

Batteries part II: *Fundamental battery concepts*

47202: Introduction to Future Energy; 2023-11-14

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$$\Delta E = 0 \quad \Delta S \geq 0 \quad \int_a^b \mathcal{E} \Theta + \Omega \int_0^{\sqrt{17}} \delta e^{i\pi} = \\ \infty = \{2.7182818284 \dots\} \quad \sum_{n=0}^{\infty} n!'$$

Electrochemical Reactions

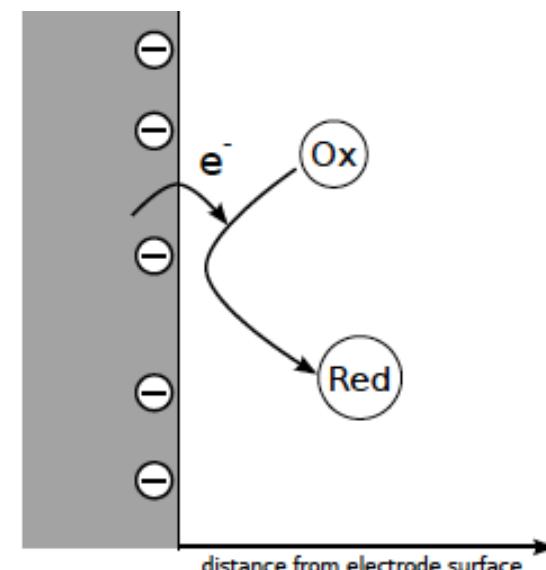
Many chemical substances can exist in more than one oxidation state: that is to say, they can donate or accept electrons from other species.



Electrochemical reactions, reduction and oxidation reactions, or *redox* reactions, can take place between species in solution (or solids):



Such reactions can also take place at the interface of an *electrode* (often a solid metallic conductor) and an electrolyte containing a redox active species (a redox couple)



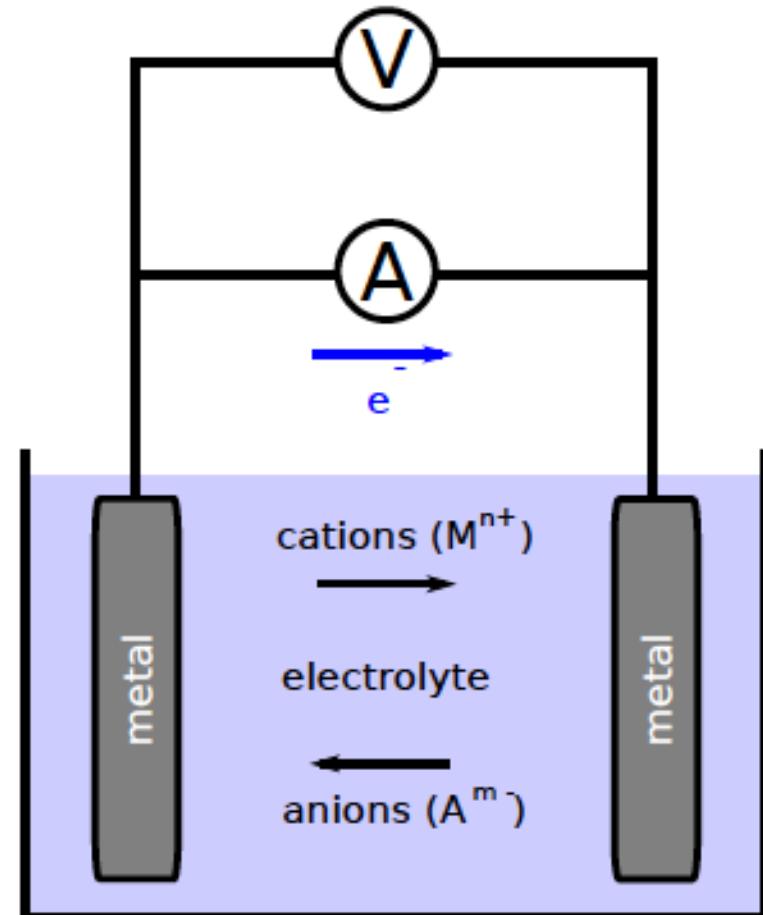
Electrochemical Cells

Formed by two electrodes (one positive, one negative) and separated by an electrolyte.

The **electrodes** need to be *electronically conducting*, and are often metals, but can also be made from many other materials, e.g. graphite, metal oxides, etc

The **electrolyte** is (ideally) *ionically conducting*, but electronically insulating.
An electrolyte in a battery is typically a solvent, or solid polymer, with some amount of salt dissolved to provide ionic conductivity.

High input impedance, $i \sim 0$



Definitions – anode and cathode

The **anode** is the electrode where **oxidation** takes place

An **anodic** process is an **oxidation** process.

Something is **oxidized** at the **anode** and

Electrons are **liberated** at the **anode**

The **cathode** is the electrode where **reduction** takes place

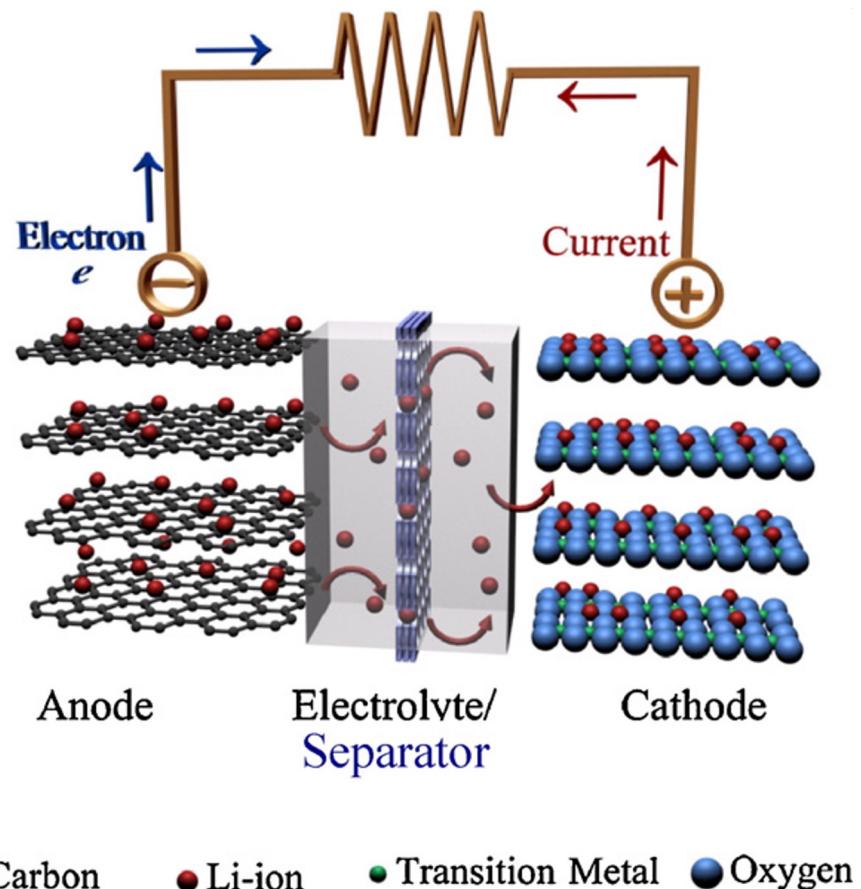
An **cathodic** process is a **reduction** process.

Something is **reduced** at the **cathode**

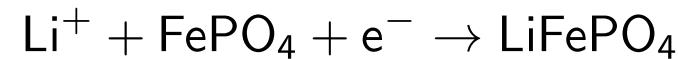
Electrons are **consumed** at the **cathode**

Battery Cells

Formed by two electrodes (one positive, one negative) and separated by an electrolyte.



Consider FePO₄/LiFePO₄ (LFP) used as the positive electrode material:

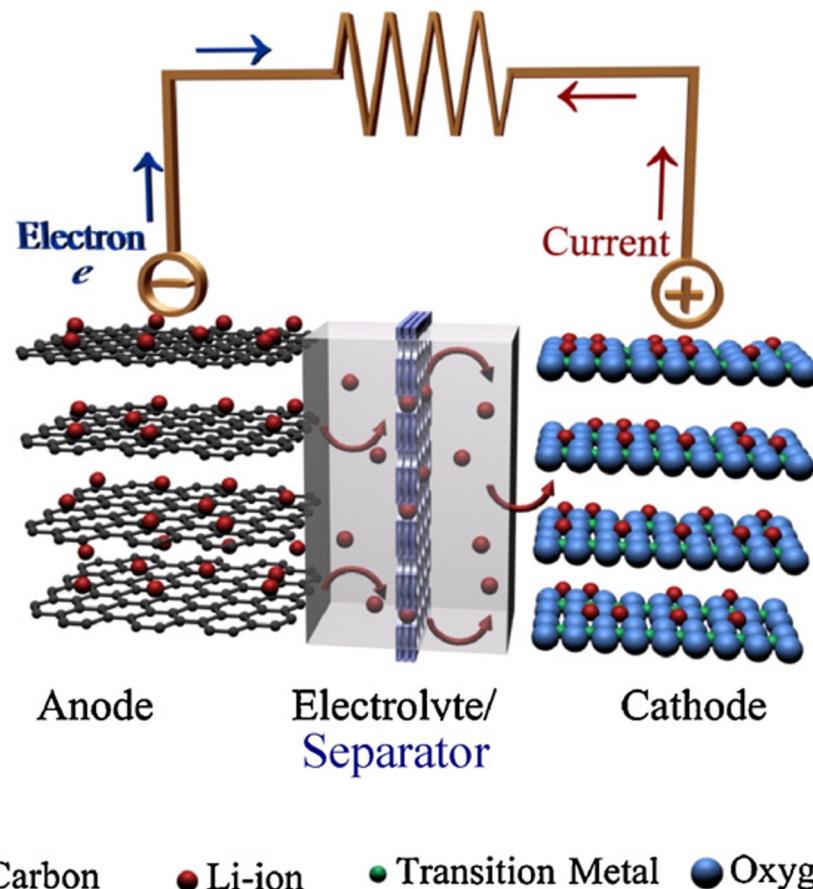


What is reduced during discharge in this cell?

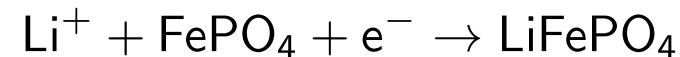
Source: Image from Song et al, Materials Science and Engineering: R: Reports 2011, 72 (11), 203–252.

Battery Cells

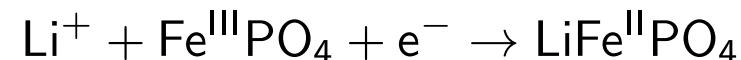
Formed by two electrodes (one positive, one negative) and separated by an electrolyte.



Consider $\text{FePO}_4/\text{LiFePO}_4$ (LFP) used as the positive electrode material:



What is reduced during discharge in this cell?



Source: Image from Song et al, Materials Science and Engineering: R: Reports 2011, 72 (11), 203–252.

Electrochemical Power Sources

Batteries and fuel cells are electrochemical cells where *faradaic* reactions take place.

This means that reactants are changing redox state.

There is also power sources such as capacitors / supercapacitors, but here the energy is stored *electrostatically* rather than *chemically*.

Electrochemical Power Source (Galvanic Cells - Discharge)	Reactants contained inside cell (mostly)	Primary cells (discharge only)
	Battery	Secondary cells (rechargeable)
Fuel Cell	Reactants supplied	

Current, Current Density

Current is a flow of charge per unit of time. The coulomb (unit symbol: C) is the International System of Units (SI) unit of electric charge.

Current $I = \frac{dQ}{dt}$ Units: $C\ s^{-1} = A$

Current density $j = \frac{dQ}{A \cdot dt}$ Units: $A\ cm^{-2}, A\ m^{-2}$

1 Coulomb is the charge (symbol: Q or q) transported by a constant current of 1 ampere in 1 second.

The rate of an electrochemical reaction can be followed by counting the number of charges released per unit of time (by measuring the resulting current).

The [capacity of a battery](#) can be measured by [counting the amount of charge](#) released during discharge.

Faraday's law

The current flowing at any time as a consequence of an electrochemical reaction is related to the amount of material converted per unit time:

$$I = zF \frac{dn}{dt}$$

where **n** is the number of moles of converted material, **z** is the number of electrons involved in the reaction and **F** is Faraday's constant.

The *total amount* of converted material in a reaction is the integral of the previous expression:

$$n = \frac{1}{zF} \int_0^t I dt = \frac{Q}{zF}$$

For a reaction running at a constant rate,
i.e. at a constant current, the charge passed is simply: $Q = It$

Theoretical Capacity of a Battery

Now when we know how to relate the amount of converted material with the charge passed in an electrochemical reaction we can use this to calculate the ***theoretical capacity*** (*i.e.* the total amount of charge released) of any electrode material that could be used in a battery.

So, for a given amount of active material the theoretical capacity, Q_T is

$$Q_T = znF \quad \text{Theoretical Capacity}$$

and

$$n = \frac{m}{M_w} \quad \text{Number of moles of active material}$$

where M_w is the molecular (or formula) weight of the active material, and m is the mass of the active material (z is the number of electrons involved in the reaction).

Thus:

$$Q_T = \frac{zmF}{M_w}$$

or, for $m = 1$ g
it becomes:

$$Q_T = \frac{zF}{M_w}$$

Question

Take 5 min to think about this (you can team up in pairs/chat/whatever):

For practical reasons the unit used is often mAh (milli-ampere hours) per g of active material. A = C/s, thus C = As, but how many C (Coulombs) is one Ah? and one mAh?

Question

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$$1 \text{ C} = 1 \text{ As}, 1\text{h} = 3600 \text{ s} \rightarrow 3600 \text{ As} = 1 \text{ Ah} = 3600 \text{ C}$$

$$1 \text{ mAh} \text{ is } 0.001 * 3600 \text{ As} = 3.6 \text{ As} = 3.6 \text{ C}$$

Thus, if we want to give the theoretical capacity in mAh/g we would use:

$$Q_{T,\max} = \frac{zF}{3.6M_w}$$

The Reversible Cell Voltage

The cell voltage, E , of a cell, at equilibrium ($i = 0$), is related to the maximum work that can be done by the cell, which corresponds to ΔG :

$$\Delta G_r^\circ = \Delta H_r^\circ - T\Delta S_r^\circ = -nFE^\circ$$

$$-\frac{\Delta G_r^\circ}{nF} = E^\circ$$

This important relationship provides a link between thermodynamics and electrochemical cells at equilibrium. [n - number of electrons, F - Faraday's const.]

The $^\circ$ symbol indicates that we are referring to standard conditions (activities = 1, $T = 298$ K, $P = 1$ atm) in this case. This is often referred to as the reversible cell voltage. A more general term would be electric potential difference*

For non-standard conditions we often use the term “open-circuit voltage” for the cell and Nernst voltage / electrode potential for the half-cells.

* <http://goldbook.iupac.org/E01934.html>

Half-Cell Standard Reduction Potentials

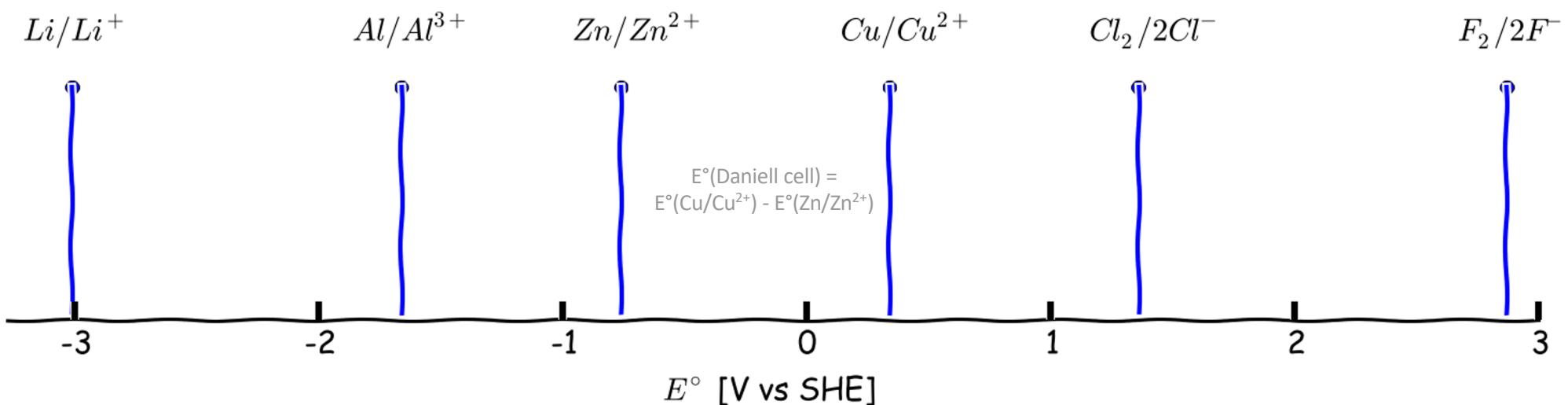
Listing of half-cell reactions written as reduction reactions with potentials given at standard conditions, *i.e. standard reduction potentials*

Electrode reaction	E^0 (V)	Electrode reaction	E^0 (V)	Reference reaction with $\Delta G_r = 0$ by convention
$\text{Li}^+ + \text{e} \rightleftharpoons \text{Li}$	-3.01	$\text{Tl}^+ + \text{e} \rightleftharpoons \text{Tl}$	-0.34	
$\text{Rb}^+ + \text{e} \rightleftharpoons \text{Rb}$	-2.98	$\text{Co}^{2+} + 2\text{e} \rightleftharpoons \text{Co}$	-0.27	
$\text{Cs}^+ + \text{e} \rightleftharpoons \text{Cs}$	-2.92	$\text{Ni}^{2+} + 2\text{e} \rightleftharpoons \text{Ni}$	-0.23	
$\text{K}^+ + \text{e} \rightleftharpoons \text{K}$	-2.92	$\text{Sn}^{2+} + 2\text{e} \rightleftharpoons \text{Sn}$	-0.14	
$\text{Ba}^{2+} + 2\text{e} \rightleftharpoons \text{Ba}$	-2.92	$\text{Pb}^{2+} + 2\text{e} \rightleftharpoons \text{Pb}$	-0.13	
$\text{Ca}^{2+} + 2\text{e} \rightleftharpoons \text{Ca}$	-2.84	$\text{H}^+ + \text{e} \rightleftharpoons \frac{1}{2}\text{H}_2$	0.000	
$\text{Na}^+ + \text{e} \rightleftharpoons \text{Na}$	-2.71	$\text{Cu}^{2+} + 2\text{e} \rightleftharpoons \text{Cu}$	0.34	
$\text{Mg}^{2+} + 2\text{e} \rightleftharpoons \text{Mg}$	-2.38	$\frac{1}{2}\text{O}_2 + \text{H}_2\text{O} + 2\text{e} \rightleftharpoons 2\text{OH}^-$	0.40	
$\text{Ti}^{2+} + 2\text{e} \rightleftharpoons \text{Ti}$	-1.75	$\text{Cu}^+ + \text{e} \rightleftharpoons \text{Cu}$	0.52	
$\text{Be}^{2+} + 2\text{e} \rightleftharpoons \text{Be}$	-1.70	$\text{Hg}^{2+} + 2\text{e} \rightleftharpoons \text{Hg}$	0.80	
$\text{Al}^{3+} + 3\text{e} \rightleftharpoons \text{Al}$	-1.66	$\text{Ag}^+ + \text{e} \rightleftharpoons \text{Ag}$	0.80	
$\text{Mn}^{2+} + 2\text{e} \rightleftharpoons \text{Mn}$	-1.05	$\text{Pd}^{2+} + 2\text{e} \rightleftharpoons \text{Pd}$	0.83	
$\text{Zn}^{2+} + 2\text{e} \rightleftharpoons \text{Zn}$	-0.76	$\text{Ir}^{3+} + 3\text{e} \rightleftharpoons \text{Ir}$	1.00	
$\text{Ga}^{3+} + 3\text{e} \rightleftharpoons \text{Ga}$	-0.52	$\text{Br}_2 + 2\text{e} \rightleftharpoons 2\text{Br}^-$	1.07	
$\text{Fe}^{2+} + 2\text{e} \rightleftharpoons \text{Fe}$	-0.44	$\text{O}_2 + 4\text{H}^+ + 4\text{e} \rightleftharpoons 2\text{H}_2\text{O}$	1.23	
$\text{Cd}^{2+} + 2\text{e} \rightleftharpoons \text{Cd}$	-0.40	$\text{Cl}_2 + 2\text{e} \rightleftharpoons 2\text{Cl}^-$	1.36	
$\text{In}^{3+} + 3\text{e} \rightleftharpoons \text{In}$	-0.34	$\text{F}_2 + 2\text{e} \rightleftharpoons \text{F}^-$	2.87	

Negative and Positive Electrodes

When dealing with reversible electrochemical cells, such as rechargeable batteries, we have the problem that the **anode** and **cathode** *switches places* when switching between discharge (galvanic) and charge (electrolytic) modes.

Confusion can be avoided if we refer to the anode during discharge as the negative electrode (it will always be at a more negative voltage)



For example, the Daniell Cell, which relies on the Zn and Cu half-cell reactions, Zn would always be the negative electrode, and in a Li-battery the Li electrode would be the negative electrode.

Electrodes & Processes

Characteristics of electrochemical systems with forced or spontaneous current flow:

Battery	Discharge	Charge
Reactions	spontaneous	non-spontaneous
Positive Electrode	cathode (reduction)	anode (oxidation)
Negative Electrode	anode (oxidation)	cathode (reduction)

We (try) to stick to the terminology “positive” and “negative” electrodes

but

often you will hear/read about “battery anodes / anode materials” and “battery cathodes / cathode materials”, and then it generally refers to the situation in discharge, i.e. as it applies to a galvanic cell.

Energy Stored in a Battery

Practical Measurement of the Energy Content of Batteries:

Often more useful and more practical to calculate the energy content, U of the battery based on the full time course of its discharge voltage, $E_{cell}(t)$, measured at the current, $I_{cell}(t)$:

$$U = \int_0^t E_{cell}(t) \cdot I_{cell}(t) dt$$

For the case of discharge at constant current, and with a negligible change in cell voltage (e.g. a LiFePO₄ based battery) during discharge:

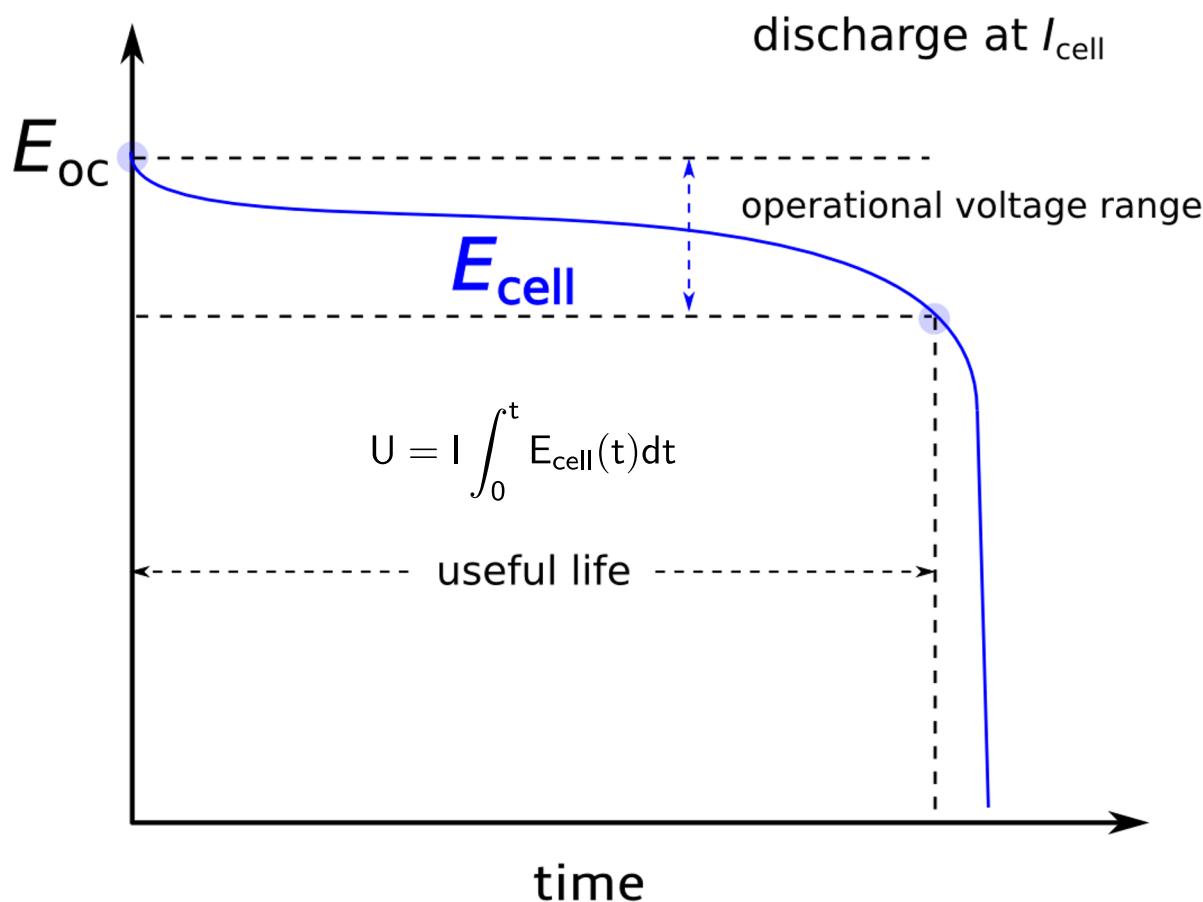
$$U = E_{cell} \cdot I_{cell} \cdot t$$

Note that in reality, one should include the weight of both electrodes, and the weights of the various components in the cell in reporting the energy density...

Energy Stored & Charge-Discharge Curves

To increase the energy of a battery, there are two main options:

- 1) increase the capacity or
- 2) increase the (operational, or average) voltage

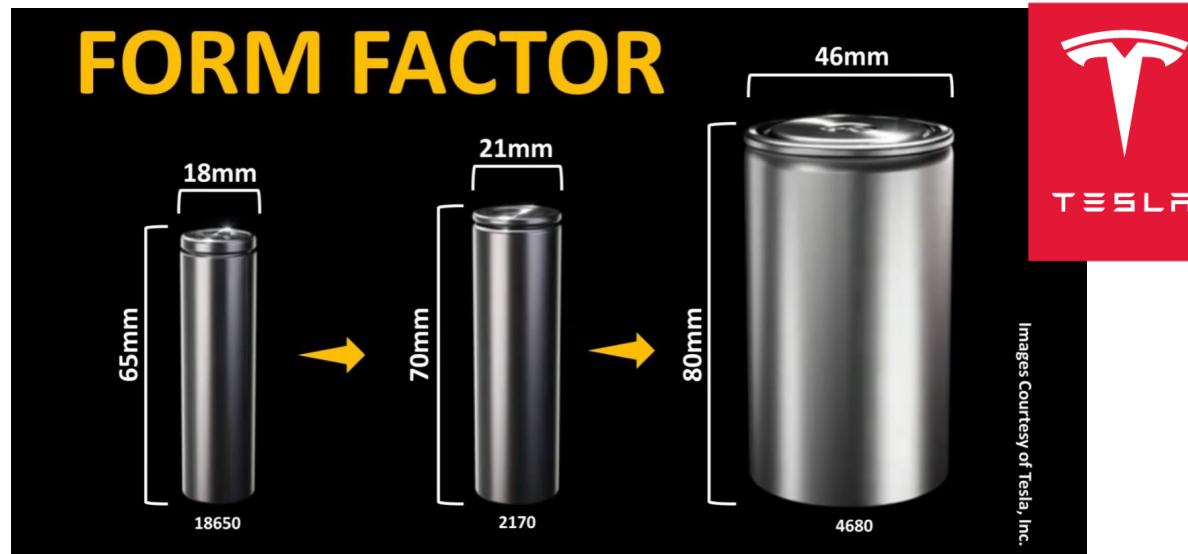


So, we can obtain the amount of energy stored in a battery from a discharge curve...

Short reflection break (2 min to let it sink in)?

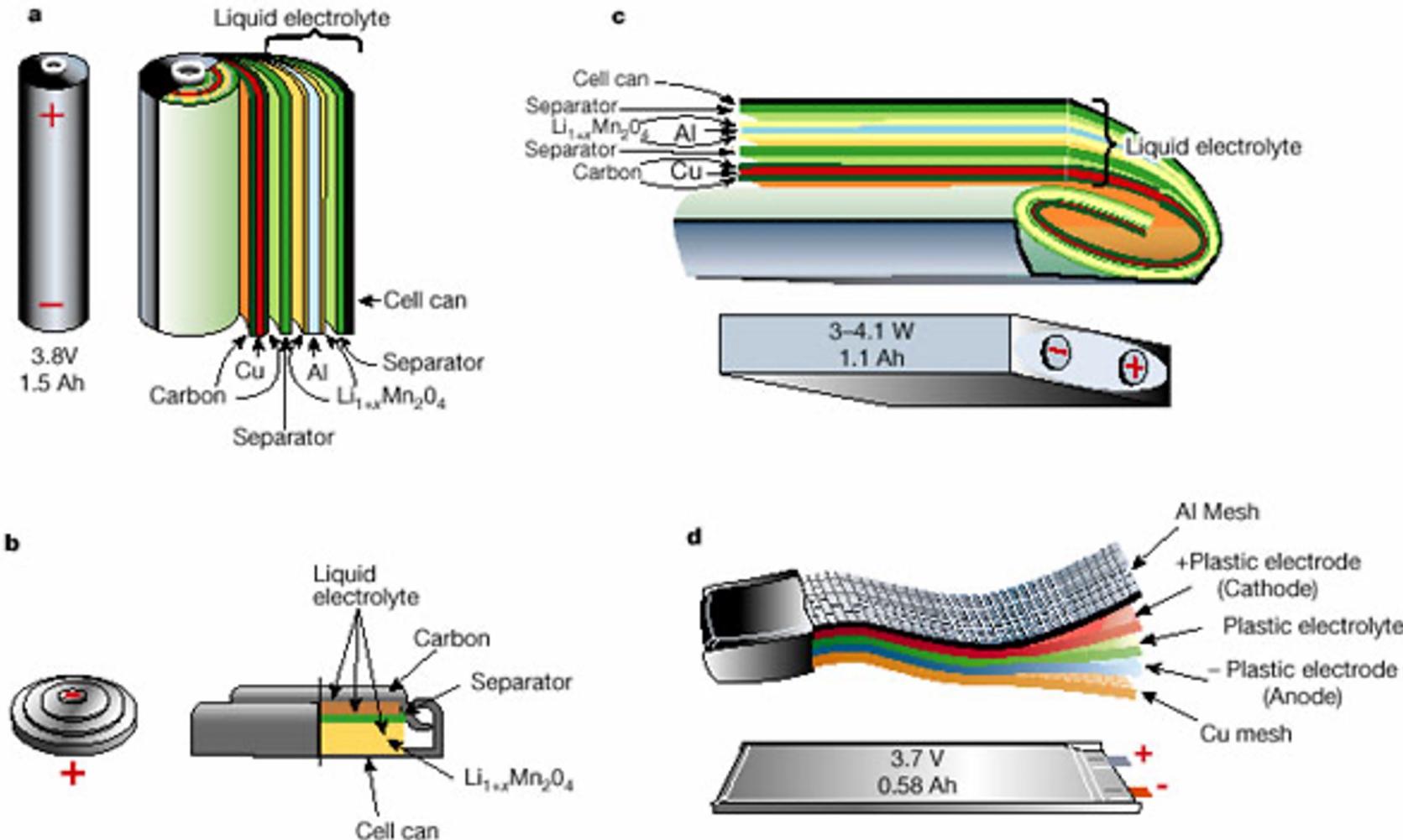
Changing the battery cell design...

- Changing the cell design can also have substantial impact on the energy and power density
- It can also change the limiting processes



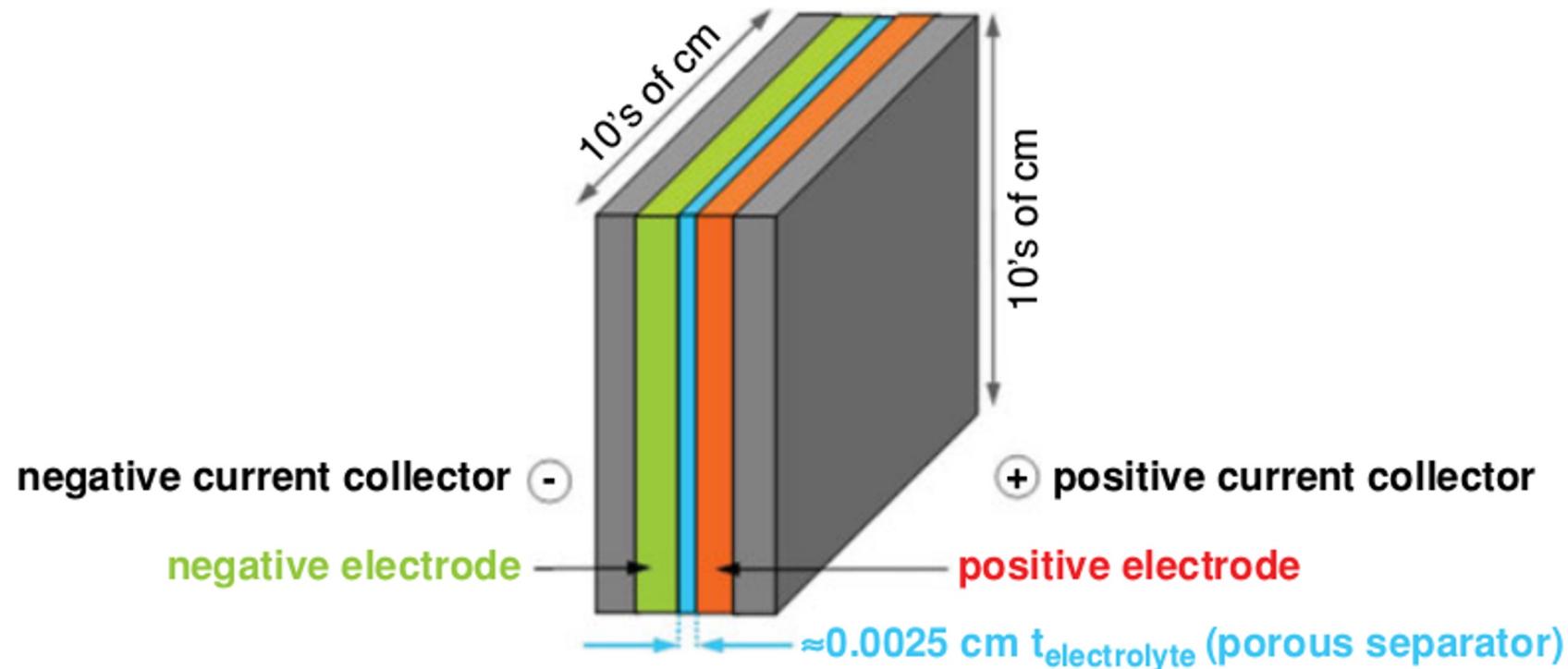
Tesla@Texas: 625,000 cells per week!

Common Battery Configurations



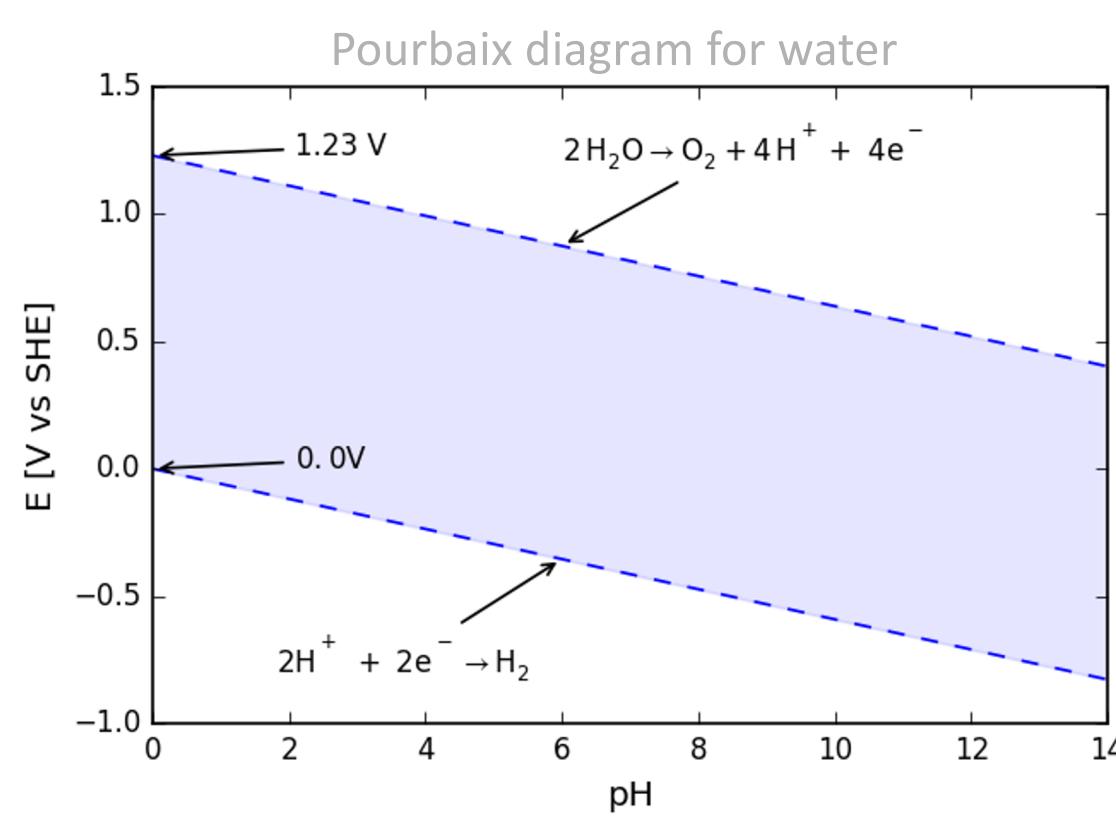
Source: Tarascon, J.-M.; Armand, M. Issues and Challenges Facing Rechargeable Lithium Batteries. *Nature* 2001, 414, 359–367.

Configuration of a typical Li-ion Battery



Aqueous Electrolytes

e.g. water mixed with sulfuric acid (Lead – Acid), or water with some dissolved salt



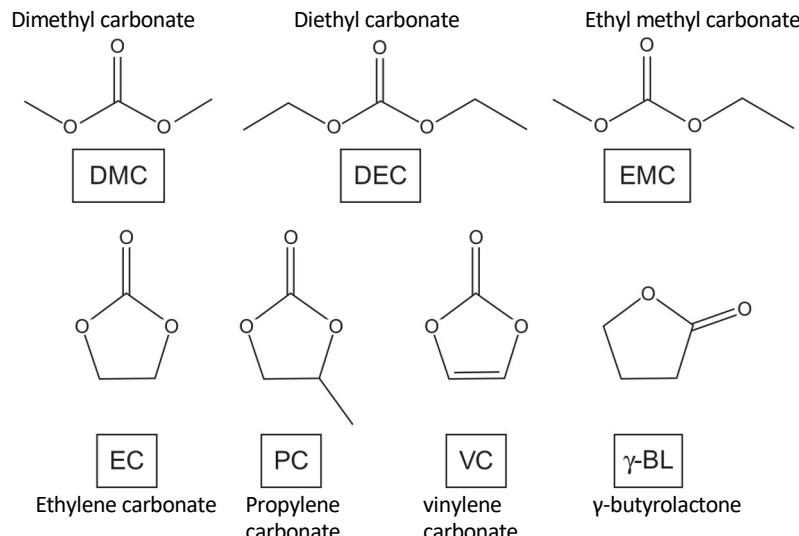
Advantages: Environmentally benign, cheap, abundant, high conductivity (with salts)

Disadvantage: A narrow “stability window”, risk of hydrogen/oxygen evolution

Organic Electrolytes

Organic solvent + dissolved (and highly dissociated) electrolyte salt

Low dielectric constant, low viscosity (DEC, EMC)



High dielectric constant,
high viscosity

EC, VC: good film
formers on carbon

Solvent	Molecular weight	Boiling point (°C)	Dielectric constant	Viscosity (cP)	Density (g cm ⁻³)
ACN	41.05	81.6	35.95	0.341	0.777
γ-BL	86.09	204	39.1	1.75	1.13
DEC	118.13	126	2.84	0.81	0.975
DMC	90.08	90.1	3.1	2.4	1.07
DME	90.12	84.0	7.20	0.455	0.859
DMF	73.10	158	36.71	0.796	0.944
DMSO	78.13	189.0	46.45	1.991	1.095
EC	88.06	248	89.6	1.85 (40 °C)	1.322
EMC	104.1	109	2.4	0.65	1.00
MF	60.06	31.5	8.5	0.333	0.974
NM	61.04	101.2	35.94	0.694	1.131
PC	102.1	241	64.4	2.53	1.19
THF	72.12	65.0	7.39	0.46	0.880
VC	86.05	162	127	–	1.36

Properties of a good electrolyte for Li ion batteries

- High dielectric constant (to favour dissociation of the lithium salt).
- Low volatility (*i.e.* high boiling point).
- Low viscosity (assuring fast ion movement).
- No reactivity toward electrode materials (film formation is an exception).

Source: Montanino et al; 4 - Electrolytes for Rechargeable Lithium Batteries. In Rechargeable Lithium Batteries; Franco, A. A., Ed.; Woodhead Publishing Series in Energy; Woodhead Publishing, 2015; pp 73–116.

Electrolyte Salts – Organic Electrolytes

One of the most common salts:



Table 1. Anodic stability of some conventional lithium salts.

Solvent	Working electrode	Oxidation potential (vs. Li^+/Li) [V]					
		ClO_4^-	PF_6^-	BF_4^-	AsF_6^-	$\text{N}(\text{CF}_3\text{SO}_2)_2^-$	CF_3SO_3^-
EC/DEE ^[24]	$\text{Li}_{1+x}\text{Mn}_2\text{O}_4$	4.55	3.8	3.4	3.9	4.4	4.1
EC/DMC ^[24]	$\text{Li}_{1+x}\text{Mn}_2\text{O}_4$	>5.1	>5.1	>5.1	4.7	4.35	3.2
EC/DMC ^[25]	AC	-	4.55	4.78	4.96	4.33	4.29

Source: Tan et al; Recent Progress in Research on High-Voltage Electrolytes for Lithium-Ion Batteries.
 ChemPhysChem 2014, 15 (10), 1956–1969.

Discharge at Constant Current

Galvanic cell (Discharge):

$$E_{\text{cell}} = E_{\text{reversible}} - iR_{\text{internal}} = E_{\text{reversible}} - \Delta E_{\text{losses}}$$

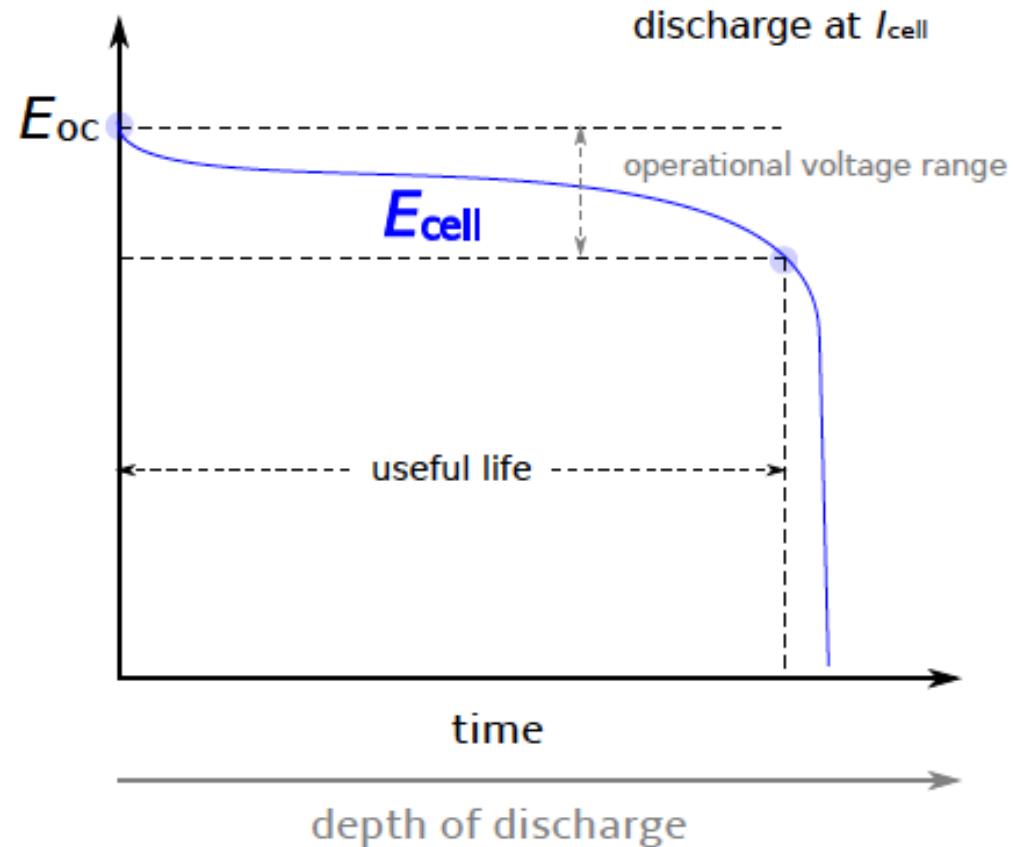
A discharge curve:

C-rate:

Describes how many times per hour the battery capacity is discharged (or charged).

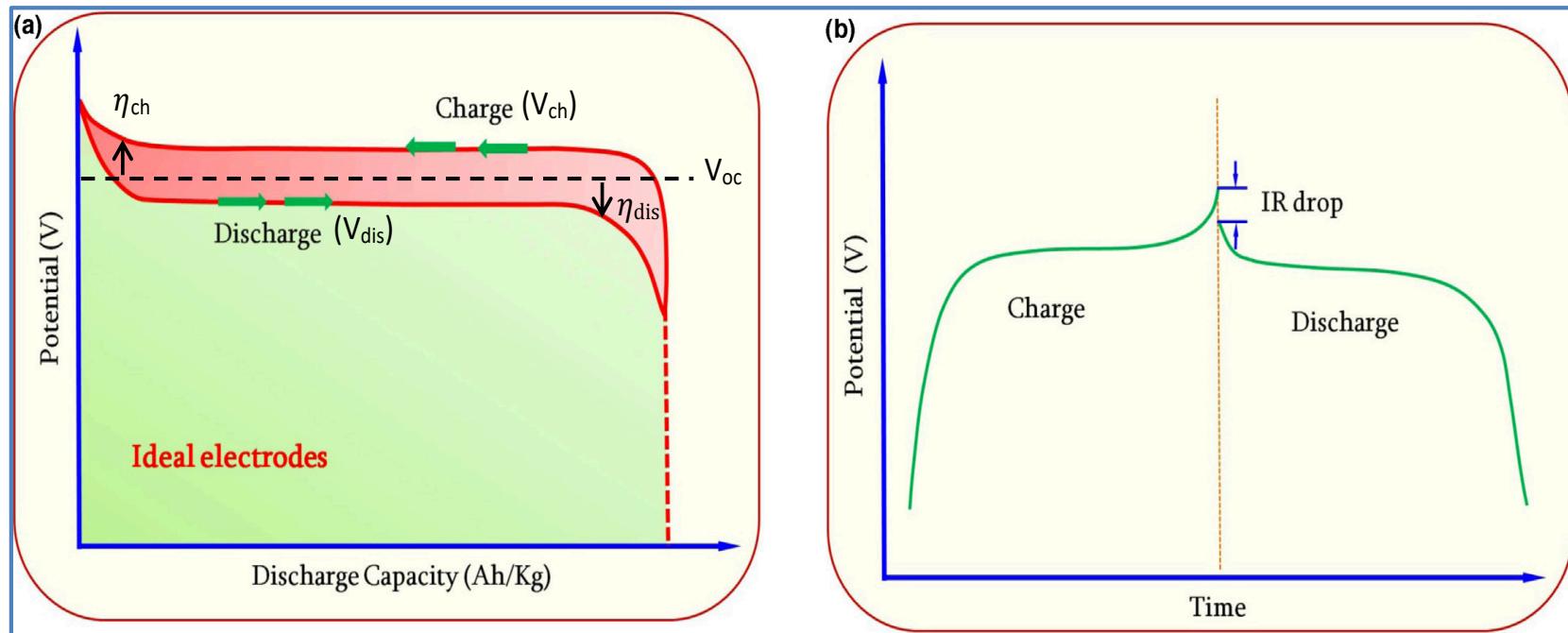
20 complete discharges per hour is a C-rate of 20C.

One discharge per 5 hours is a C-rate of C/5



Real batteries are not ideal

- Overpotentials (overvoltages) $\eta_{\text{dis}}(q, I_{\text{dis}})$ and $\eta_{\text{ch}}(q, I_{\text{ch}})$ limits the efficiency
- $V_{\text{dis}} = V_{\text{oc}} - \eta_{\text{dis}}(q, I_{\text{dis}})$ (1) and $V_{\text{ch}} = V_{\text{oc}} + \eta_{\text{ch}}(q, I_{\text{ch}})$ (2)
- $V_{\text{OC}} = (\mu_A - \mu_C)/e$ (4)

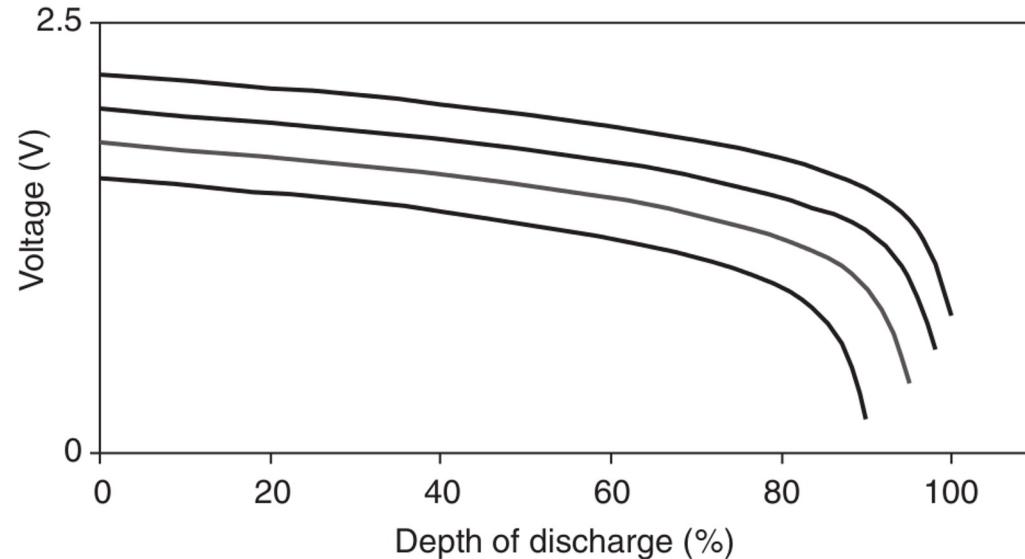
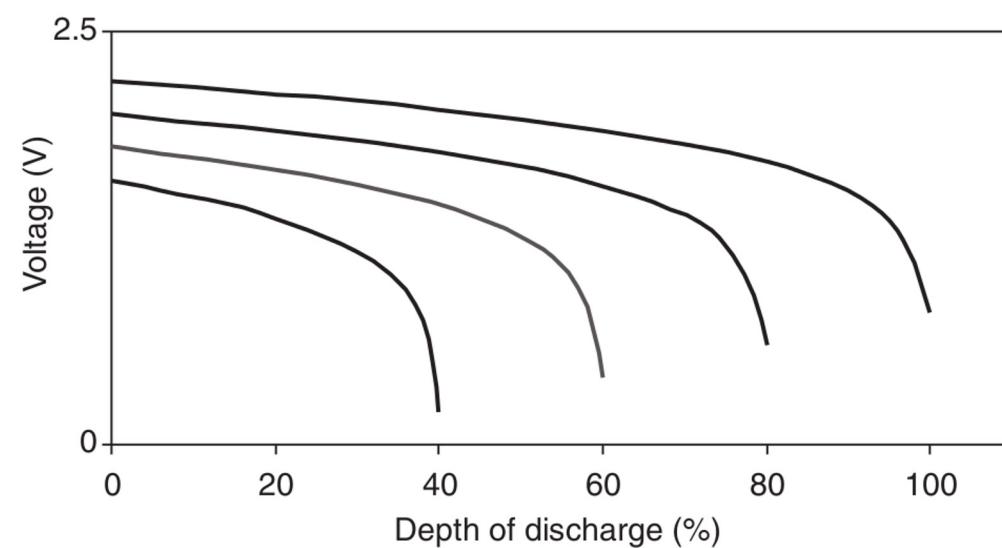


Effect of Current Density / C-rate

Discharge at higher current densities (or C-rate) causes the apparent capacity to decrease.

A battery with poor rate capability suffers a large decrease in apparent capacity with increasing C-rate

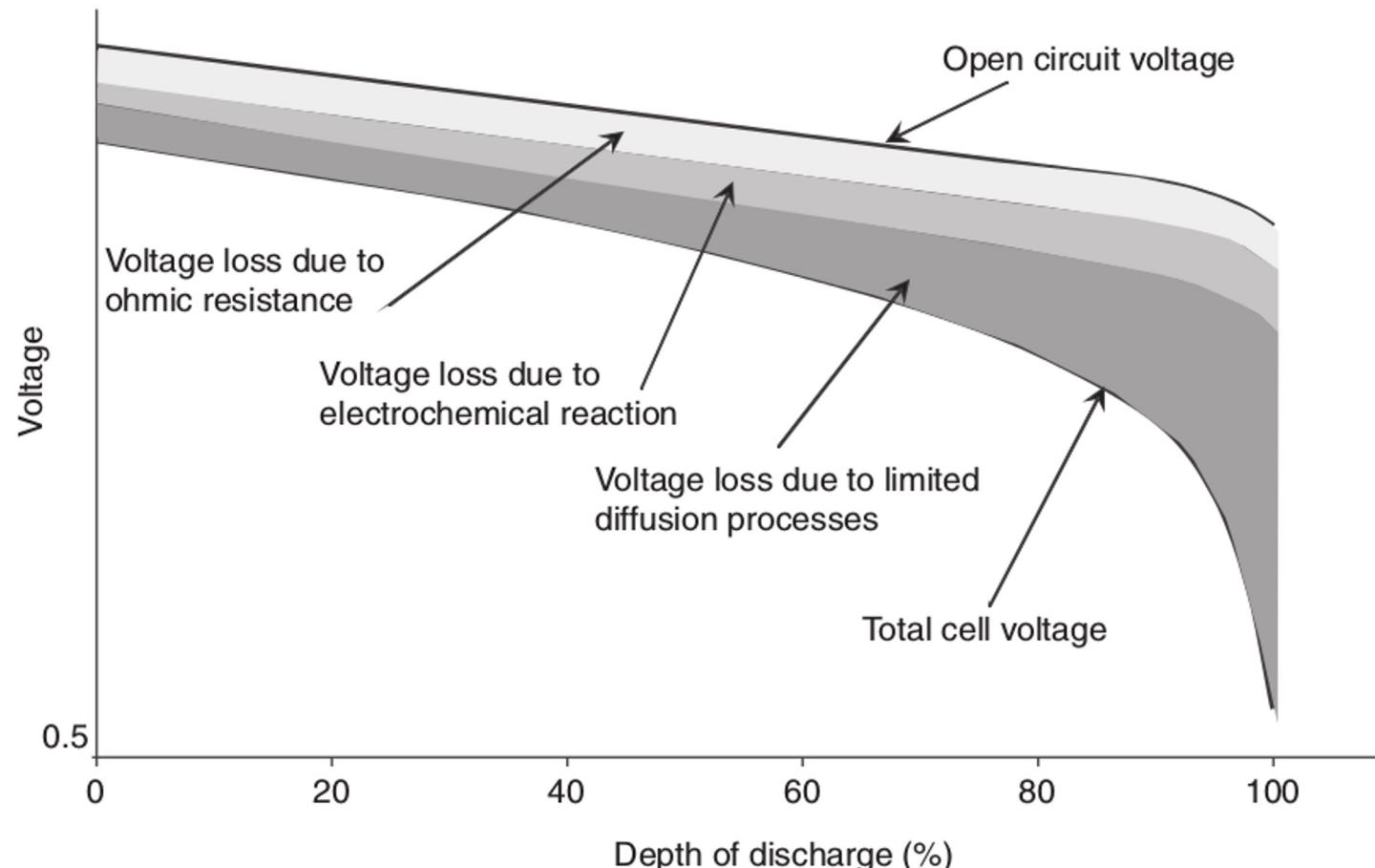
A battery with good rate capability only suffers a small decrease in apparent capacity with increasing C-rate



Losses in Battery Cells

Galvanic cell: $E_{\text{cell}} = E_{\text{reversible}} - iR_{\text{internal}} = E_{\text{reversible}} - \Delta E_{\text{losses}}$

Internal Resistance: $R_{\text{internal}} = R_{\text{Ohmic}} + R_{\text{Kinetic}} + R_{\text{MassTransport}} + \dots$



Battery Efficiency (Secondary Batteries only)

The electrical efficiency (ϵ) of secondary batteries and supercapacitors is determined by the voltage efficiency and the coulombic efficiency:

$$\epsilon = \epsilon_{\text{voltage}} \cdot \epsilon_{\text{coulombic}}$$

$$\epsilon_{\text{voltage}} = \frac{\text{Average voltage during discharging}}{\text{Average voltage during charging}}$$

$$\epsilon_{\text{coulombic}} = \frac{Q_{\text{discharge}}}{Q_{\text{charge}}} = \frac{1}{CF}$$

So, a battery with a low internal resistance (and thus a small overpotential) will have a high voltage efficiency...

Battery Efficiency - Coulombic

The **coulombic efficiency** (sometimes called “cycle efficiency”) is very sensitive to how one carries out the measurement of this quantity, so it is very important to be explicit about the strategy chosen. Charge retention can be quantified in a similar way, and is also dependent on cut-off voltages etc.

$$\epsilon_{\text{coulombic}} = \frac{Q_{\text{discharge}}}{Q_{\text{charge}}} = \frac{1}{CF}$$

A Coulombic efficiency lower than 1 (unity) means some side reactions are taking place, or other irreversible processes that “consumes” electrons.

