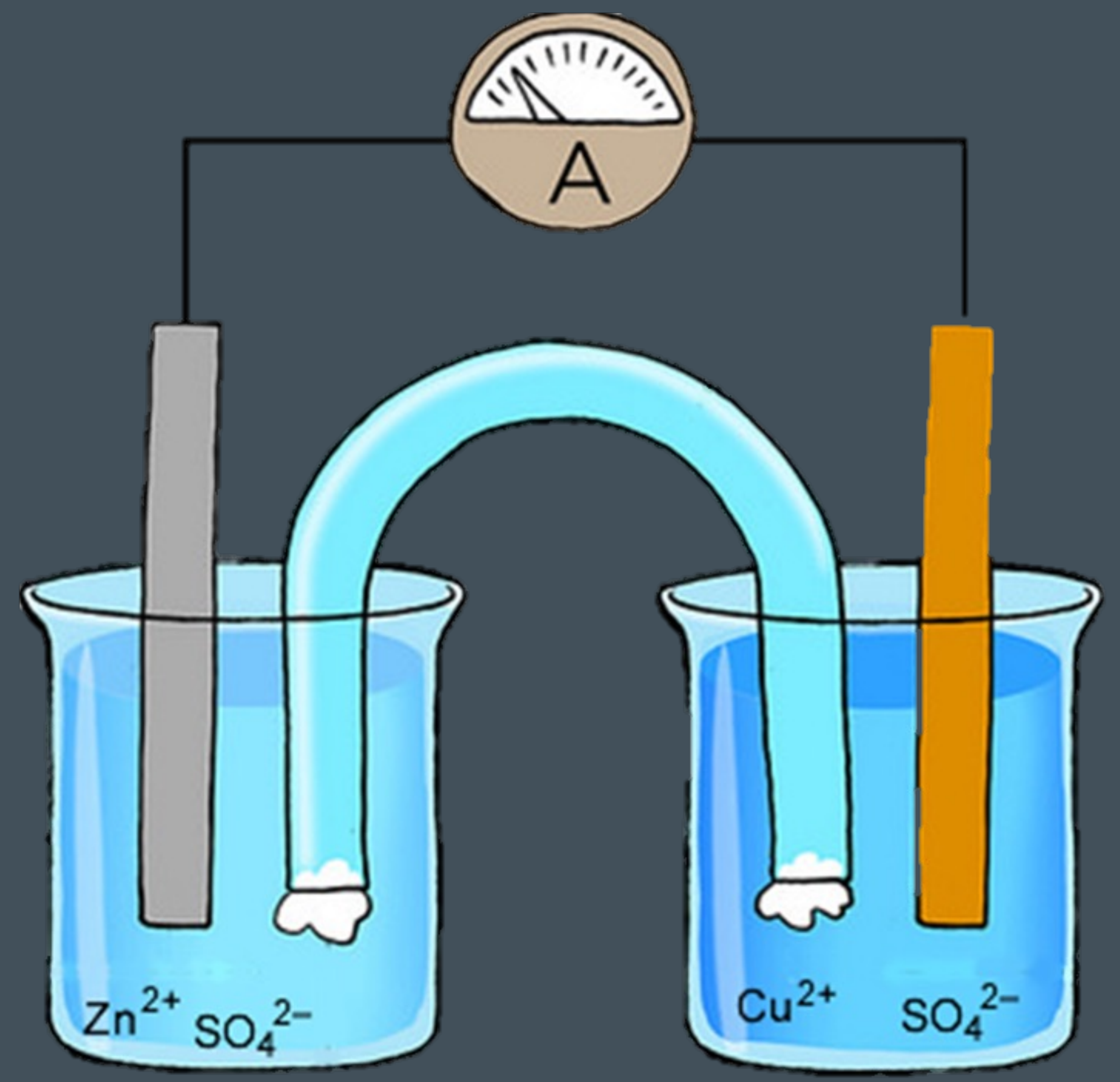
Unit 1 – Deck 6

ELECTROCHEMISTRY

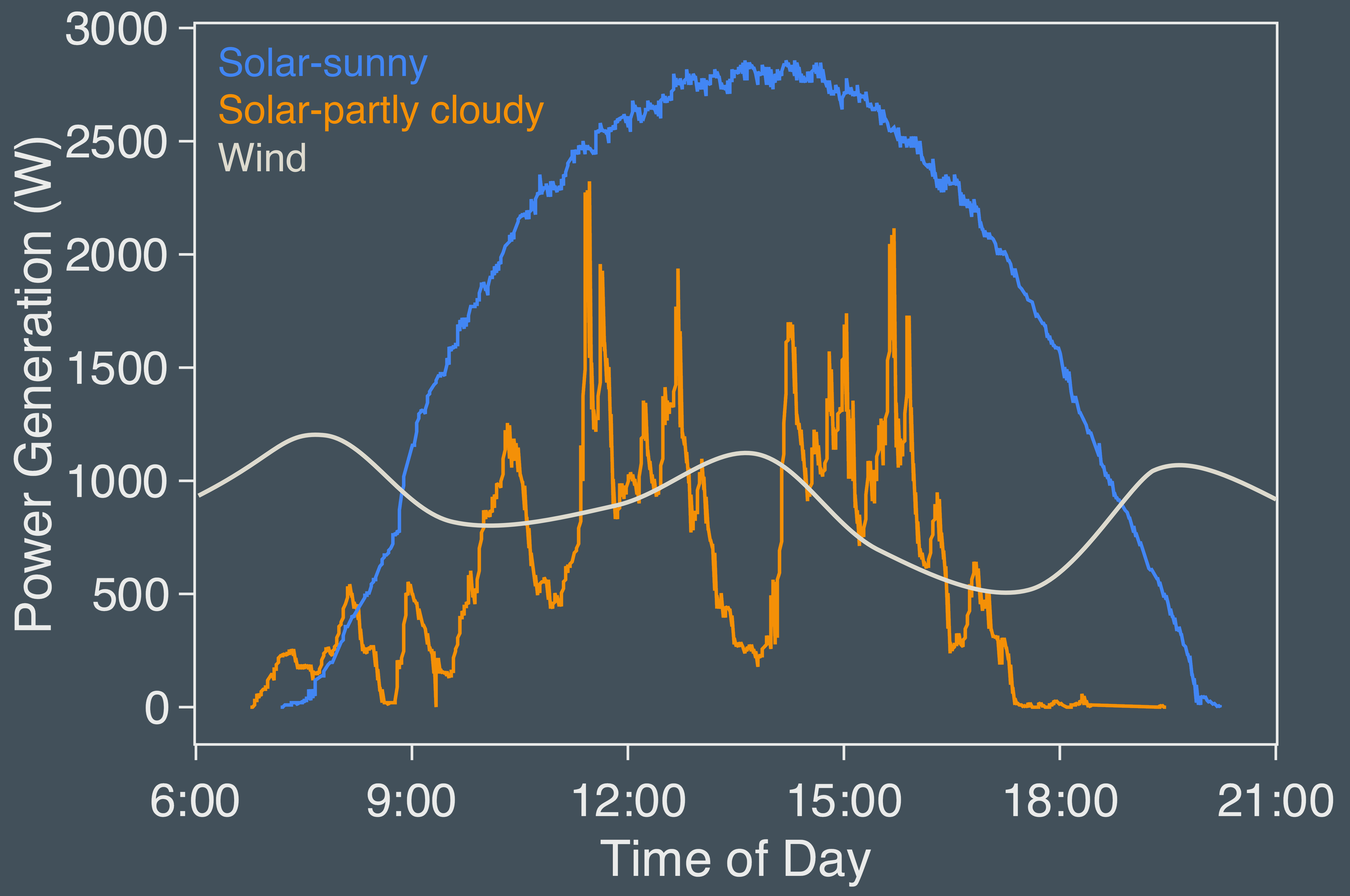
Energy Storage Applications

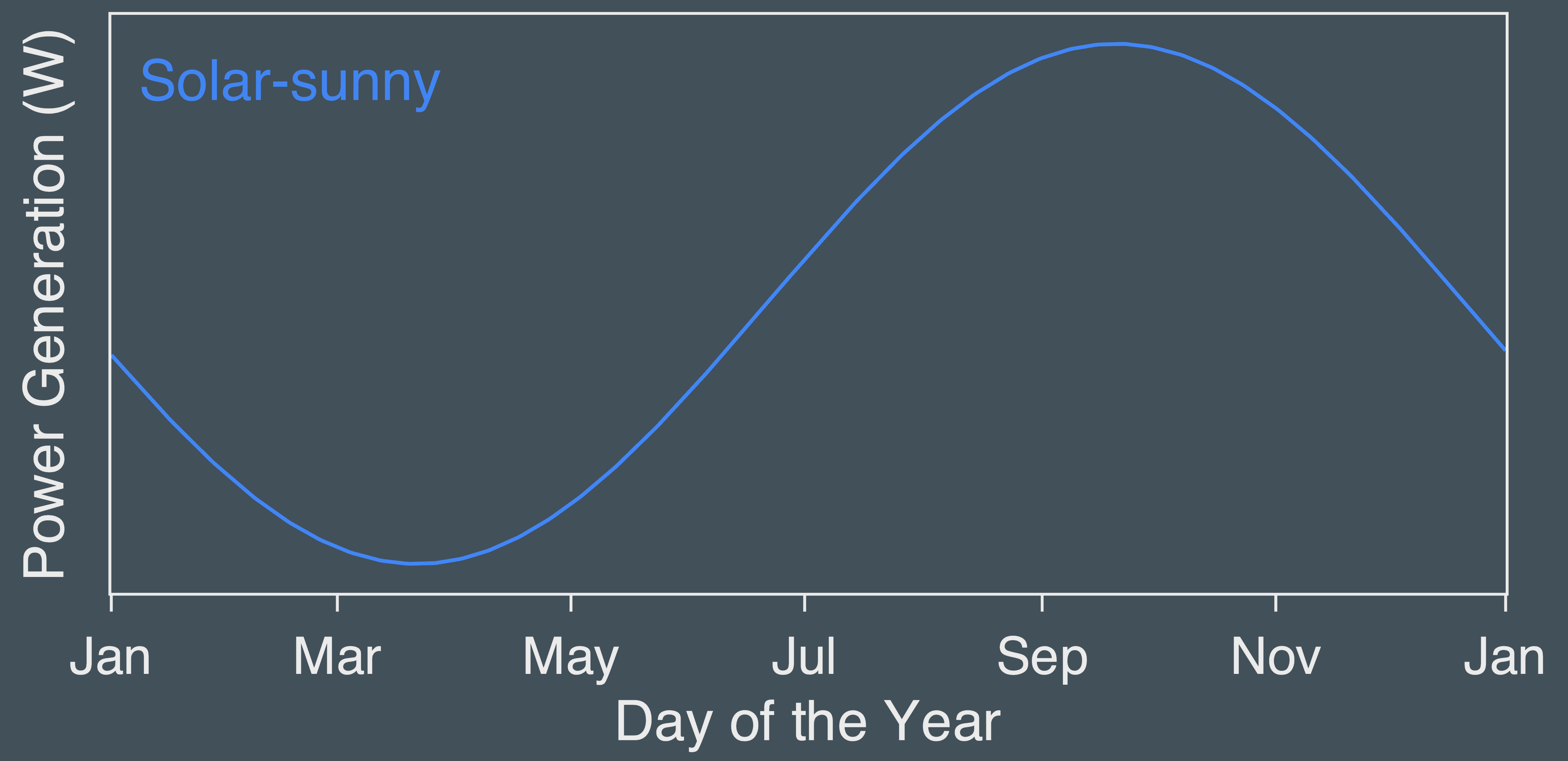
Topics – Energy Storage

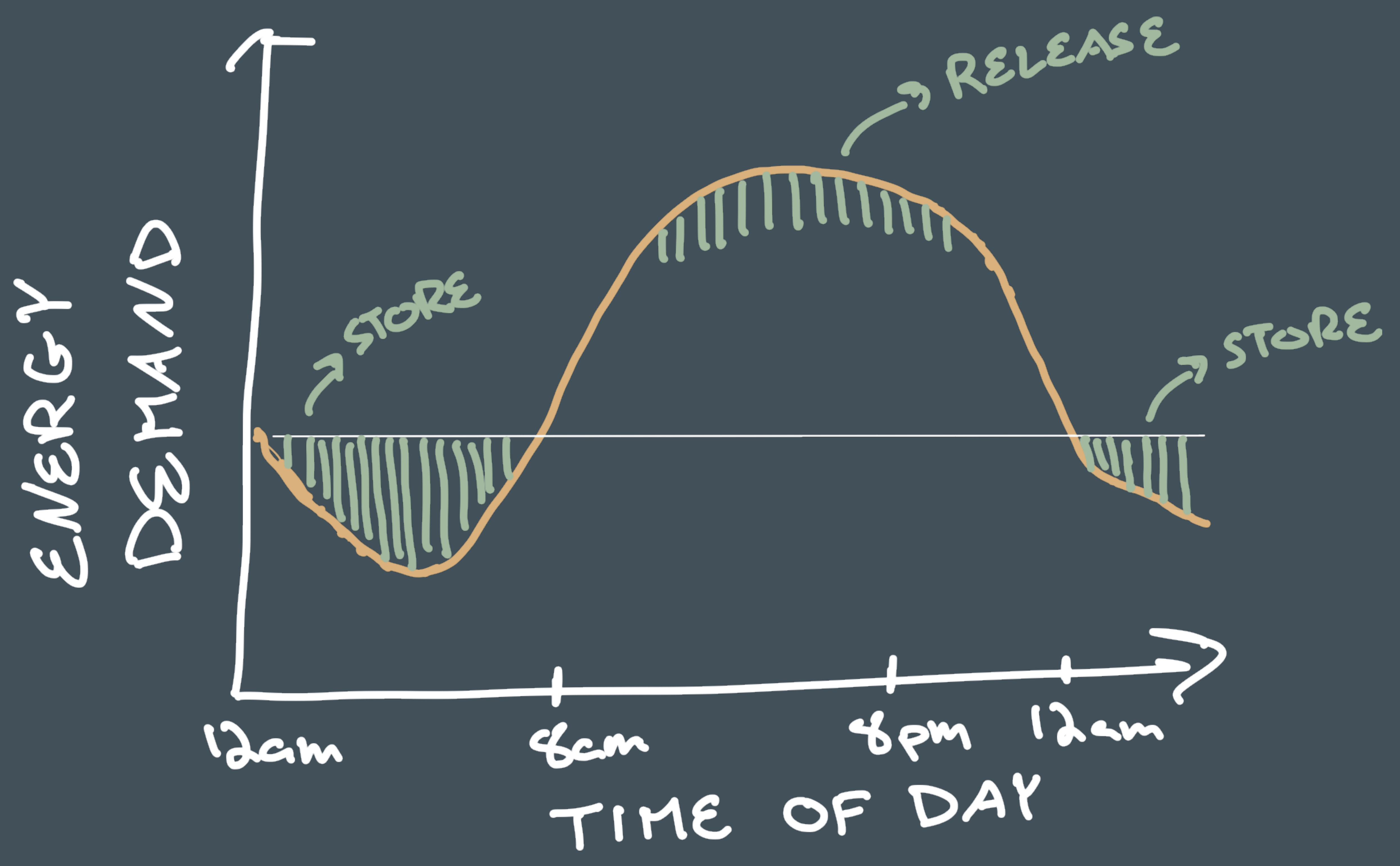
1. **Batteries**
2. Fuel Cells
3. Supercapacitors



Energy generation : transients in renewables







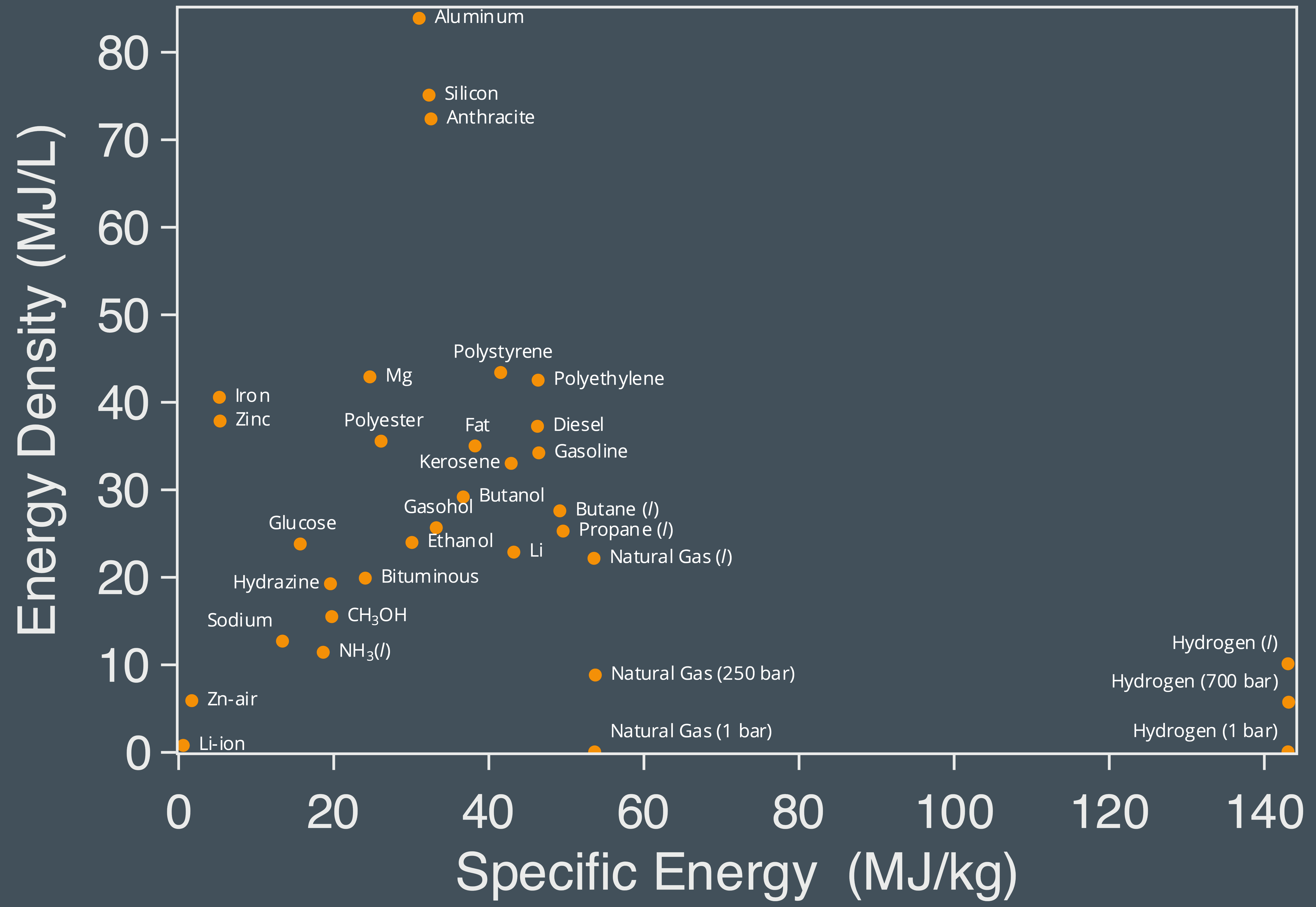
Energy Storage: Energy Density & Specific Energy

Energy --> $Units = J$

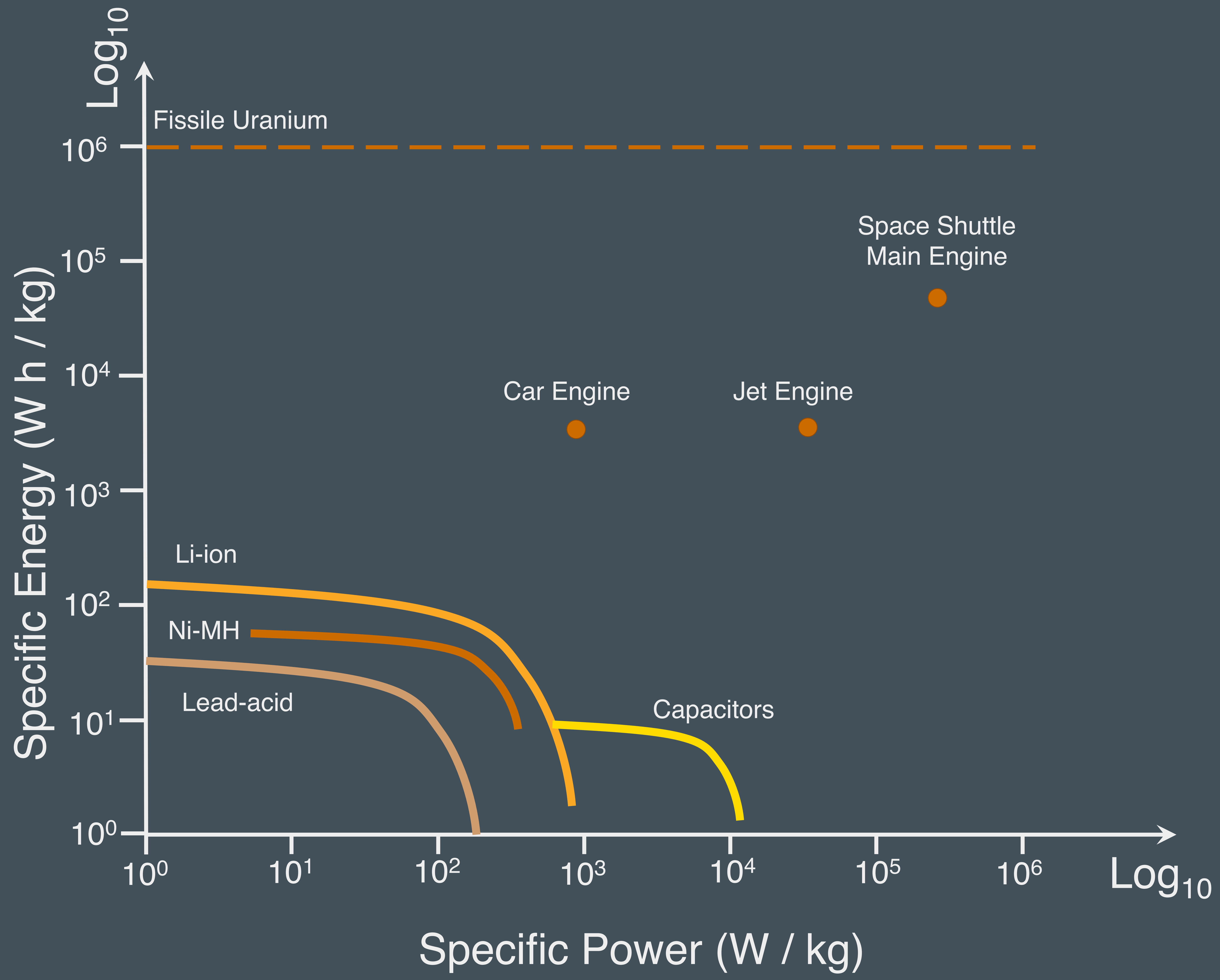
Engineering Unit: $Wh = 3600\,J$

Specific Energy:

Energy Density:



Ragone plot



Power

$$1\,Watt = 1\,J/s$$

$$Power \times Time = Energy$$

$$W \times s = J$$

Specific Power:

Power Density:

Energy Stored by Batteries

Specific Capacity (Batteries)

$$Li + CoO_2 \rightarrow LiCoO_2 \; E^\circ = E^\circ_{CoO_2} - E^\circ_{Li} = 3.5$$

"e^- transferred per unit mass of reactants" Units: $\frac{C}{kg}$ or mAh/g or Ah/kg

Maximum Theoretical Specific Energy

$$MTSE = Specific\ Capacity \times E^\circ_{cell}$$

Units: J/g or Wh/kg

Energy Stored by Batteries

What is the specific capacity of a battery based on the following electrochemical reaction?

$$Li + CoO_2 \rightarrow LiCoO_2$$

a. 0.27 Ah/g
b. 0.54 Ah/g
c. 985 Ah/g
d. 492 Ah/g

What is the maximum theoretical specific energy of the following electrochemical reaction?

$$Li^+ + e^- \rightarrow Li \qquad E^\circ = -3.05\ V$$

$$CoO_2 + e^- \rightarrow CoO_2^- \qquad E^\circ = +0.45\ V$$

a. 1 Wh/g
b. 2 Wh/g
c. 10 Wh/g
d. 20 Wh/g

Energy Stored by Batteries

Which battery reaction has the highest specific energy?

$$Pb + PbO_2 \xrightarrow{H_2SO_4} 2PbSO_4$$

$$NiO(OH) + Cd + 2H_2O \xrightarrow{H_2SO_4} 2Ni(OH)_2 + Cd(OH)_2$$

$$Cd^{2+} + 2e^- \rightarrow Cd \qquad E° = -0.6\,V$$

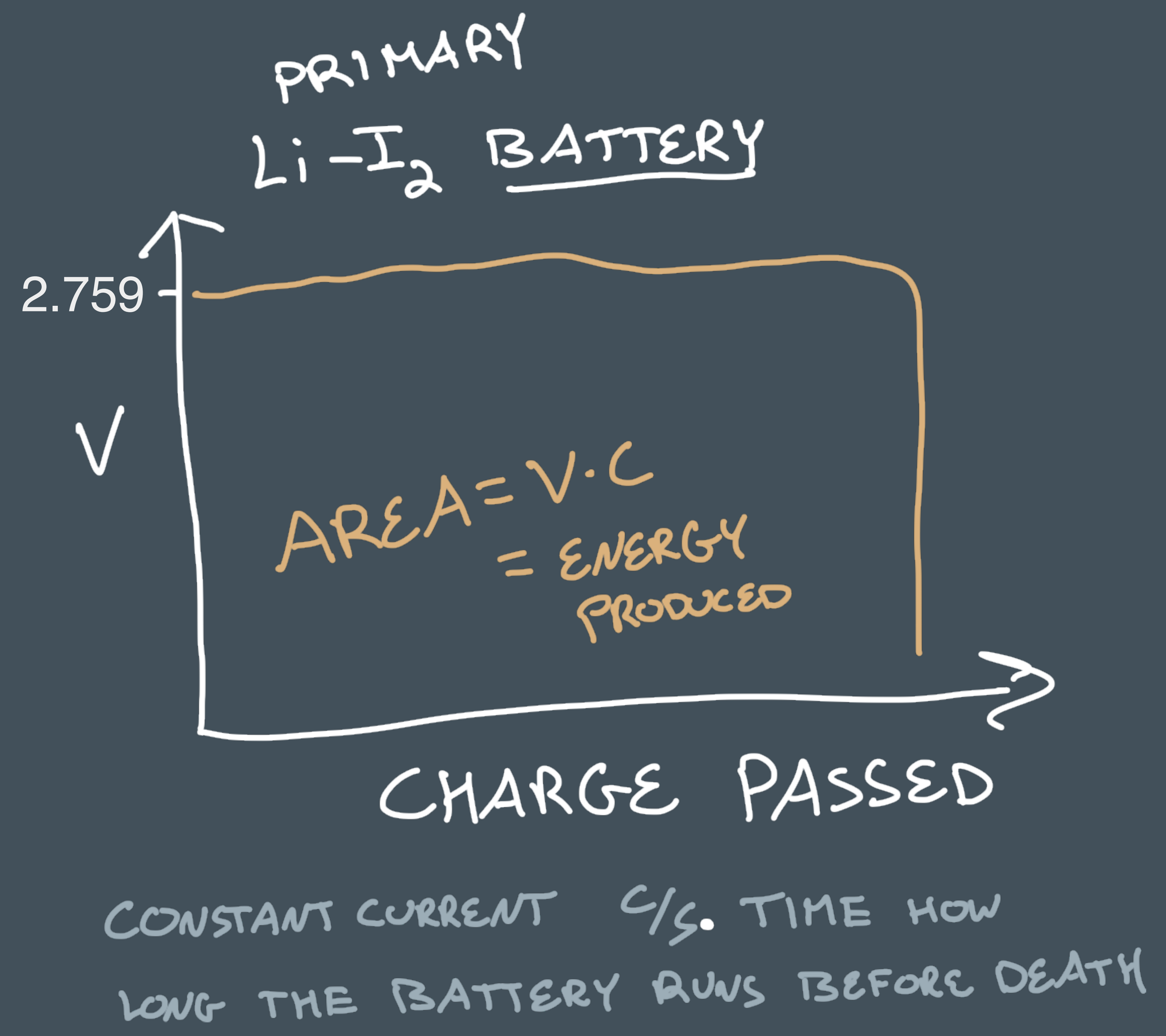
$$NiO(OH) + e^- + H^+ \rightarrow Ni(OH)_2 \qquad E° = +0.6\,V$$

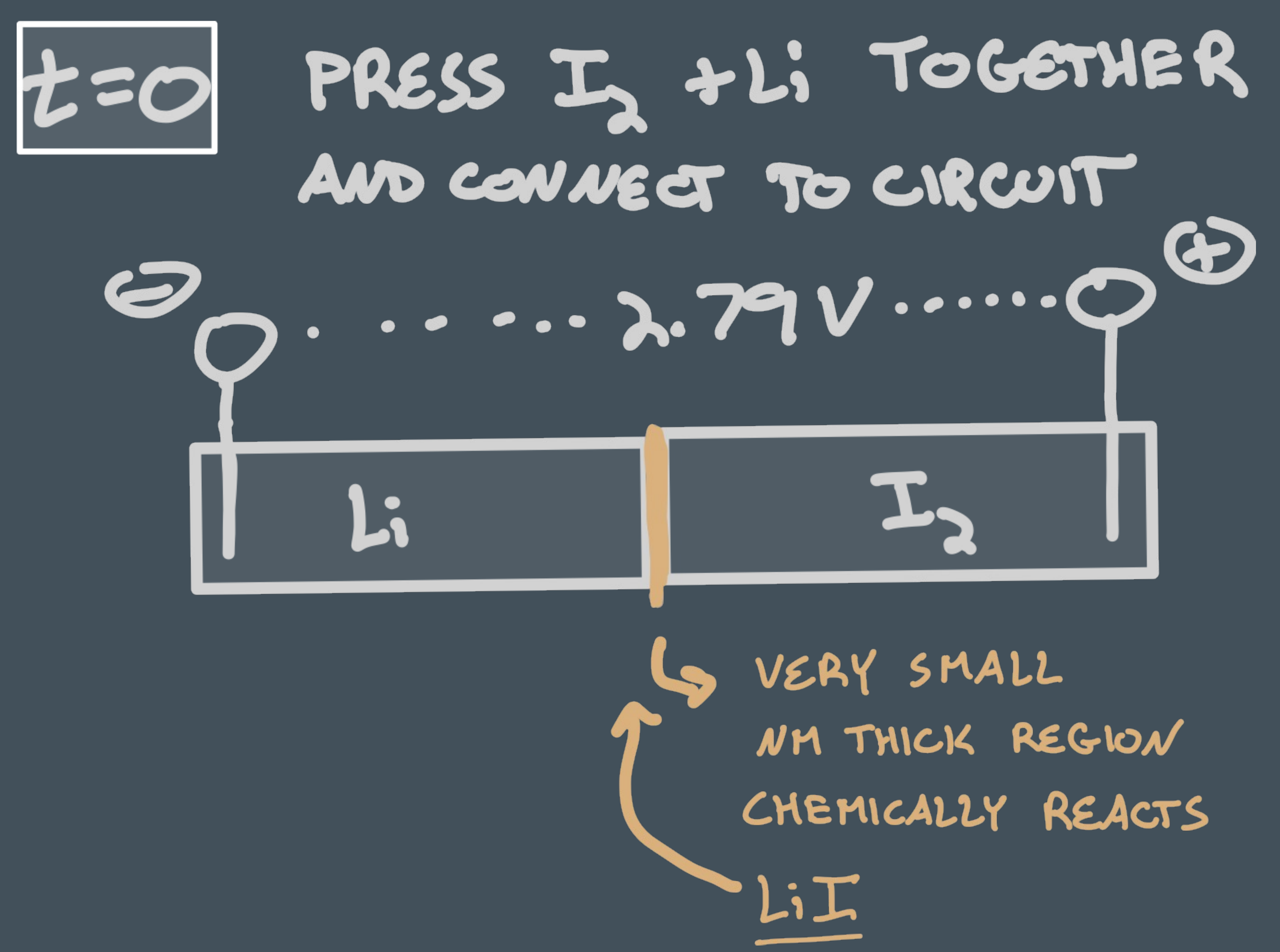
$$PbSO_4 + 2e^- \rightarrow Pb \qquad E° = -0.36\,V$$

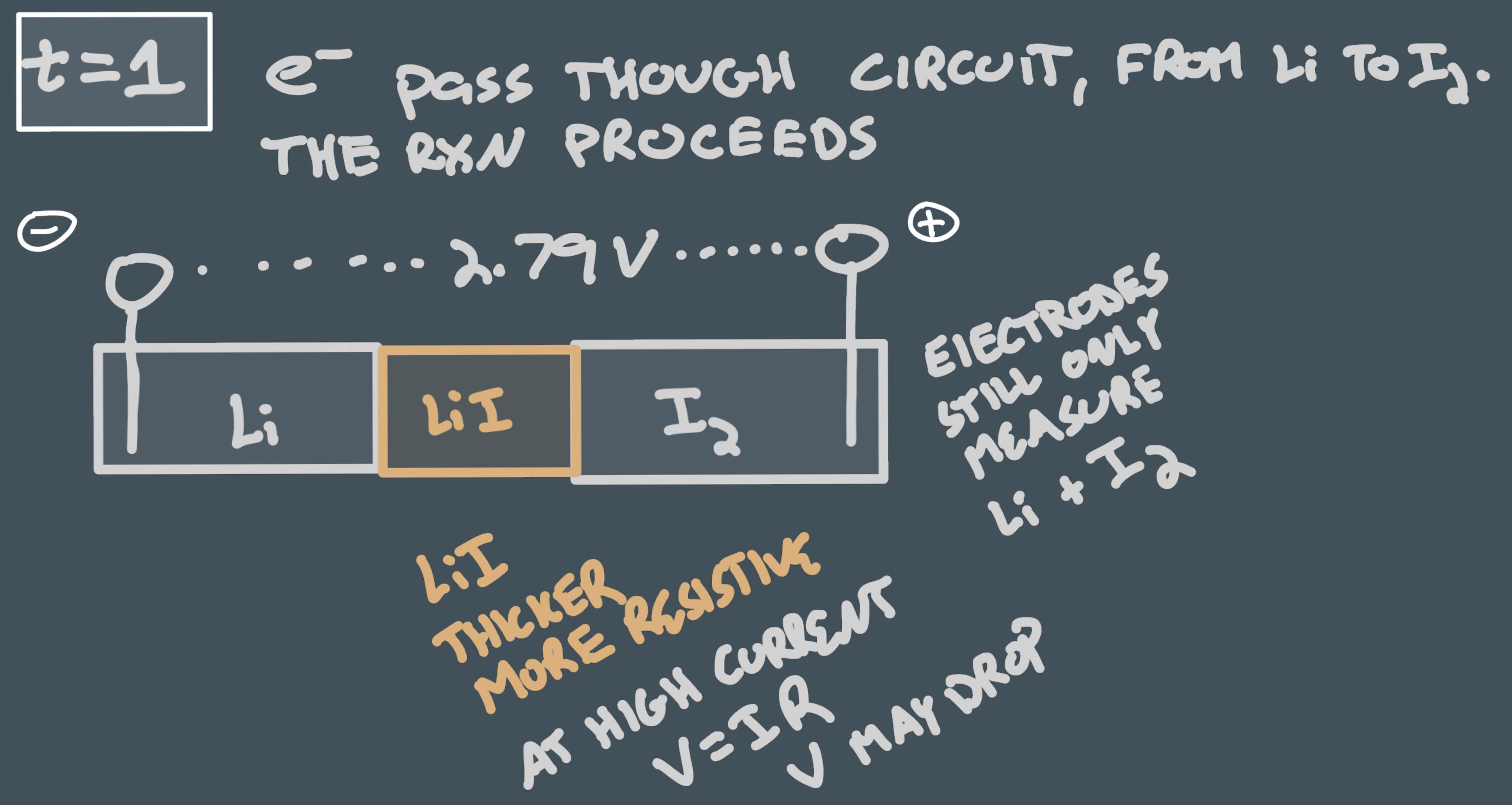
$$Pb^{4+} + 2e^- \rightarrow Pb^{2+} \qquad E° = +1.67\,V$$

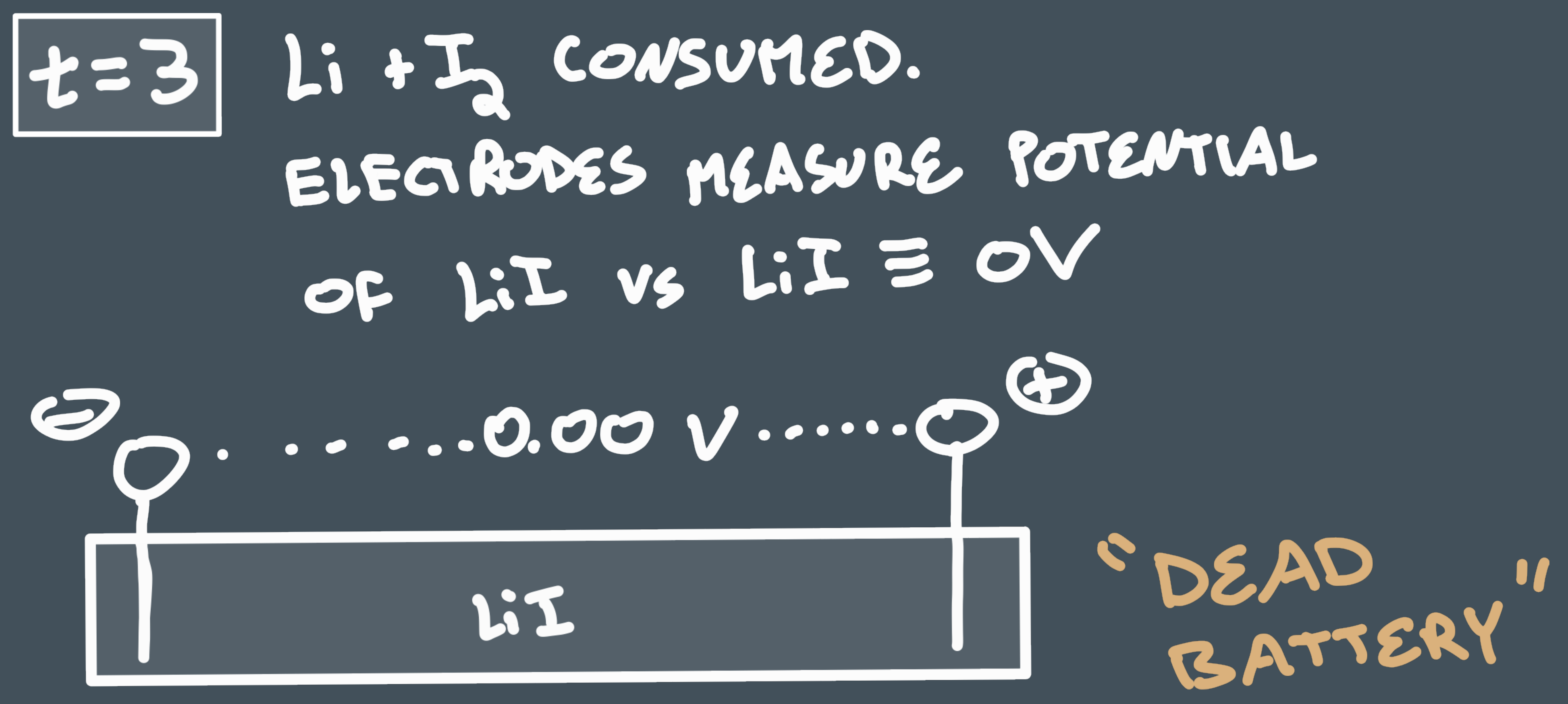
Character of a battery

1. Fixed Electrodes
2. Faradaic $2Li + I_2 \rightarrow 2\,LiI \quad E^\circ = 2.759\,V$
3. Can be primary or secondary (rechargeable) storage media
4. Fixed Volume
5. Fixed amount of reagents

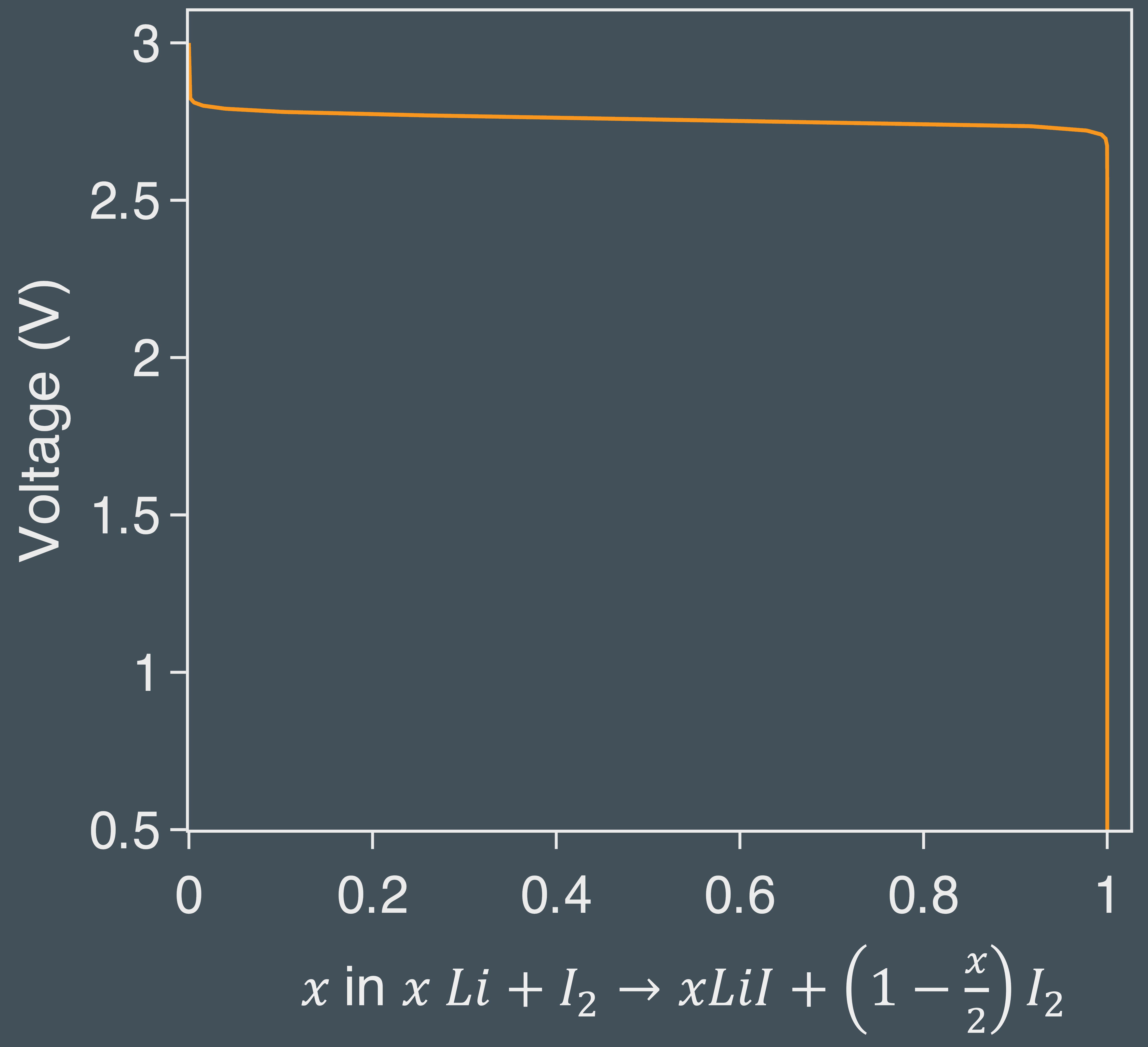






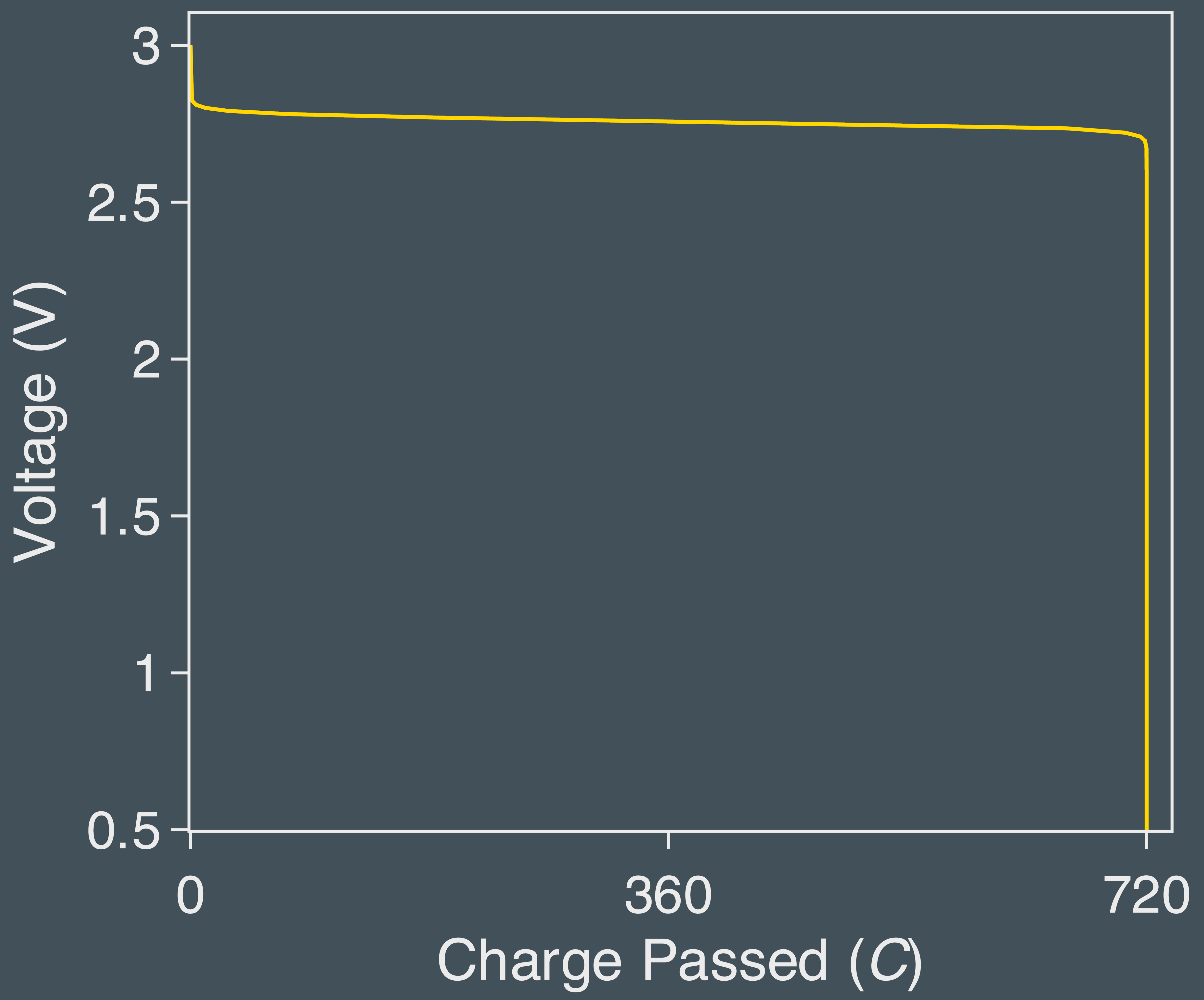


Measuring voltage as a reaction progresses



What does the Nernst equation tell us about this reaction?

Coulombic Titration:

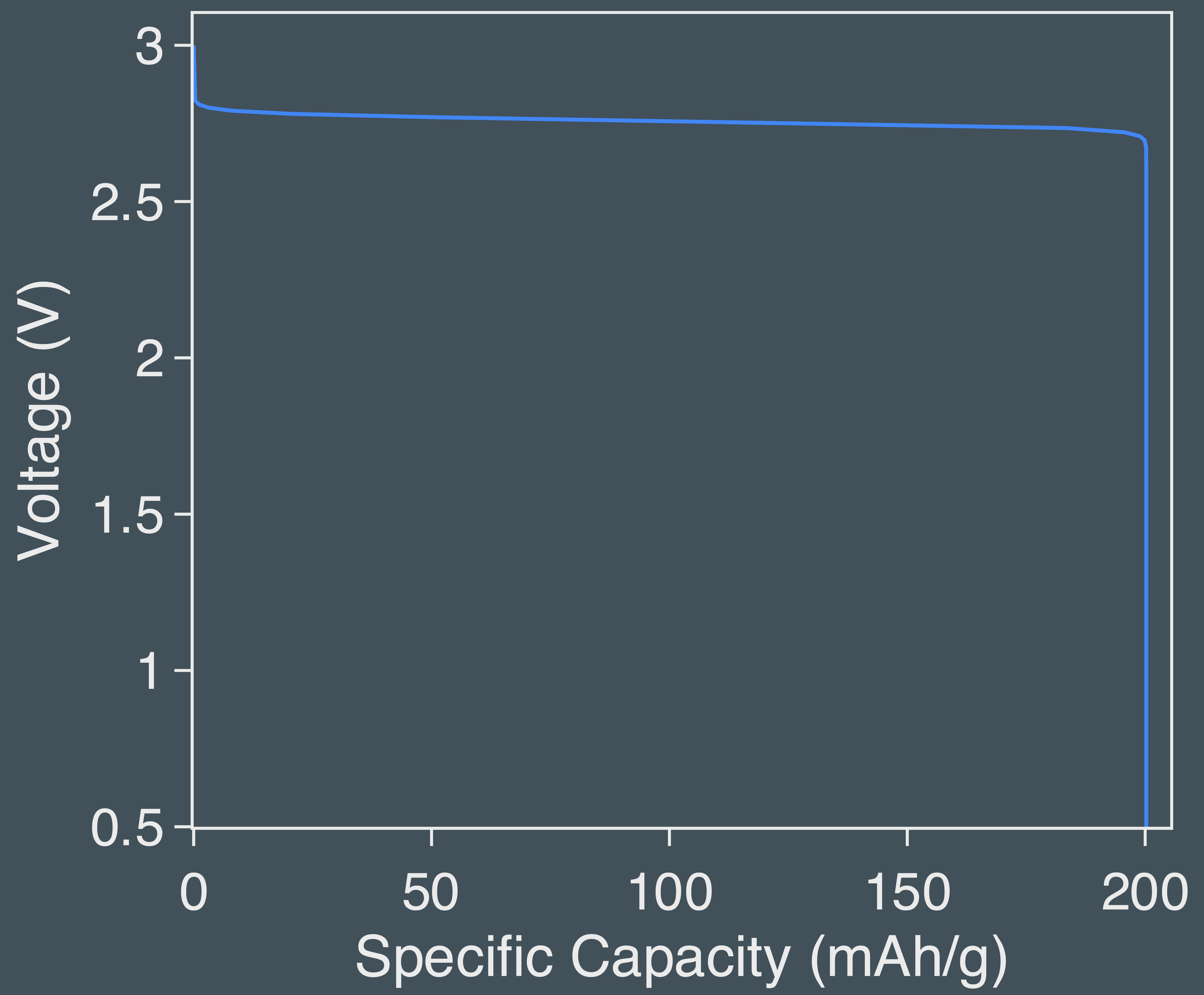


Measuring Discharge Capacity vs Potential.
Potential × Charge = Energy (area)

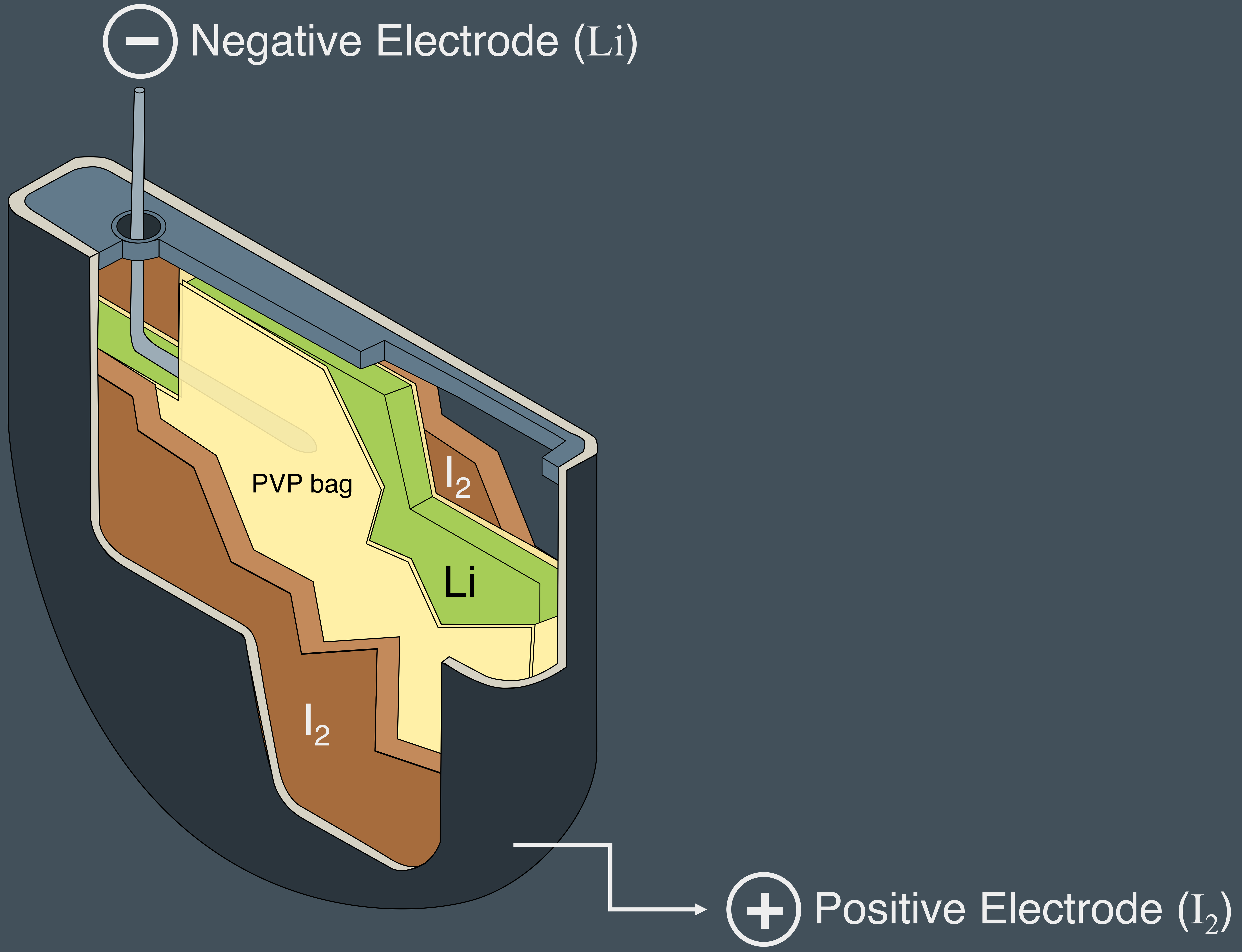
How much energy was expended?

a. 500 J
b. 1000 J
c. 2000 J
d. 4000 J

Divide charge passed by reactant mass:
Specific Capacity & Specific Energy



Battery design: The lithium-iodine battery



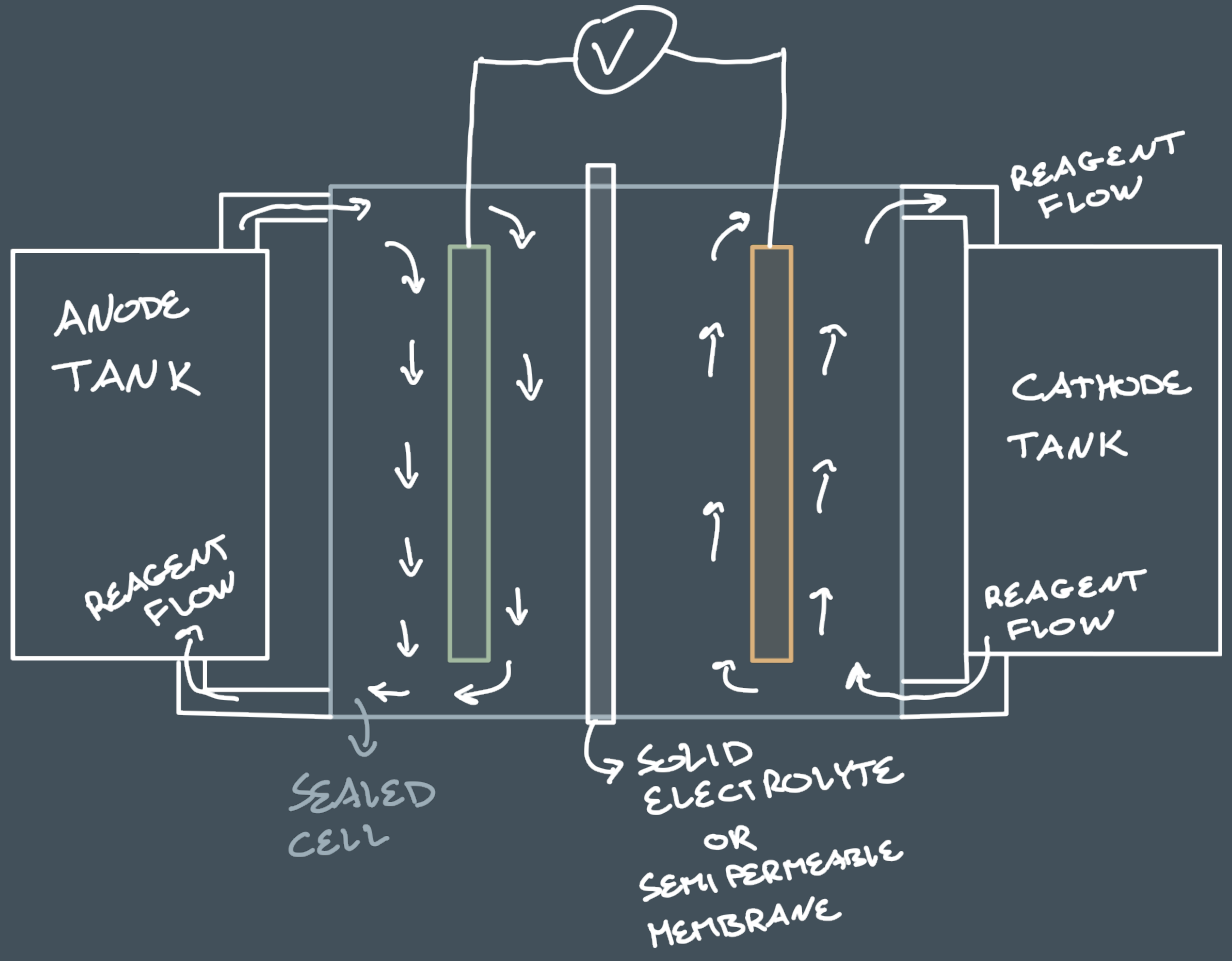
Pacemakers

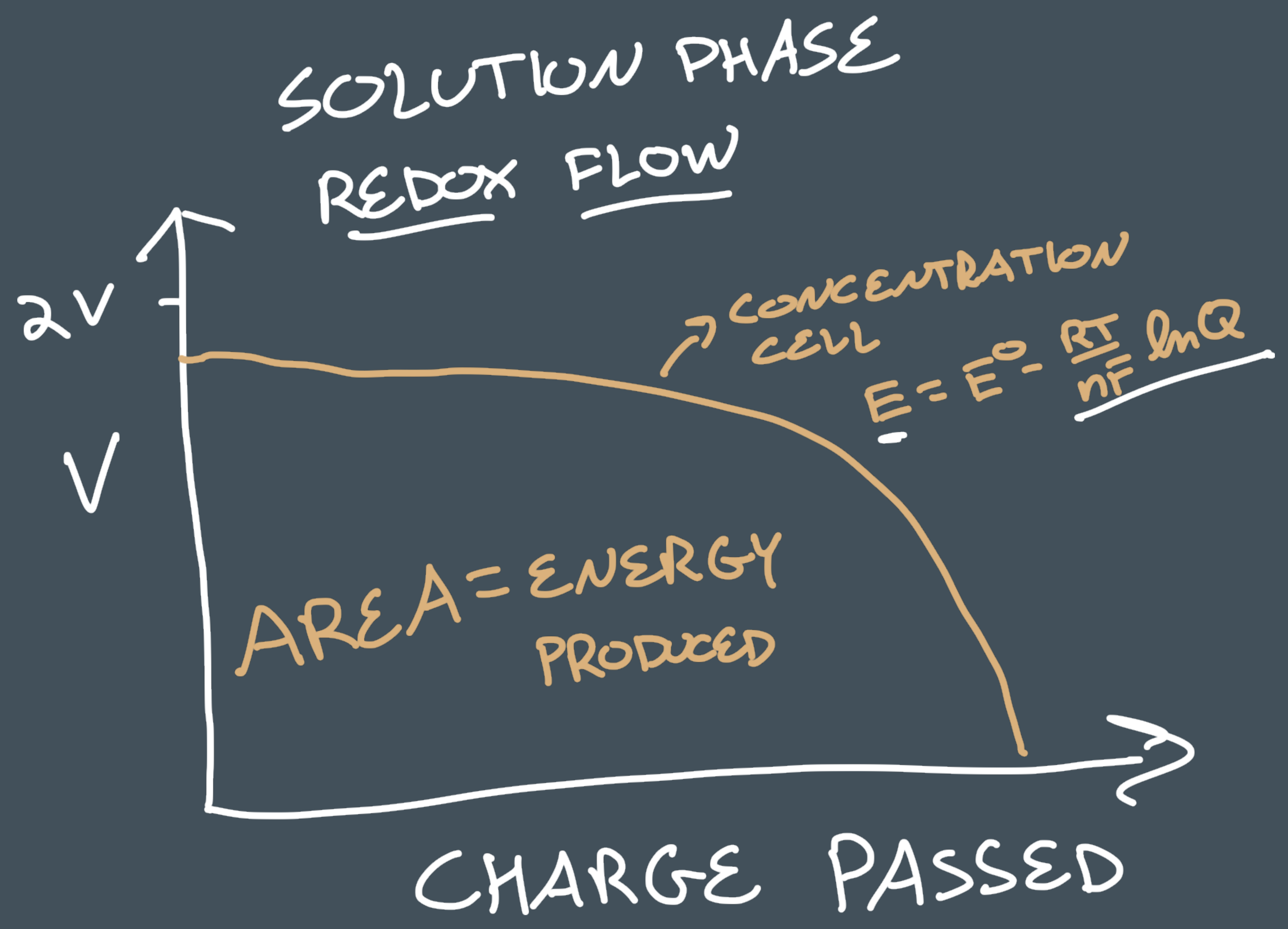
Battery design: the electrochemical series

Which half reactions would you choose to make the battery with the highest energy density?

Fe^{3+}/Fe^{2+}	$Fe^{3+}(aq) + e^- \longrightarrow Fe^{2+}(aq)$	+0.77
I_2/I^-	$I_2(s) + 2\ e^- \longrightarrow 2\ I^-(aq)$	+0.54
$O_2,H_2O/OH^-$	$O_2(g) + 2\ H_2O(l) + 4\ e^- \longrightarrow 4\ OH^-\ (aq)$	+0.40; +0.82 at pH = 7
Cu^{2+}/Cu	$Cu^{2+}(aq) + 2\ e^- \longrightarrow Cu(s)$	+0.34
$AgCl/Ag,Cl^-$	$AgCl(s) + e^- \longrightarrow Ag(s) + Cl^-\ (aq)$	+0.22
H^+/H_2	$2\ H^+(aq) + 2\ e^- \longrightarrow H_2(g)$	0, by definition
Fe^{3+}/Fe	$Fe^{3+}(aq) + 3\ e^- \longrightarrow Fe(s)$	−0.04
$O_2,H_2O/HO_2^-,OH^-$	$O_2(g) + H_2O(l) + 2\ e^- \longrightarrow HO_2^-(aq) + OH^-(aq)$	−0.08
Pb^{2+}/Pb	$Pb^{2+}(aq) + 2\ e^- \longrightarrow Pb(s)$	−0.13

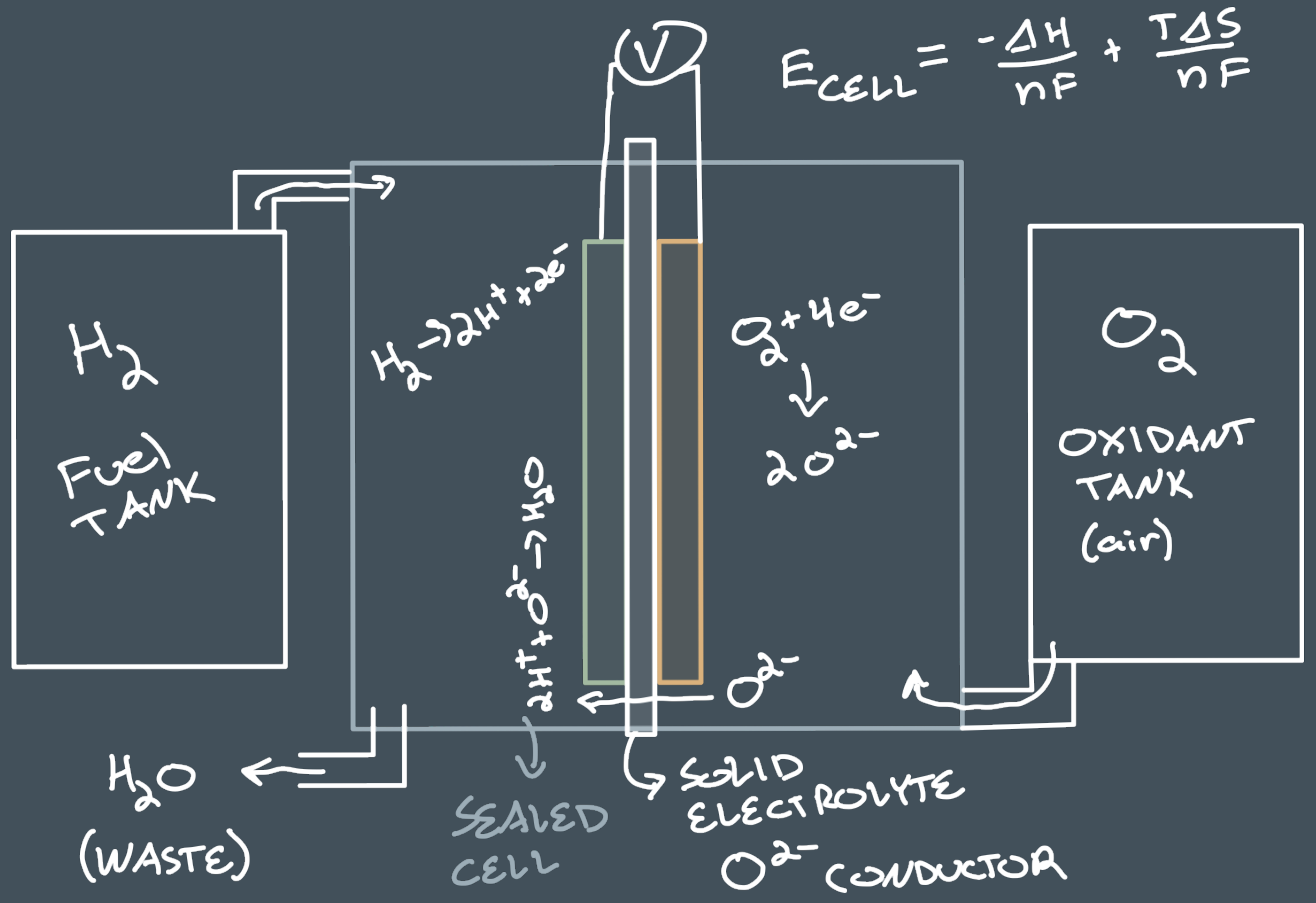
Redox flow battery

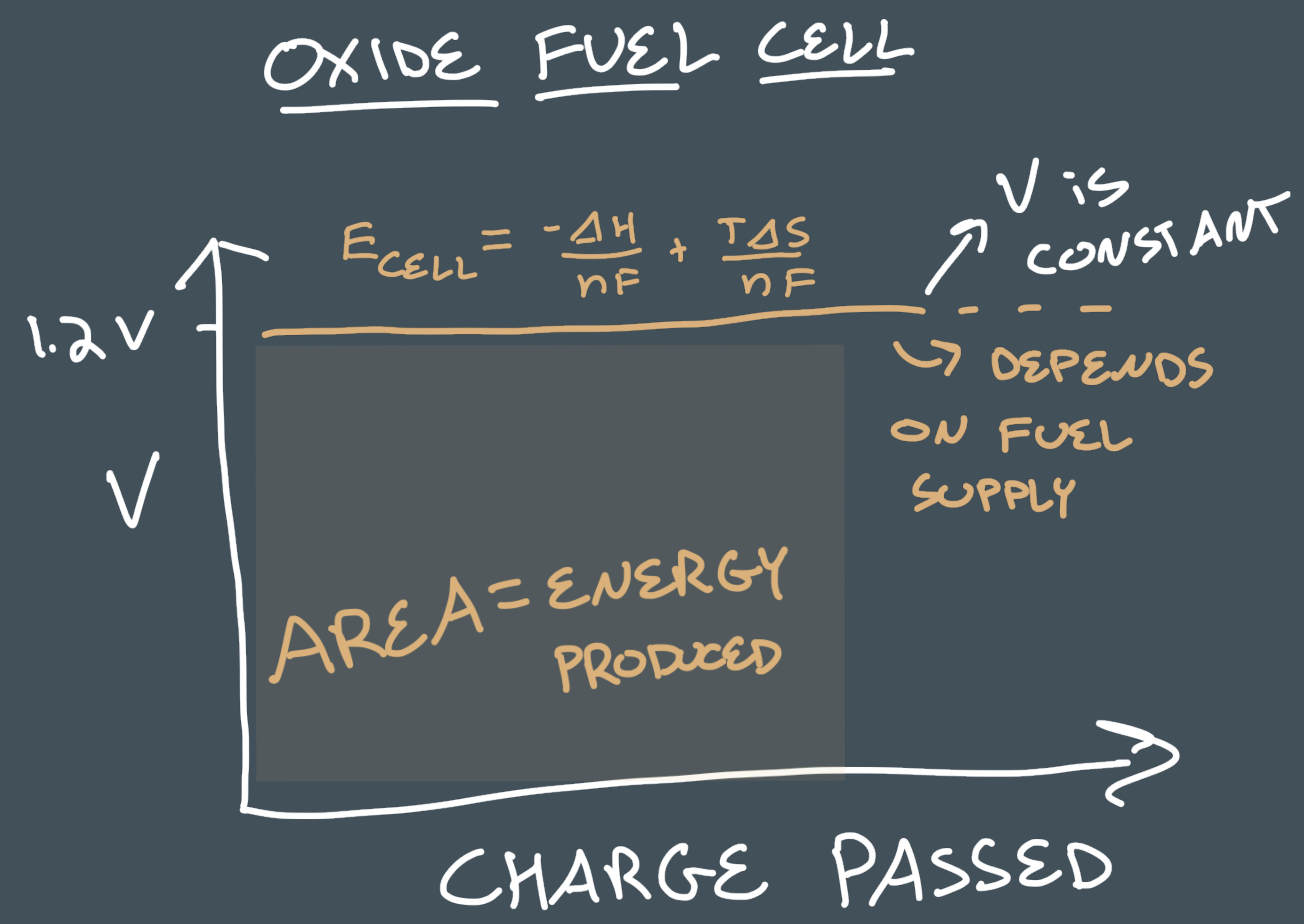




1. Battery
2. Secondary (rechargeable)
3. Faradaic
4. Liquid/Soln. Phase Reactants
5. Semi-fixed volume (i.e. amount of reactants)
6. Some grid scale implementations
7. Nernst Equation Determines E_{cell} (concentration dependent voltage)

Fuel Cells

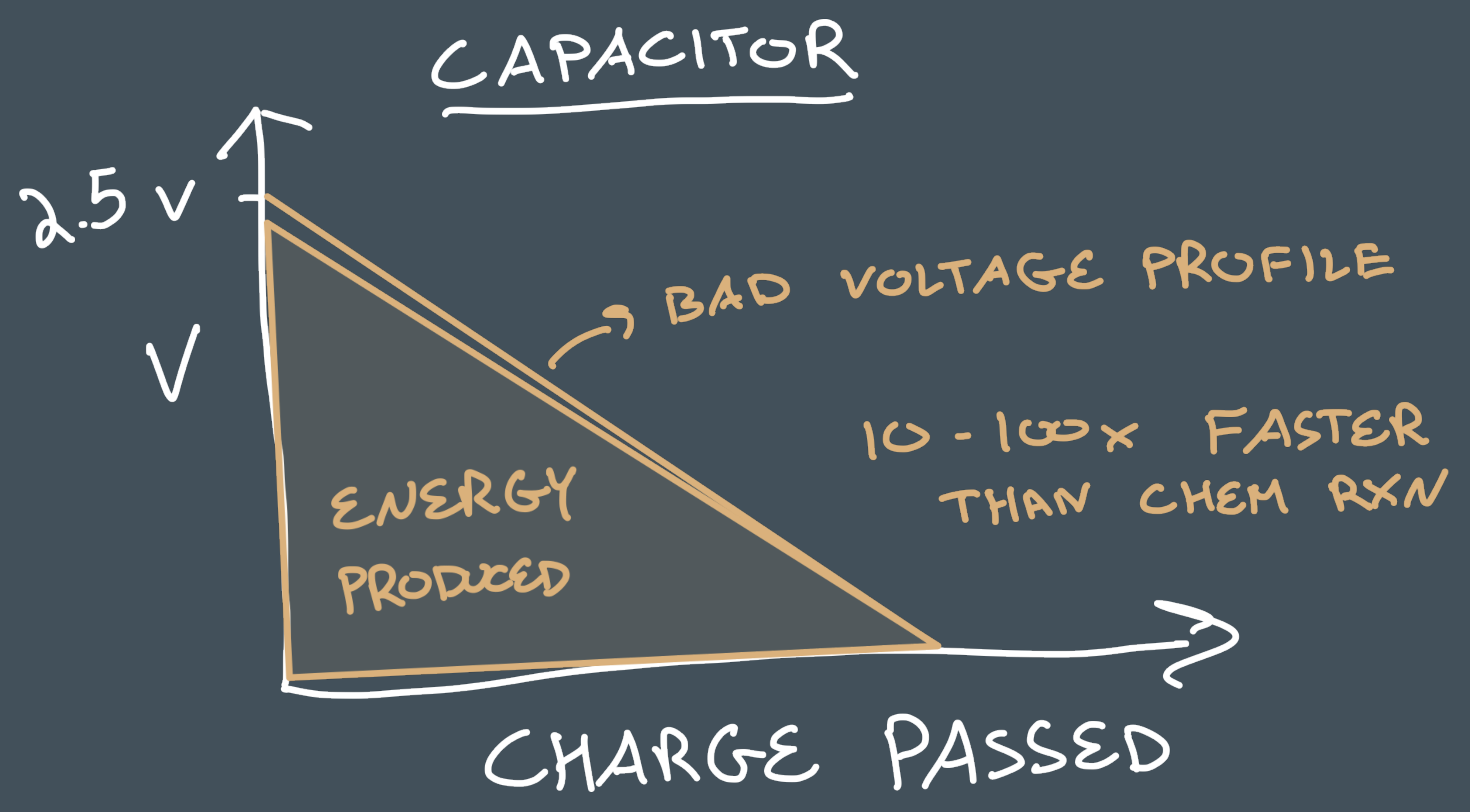




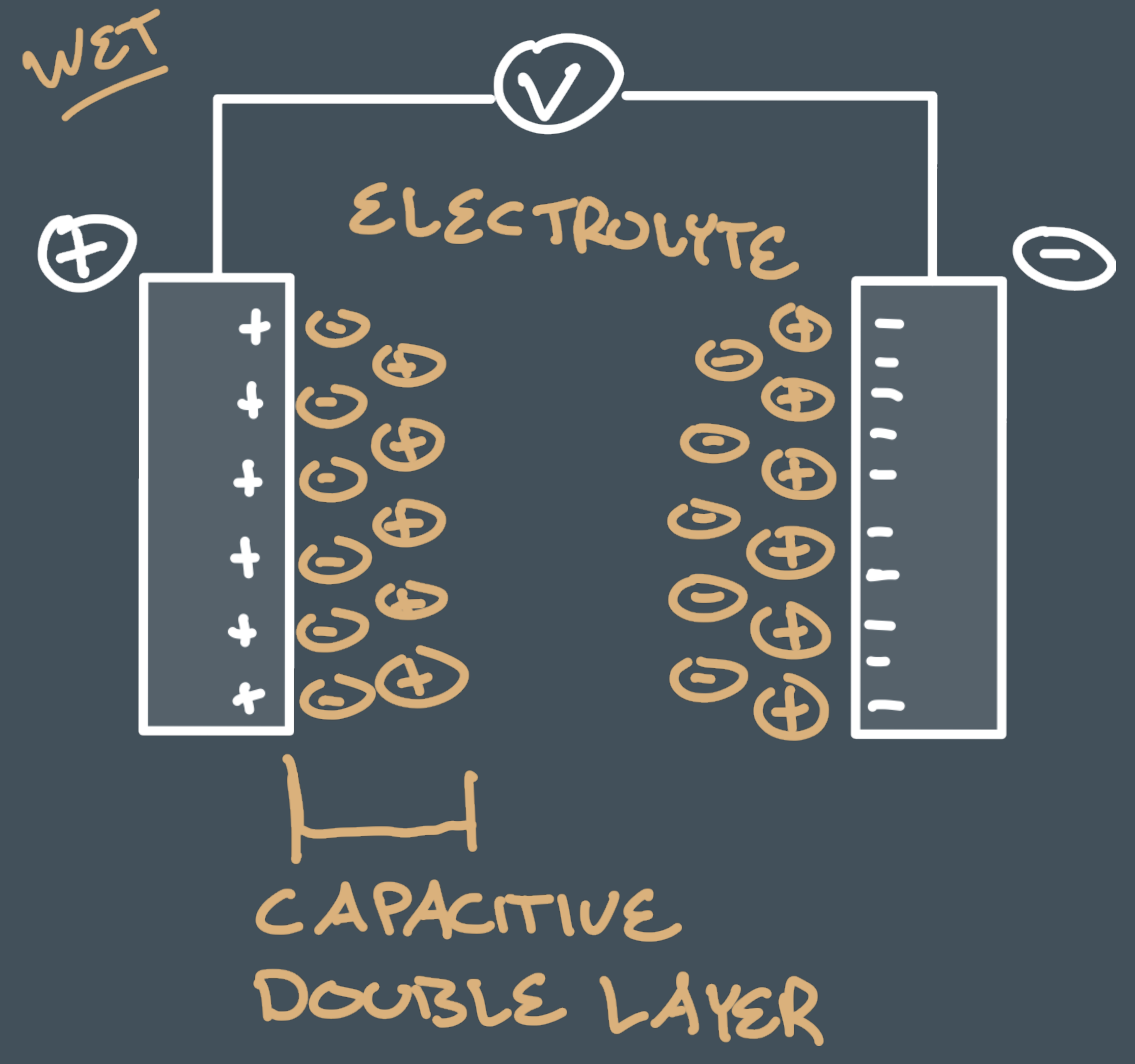
1. Like Redox Flow
2. Primary cell
3. Just need to add a fuel
4. Variable / potentially infinite capacity
5. Typically, low voltages
6. Engineering challenge
7. Closest technology to how biology generates electricity

Supercapacitors ("electrolytic")

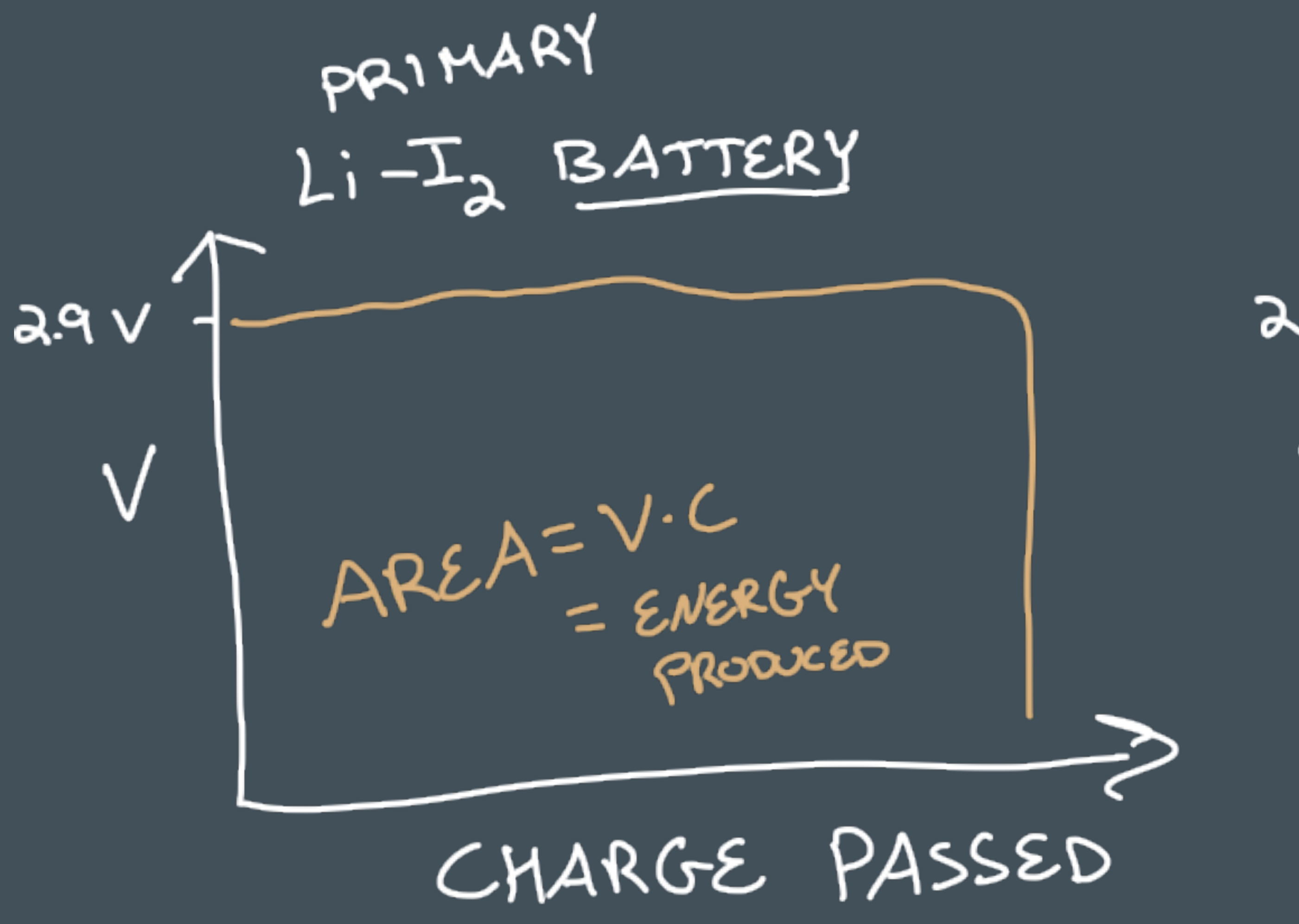
(really big capacitors)



1. No chemical reaction
2. Not Faradaic
3. Charge capacity based on dielectric constant (dry cell)
   Or
   An electrolyte's double layer capacitance (electrochemical cell)
4. Extremely fast to charge and discharge (high power, short duration)



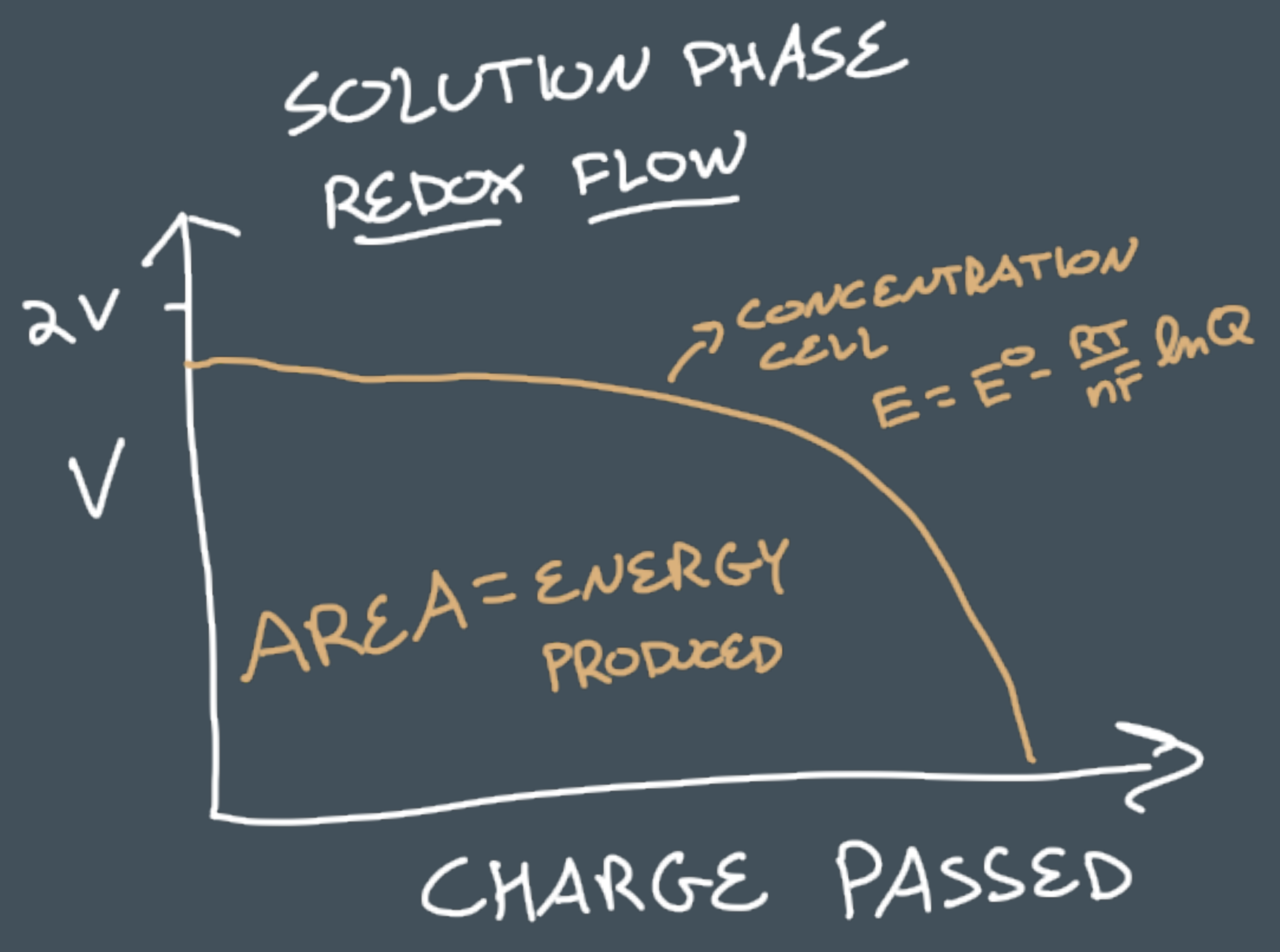
Battery



CONSTANT CURRENT C/5. TIME HOW LONG THE BATTERY RUNS BEFORE DEATH

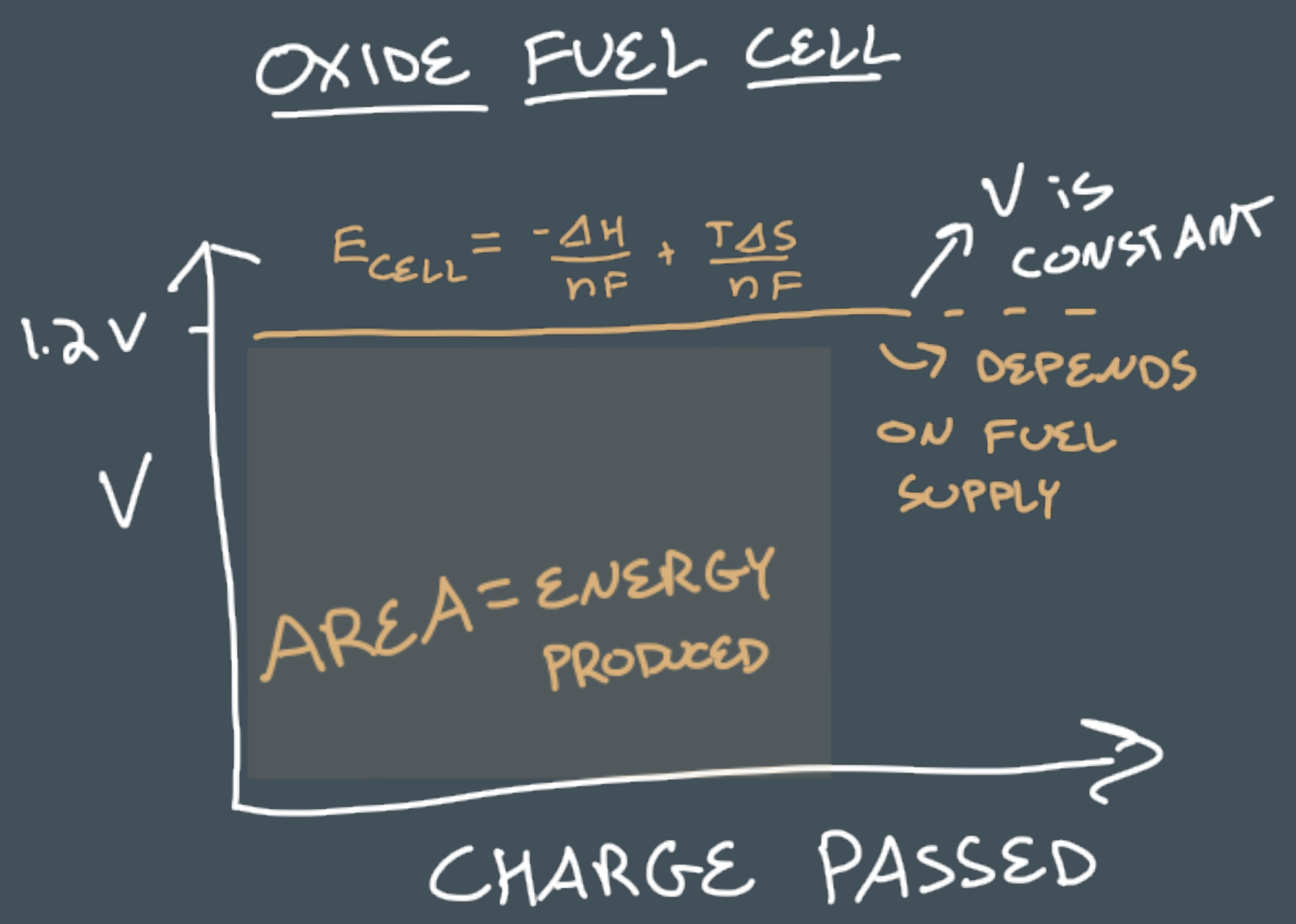
- HIGH DENSITY
- HIGH POWER
- FIXED SIZED
- LOW CAPACITY
- SLOW CHARGE
- NO FUEL SUPPLY

Flow-Battery



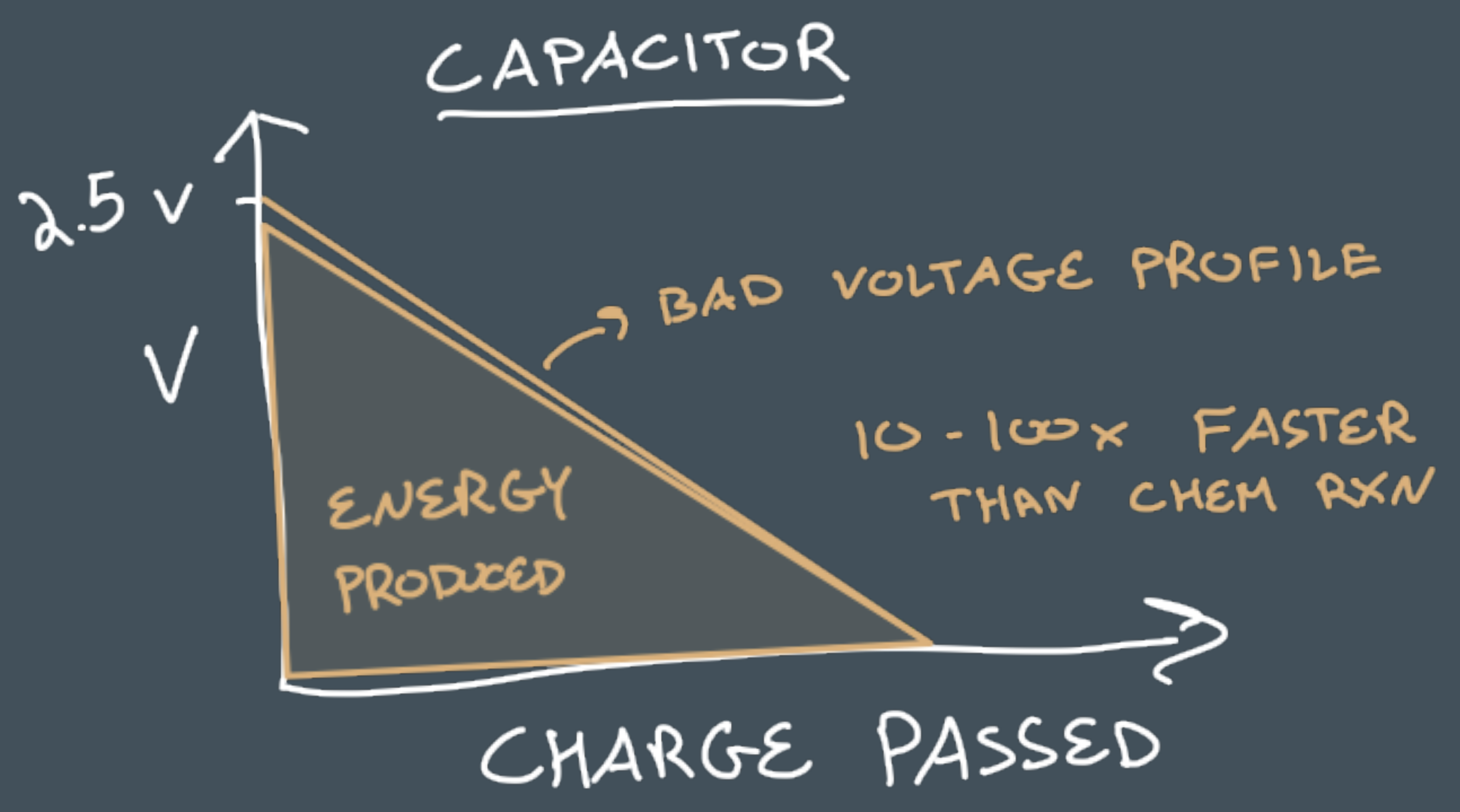
- LOW DENSITY
- MODERATE POWER
- SEMI FIXED SIZE
- LARGE CAPACITY
- SLOW CHARGE
- NO FUEL SUPPLY

Fuel Cell



- LOW ENERGY DENSITY
- MODERATE POWER
- VERY LARGE CAPACITY
- NEVER NEED TO CHARGE
- MUST HAVE FUEL SUPPLY

Capacitor



- LOW ENERGY DENSITY
- VERY HIGH POWER
- RAPID CHARGE
- RAPID DISCHARGE
- VERY POOR VOLTAGE CONTROL
- FIXED SIZE

Capacitor, battery, or fuel cell?

1. Bridge gaps in power generation for shadows cast on solar panels.

2. Store solar panel generated electricity for use at night.

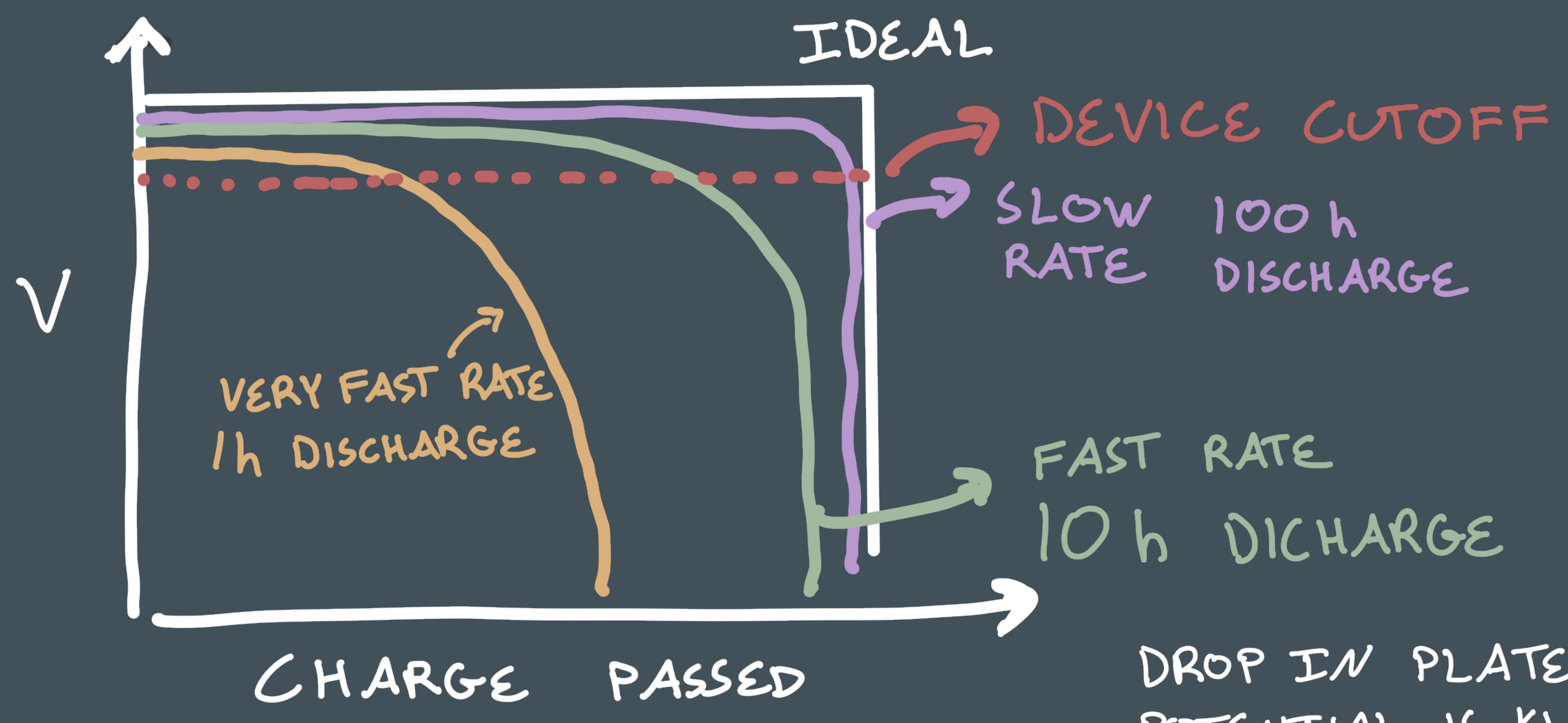
3. Store solar energy generated in the summer for use in the darker days of winter.

Shapes of Battery Discharge Curves

"Kinetics and Overpotential"

1. Depends on chemistry of the electrode
2. Depends on the reaction rate at the electrode

Side Note:
Thermodynamics also change shape of discharge curve --> see Gibbs Phase Law



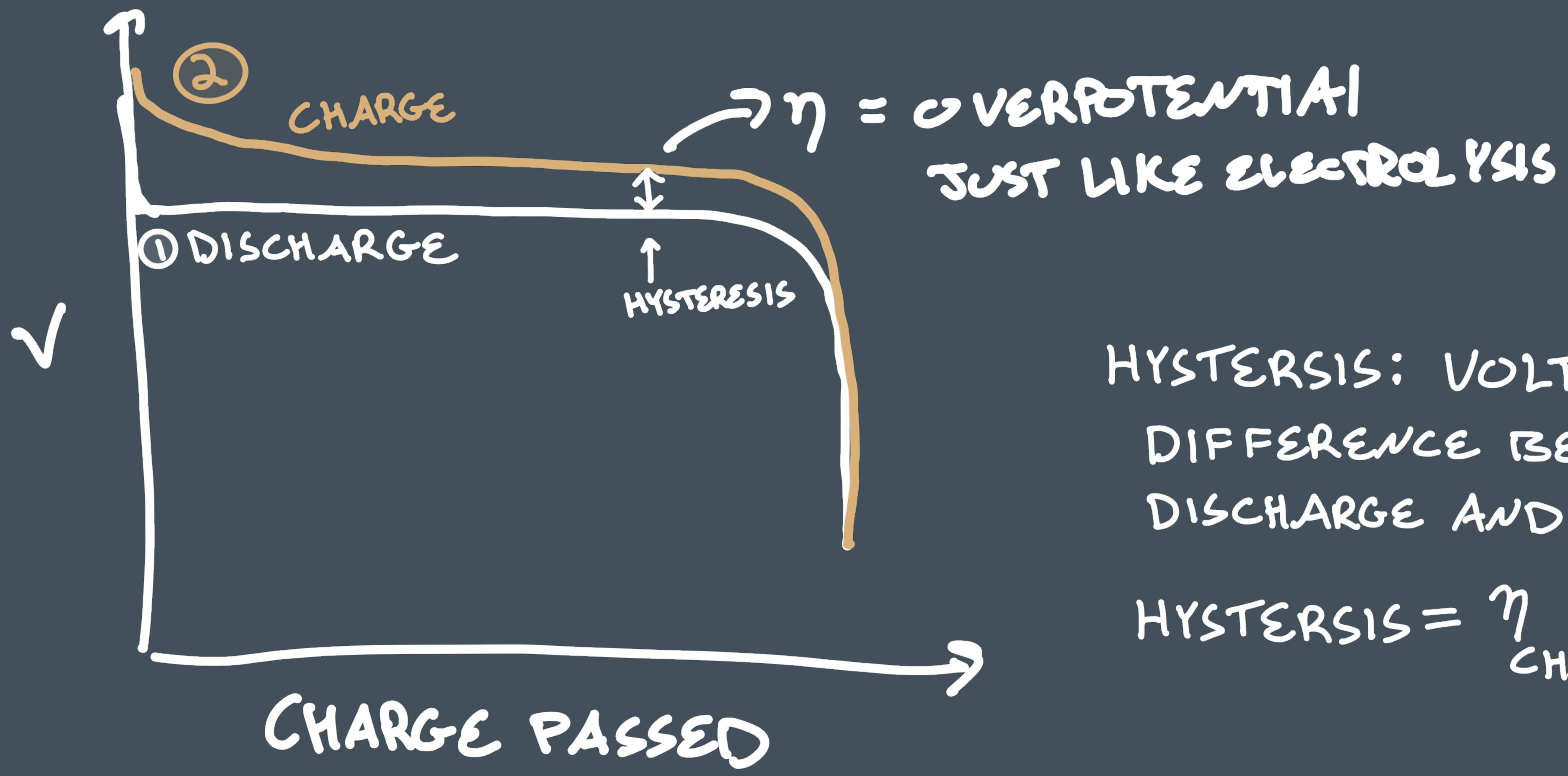
DROP IN PLATEAU OPERATING POTENTIAL IS KINETIC OVERPOTENTIAL JUST LIKE DURING ELECTROLYSIS.

Shapes of Battery Discharge Curves in Rechargeable Batteries

Also called "Secondary cells"
(electrochemical reaction is reversible)

1. Discharge Curve
2. Charge curve

$$\mathrm{Pb}^\circ + PbO_2 \xrightleftharpoons{H_2SO_4} 2PbSO_4$$

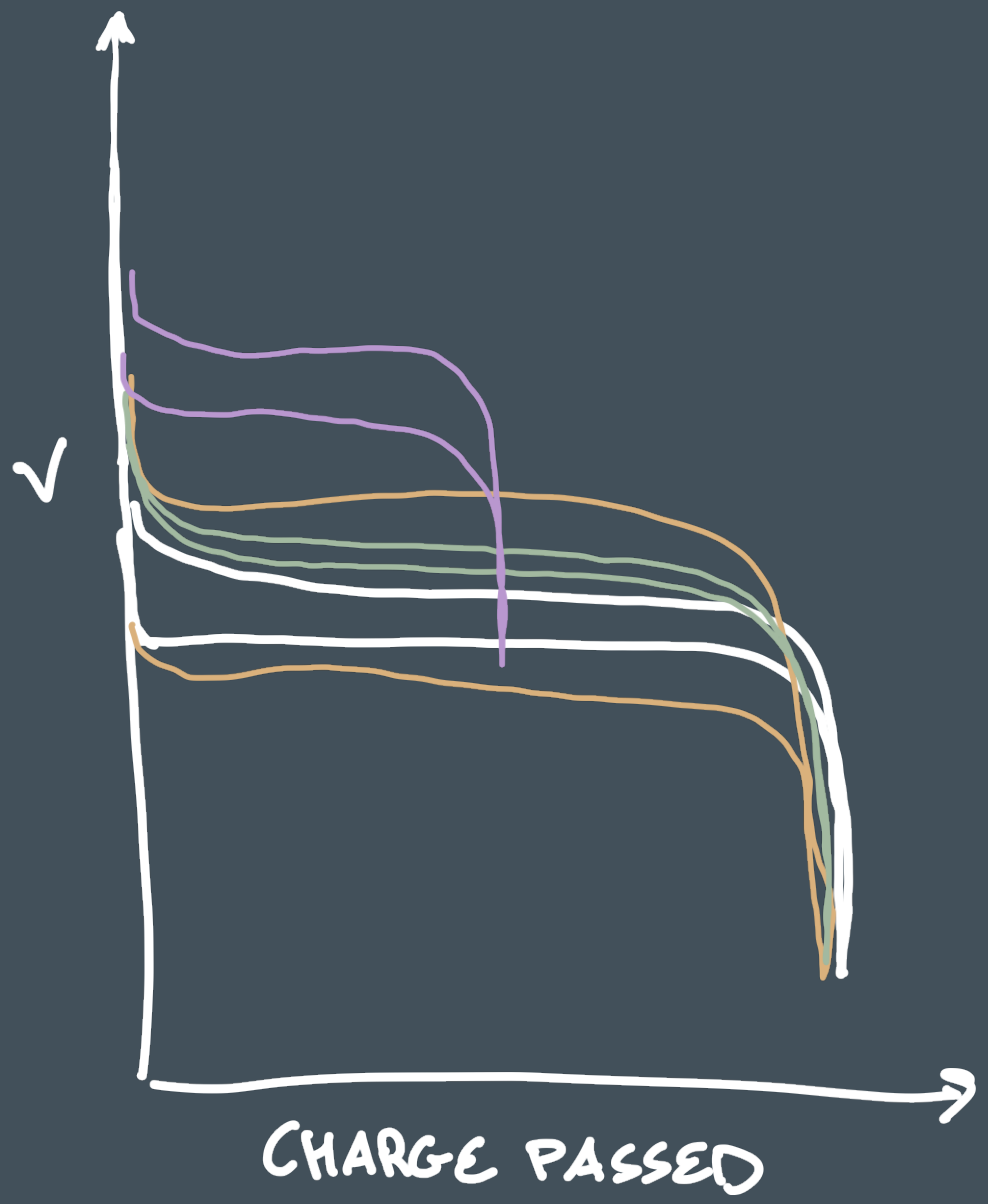


HYSTERSIS: VOLTAGE DIFFERENCE BETWEEN DISCHARGE AND CHARGE

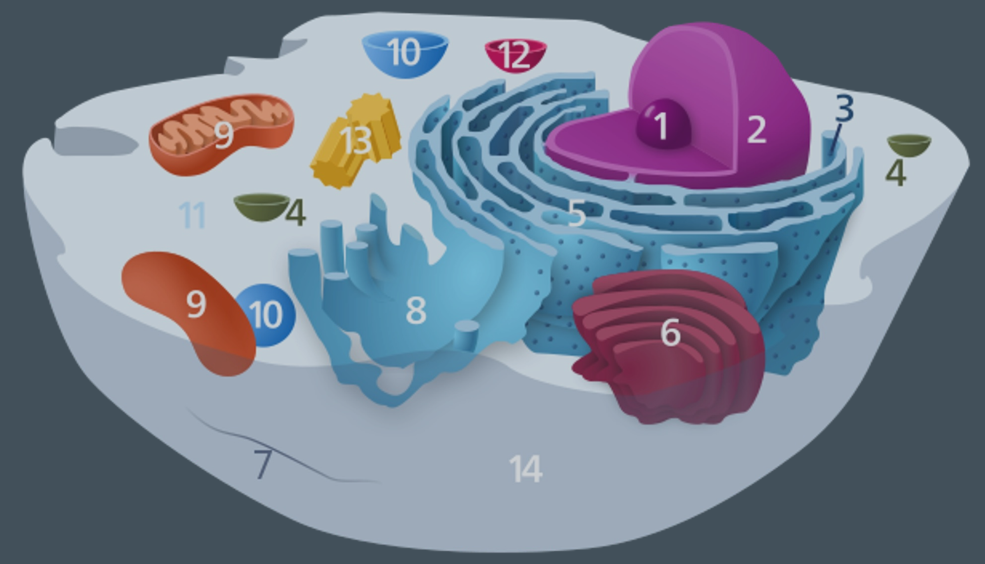
$$\text{HYSTERSIS} = \eta_{\text{CHARGE}} + \eta_{\text{DISCHARGE}}$$

Poll

1. Which of the following batteries charge-discharge curves shows the lowest overpotential?
2. Which has the best kinetic performance?
3. Which has the highest specific capacity?

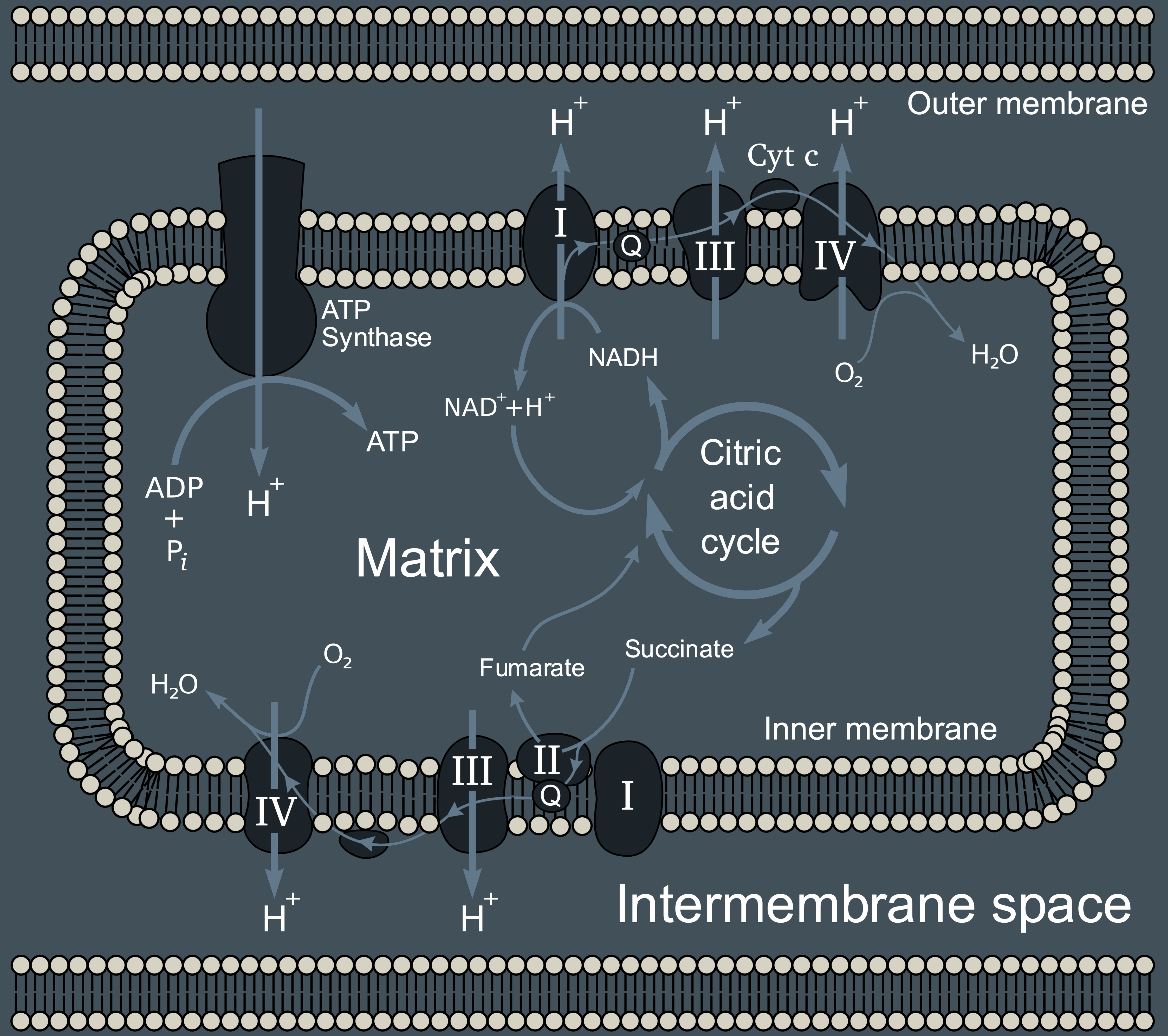


Mitochondria – An electrochemical cell of another kind



Glycolysis

Glucose + 6 O2 + ~38 ATP---> 6 CO2 + 6 H2O + ~38 ATP (not balanced)



Oxidative phosphorylation responsible for 34/38 ATP's