

Batteries!

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What is a Battery?

A “Battery” Is

- A pair of electrochemical reactions in which electrons are passed through an external circuit
- The external circuit is your device
- A cell is one pair
- A battery is a series of cell

Series vs. Parallel

- In series, potential adds, capacity is constant
- In parallel, capacity adds, potential is constant
- Either way the energy is the same
- The efficiency/accessibility depends on your device

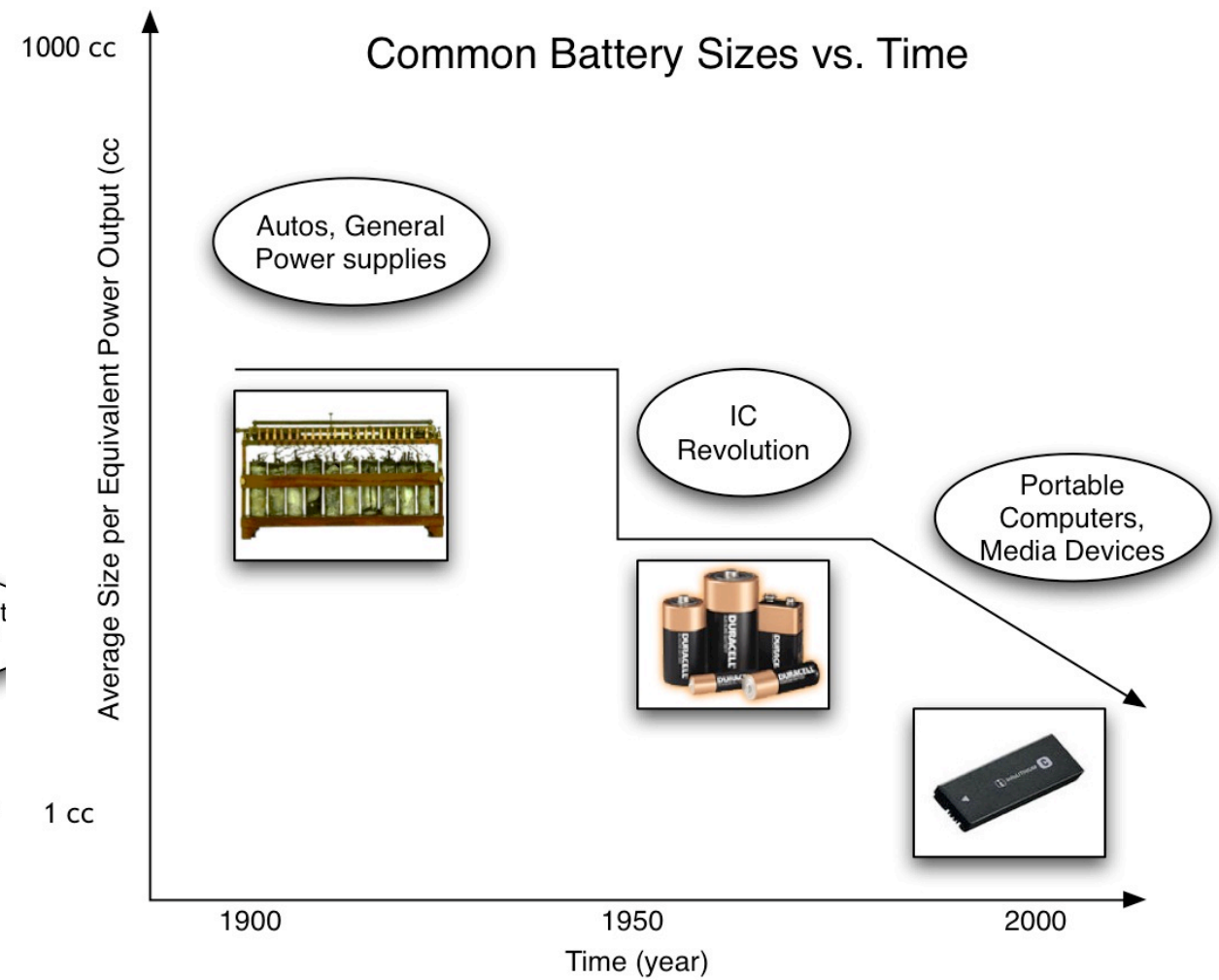
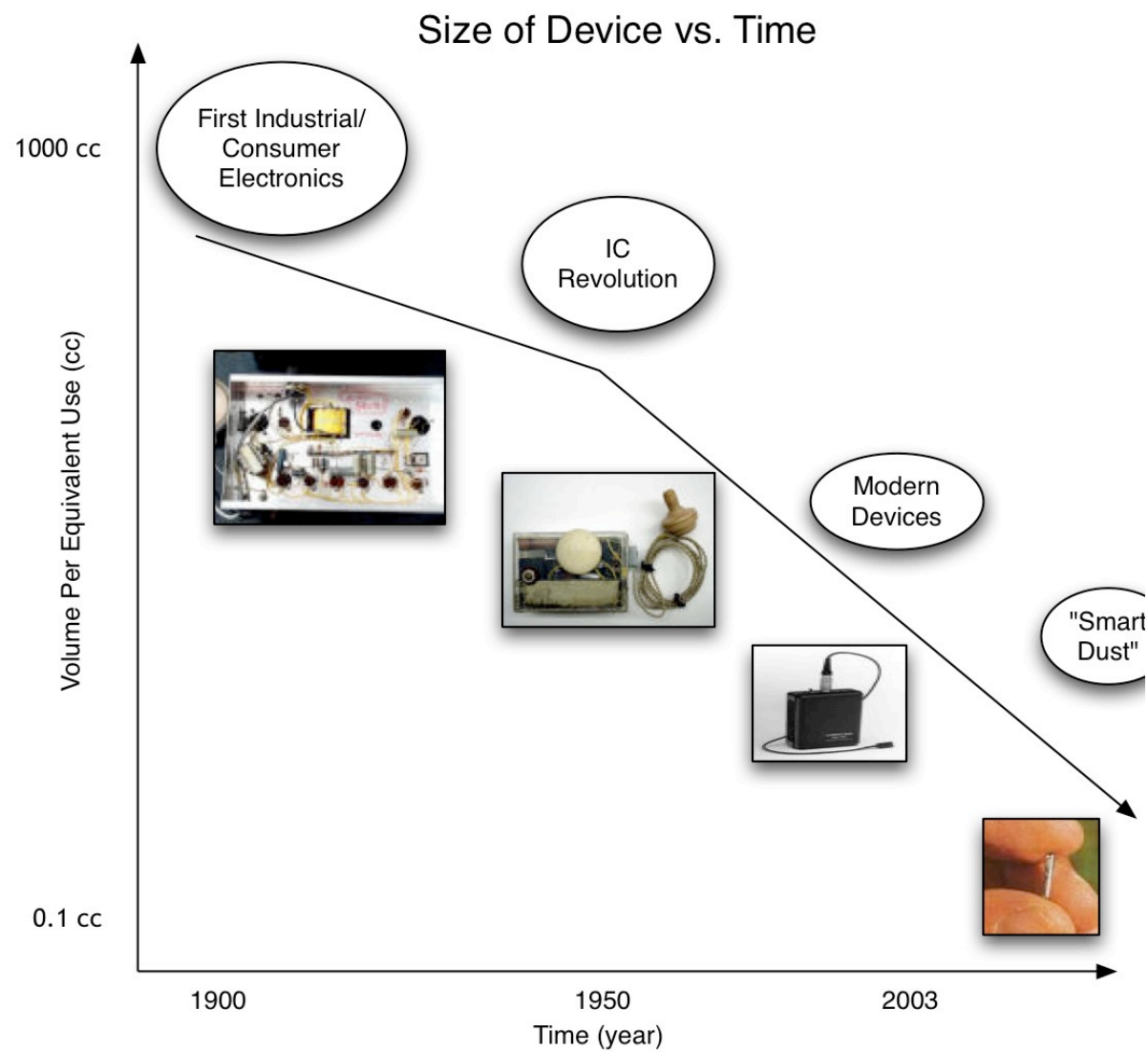
Electrochemical Reactions

- Are just like any other reaction, but mediated by an electron transfer
- Just like fuel + oxygen leads is required for combustion, a battery, internally, undergoes the same process
 - only much more controlled

Electrochemical Reactions

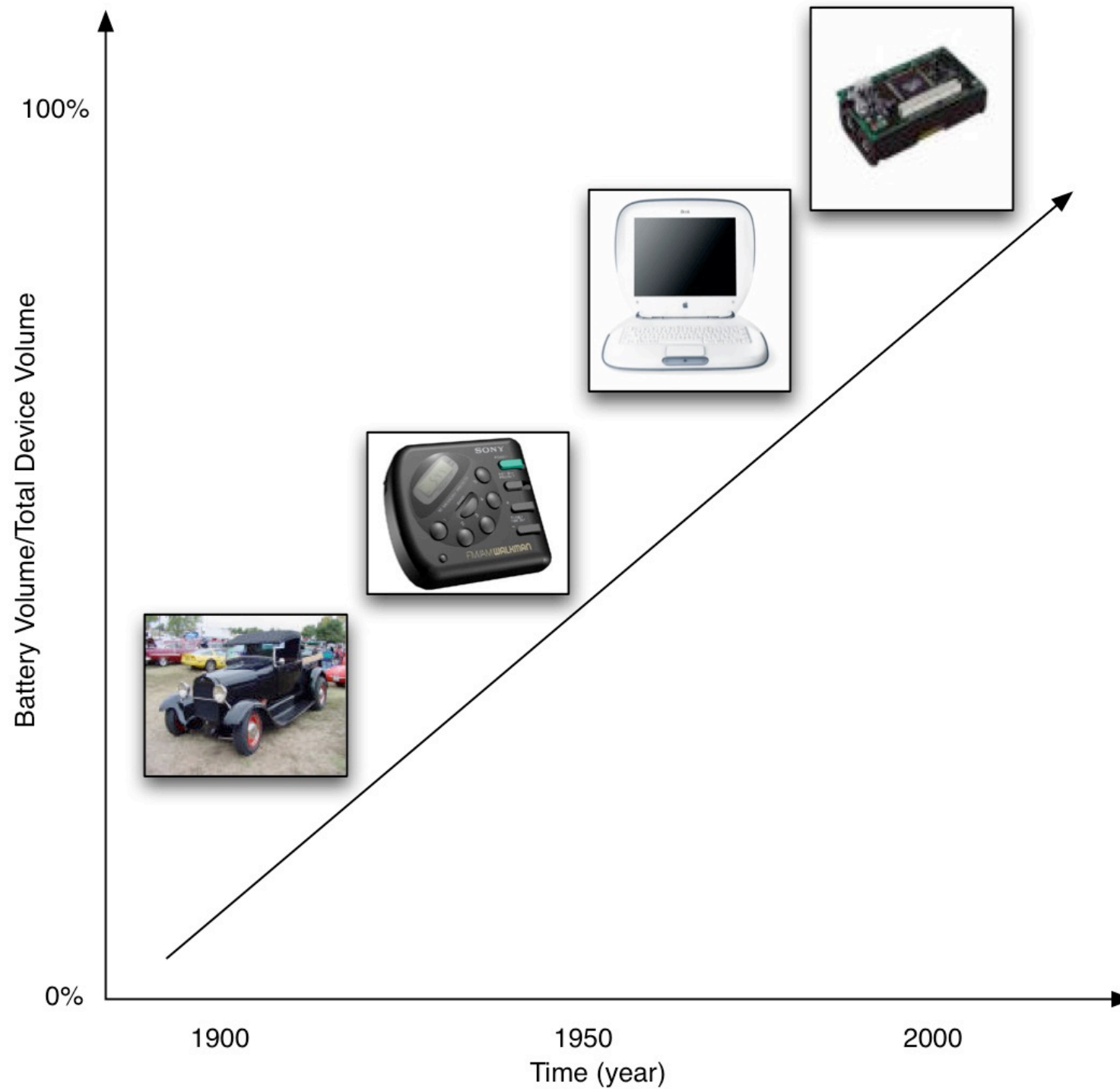
- Are critical beyond batteries
 - Metal Plating
 - Corrosion
 - Sensors

Batteries vs. Devices



Batteries vs. Devices

Battery Volume/Total Device Volume vs. Time



Battery Basics

Battery Ideals

- Chemistry

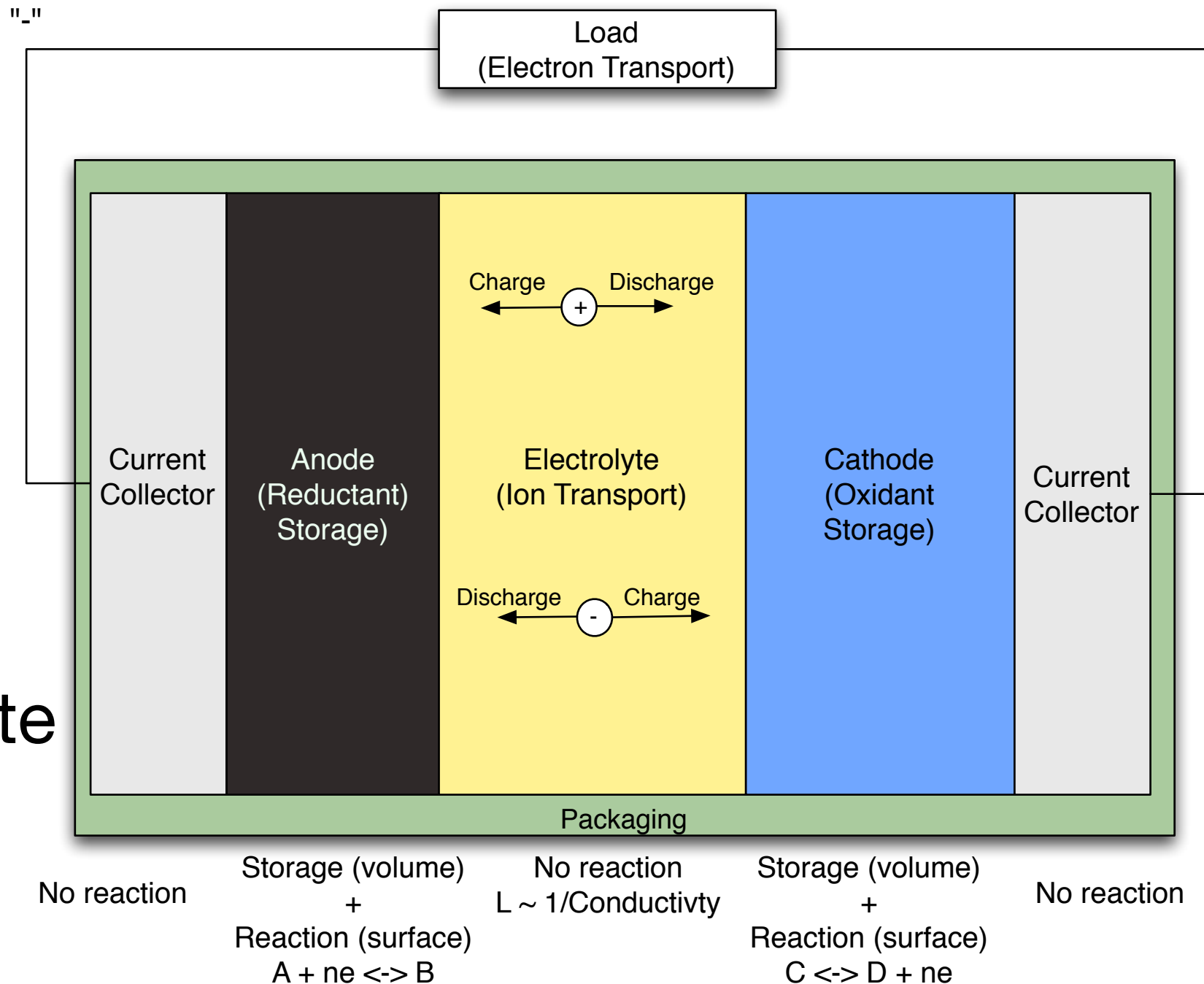
- Potential
- Energy Density
- Power Density

- Electrode Volume

- Absolute Energy

- Area of Electrodes exposed to Electrolyte

- Absolute Power



Battery Ideals

- The potential of a reaction is determined by the Gibbs Free Energy of a reaction:

$$\Delta G = - nF\Delta E$$

n = # of electrons transferred per molecule

E = Potential (V)

F = Faraday's Constant (C/mol of electrons)

G = Free Energy of Reaction (J)

- What determines the Gibbs free energy is well beyond me

Battery Ideals

- The *capacity* of the anode and cathode should be balanced to optimize the energy and power density
 - However, there are tradeoffs
- The *effective capacity* of the device can be modeled using Faraday's law and the *active mass* of the limiting electrode

Battery Ideals

- The *power density* is determined by how fast the slowest reaction involved can occur. The faster the reaction, the faster energy can be spent, the higher the

power

$$P = E/s$$

P = Power (W)

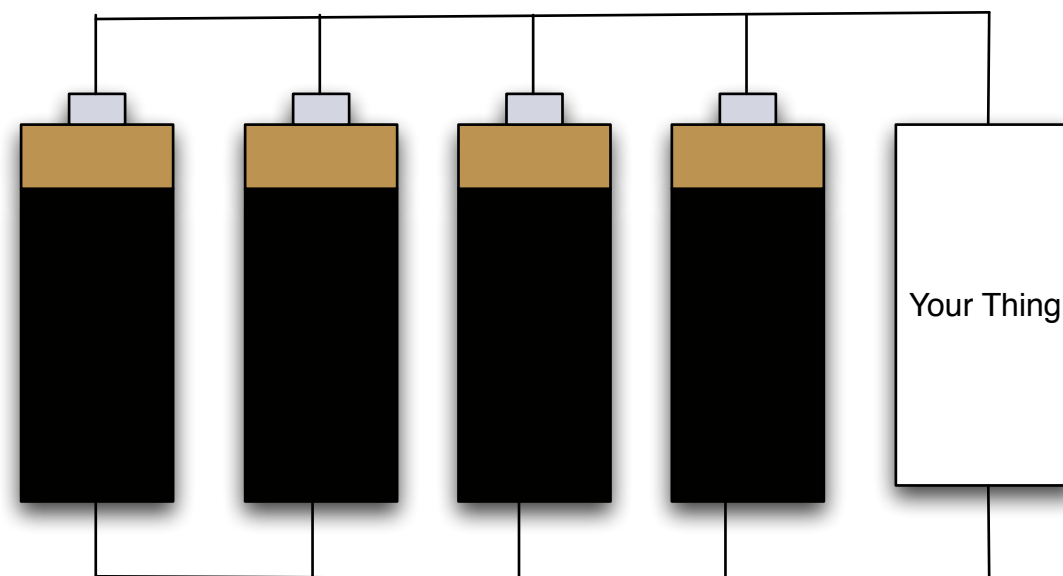
E = Energy (J)

s = Time (s)

- The rate of reaction is determined by the elements in play

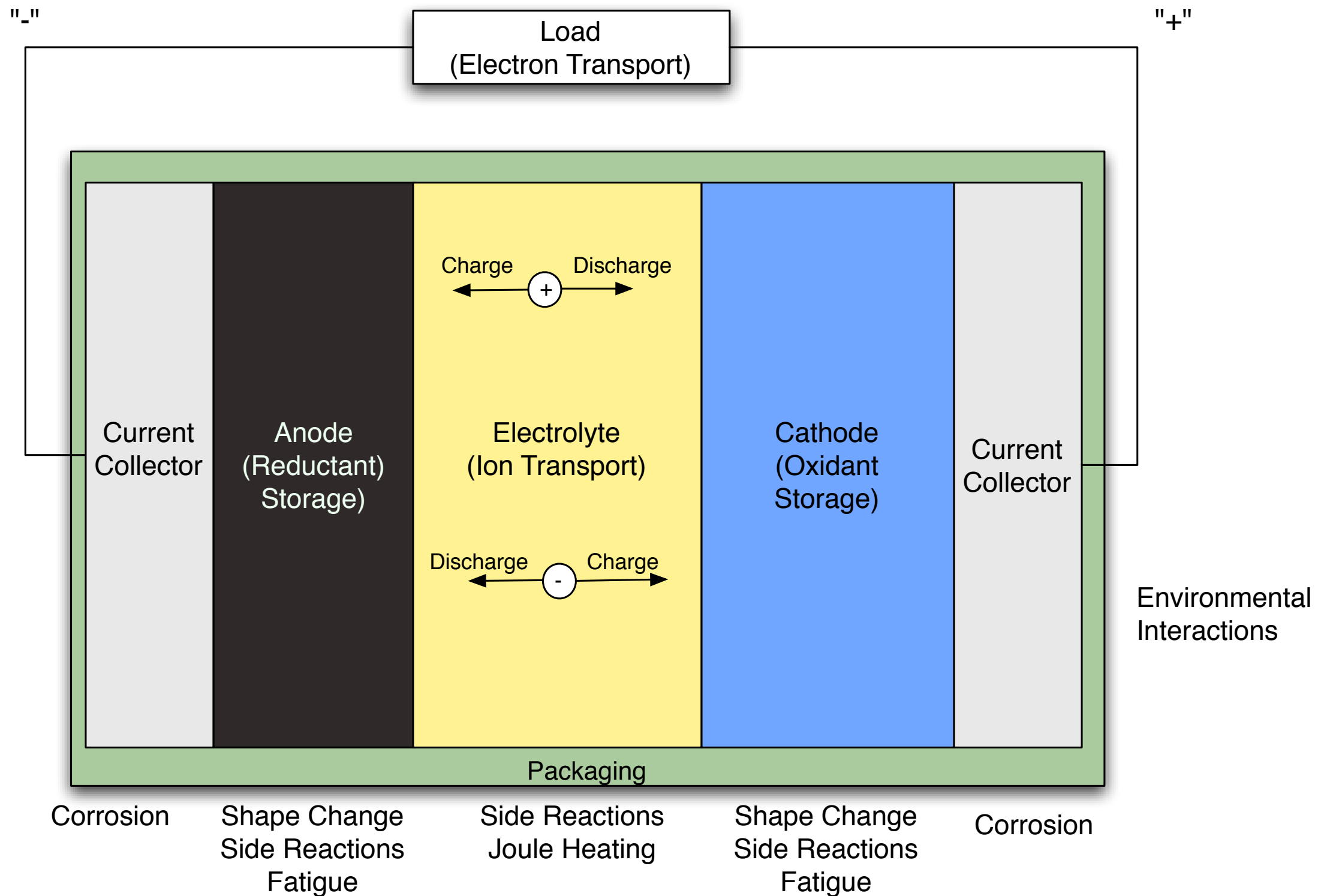
Battery Ideals

- For any given reaction, having larger electrodes will increase capacity, and having more area exposed for reaction will improve power delivery
- (Just add batteries in parallel*)



* not quite that easy

Battery Realities



Battery Realities

- The faster a battery can provide its power, the less time it can sit on a shelf
 - Not a hard and fast rule, but generally true for cheaper cells

Battery Realities

- Primary vs. Secondary
 - Primary batteries cannot be recharged
- Why do we even bother?
 - Cost (your duracell)
 - Energy Density (your watch battery)
- Why can't they be recharged?
 - All sorts of reasons

The “C” Myth

- As rates increase over $C/5$, *cheap and small* batteries demonstrate less capacity
 - C may mean 50 minutes
 - 10 C may mean 1 minute
- Dependent on a host of factors
 - Internal heating
 - Diffusion rates
 - Electrolyte ohmic drops

Battery Realities

- Secondary batteries don't last for ever
- When they fail, they are failing because they are breaking themselves apart to work for you (literally dying for you)
- All secondary batteries *except* NiCd last longer when minimally discharged
 - Really

Battery Nonlinearity

- Batteries are rated for a given capacity
 - A good NiMH provides 2500 mAh @ 1.2 V
- C rating is discharge rate, thus
 - $C/10$ (250 mA) = 10 hours to full discharge
 - $C/5$ (500 mA) = 5 hours to full discharge
 - C (2.5 A) = 1 hour (or is it?)
 - $10 C$ (25 A) = 6 minute discharge (really?)

Battery Non-linearity

- If you to spend X coulombs in Y seconds, why does it matter if X is getting larger and Y is getting smaller?
- Batteries are **non linear** devices
 - As current draw from a battery increases, the capacity consumed is **disproportionally higher**

What this means

- To preserve the life of a battery, design at least 2 hours of battery life into the product
 - More on this later

Battery Types

Battery Comparison

	Energy density [W-hr/kg]	Cost [\$/W-hr]	Cycle life	Temperature [K]	Notes
Zn-MnO ₂	55-60	0.05	1-50	Ambient	Cheap! Primary (non rechargeable)
Lithium Metal	1000	1	1-10	Ambient	Best energy density, Primary
Zn-NiOOH	55~80	0.15~0.25	~500	Ambient	Relatively high energy density, deep cycling, low cost, limited cycle life
Li-ion	100~200	1	~1200	Ambient	High energy density, high cost, difficult to scale
Na-S	180	~0.6	500~2000	620K	High Temperature, Molten Na Dangerous
Zn-Br ₂	30	0.3	2000	Ambient	Complex reaction, Bromine Dangerous
Lead-Acid	30~50	~0.4	~500	Ambient	Low energy density, limited cycle life
MH-NiOOH	60~75	~0.4	1000	Ambient	Consumer Electronics / Hybrid Vehicles

Zn-MnO₂

- The backbone of both alkaline and acidic (zinc-carbon) batteries, though the reaction is different
- As cheap as batteries come
- The complexities of various manganese oxides and zinc morphologies make it hard to recharge
- 1.6 V to 1.1 V over a useful discharge

Zn-Air

- By using ambient oxygen as the oxidant, these batteries provide the best energy density of any system
- Air electrodes are complex beasts, a “bifunctional” air electrode does not yet exist
 - we’re trying
- Once the battery is activated, reacts to completion regardless of what you do
 - energy vs. corrosion

Lithium Metal

- Batteries with a pure lithium negative electrode
- High energy density, long lasting
 - watch batteries, pace makers
- Low power density by design to improve shelf life
- Instability of lithium plating prevents cyclability
 - explosive
- Lithium batteries have non-aqueous electrolytes, cannot be exposed to air or oxygen
 - explosive!

Lead Acid

- Overall 140 years old
- The most common, lowest cost secondary battery
- Excellent power delivery
- Heavy
- Poor deep discharge performance
 - ~500 cycles
- Nominally ~2 V per cell, dropping to ~1.5 over useful discharge life



NiMH

- A very popular secondary battery, second now to lithium ion in consumer electronics
- Essentially a “closed” fuel cell, hydrogen is stored as a metal hydride, oxygen is stored in the nickel oxide
- Excellent cycle life, moderate cost
- Low operating potential (~1.4 V to 1.2 V)

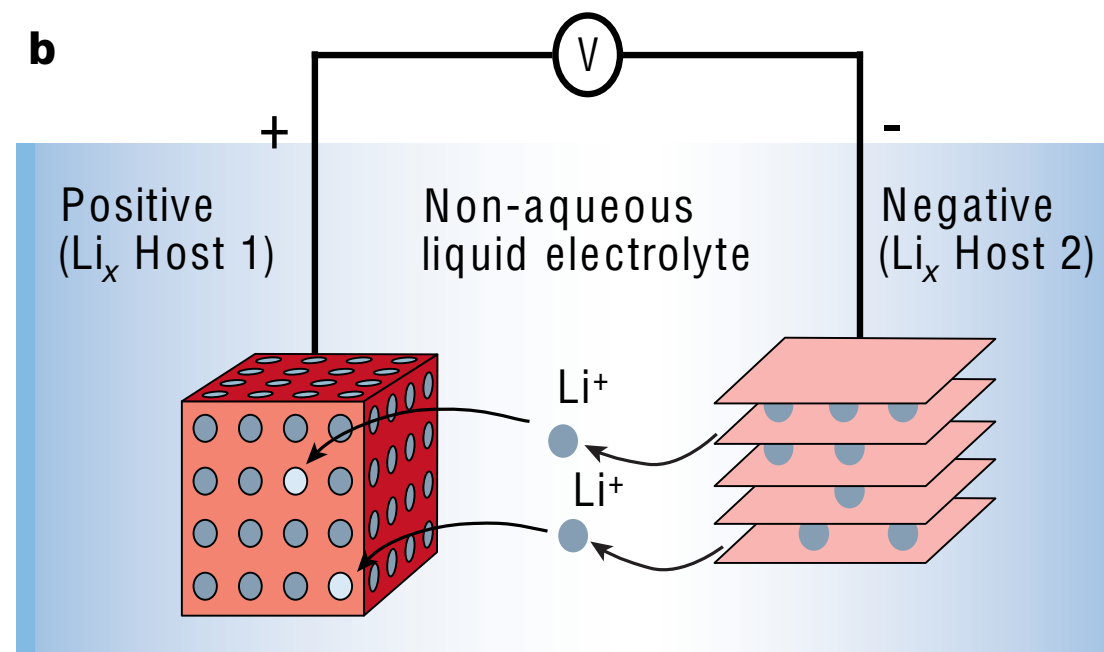
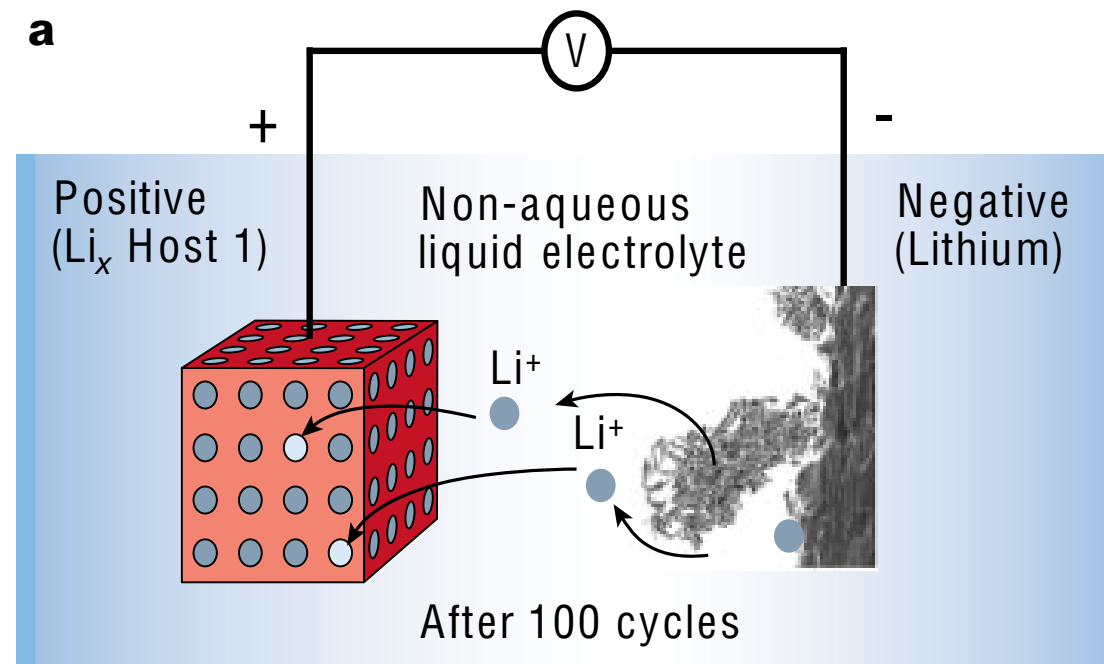
NiCd

- Like NiMH, but a bit cheaper, much less robust, and quite toxic internally
- Pro Tip: don't use these!



Lithium Ion

- Similar to Lithium metal, but with an *intercalation host* for an anode



Nature 2001 Tarascon

Lithium Ion Cells

- A feat of materials and packaging engineering
- A completely engineered structure containing less than 1 PPM H₂O and O₂ leads to unprecedented shelf life and cycle life

Lithium Ion Cells

- Many intercalation hosts available, most common are graphite as the anode and LiCoO_2 as the cathode
- Charged potential of 4.2 V, down to ~ 2.5 V at full discharge (but you don't want to pull past 3.5 V if you can help it)
 - Since $P = IV$, there's a bigger penalty the lower you go

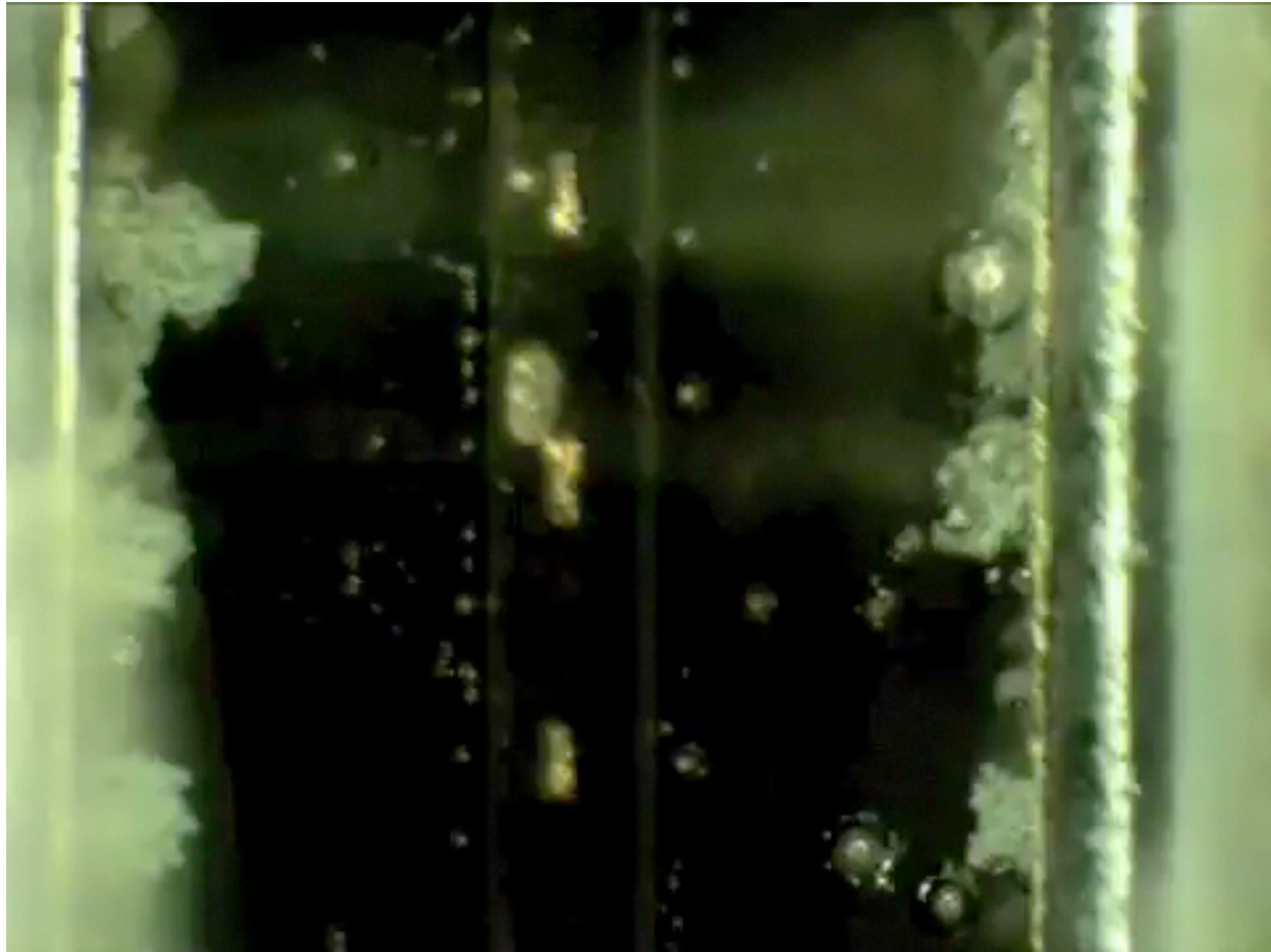
Why Do Batteries Break?

Mass transfer

- Basically related to the issues of reacting and moving a significant fraction of mass quickly in a small space

Uneven Surfaces over Cycles

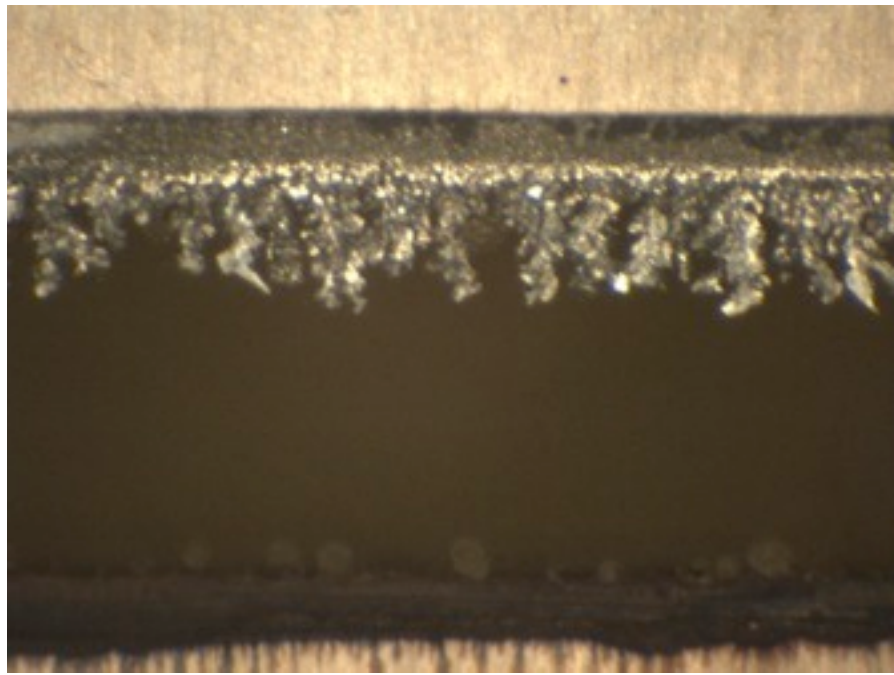
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Flow



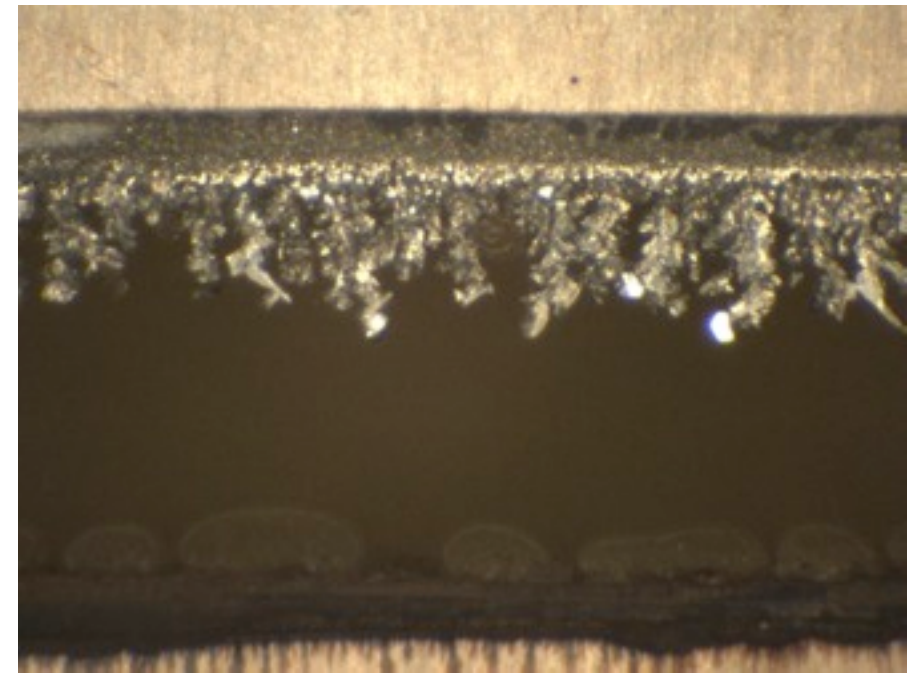
Ito et. al. JOPS 2010

2mm

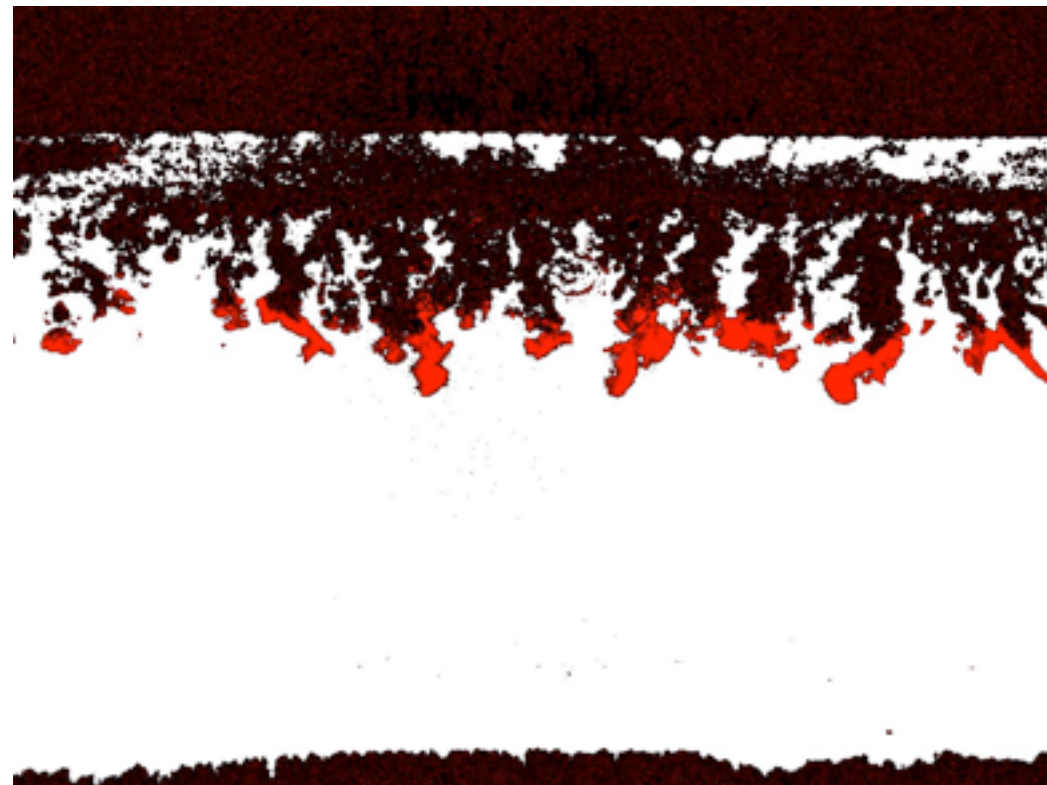
Uneven Surfaces over Cycles



→
100 s



500 μm



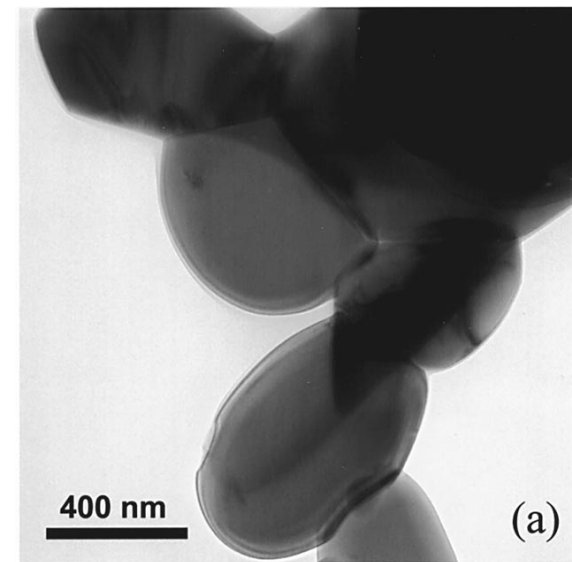
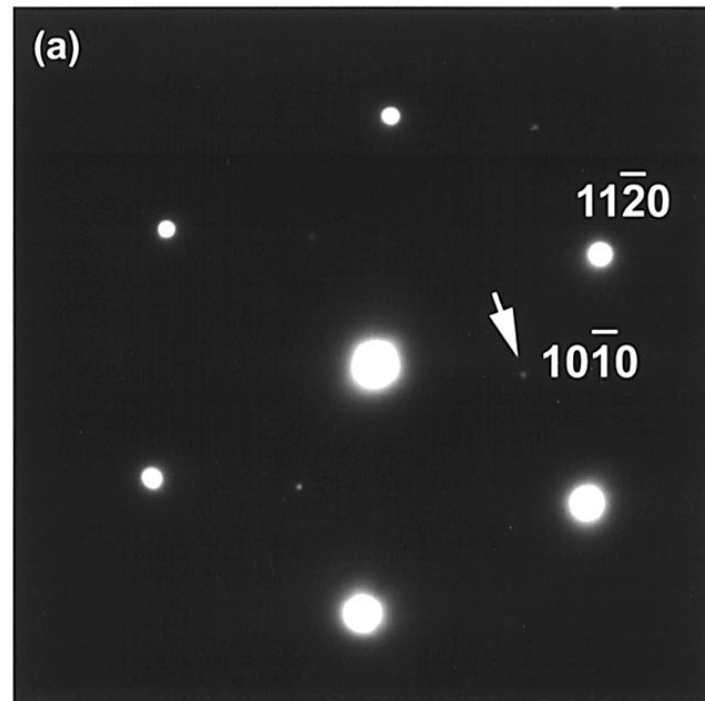
Microscopic Fracture

Red = Zinc Loss
Blue = AgO \rightarrow Ag + ?

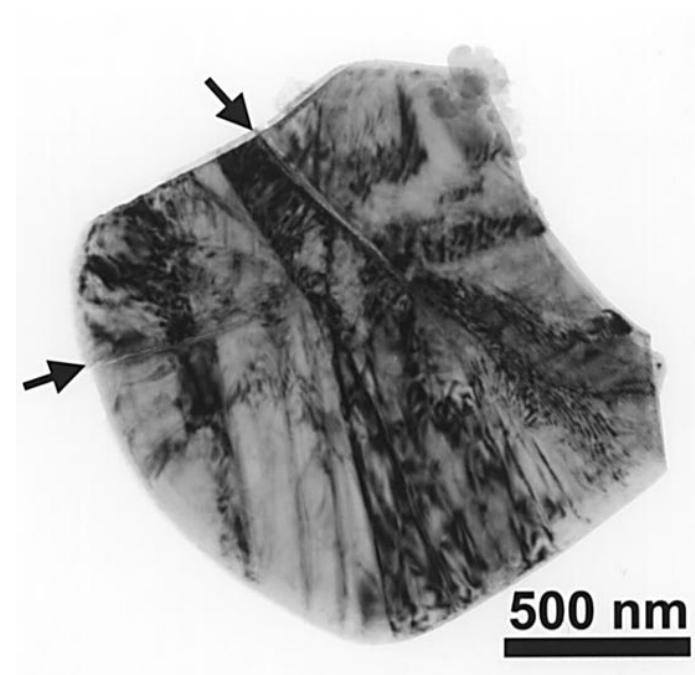
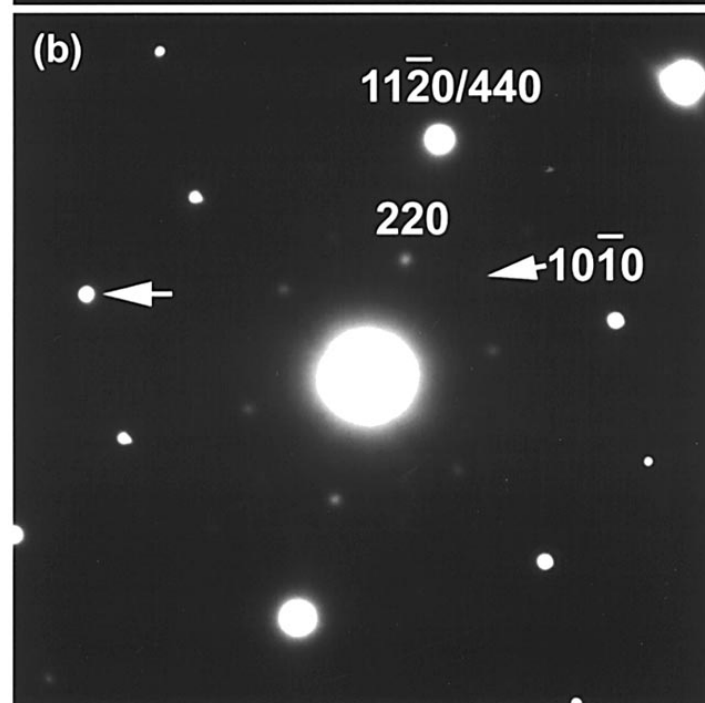
Zn on
Printed Ag $\xrightarrow{200\ \mu\text{m}}$ AgO
 $\xrightarrow{\text{Flow}}$

Nano & Atomic Scale Stress

Before Cycling



After 50 Cycles



What battery should you use?

Lithium Ion Polymer

(99% of the time)

Why?

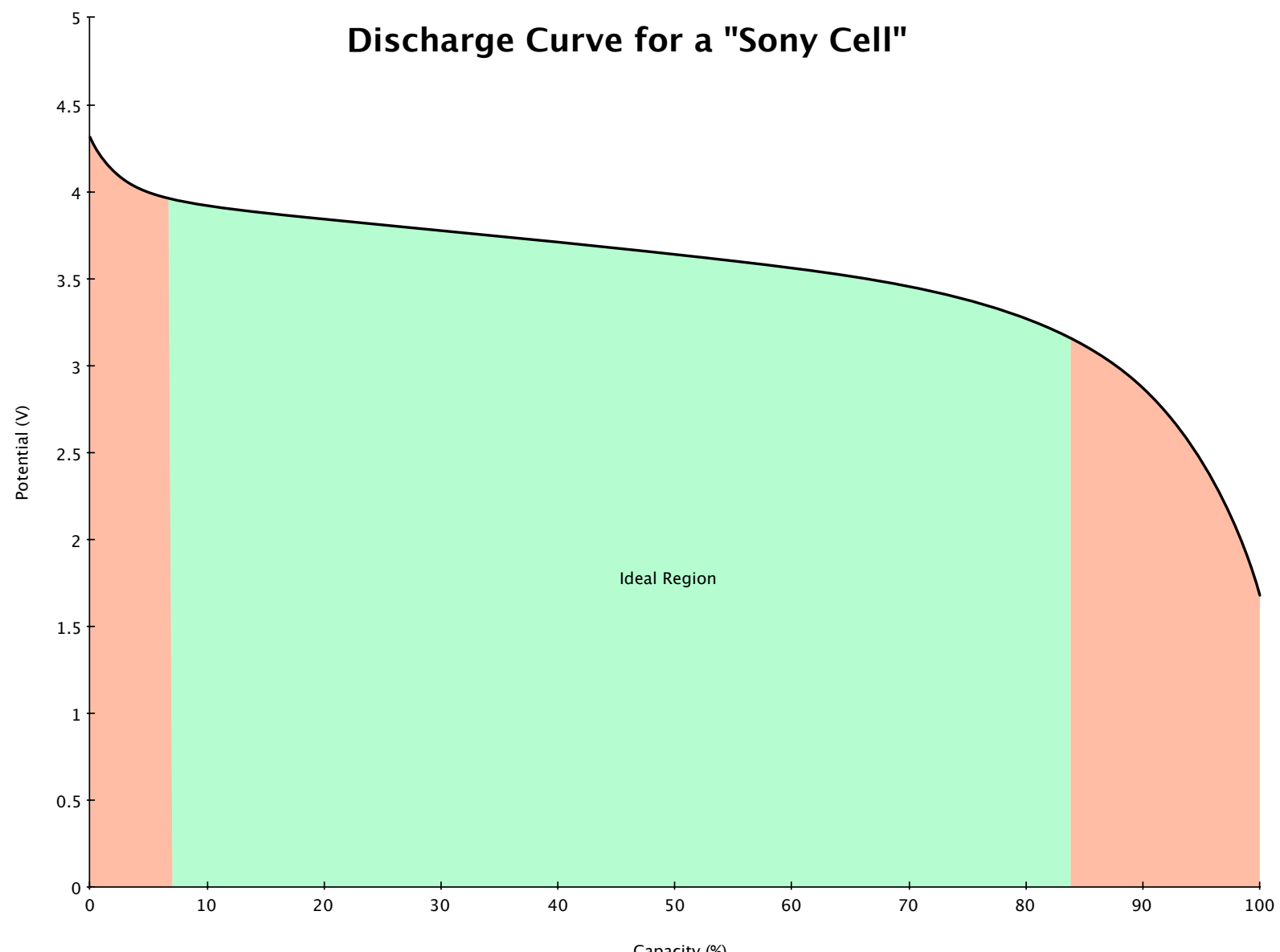
- Charge retention
- Energy Density
- Power Density
- *Loves Shallow Discharge*
 - No memory effect

Overspec the battery

- For long term applications
- At 80% Depth of Discharge (DoD) 500 Cycles
- At 50% DoD, 1500 Cycles
- At 10% DoD, > 10000 Cycles
- So if you use 10% of the battery, you ultimately get > 2.5 times the energy delivered

Undercharge the battery

- For an LiCoO_2 cell, charge to 4 V instead of 4.2 V



Different Li Ion Cells

- Three years ago, there was just one type of cell to buy, but now there are a few.
- An easy guide:
 - If you want **more capacity for a given size** use cells with a **LiCoO₂** cathode
 - If you want **more power for a given size** use cells with a **LiFePO₄** cathode
 - If you want **even more power**, use the above cathode with a **Li₄Ti₅O₁₂** anode

But?

- Large Li-Polymer-Ion batteries generate a lot of heat, and to handle them safely serious regard must be given to cooling



source: tesla motors

Also, Money

- They're quite expensive, roughly ~5 to 10 times more per unit energy than lead acid, and 2-3 times more than NiMH

In fact

- If you want to “set it and forget it”*, you may want to think about using alkaline primaries
- Easier to implement, better energy density than any secondary cell, and a fraction the cost of any secondary cell per unit energy

* please don't forget it

Overall

Batteries...

- Combine controlled chemical reaction and mass transfer within confined spaces
- Have benefited from materials engineering, but not to the degree enjoyed by ICs
- Will provide more energy over their lifetime if cycled shallow and gently

Questions and Next Steps?

- Questions?
- Would you be interested in a “future of batteries talk”?
- Or a workshop where you build and test your own batteries?