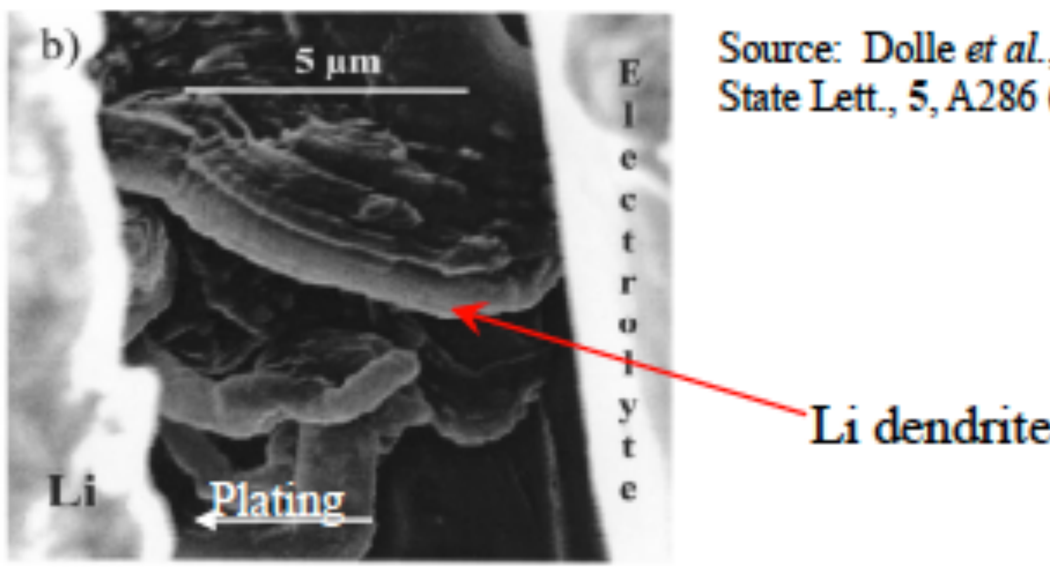
Anode materials
Graphite: 370 mAh/g

Cathode Materials
$LiCoO_2$ 150 mAh/g
$LiMn_2O_4$ 140 mAh/g
$LiFePO_4$ 170 mAh/g

Need new high capacity materials
Anode: Si, Sn etc., Li metal?
Cathode: Sulfur, air etc.

Lithium Metal Anodes

Lithium Dendrite formation



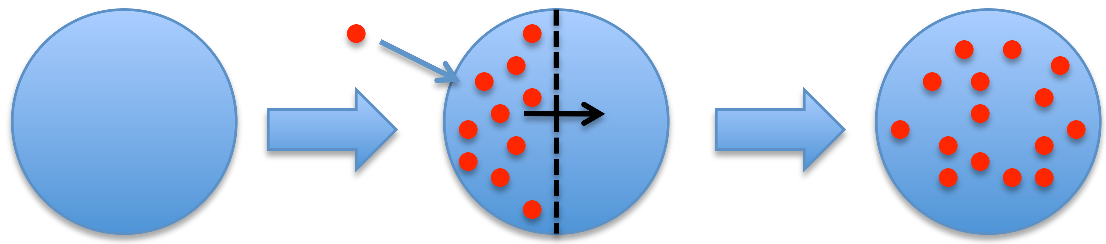
Source: Dolle *et al.*, Electrochem. Solid State Lett., 5, A286 (2002)

Challenges of Alloy Anodes

Existing anode materials

Graphite: 370 mAh/g

$C_6 \longleftrightarrow LiC_6$



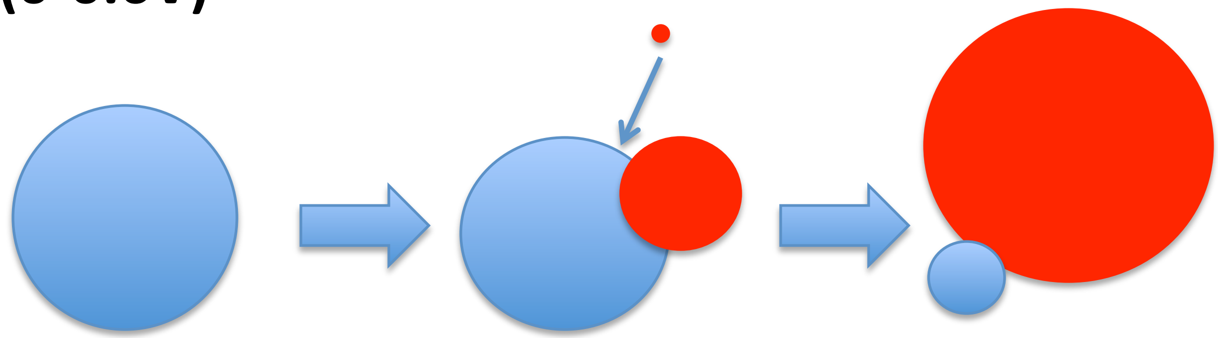
Little structure change, <10% volume expansion.

New anode materials (0-0.6V)

Si: 4200 mAh/g

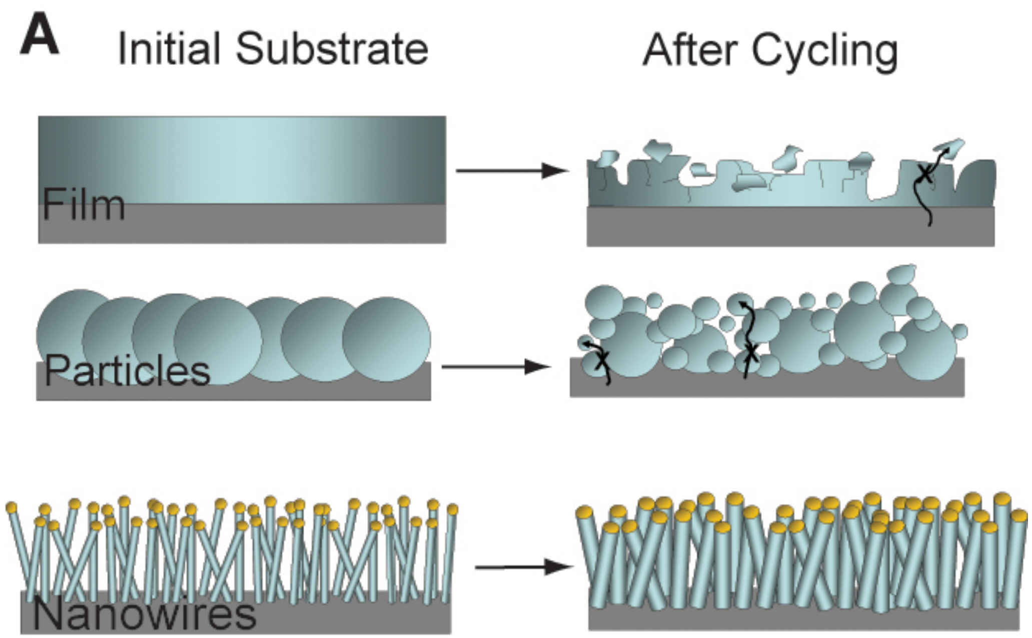
Sn: 1000 mAh/g

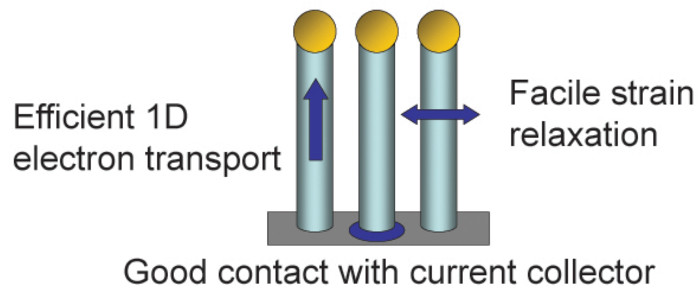
$Si \longleftrightarrow Li_{4.4}Si$



For Si: volume expansion by 300%.

Silicon Nanowires Anodes





C. K. Chan and Y. Cui, Nature Nanotechnology 3, 31 (2008).

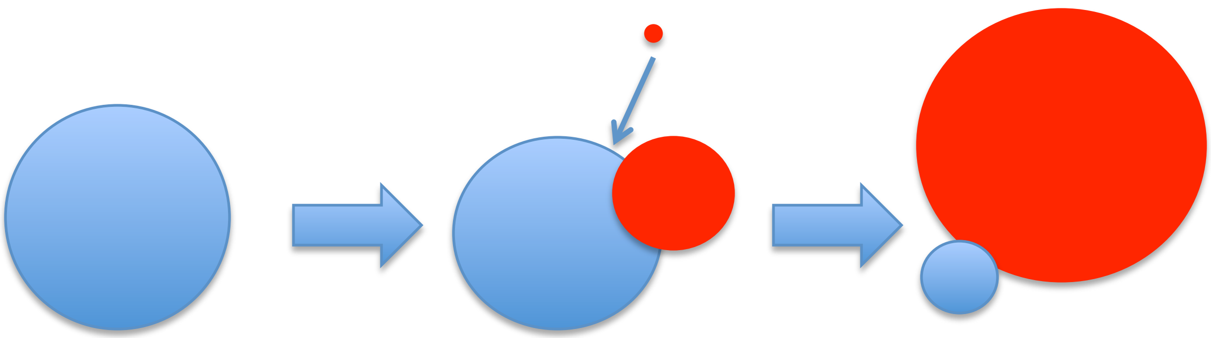
Sulfur Cathodes

Lithium metal-Sulfur batteries

$$2Li(s) + S(s) \longrightarrow Li_2S(s)$$

1700 mAh/g, 2.2V, 2600wh/kg.

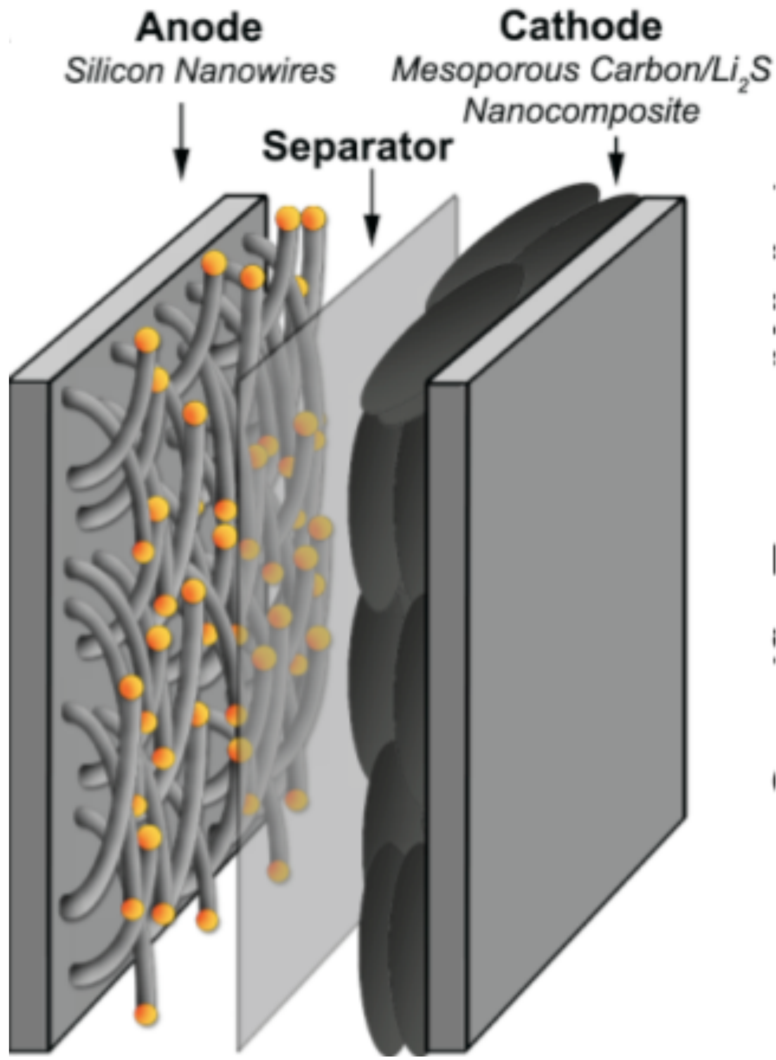
Two phase reaction



Challenges:

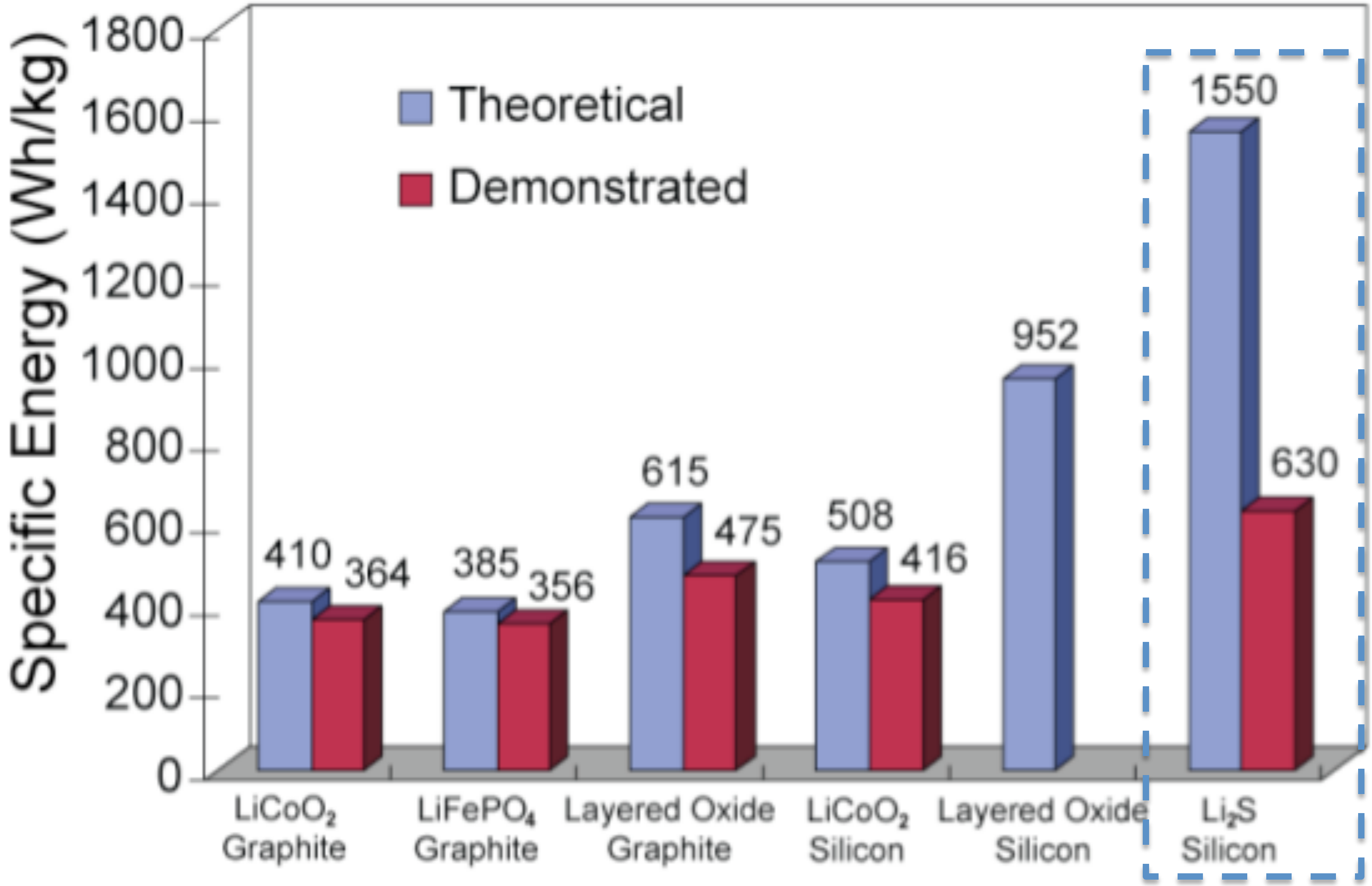
1) Large structure change and volume expansion.
2) S and Li_2S are electronically insulating
3) The intermediate phase (lithium polysulfide) is soluble in electrolyte.
4) Li metal is dangerous.

Si Nanowire Anodes and Li_2S Cathodes



Yuan Yang, Matt McDowell, Ariel Jackson and Y. Cui (Nano Letters, 2010)

Full Batteries: Si-Li_2S



Metal-air batteries

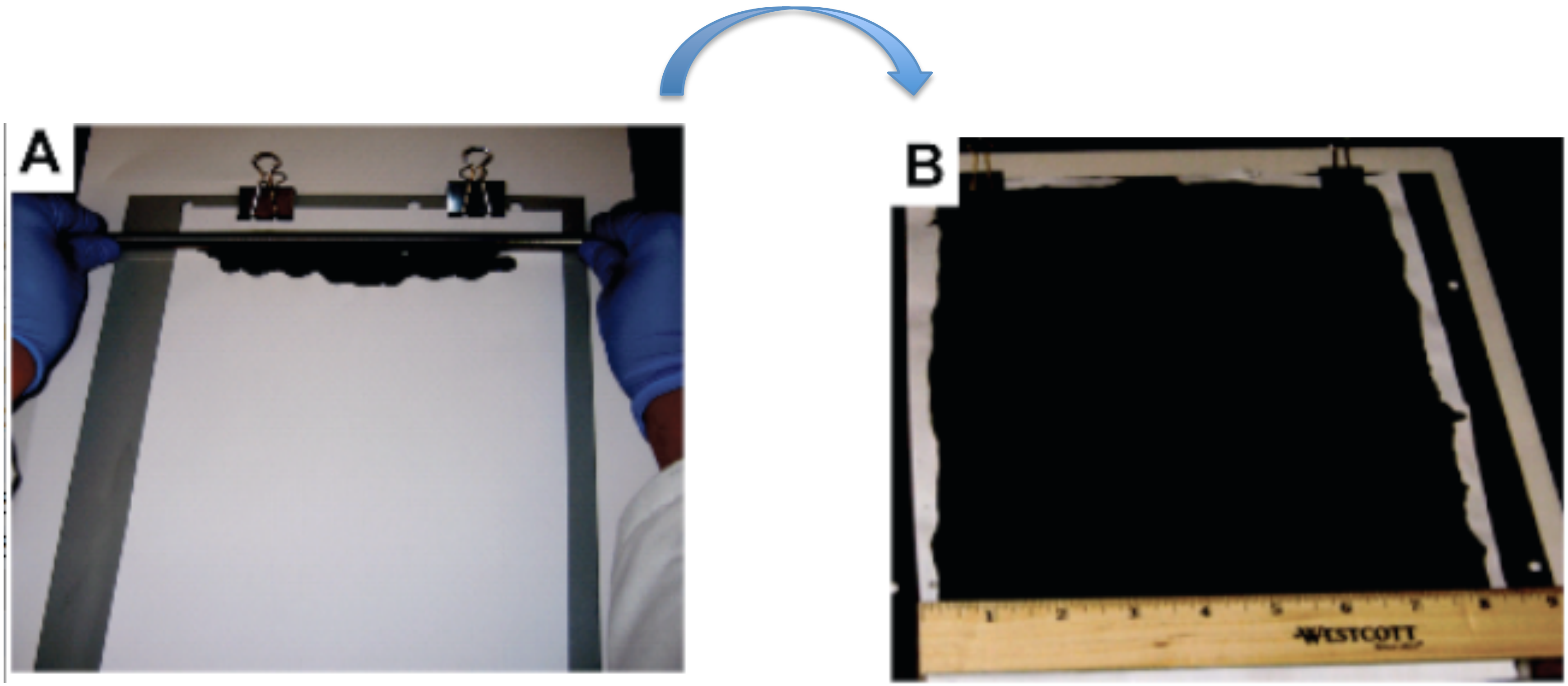
$4Li(s) + O_2(air) \longrightarrow 2Li_2O(s)$ 2.9V, 3500wh/kg. (9 times of current Li-ions)

$Zn(s) + O_2(air) \longrightarrow 2ZnO(s)$ 1.66V, ~1200wh/kg. (3 times of current Li-ions)

Low-cost Manufacturing of Batteries:
Using Paper and Textile Processing to Make Batteries

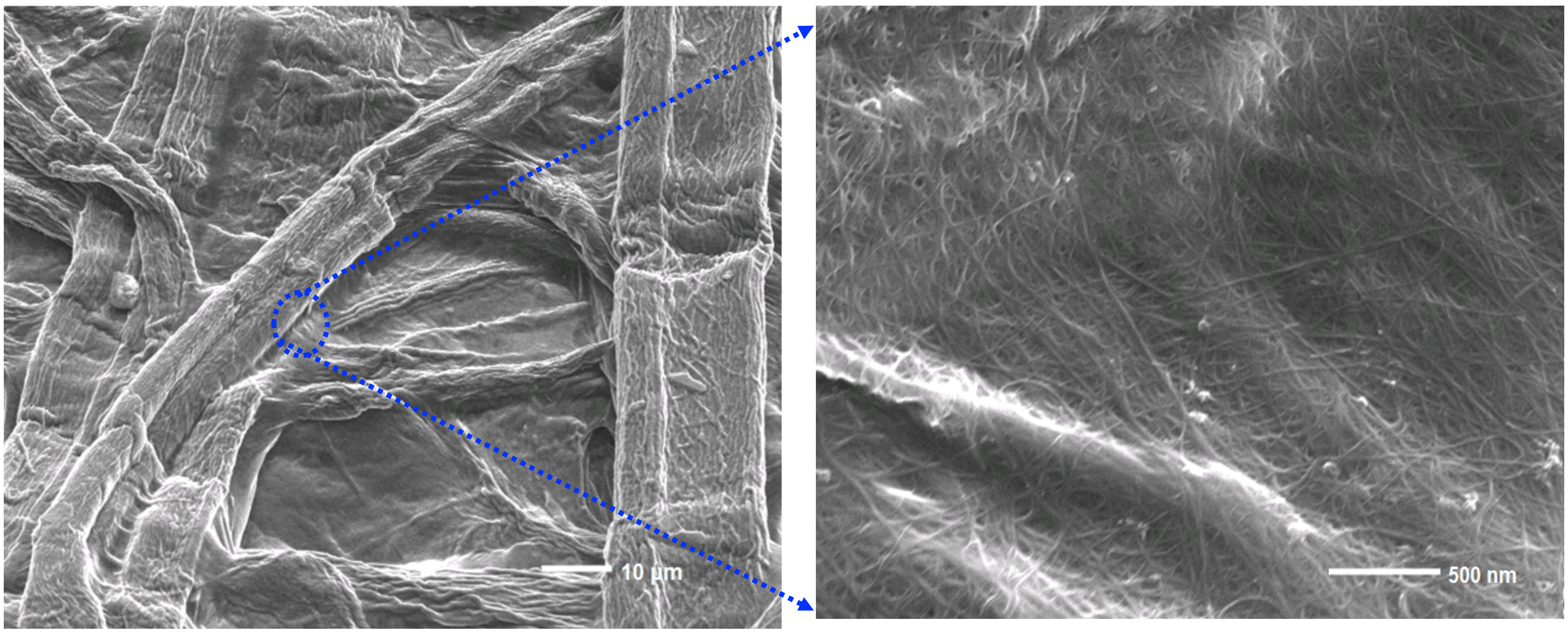
Turning Paper and Textile into Supercapacitors and Batteries for Large Scale Energy storage

Carbon nanotube and nanomaterials ink



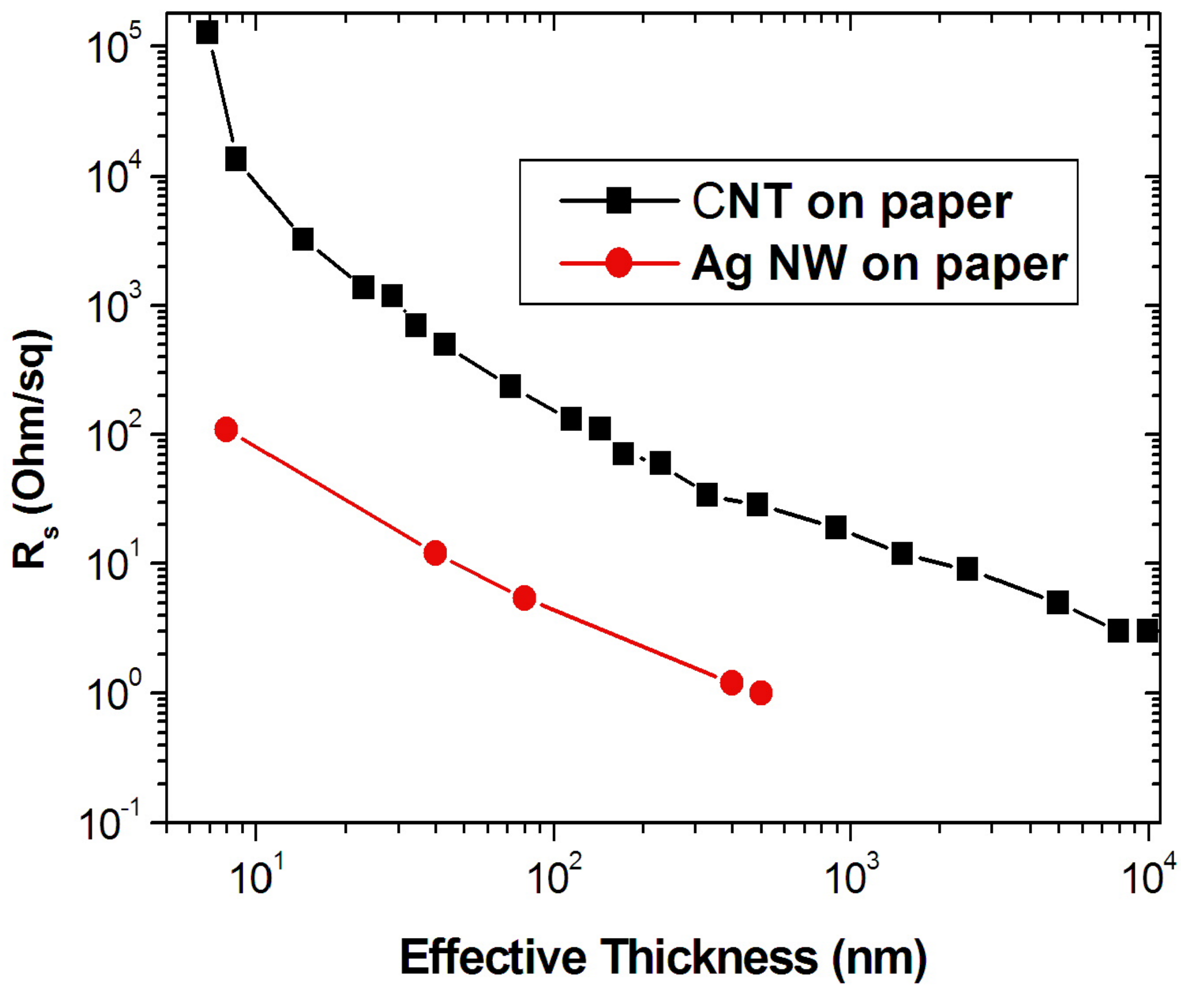
- L. Hu, J. W. Choi, Y. Yang, Y. Cui ***Proceedings of the National Academy of Science*** 106, 21490 (2010).
- L. Hu, Y. Cui, ***Nano Lett***., 10, 708 (2010).

Porous Paper and Textile with Nanomaterials



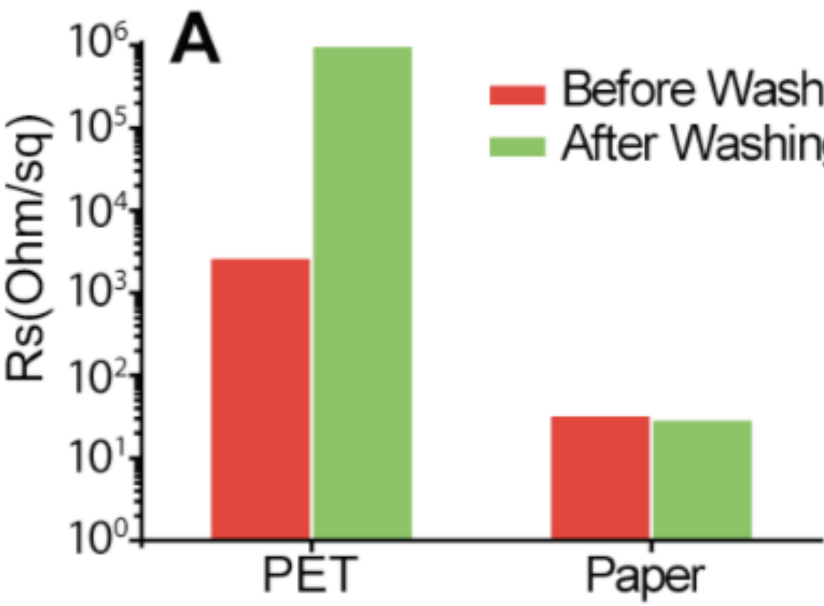
- Paper consist of 3D microfibers.
- Nanotubes can conformally coat onto paper.
- Porous structure allows the fast access of ions to nanotubes.

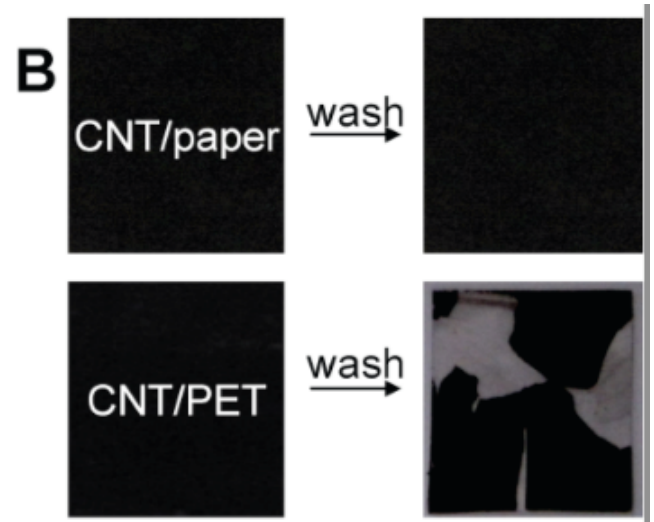
Highly Conductive Nanotube/Nanowire Paper



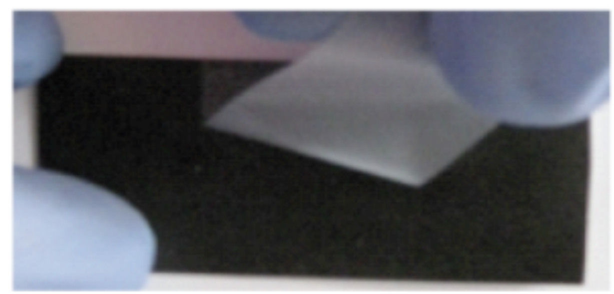
Outstanding Properties of Nanotube Paper

Strong adhesion

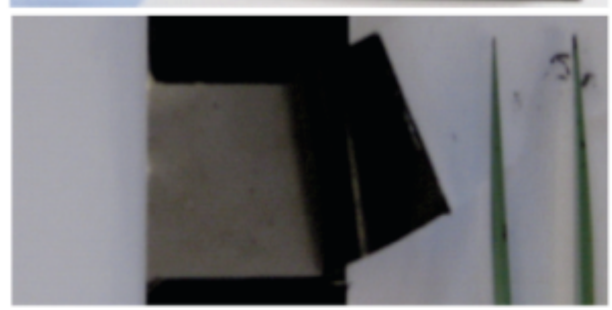




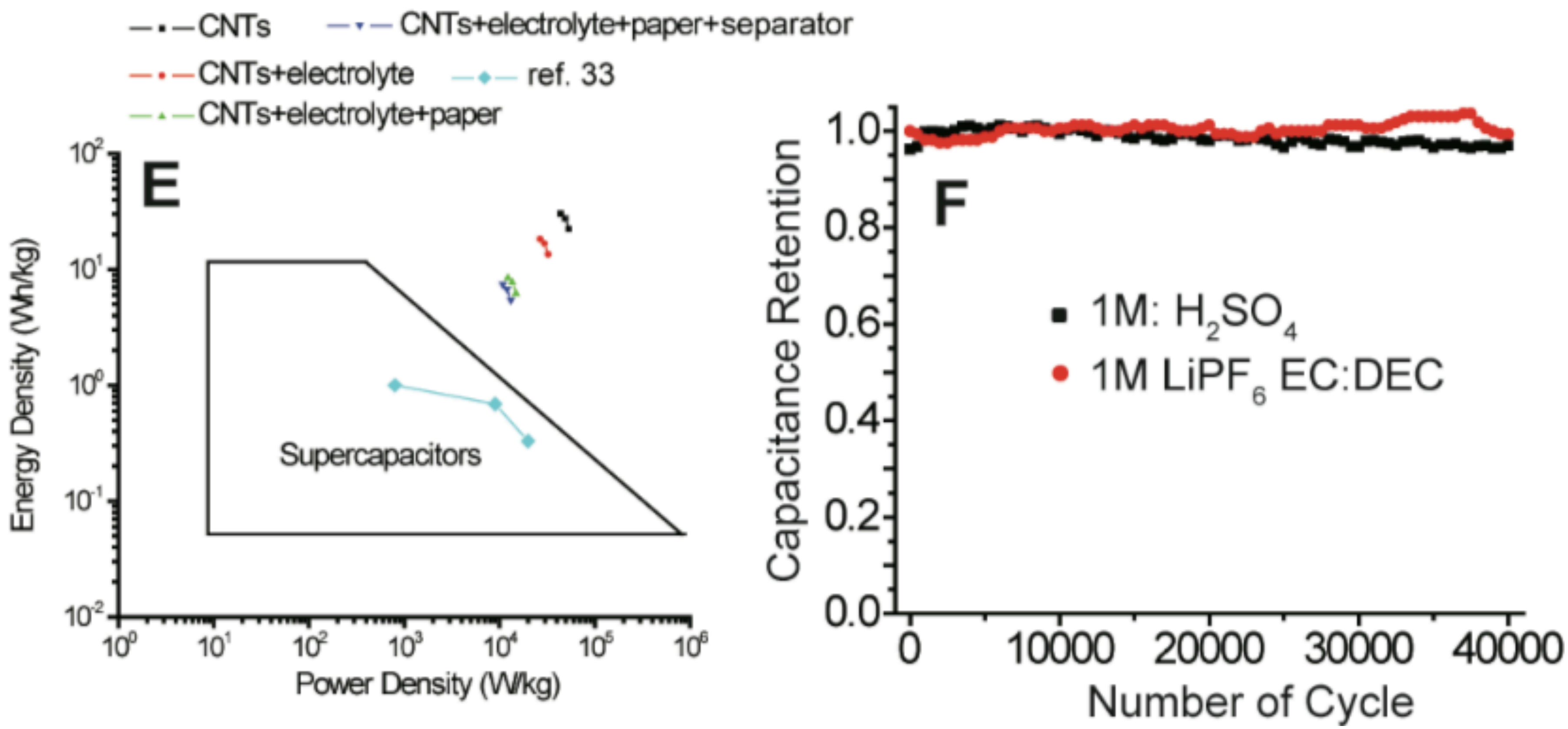
CNT/paper



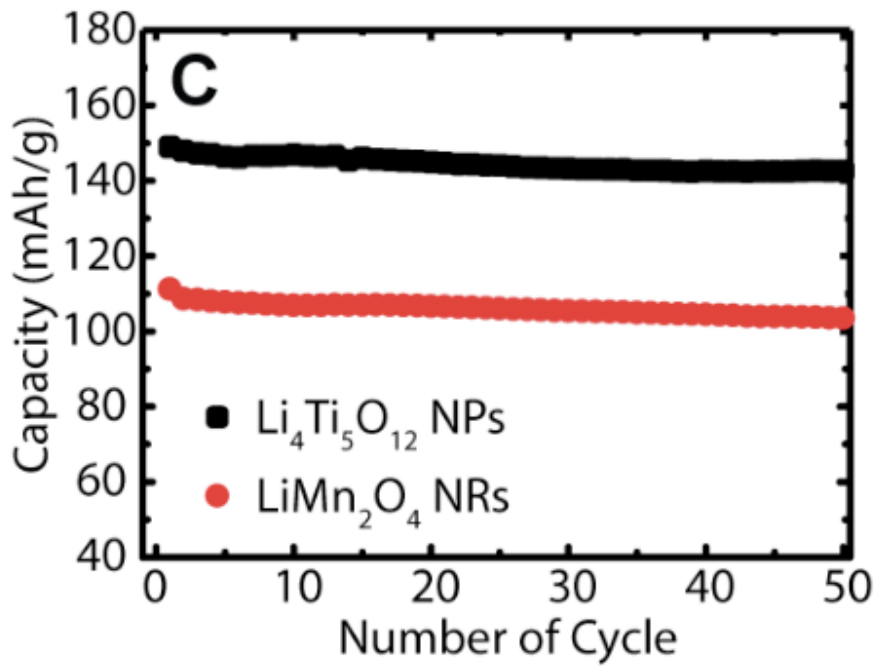
CNT/PET



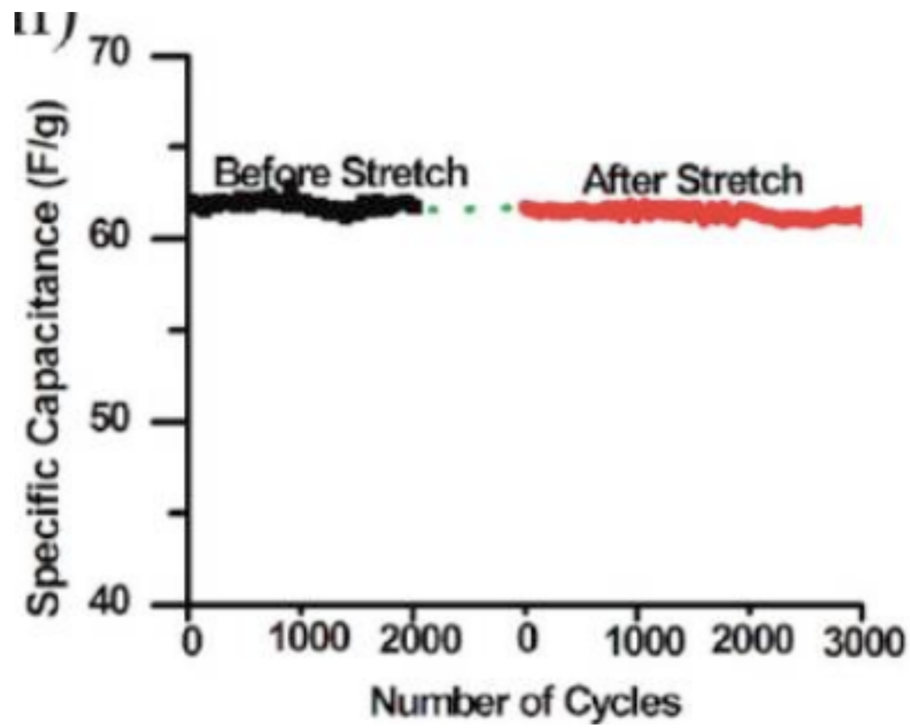
Excellent Performance of Paper Supercapacitors



Paper Batteries



Stretchable Textile Batteries



Different Types of Batteries (Solid, Liquid, Gas)

Battery Type	Negative Electrode	Electrolyte	Positive Electrode
Li ion	Solid Carbon	Liquid LiPF6 in carbonate solvent	Solid LiCoO2
Na-S (350C)	Liquid Na(molten)	Solid Beta Alumina	Liquid Sulfur (molten)
Thin film	Solid Carbon	Solid Lithium Phosphorous Oxynitride (LiPON)	Solid LiCoO2
Liquid metal (700C)	Liquid Metal (molten)	Liquid Salt (molten)	Liquid Metal (molten)
Lithium air	Solid Lithium	Liquid LiPF6 in carbonate solvent	Gas Oxgen (air)