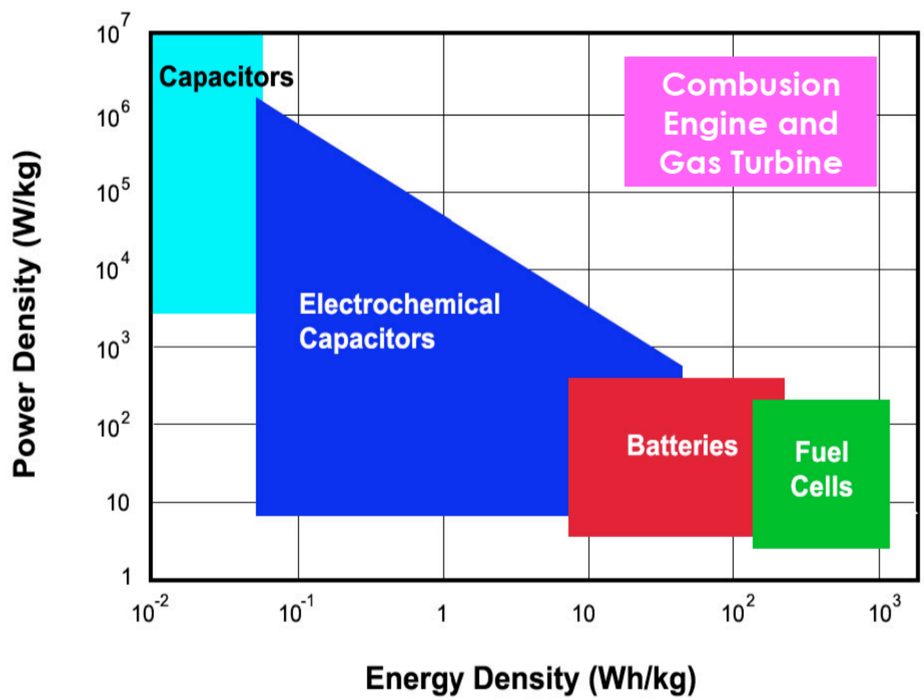
Two Major Types of Electrochemical-Based Energy Storage Devices

- **Batteries**
  - ❖ Store energy in chemical reactants capable of generating charge
  - ❖ High energy densities
  - ❖ Many different varieties

- **Electrochemical Capacitors**
  - ❖ Store energy as charge
  - ❖ High power densities
  - ❖ Sub-second response time



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Application for LIBs and Supercapacitors

- *Mobile Electronic Devices*
- *Power-Tools*
- *Electrical Vehicles (HEVs and PEVs)*

Ma, *Science*, 2013

Requirements

- **High Power for Intensity of Use**

❖ More positive redox potential (cathode)

❖ Fast charge transfer kinetics (large current output)

- **High Energy (High Capacity) for Length of Use**

❖ More charge per weight/volume

- **Safety**
- **Cost**

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Classifications of Cells and Batteries

Primary cells
- Not capable of being recharged electrically
- Good shelf life,
- high energy density at low to moderate discharge rate,
- No or little maintenance
- Ease of use

Secondary or rechargeable cells
- Can be recharged electrically
- High power density
- High discharge rate
- Flat discharge curve
- Good low temperature performance

Reserve batteries
- Primary type
- long term storage

Fuel cells
- Active material are fed into the cell from an external source
- Capable of producing electrical energy as long as the active materials are fed to the electrodes

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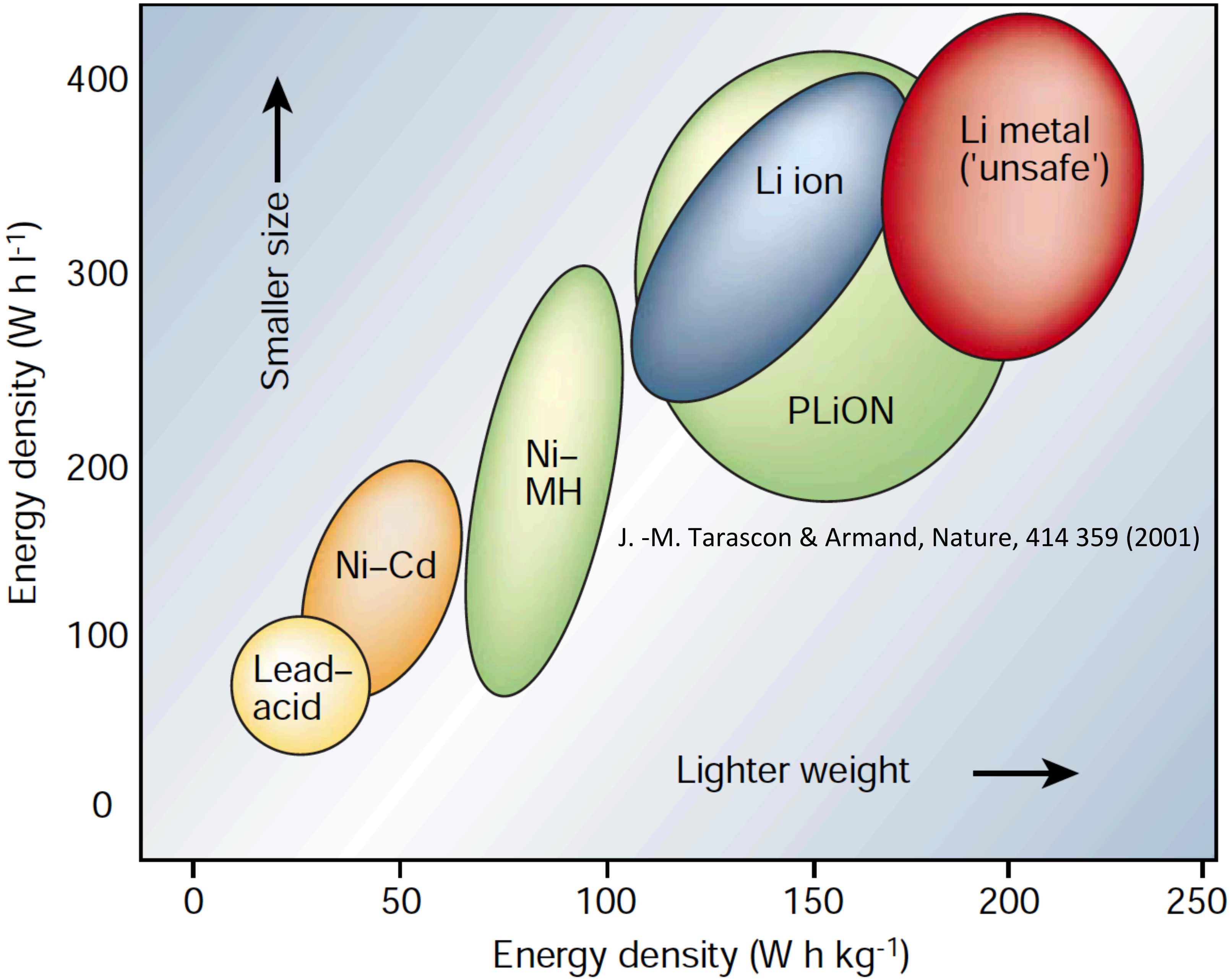
Energy Density for Secondary Batteries



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

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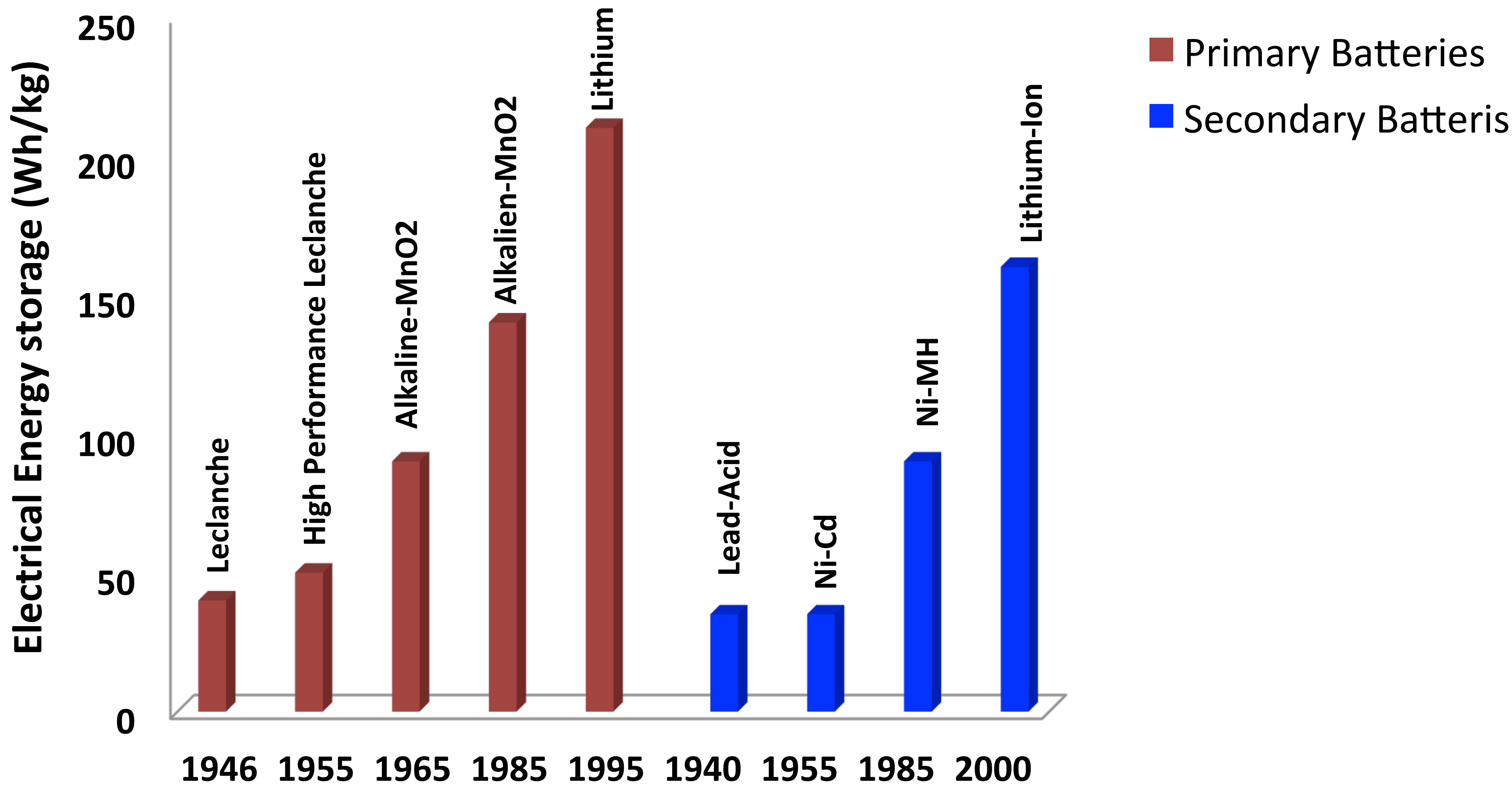
Battery Performance-Upper limits of Energy Density



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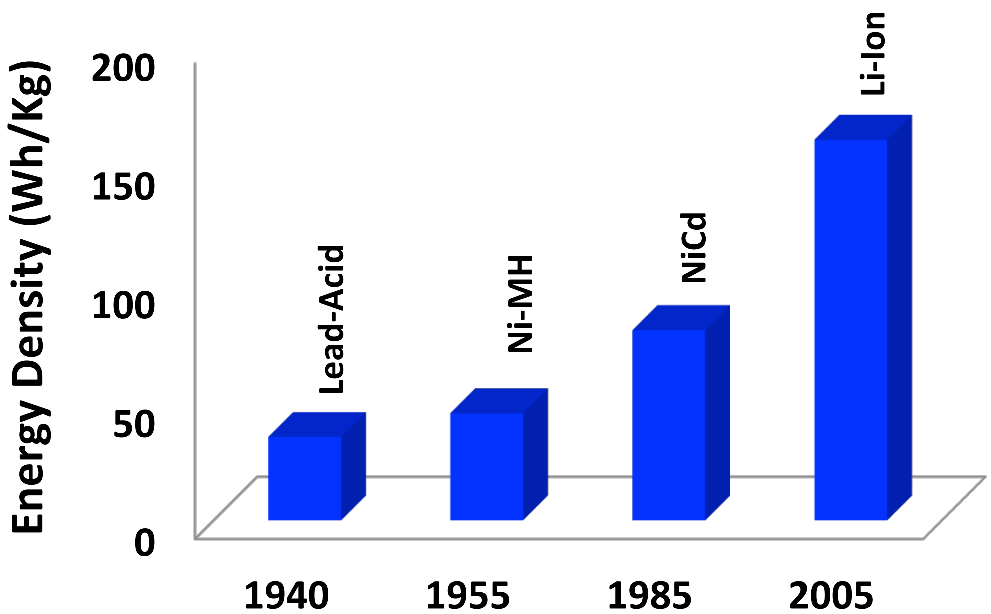
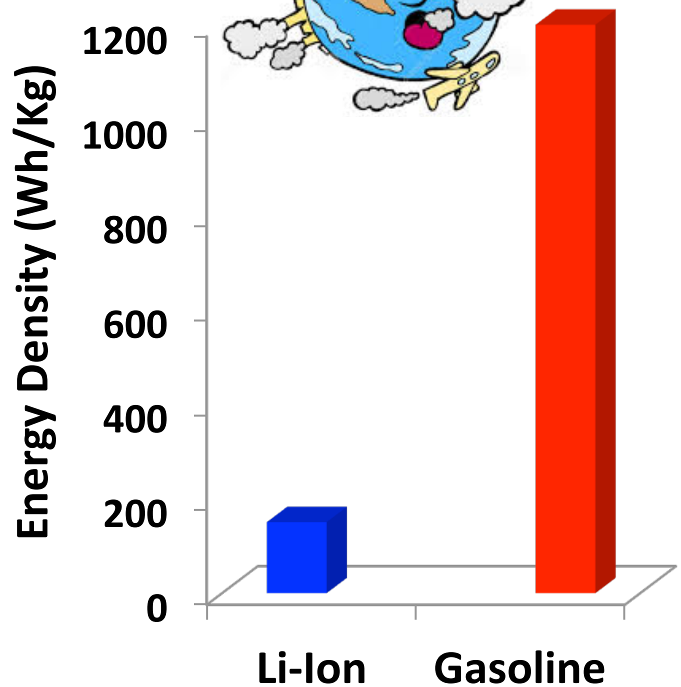
Batteries and Fuels

Rechargeable Batteries:

- High power density
- High discharge rate
- Flat discharge curve
- Good low temperature performance





1 Wh/kg ~ 1 mile driving range

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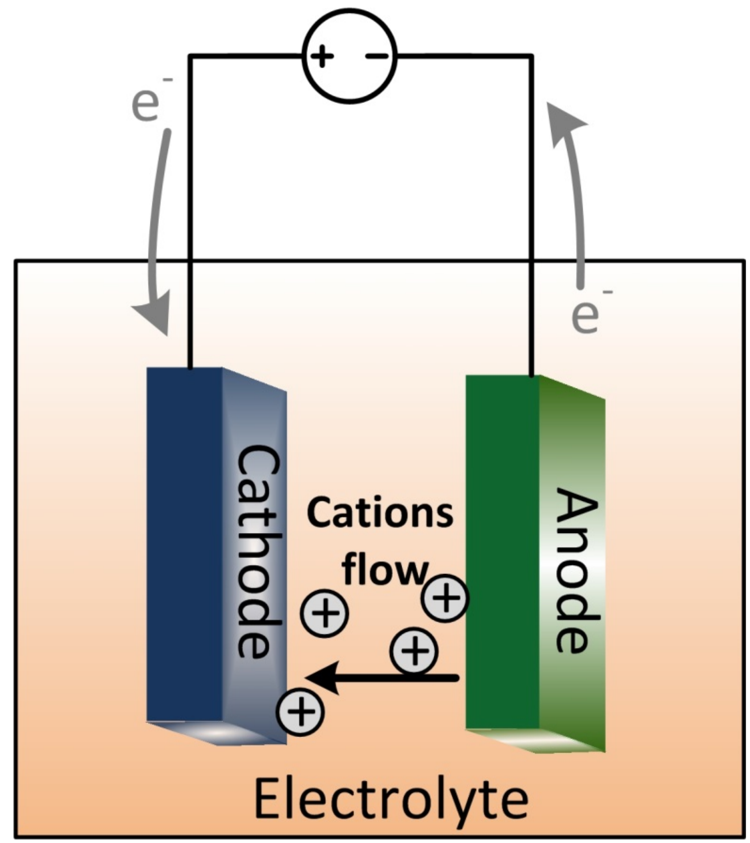
Batteries: Concept and Principle

Battery is a storage device which converts chemical energy into electrical energy

- Main components:
  - **Anode or negative electrode**
  - **Cathode or positive electrode**
  - **Electrolyte – flow of ions**



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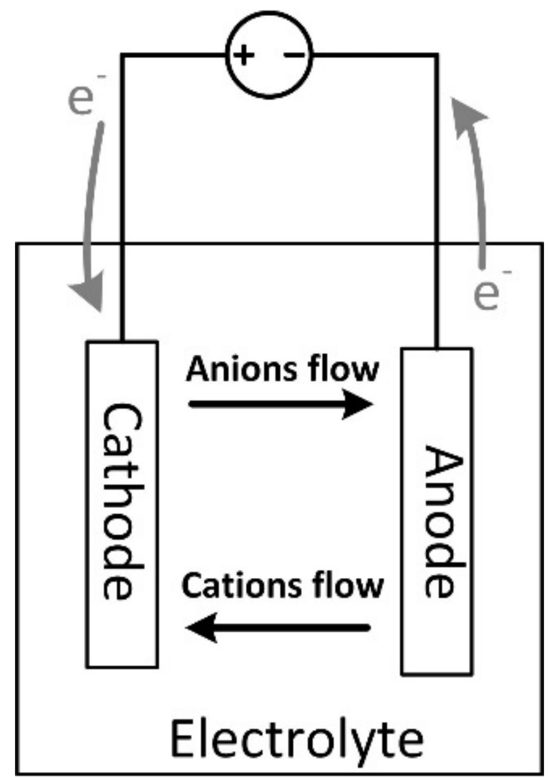
Operation of a cell

- **Discharge:**
  - When cell is connected to an external load, electrons flow from the anode, which is oxidized, through the external load to the cathode, where the electrons are accepted and the cathode material is reduced.
  - The electric circuit is completed in the electrolyte by the flow of anions (negative ions) and cations (positive ions) to the anode and cathode, respectively.



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Voltage, electric potential difference, electric pressure is the difference in electrical potential between two points.

Theoretical Voltage

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

- The standard potential of the cell is determined by the type pf the **active materials** (cathode and anode) in the cell.

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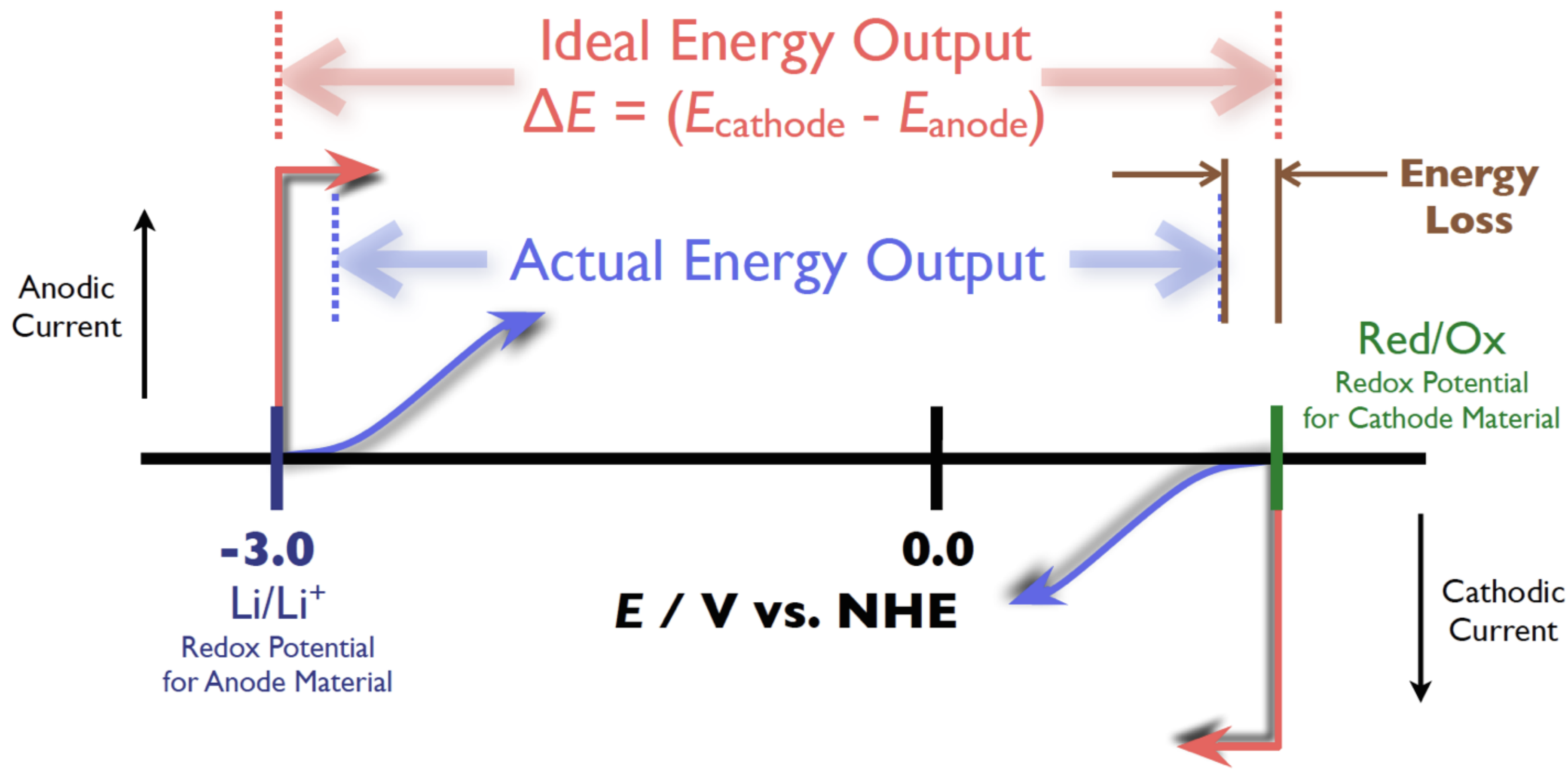
Energy Density for Secondary Batteries



Energy (Wh) = I x V x t
Power (W) = I x V

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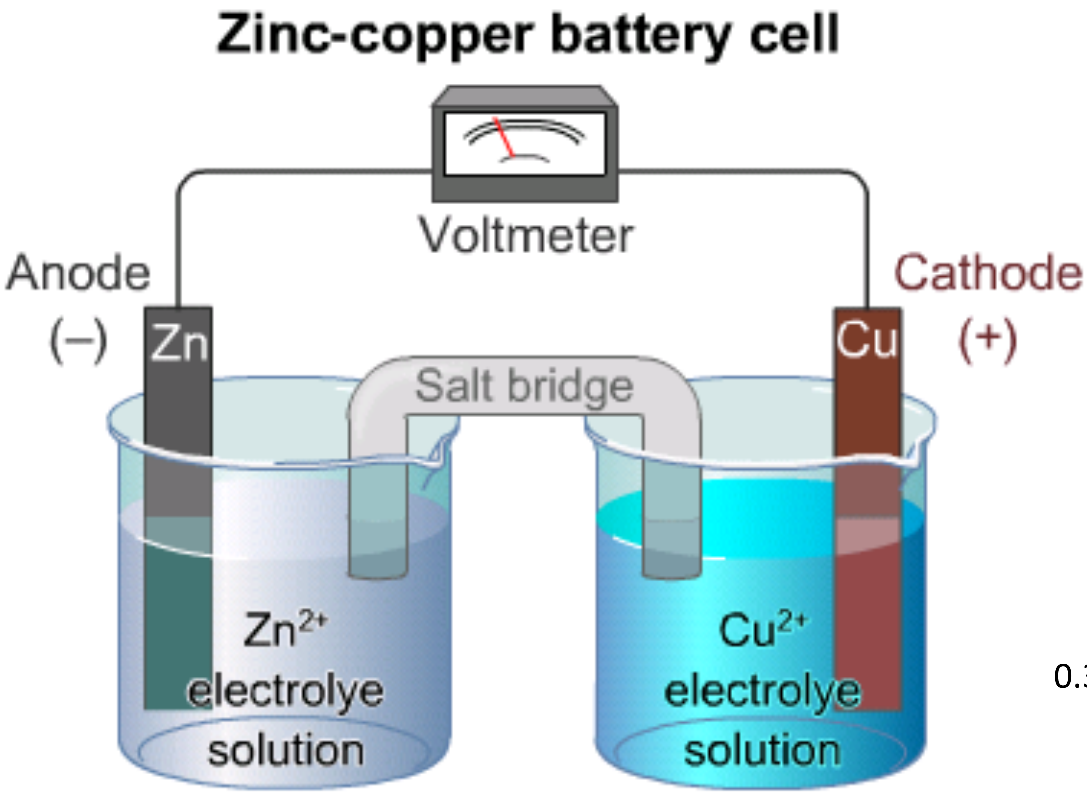
First battery



-0.76V vs SHE

0.34V vs SHE

Total voltage: 1.1 V

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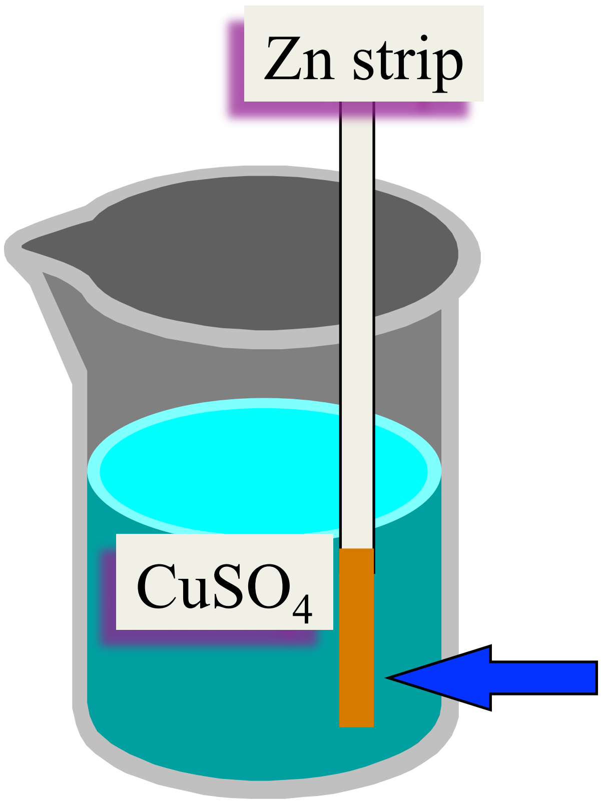
Copper Plating



With time, Cu plates out onto Zn metal strip.

Electrons are transferred from Zn to Cu^{2+}, but there is no useful electric current.

- Zn is oxidized and is the reducing agent

$$Zn(s) \rightarrow Zn^{2+}(aq) + 2e-$$

- Cu^{2+} is reduced and is the oxidizing agent

$$Cu^{2+}(aq) + 2e- \rightarrow Cu(s)$$

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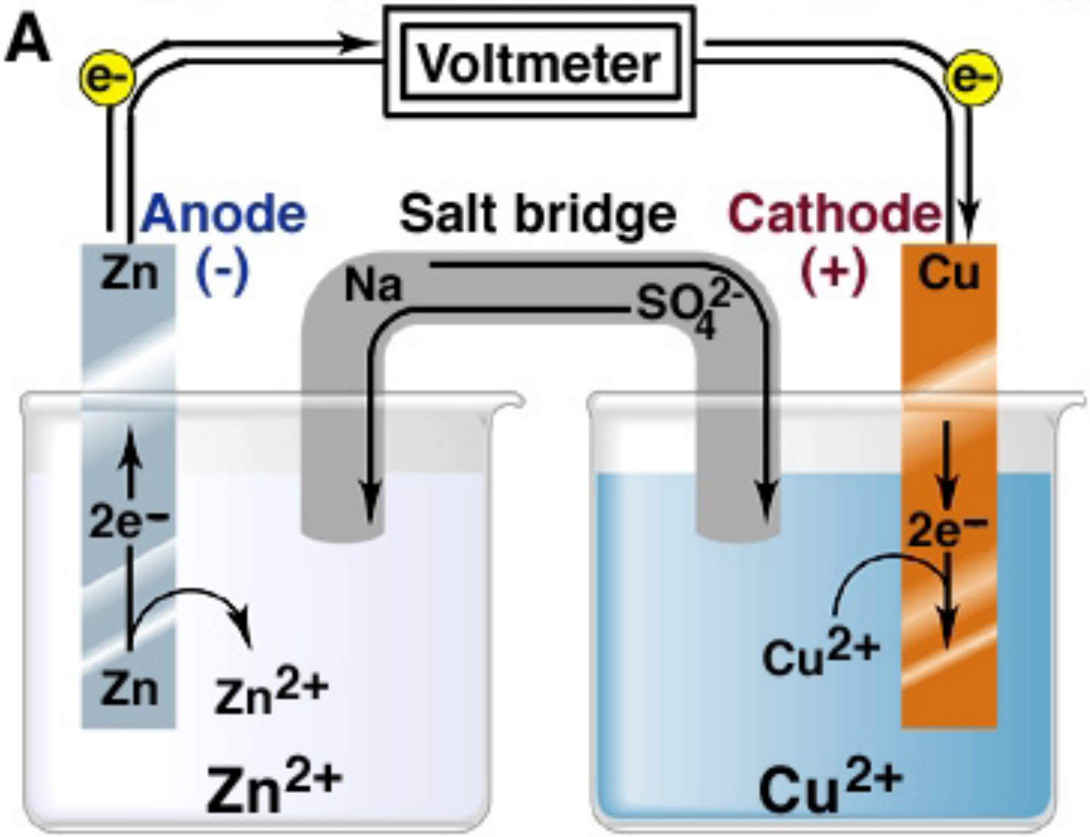
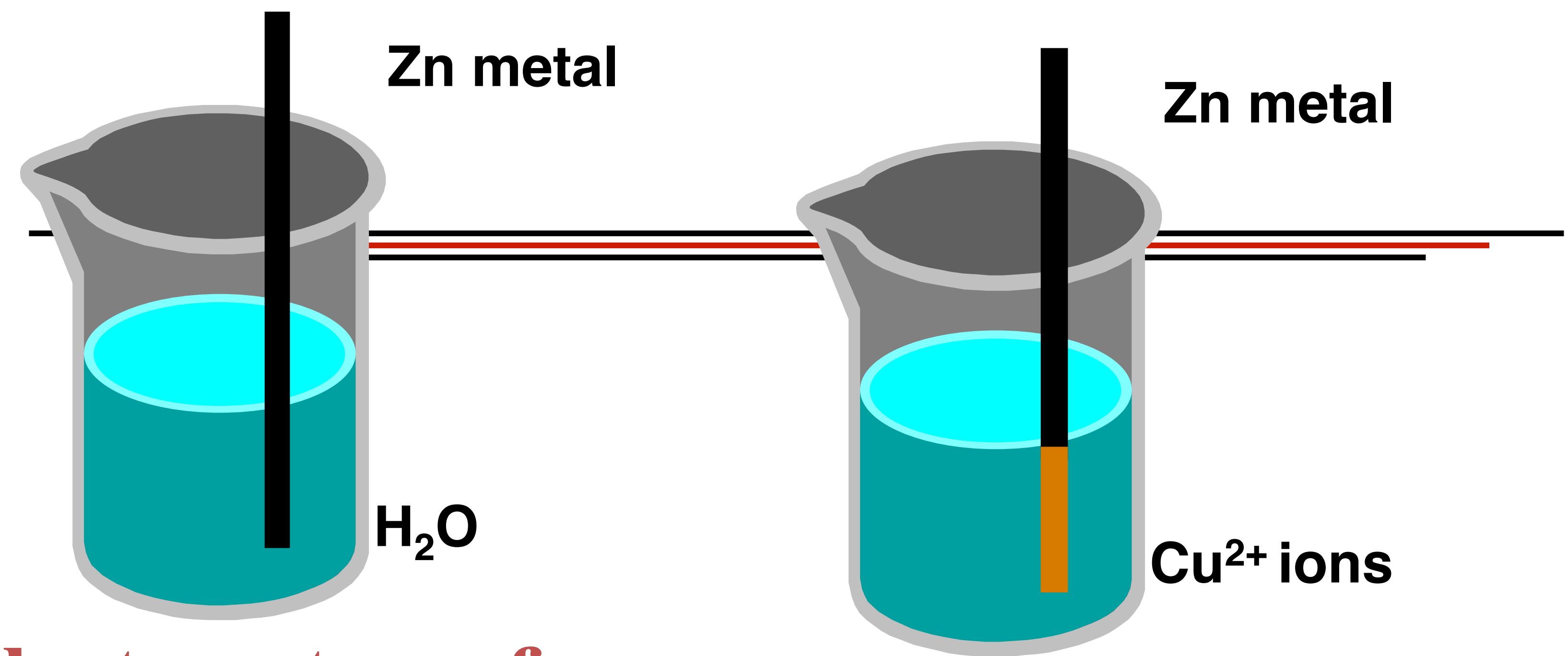
A



B

Zinc-Copper Reaction Voltaic Cell



Electron transfer

$$Zn(s) + Cu^{2+}(aq) \rightarrow Zn^{2+}(aq) + Cu(s)$$

- 2 e-

+2 e-

Loss of **E**lectrons = **O**XIDATION (**LEO**)

OiL

Gain of **E**lectrons = **R**EDUCTION (**GER**)

RiG

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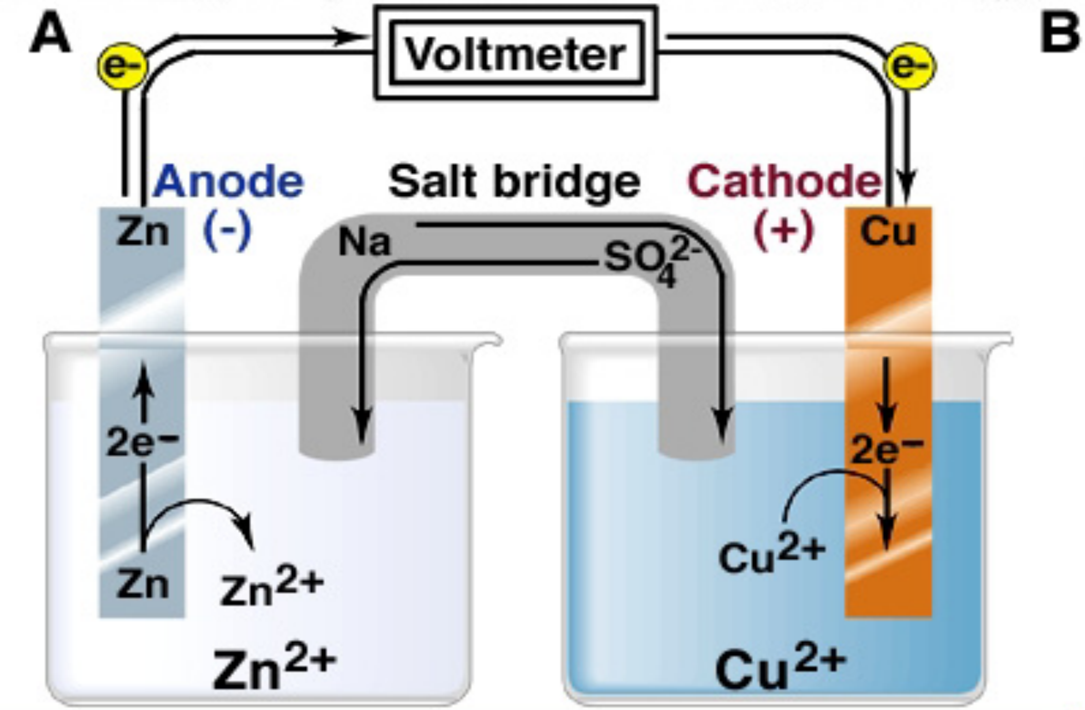
CHEMICAL CHANGE → ELECTRIC CURRENT



Oxidation half-reaction

$$Zn(s) \longrightarrow Zn^{2+}(aq) + 2e^-$$

Reduction half-reaction

$$2e^- + Cu^{2+}(aq) \longrightarrow Cu(s)$$

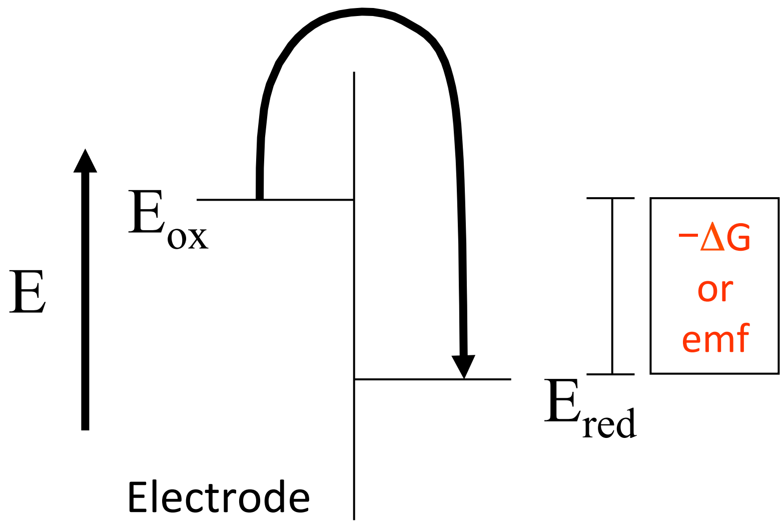
Overall (cell) reaction

$$Zn(s) + Cu^{2+}(aq) \longrightarrow Zn^{2+}(aq) + Cu(s)$$

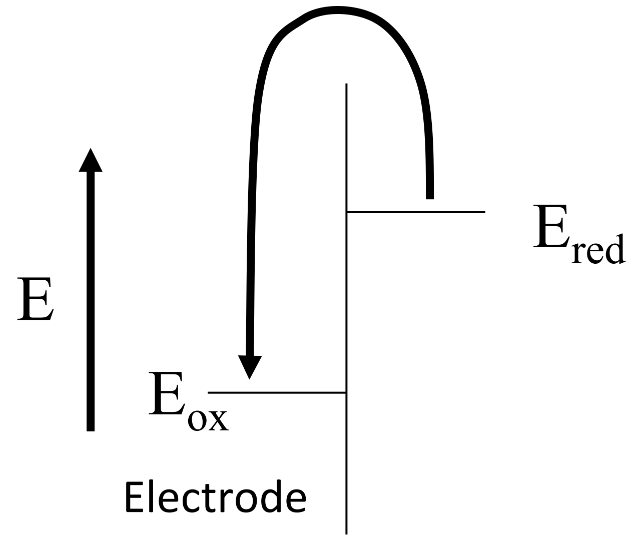
Zinc-Copper Reaction Voltaic Cell

Why Electrons Transfer

Reduction



Oxidation



- Net flow of electrons from electrode to solute
- Electromotive force (emf) is the difference between the initial energy and reduced energy
- more cathodic
- more reducing

- Net flow of electrons from solute to electrode
- Positive ΔG, negative emf
- more anodic
- more oxidizing

Cell diagrams

Rather than drawing an entire cell, a type of shorthand can be used.

For our copper - zinc cell, it is:

$$Zn \mid Zn^{2+}\,(1M) \mid\mid Cu^{2+}\,(1M) \mid Cu$$

The anode is always on the left.

| = boundaries between phases

|| = salt bridge

Anode Left, Cathode Right (Reduction, Receiving)

Electrons flow left to right (in order of species)

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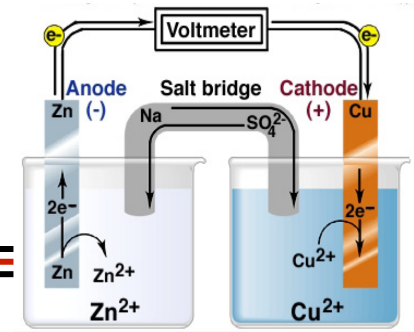
Zn/Cu Electrochemical Cell

What is E° for the Zn/Cu cell (Daniel's cell) ??



$$E^o_{cell} = E^o_{cathode} - E^o_{anode}$$

Product gets electron

Reactant gives electron

Products - reactants

Cathode: $Cu^{2+}(aq) + 2e^- \rightarrow Cu(s)$ $E^o = +0.34$ V

Anode: $Zn(s) \rightarrow Zn^{2+}(aq) + 2e^-$ $E^o = -0.76$ V

Net: $Cu^{2+}(aq) + Zn(s) \rightarrow Zn^{2+}(aq) + Cu(s)$

$$E_{cell} = E_{cathode} - E_{anode} = 0.34 - (-0.76) = +1.10 \text{ V}$$

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E^o and ΔG^o

E^o is related to ΔG^o, the free energy change for the reaction for standard state (most stable form at 25°C and 100kPa).

Michael Faraday
1791-1867

Discoverer of

- electrolysis
- magnetic properties of matter
- electromagnetic induction (electric motor)

$$\Delta G^o = -n F E^o$$

F = Faraday constant
= 9.6485×10^4 C/mol

n = number of moles of e^-'s transferred.

Zn / Zn^{2+} // Cu^{2+} / Cu

n for Zn/Cu cell ? **n = 2**

$$Cu^{2+}(aq) + Zn(s) \rightarrow Zn^{2+}(aq) + Cu(s)$$

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E^o and ΔG^o

$$\Delta G^o = -nFE^o$$

- For a **product-favored** reaction
  - Galvanic cell: Chemistry → electric current

Reactants → Products

$\Delta G^o < 0$ and so $E^o > 0$ (E^o is positive)

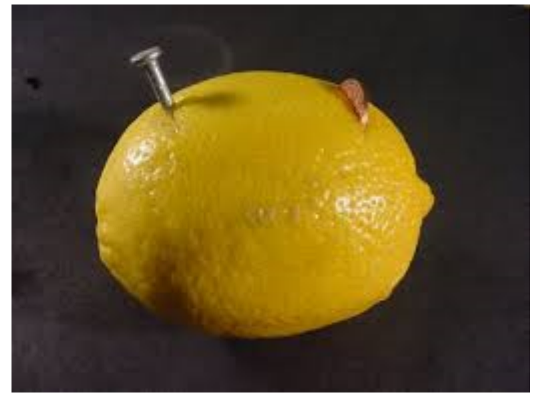
- For a **reactant-favored** reaction
  - Electrolytic cell: Electric current → chemistry

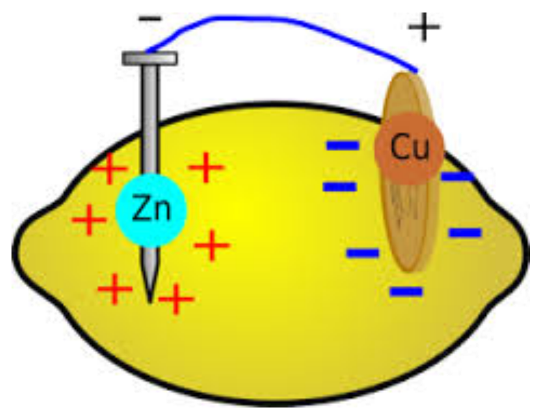
Reactants ← Products

$\Delta G^o > 0$ and so $E^o < 0$ (E^o is negative)

Lemon Battery

- Making a battery with a lemon, penny and galvanized nail (Zn-coated) as the electrodes
  - **Negative electrode?**
  - **Positive electrode?**
  - **Why do we need the lemon?**
  - **What if we use 2 pennies?**





$$Zn^{2+}(aq) + 2e^- \longrightarrow Zn(S) \qquad -0.76(v)$$

$$Cu^{2+}(aq) + 2e^- \longrightarrow Cu(S) \qquad 0.34\ (v)$$

- **What is the standard potential of the lemon battery?**

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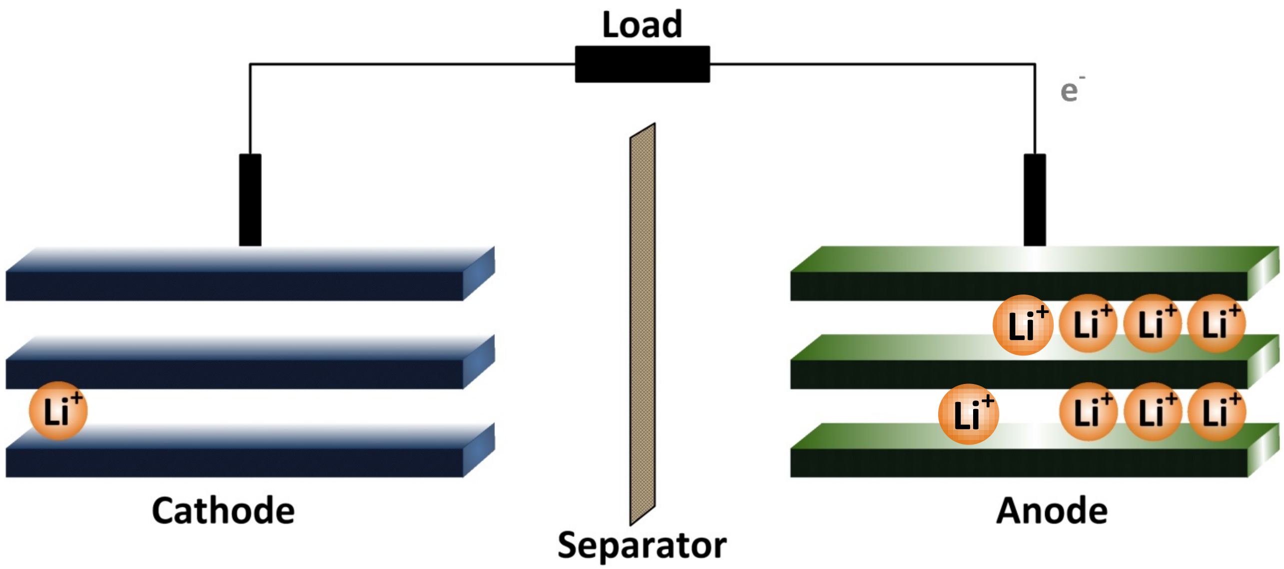
Lithium ion Batteries (LIBs)

- **LIBs are comprised of cells that employ lithium intercalation compounds as the positive and negative electrodes**



$$Li^{+} + e^{-} + Li_{x}CoO_{2} \longrightarrow Li_{1+x}CoO_{2}$$

$$Li \longrightarrow Li^{+} + e^{-}$$

$$Li^{+} + e^{-} + Co^{4+} \longrightarrow Li^{+} + Co^{3+}$$

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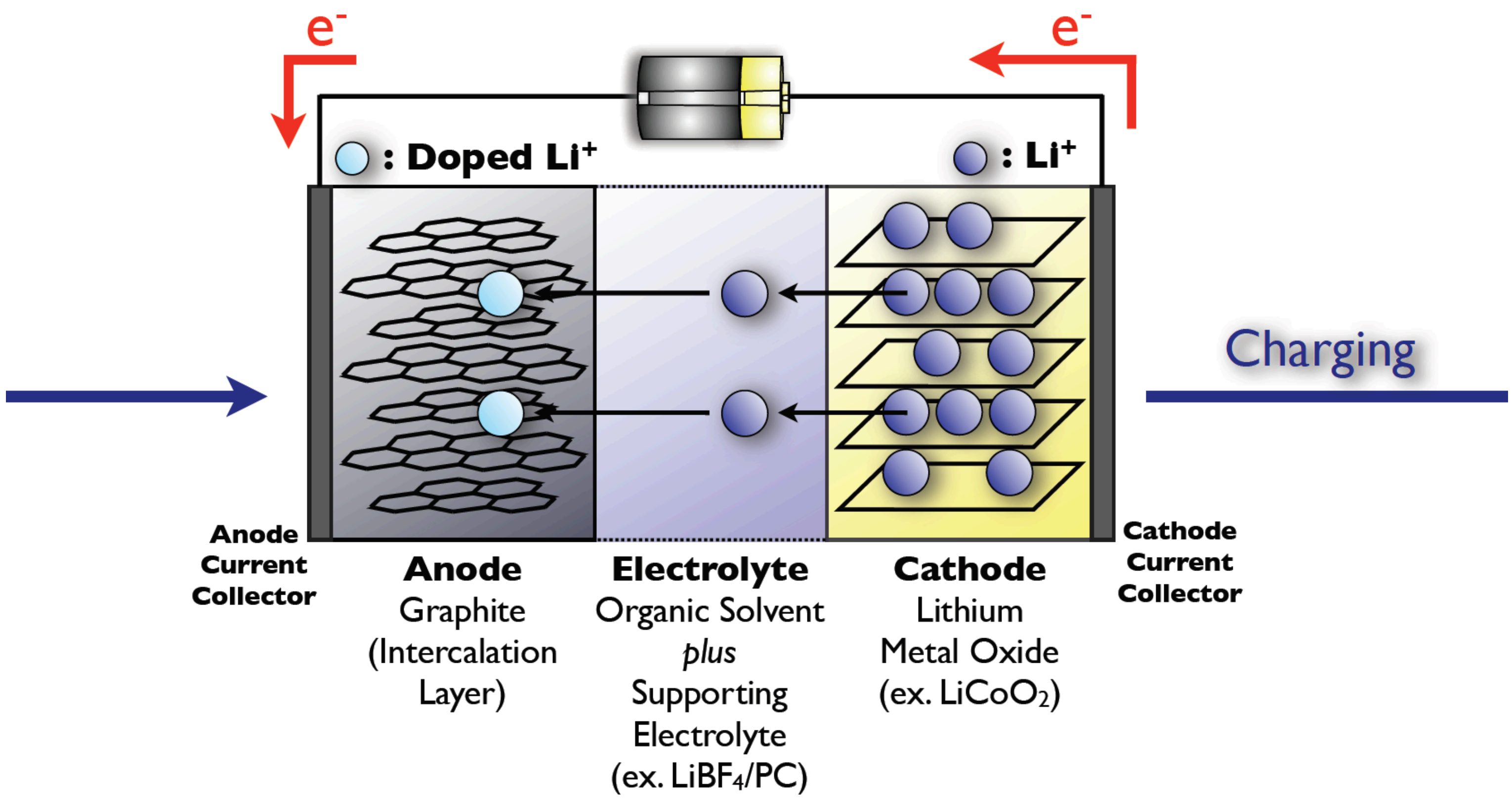
An Intercalation-based Lithium Battery Cell



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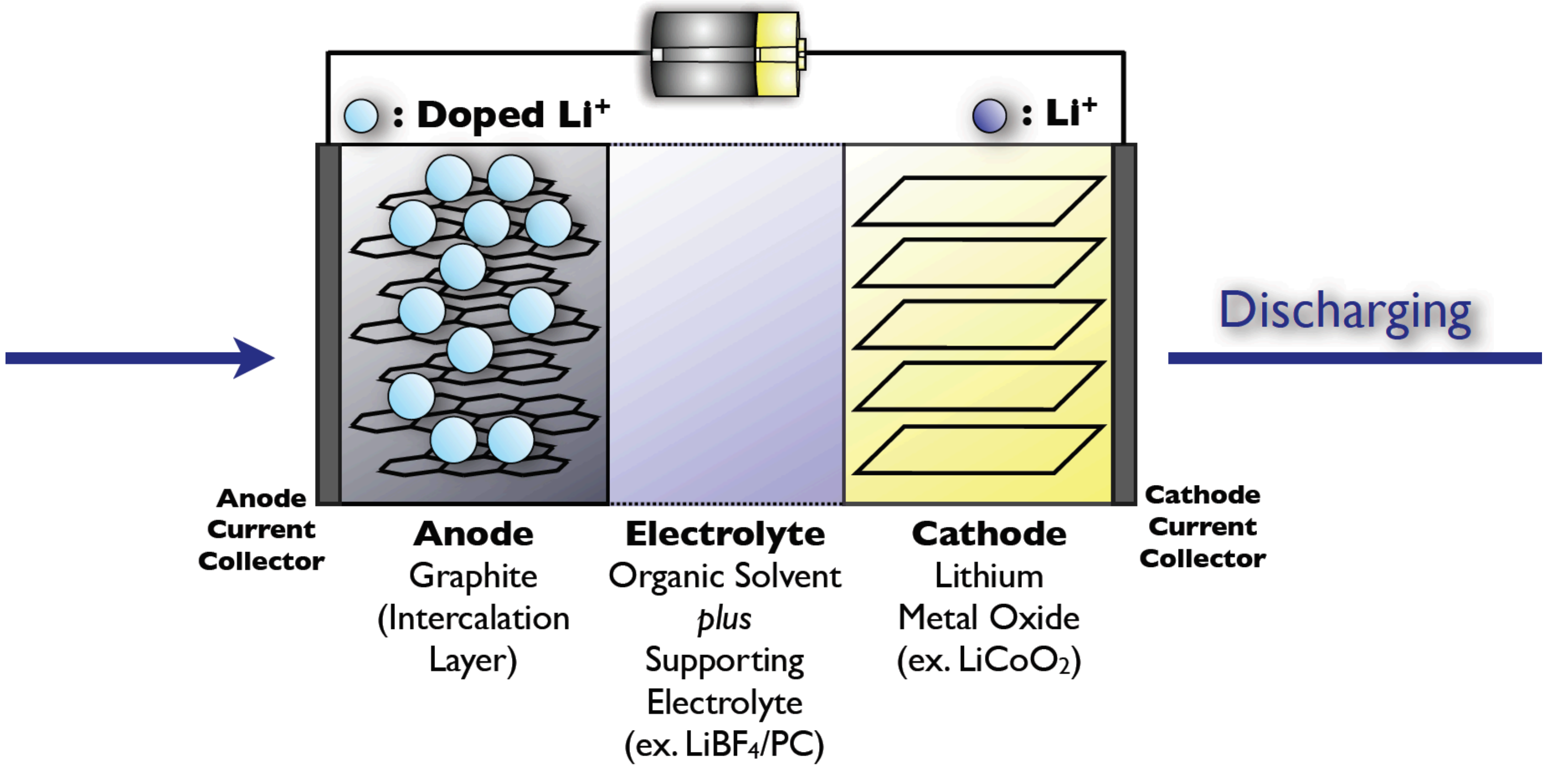
Reaction Mechanism for LIBs

Fully Charged State



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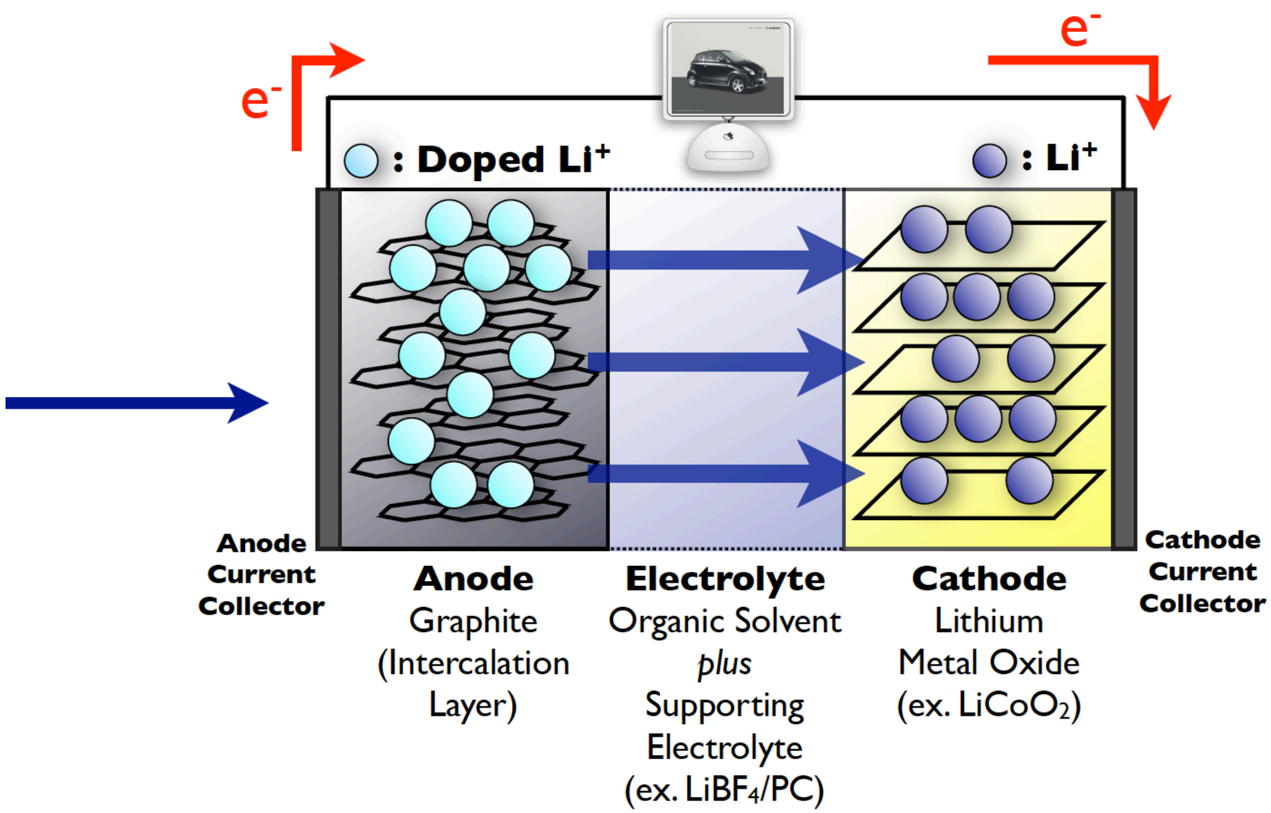
Reaction Mechanism for LIBs

Fully Discharged State



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What are the Batteries for Higher Energy Density LIBs?

Category	Material	Capacity (Ah/kg)	
		Theoretical	Actual
Cathode Material	$LiCoO_2$	274	140
	$LiMn_2O_4$	148	120
	LiV_2O_5	142	140
	$LiNiO_2$	275	200
	$LiFePO_4$	170	150
Anode Material	Carbon (LiC_6)	372	-
	Lithium	3861	-

Capacity imbalance between cathode and anode will increase further so that higher capacity cathode materials to match anode capacity will be required. Furthermore, for transportation, inexpensive and abundant materials will also be required.

Cathode vs Anode

- Negative electrode, oxidation, loss of electron

$$Li \longrightarrow Li^{+} + e^{-}$$

- Positive electrode, cathodic reaction, gain of electron

$$Cu^{2+} + 2e^{-} \longrightarrow Cu$$

Theoretical Capacity

- Theoretical capacity of a cell is determined by the amount of active materials in the cell.
- Theoretical capacity is the total quantity of electricity involved in the electrochemical reactions (in terms of coulombs or ampere-hours).
  - 1 gram-equivalent weight of material deliver **96,485 C** or **26.8 Ah**. (Farday Constant, magnitude of electric charge per mole of electrons0

Theoretical capacity for Zn
(Molecular Weight 65.4 g)

$$\mathbf{Zn^{2+}(aq) + 2e^{-} \longrightarrow Zn\,(S)}$$

$$2e- \times 96485\ A.sec/1\ mole \times 1\ hour/3600\ sec \times 1000\ mA/1Amp \times 1\ mole/65.4\ g = 820\ mAh/g$$

Cathode and Anode design consideration

- **Choose electrode materials with:**
  - High standard potential difference
  - Fast reactions at electrodes
  - High capacity
  - Stable electrodes
  - lightweight

Battery Metrics

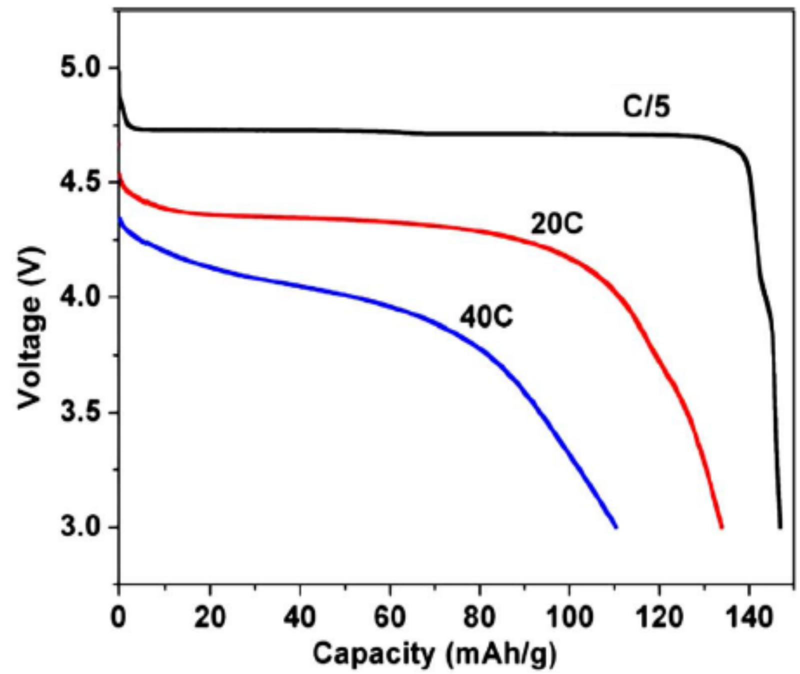
Capacity: Amount of charge stored
ie. gravimetric capacity in **mAh/g**

Energy Density: Energy stored in a cell

Wh/kg (Gravimetric)
Wh/L (Volumetric)

C-RATE: Is a measure of a rate at which a battery is discharged relative to its maximum capacity.
1C means that the discharge current will discharge the entire battery in 1 hour.

Charge or discharge rate **C/X**
X = # hours to (dis)charge



X. Ma et al. *J. Electrochem.Soc.* **157** 8 A925-A931 (2010)

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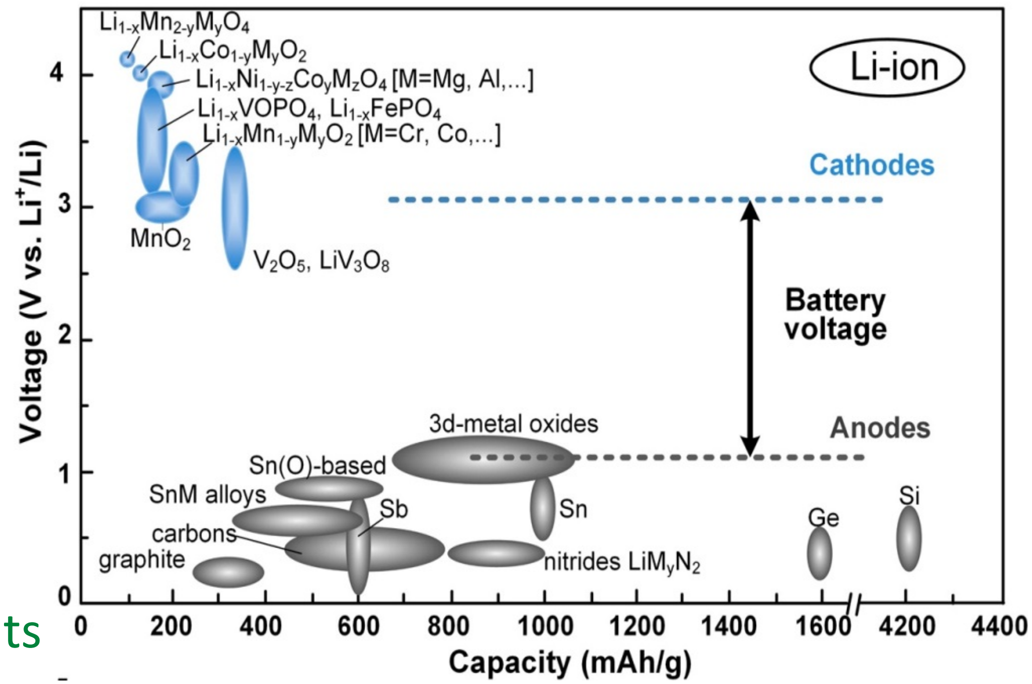
LIBs: Possibilities and Challenges

LIB electrode materials requirements:

- Reversibly incorporate Lithium without structural change
- High redox potential between anode and cathode
- Incorporate large quantities of lithium

- ❑ High lithium ion diffusivity
- ❑ Good electronic conductivity
- ❑ Prepared from inexpensive reagents
- ❑ Low cost synthesis



Capacities of common Li-ion electrode materials. *Chem. Mater. 2014, 26.*

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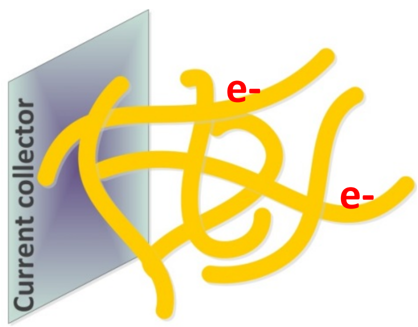
How to Improve the State of the Art?

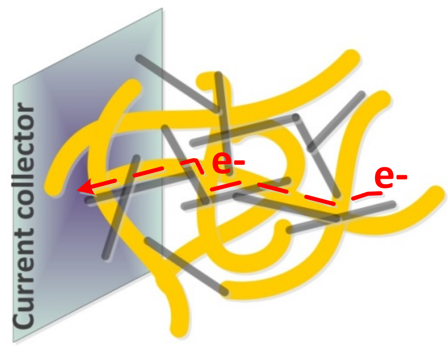
Problems:

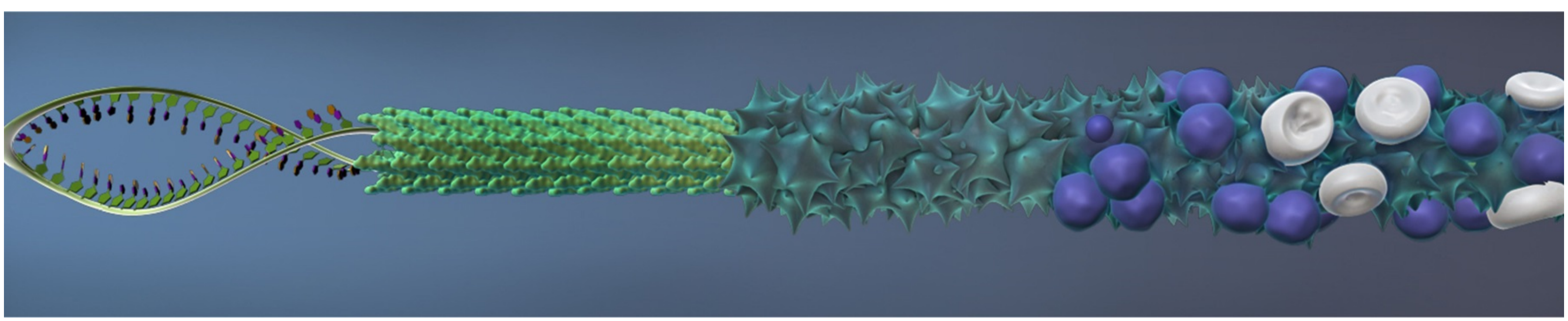
- Ion diffusivity
- Electronic conductivity

Solutions:

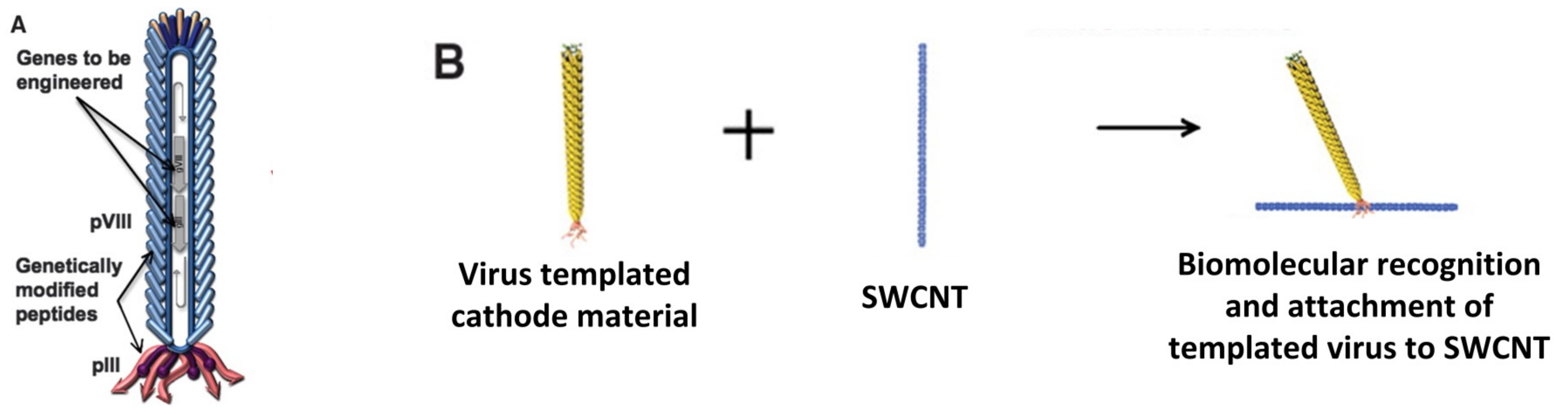
- Nano-structuring the functional materials
  - Increasing surface to volume ratio
- Increasing the electronic conductivity by integrating conductive additives
  - Creating percolating network

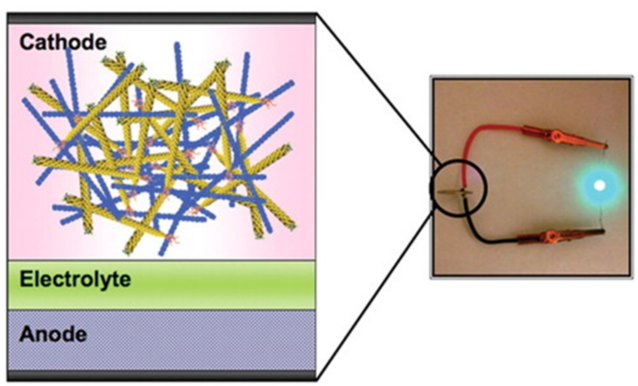






Studying Bio-templated Materials for LIBs for the First Time





- The Bio-cathode materials with SWCNT on the tail of the virus.
  - **Improved energy density**
  - **Imporved power density**

Yun Jung Lee et al., *Science* (2009)

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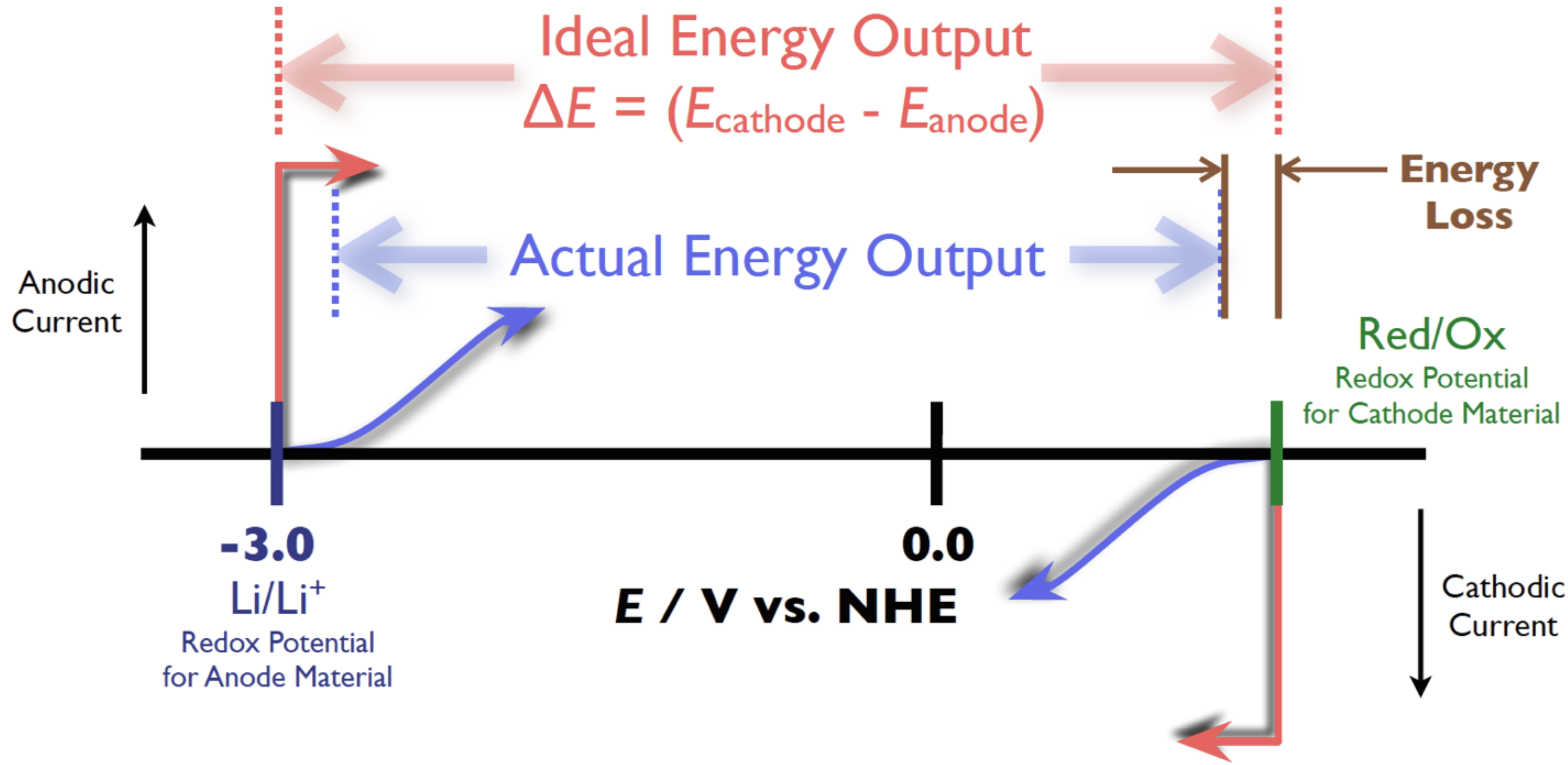
Energy Density for Secondary Batteries



Energy (Wh) = I x V x t
Power (W) = I x V

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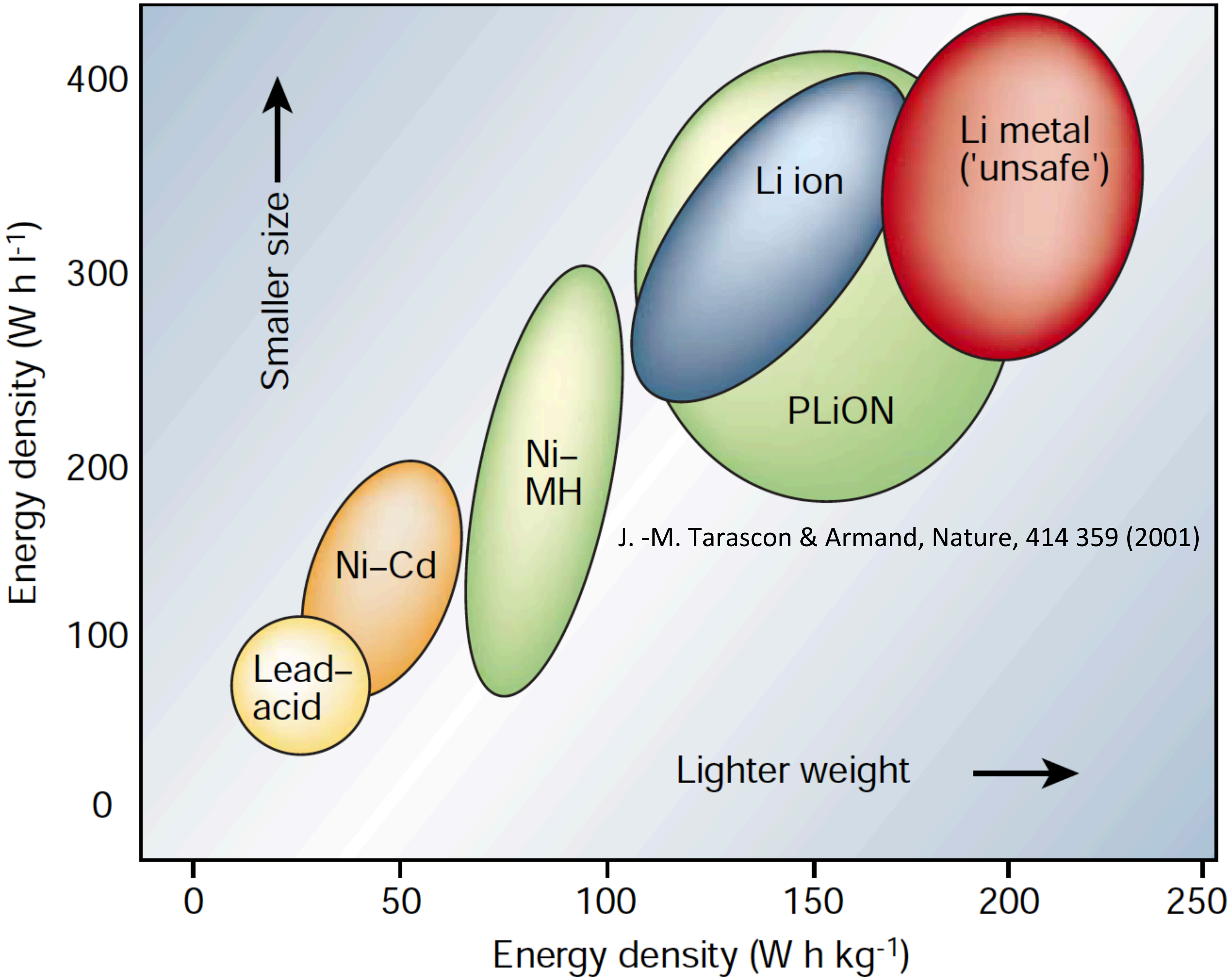
Energy Density for Secondary Batteries



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