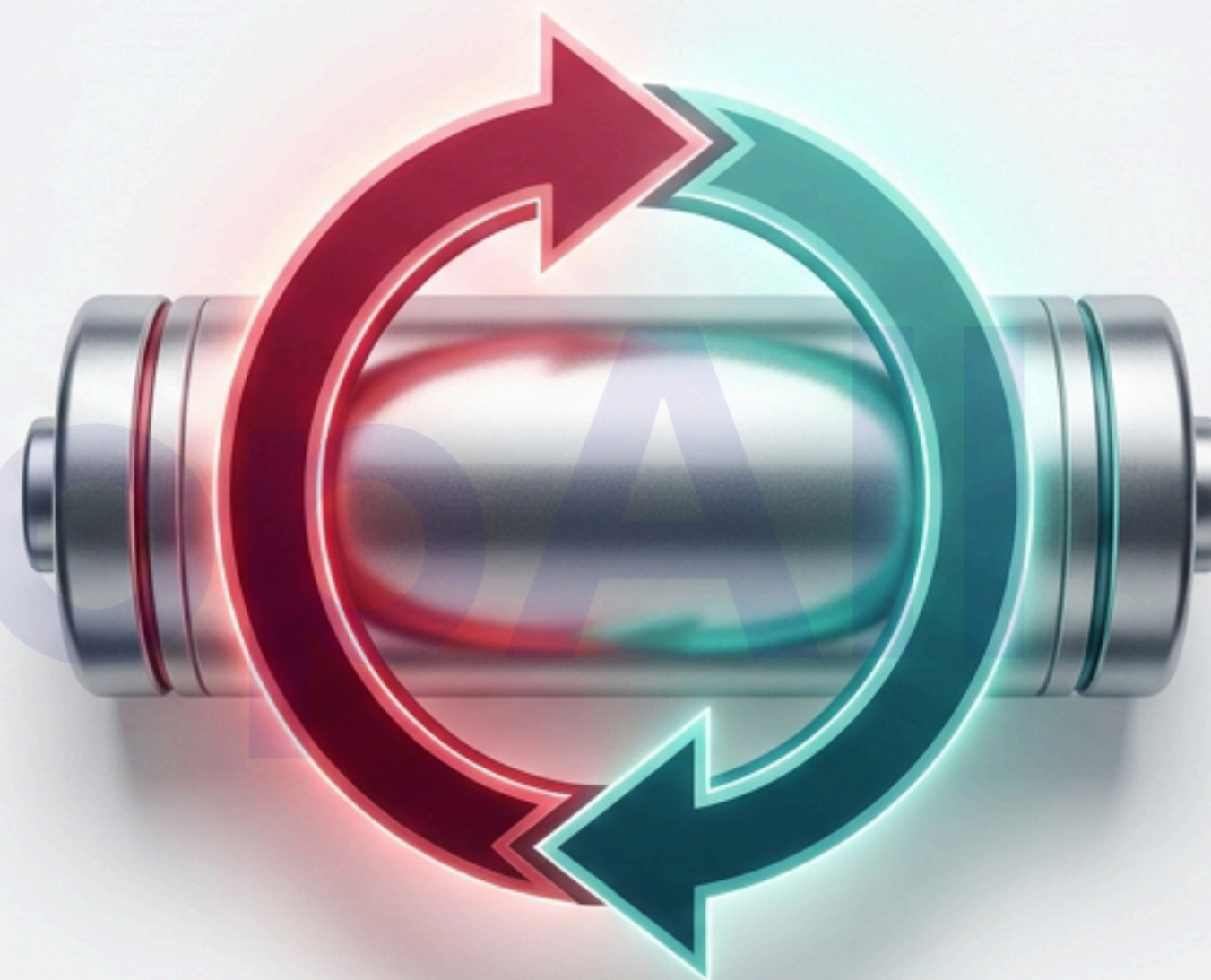


2.6.2

Secondary Batteries

The chemistry of reversible electrochemical systems.



The Dual Nature of Secondary Cells



Primary Battery

- Reaction occurs only once.
- Cannot be reused after the battery is “dead”.
- Examples: Dry cell (Leclanché), Mercury cell.



Secondary Battery

- Reaction can be reversed.
- Recharged by passing current in the opposite direction.

Galvanic

(during use)

Electrolytic

(during charging)

Key Takeaway: A secondary cell bridges two fundamental electrochemical concepts: it converts chemical energy to electrical energy (**spontaneous**) and uses electrical energy to force a chemical reaction (**non-spontaneous**).

Lead Storage Battery Construction

Negative (-)

Spongy Lead
 Pb(s)

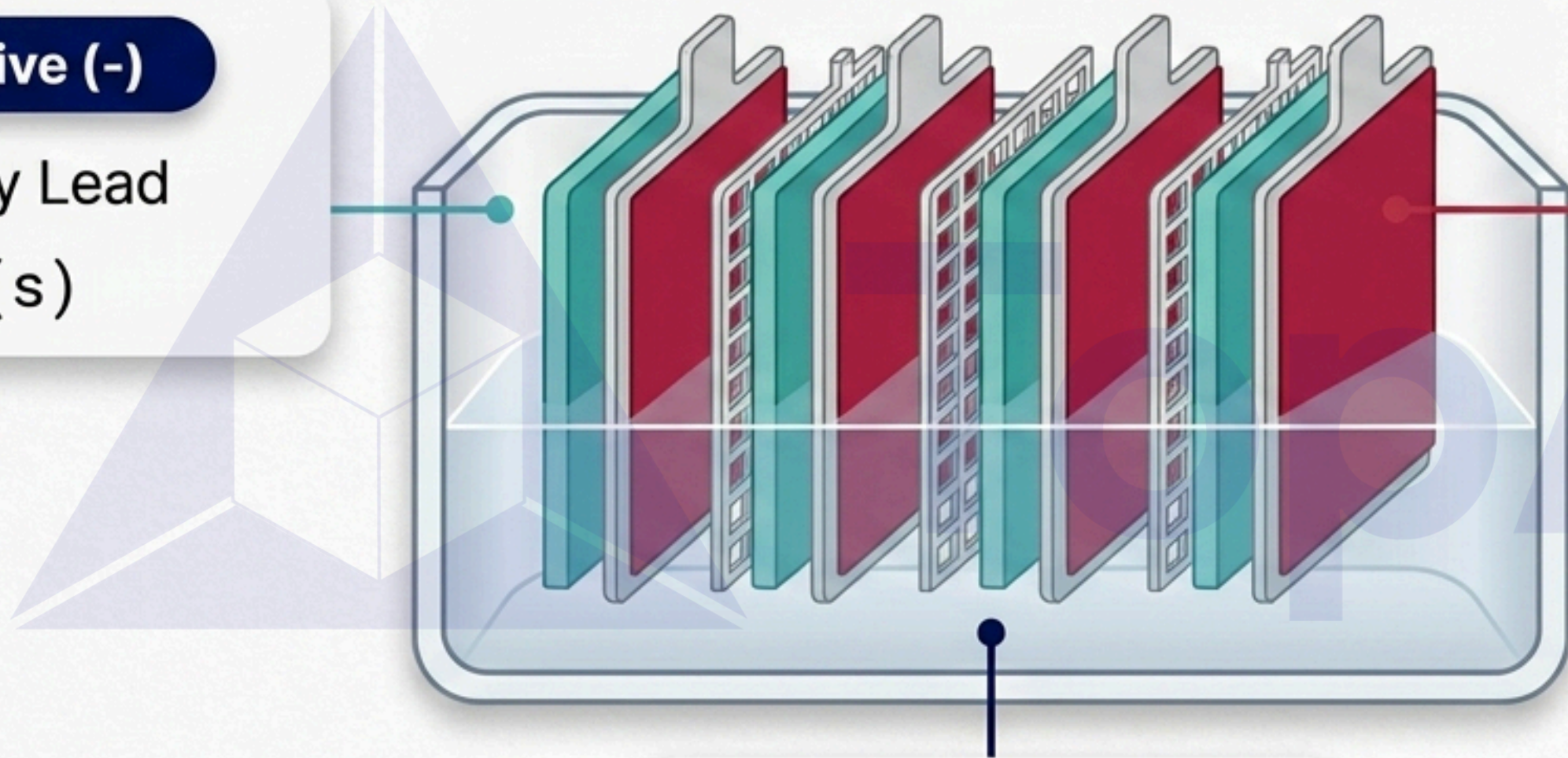
Positive (+)

Lead Grid packed
with Lead Dioxide
 $\text{PbO}_2(\text{s})$

Aqueous Solution

38% Sulphuric Acid
 $\text{H}_2\text{SO}_4(\text{aq})$

Approx. 1.35 V to 2.0 V per
cell (commonly grouped to
form 12V batteries).





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$$E=mc^2$$



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Key Highlights

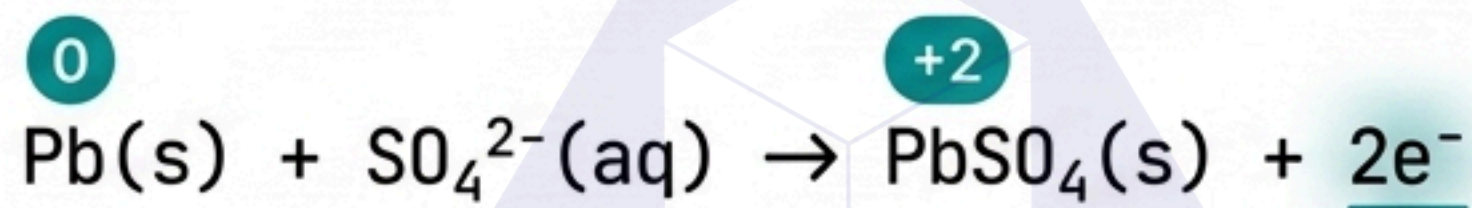
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Discharging: Supplying Power

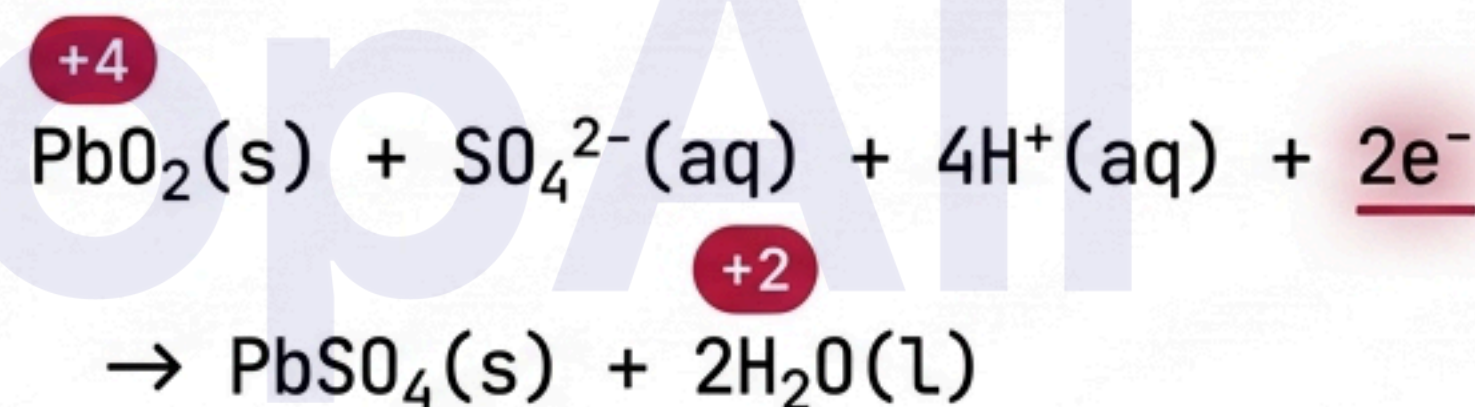
Anode / Oxidation

Lead is oxidized from 0 to +2.

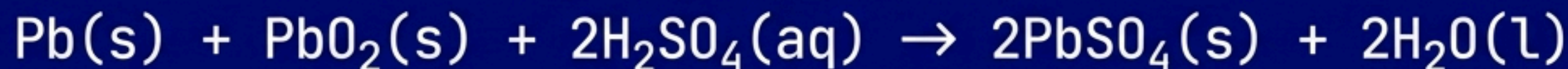


Cathode / Reduction

Lead is reduced from +4 to +2.



Spontaneous ($\Delta G < 0$)





ELECTROLYTIC MODE

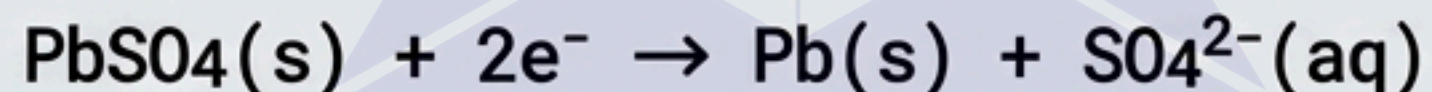
Charging: Restoring Potential

Reversing the cycle requires passing an external current ($E_{\text{ext}} > E_{\text{cell}}$) in the opposite direction.

Just like applying $E_{\text{ext}} > 1.1\text{V}$ reversed the Daniell cell, an external voltage reverses the lead storage cell.

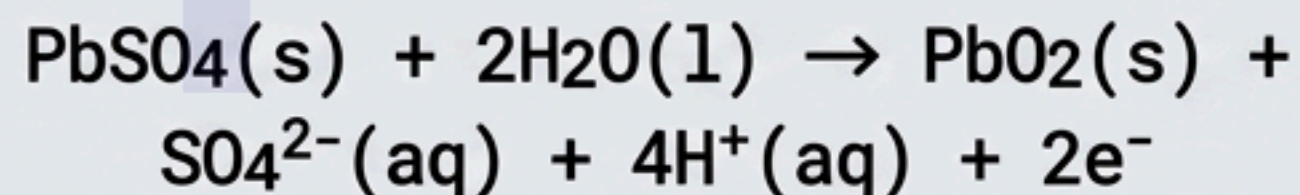
Anode Recovery

Solid Lead Sulphate is converted back to Lead.

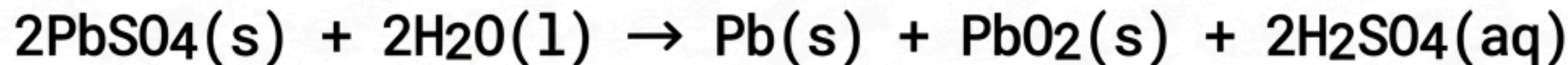


Cathode Recovery

Solid Lead Sulphate is converted back to Lead Dioxide.



Non-Spontaneous ($\Delta G > 0$)



APPLICATIONS & ALTERNATIVES

Powering the Real World



Lead Storage Battery

Lifespan: Can undergo a large number of charging/discharging cycles. The cell potential remains steady because the overall reaction doesn't rely on widely fluctuating ion concentrations.

Use Cases: Automobiles, commercial inverters.

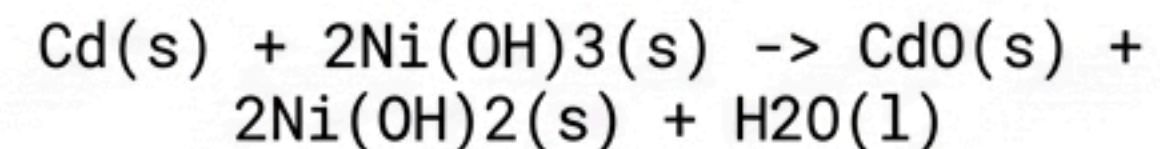


The Nickel-Cadmium (Ni-Cd) Alternative

Advantage: Longer lifespan than lead storage.

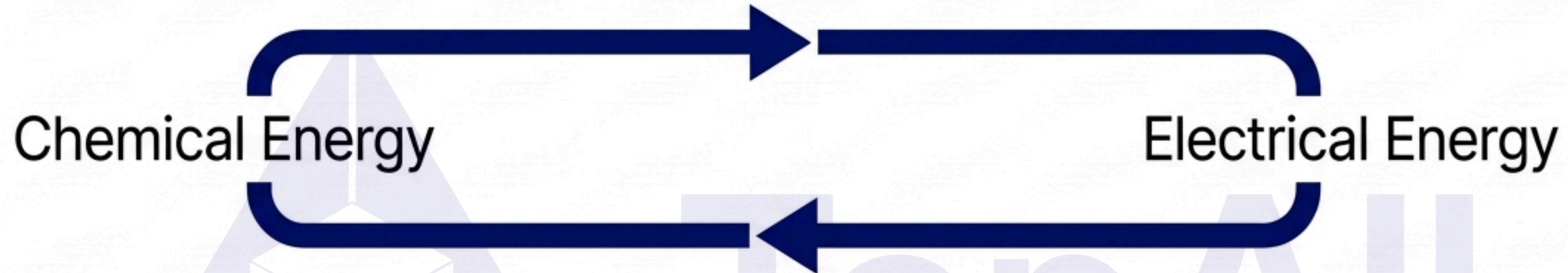
Disadvantage: More expensive to manufacture.

Discharge Reaction:



SYNTHESIS

The Secondary Battery at a Glance



The Core Mechanism

Galvanic -> Discharges spontaneously to provide current.

Electrolytic -> Recharges non-spontaneously via external current.

The Chemistry (Lead Storage)

- **Anode:** $\text{Pb} \leftrightarrow \text{PbSO}_4$
- **Cathode:** $\text{PbO}_2 \leftrightarrow \text{PbSO}_4$
- **Electrolyte:** 38% H_2SO_4
(Consumed during discharge, regenerated during charge).

Practical Value

Highly efficient energy storage capable of numerous cycles, essential for automotive and backup power systems.



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