

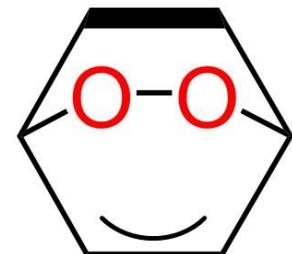
CHEM103

General Chemistry

Chapter 20: Electrochemistry

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Department of Chemistry
SUSTech



Homework 19-20

Homework 19

Due date: 26th Dec. (Mon)

Homework 20

Due date: 28th? Dec. (Wed)

Grading & Final Exam

Option 1 (Pass/Fail; No GPA)考查制

Mid-term: 40%; HW: 30%;

Attendance: 10%; Quiz: 20%

Option 2 (Count GPA)考试制

Mid-term: 30%; Final: 40%;

HW: 10%; Attendance + Quiz: 20%

Time for Final Exam (Ch 11, 13-17, 19-20):

2A. 10th Jan. (Tue)

2B. Next semester

Please choose **1** out of 3 choice **before 27 Dec**

Summary on Chapter 19

Spontaneous/Non-spontaneous process,
reversible/irreversible process, entropy

The Second law of thermodynamics (ΔS_{univ}), The Third
law of thermodynamics

Isothermal, statistical thermodynamics, microstate,
Boltzmann's equation

Gibbs free energy, standard free energy change &
equilibrium

Outline of Chapter 20

Relationships between electricity & chemical (redox) reactions; Half-reaction method

Voltaic Cells: oxidation (anode); reduction (cathode); salt bridge

Electromotive force (emf), cell potential, standard reduction potentials, standard hydrogen electrode, standard cell potentials

Free energy and redox/emf; Nernst equation

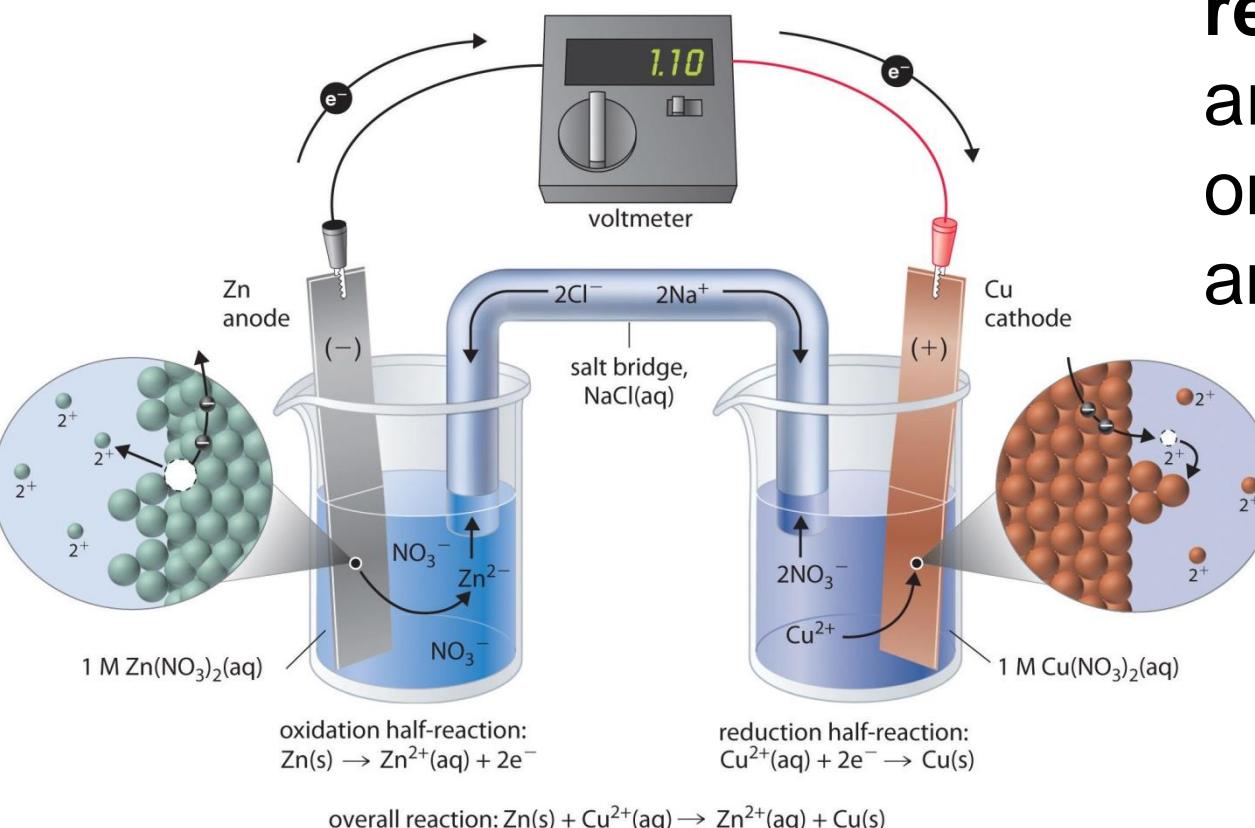
Applications: batteries, fuel cells, corrosion prevention, electrolysis

Electrochemistry/Electrochemical Reactions

- Relationships between **electricity** and **chemical reactions**. It includes the study of *both spontaneous and nonspontaneous* processes.

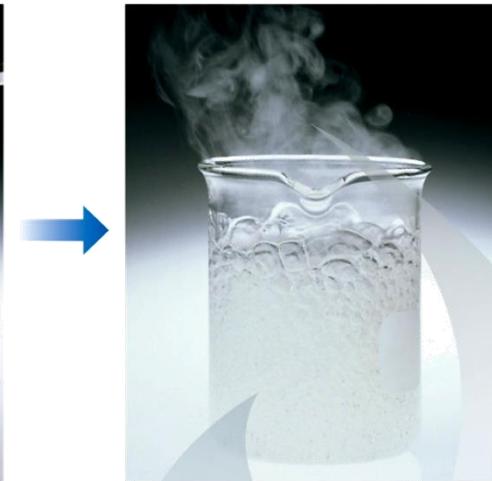
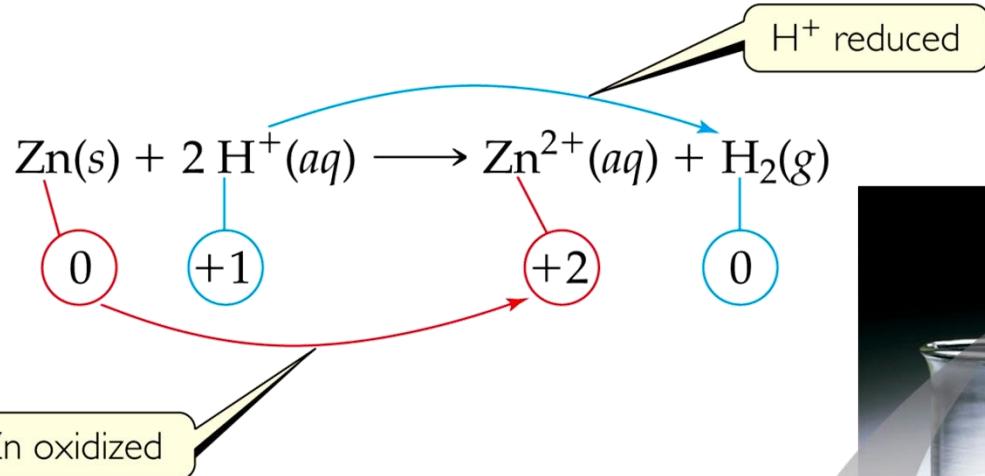
- In **electrochemical reactions**, electrons are **transferred** from one species to another:

Oxidation-Reduction (Redox) Reactions

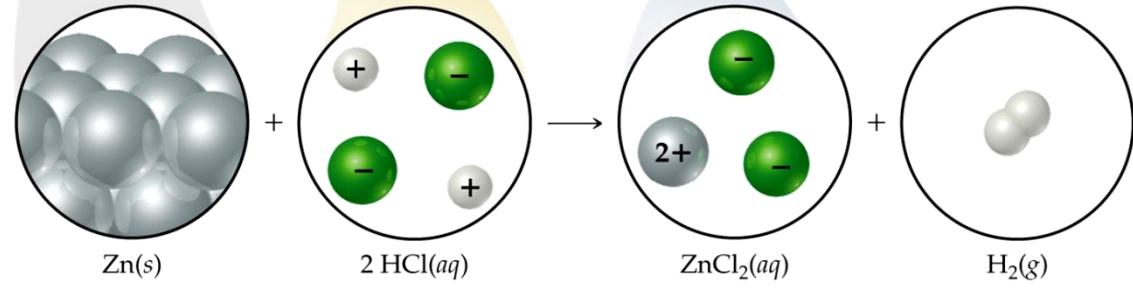


Oxidation Numbers

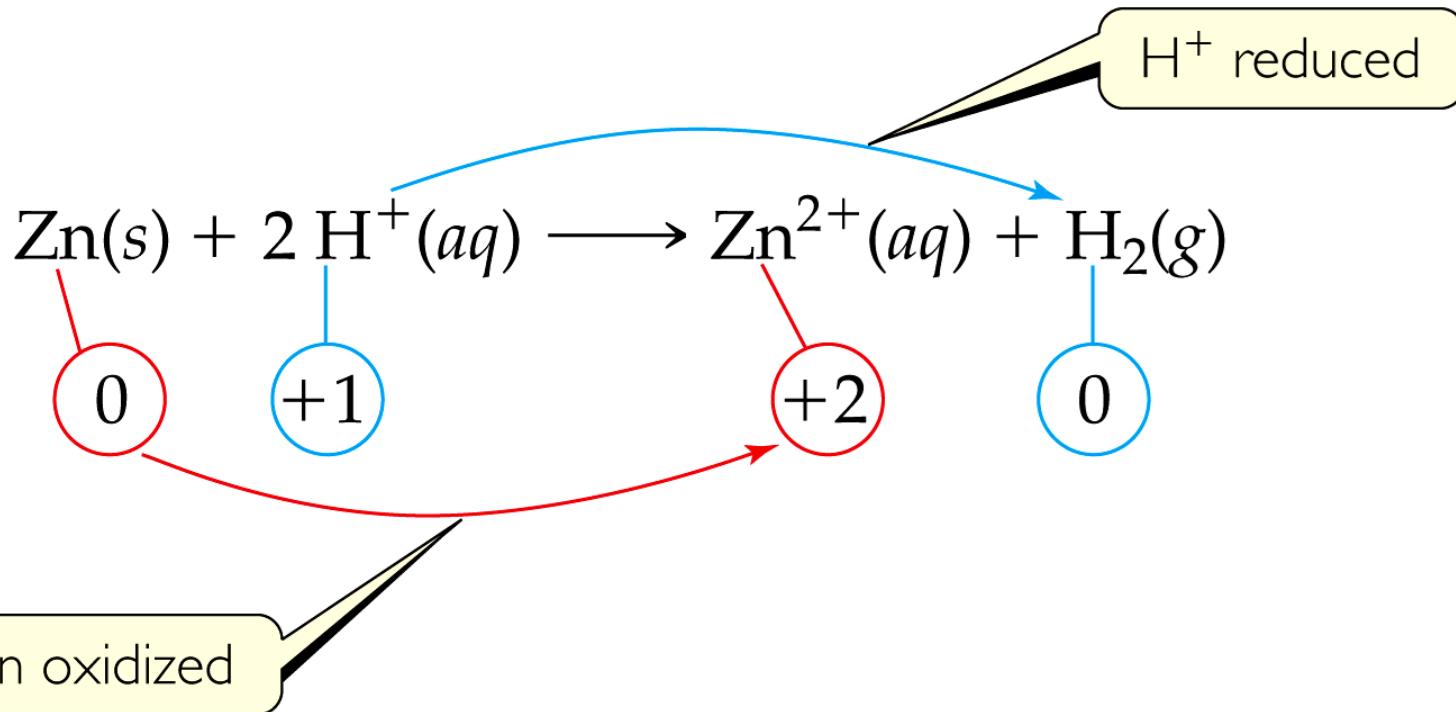
- In order to keep track of what loses electrons and what gains them, we assign **oxidation numbers**.



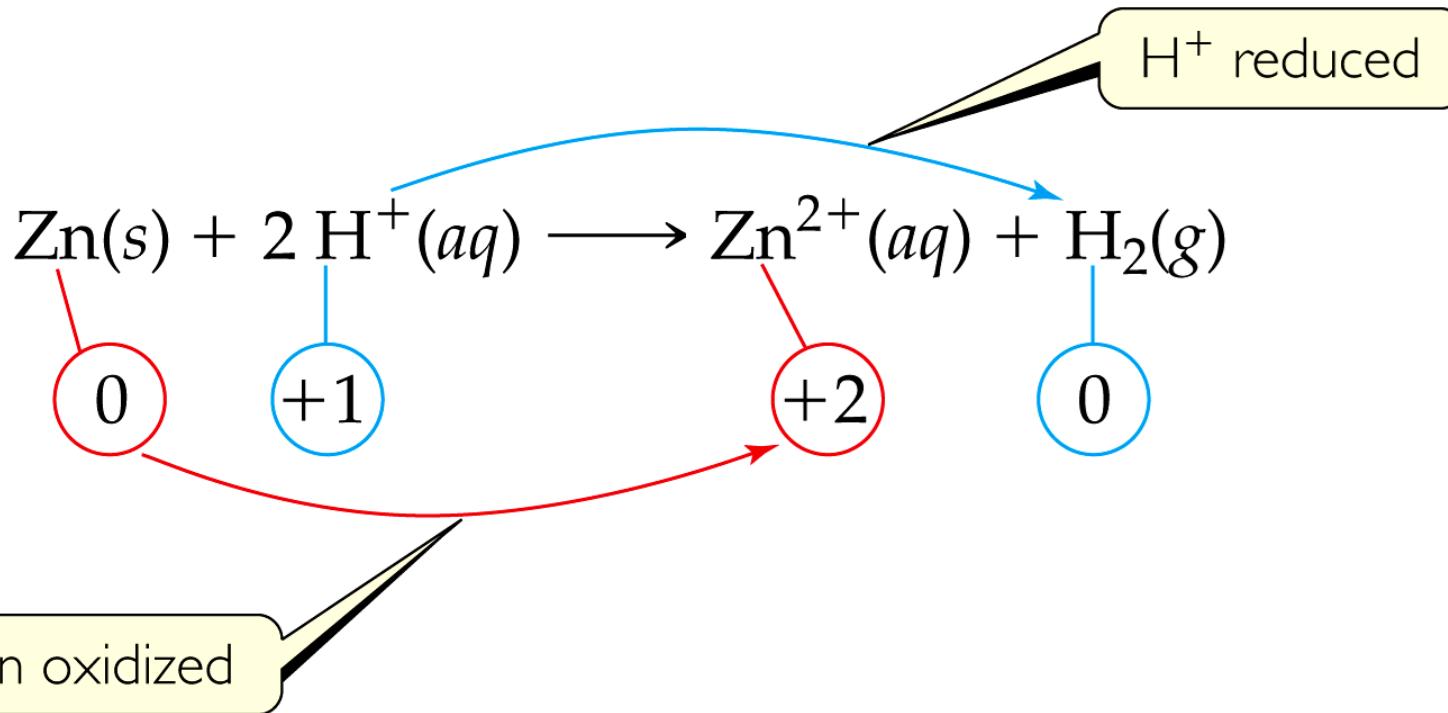
Explain (a) the vigorous bubbling in the beaker on the right and (b) the formation of steam above that beaker.



Oxidation & Reduction (Redox)



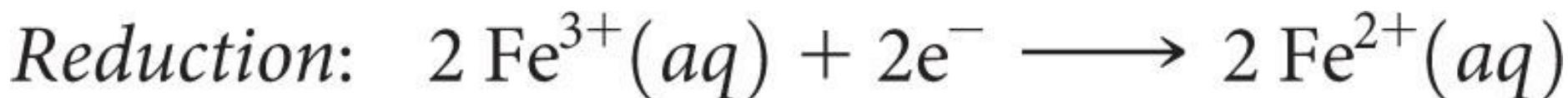
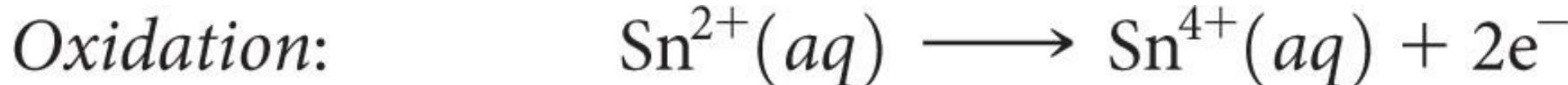
- A species is **oxidized** when it loses electrons. Zinc loses two electrons to go from neutral zinc metal to the Zn²⁺ ion.
- A species is **reduced** when it gains electrons. H⁺ gains an electron, and they combine to form H₂.



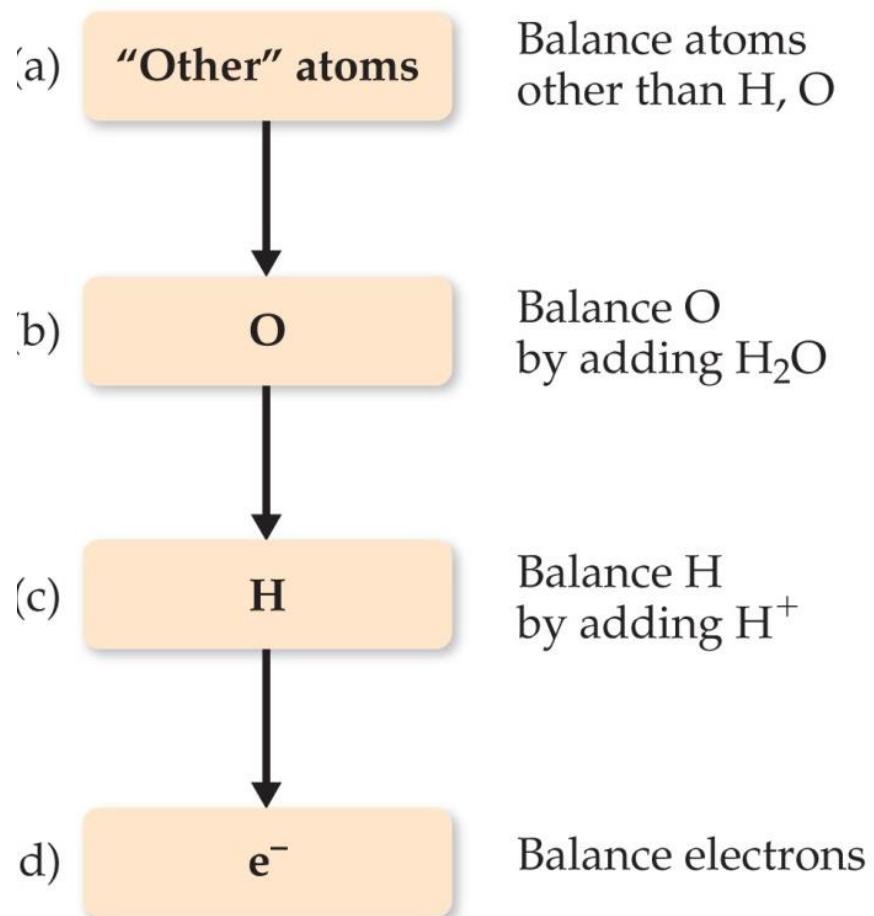
- What is reduced is the **oxidizing agent (H^+)**
- What is oxidized is the **reducing agent (Zn)**

Balancing Redox Equations

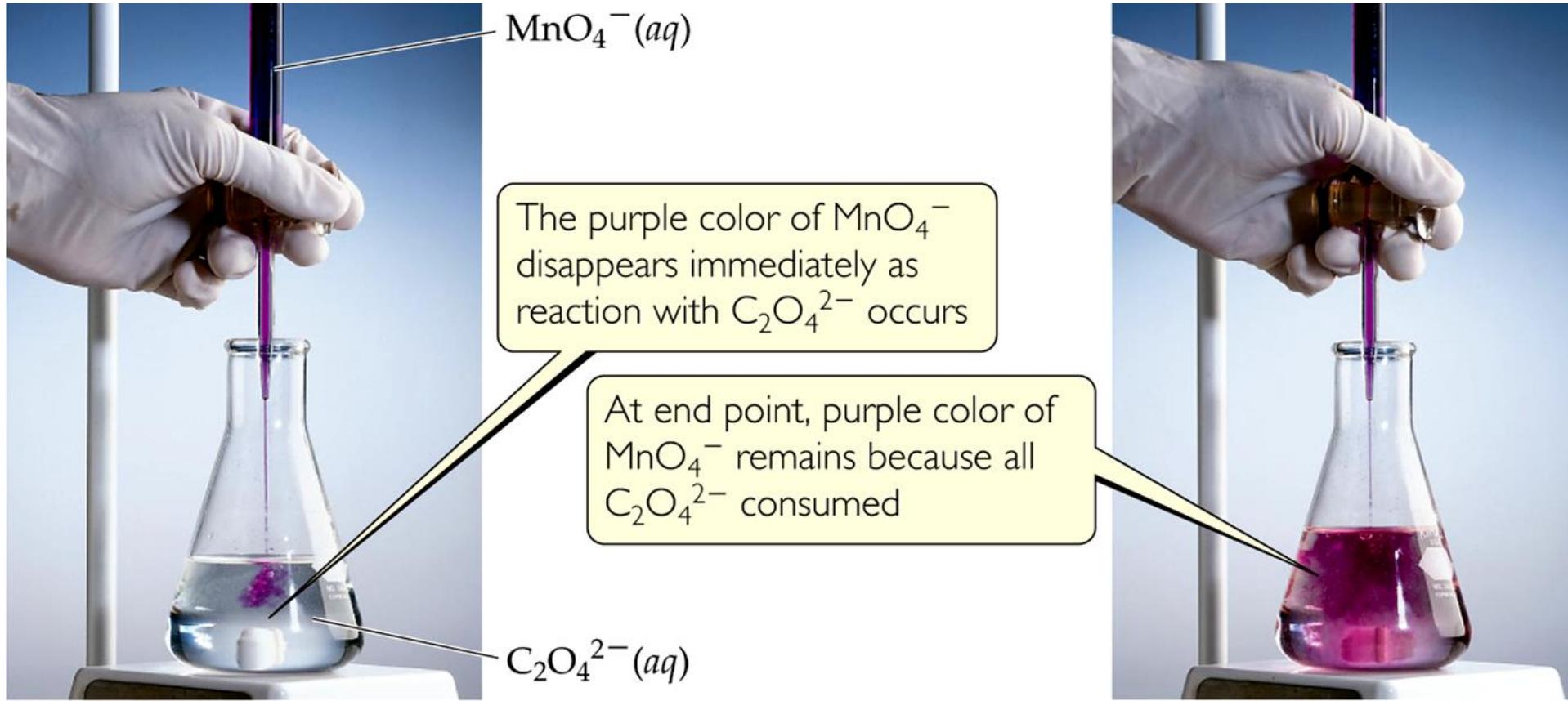
- Perhaps the easiest way to balance the equation of an oxidation-reduction reaction is via the **half-reaction method**.
- This method involves treating (on paper only) the **oxidation and reduction as two separate processes, balancing these half-reactions**, and then **combining** them to attain the balanced equation for the overall reaction.



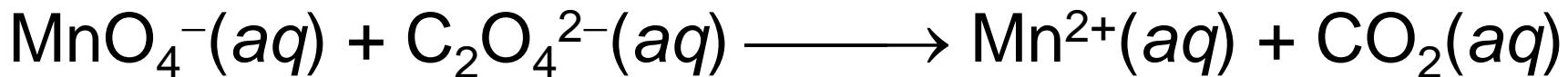
- 1) Make two half-reactions (oxidation and reduction).
- 2) Balance atoms other than O and H. Then, balance O and H using $\text{H}_2\text{O}/\text{H}^+$.
- 3) Add e^- to balance charges.
- 4) Multiply by common factor to make electrons in half-reactions equal.
- 5) Add the half-reactions.
- 6) Simplify by dividing by common factor or converting H^+ to OH^- if basic.
- 7) Double-check atoms and charges balance!



The Half-Reaction Method



Consider the reaction between MnO₄⁻ and C₂O₄²⁻:



Which species is reduced in this reaction?
Which species is the reducing agent?

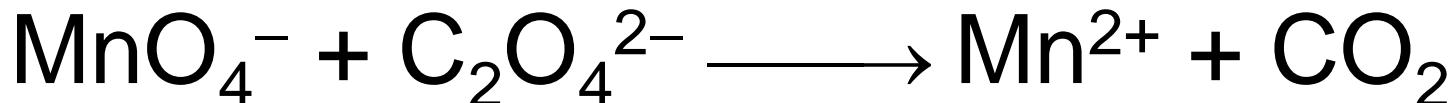
1. Assign oxidation numbers:

+7

+3

+2

+4



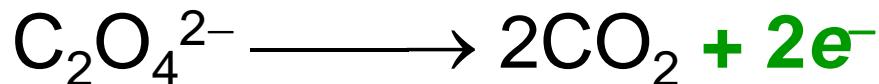
Since the manganese goes from +7 to +2, it is reduced.

Since the carbon goes from +3 to +4, it is oxidized.

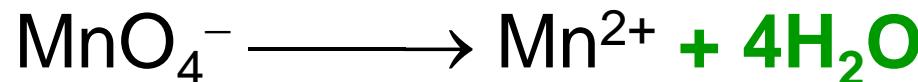
2. Balance the carbon, add a coefficient of 2:



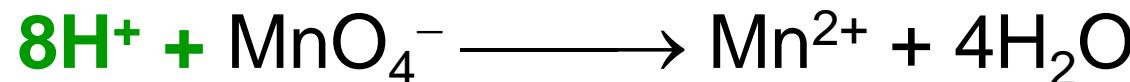
3. Balance the charge, add 2 electrons:



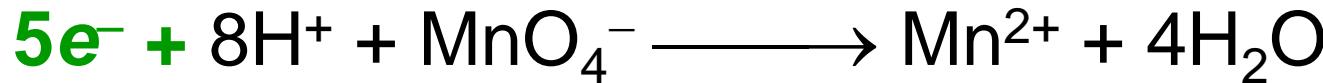
4. The manganese is balanced; **balance** the **oxygen**, add **4 waters**:



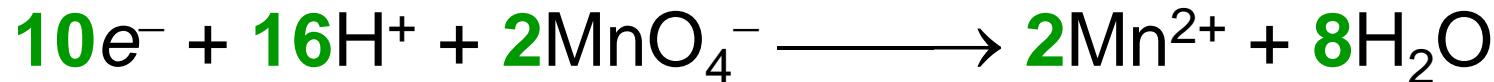
5. **Balance** the **hydrogen**, add **8H⁺**:



6. **Balance** the **charge**, add **5e⁻**:

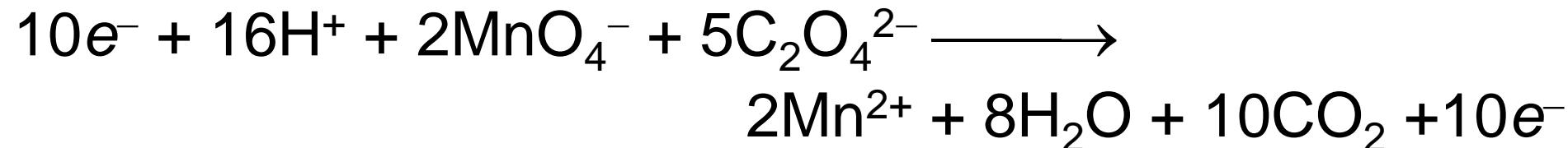


7. Evaluate the two half-reactions together & **balance** the number of **electrons**, multiply the first reaction by **5** and the second by **2**:

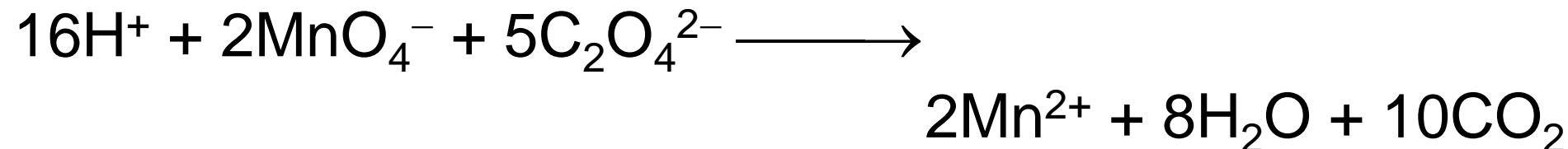


Combining the Half-Reactions

8. When we **combine** these two half-reactions together:



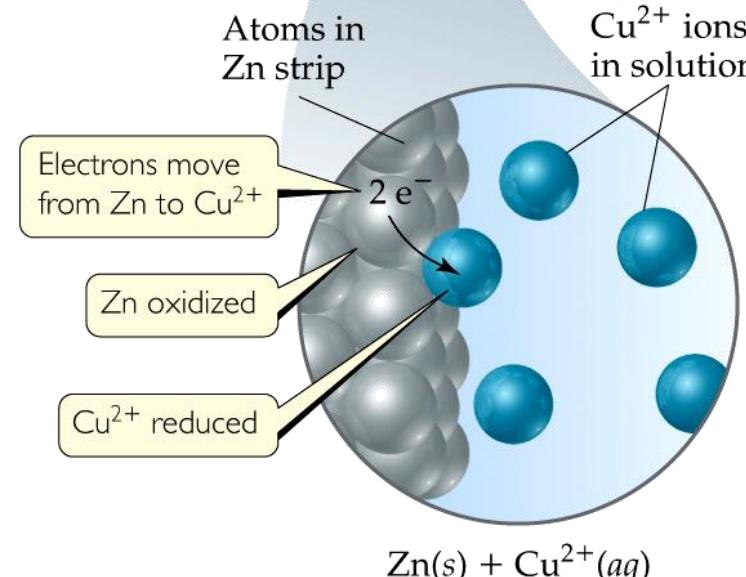
9. **Subtracting electrons** on both sides, we are left with:



Voltaic Cells

(原电池)

- In **spontaneous redox reactions**, electrons are transferred and energy is released.

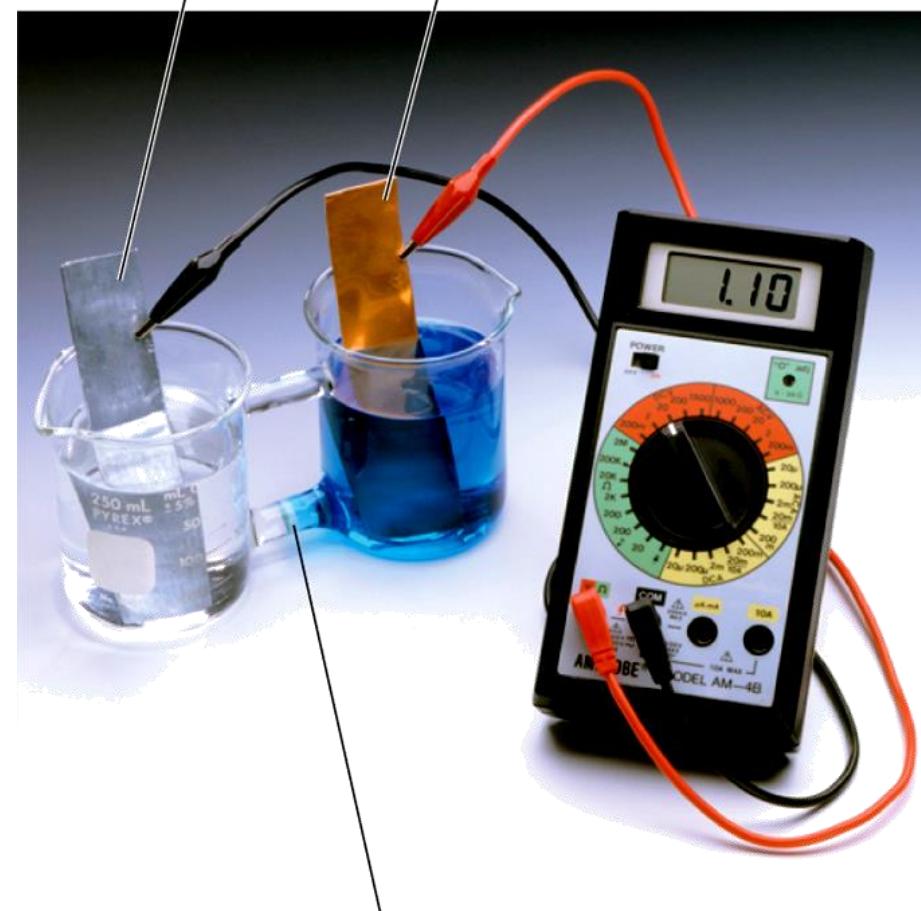


- We can **use that energy to do work** if we make the electrons flow through an external device.
- We call such a setup a **voltaic cell**.

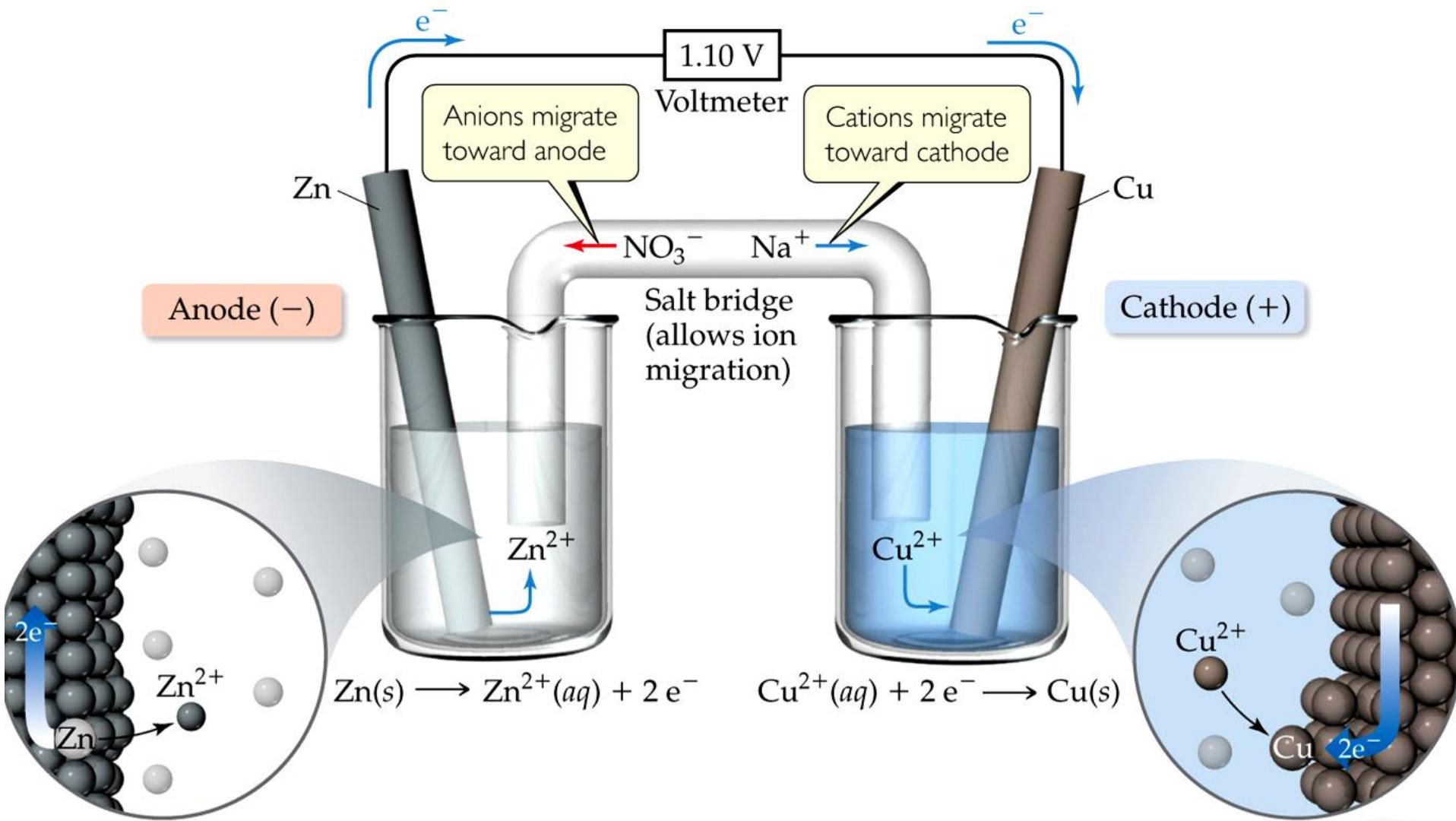
Which metal, Cu or Zn, is oxidized in this voltaic cell?

Zn electrode in
1 M ZnSO₄ solution

Cu electrode in
1 M CuSO₄ solution

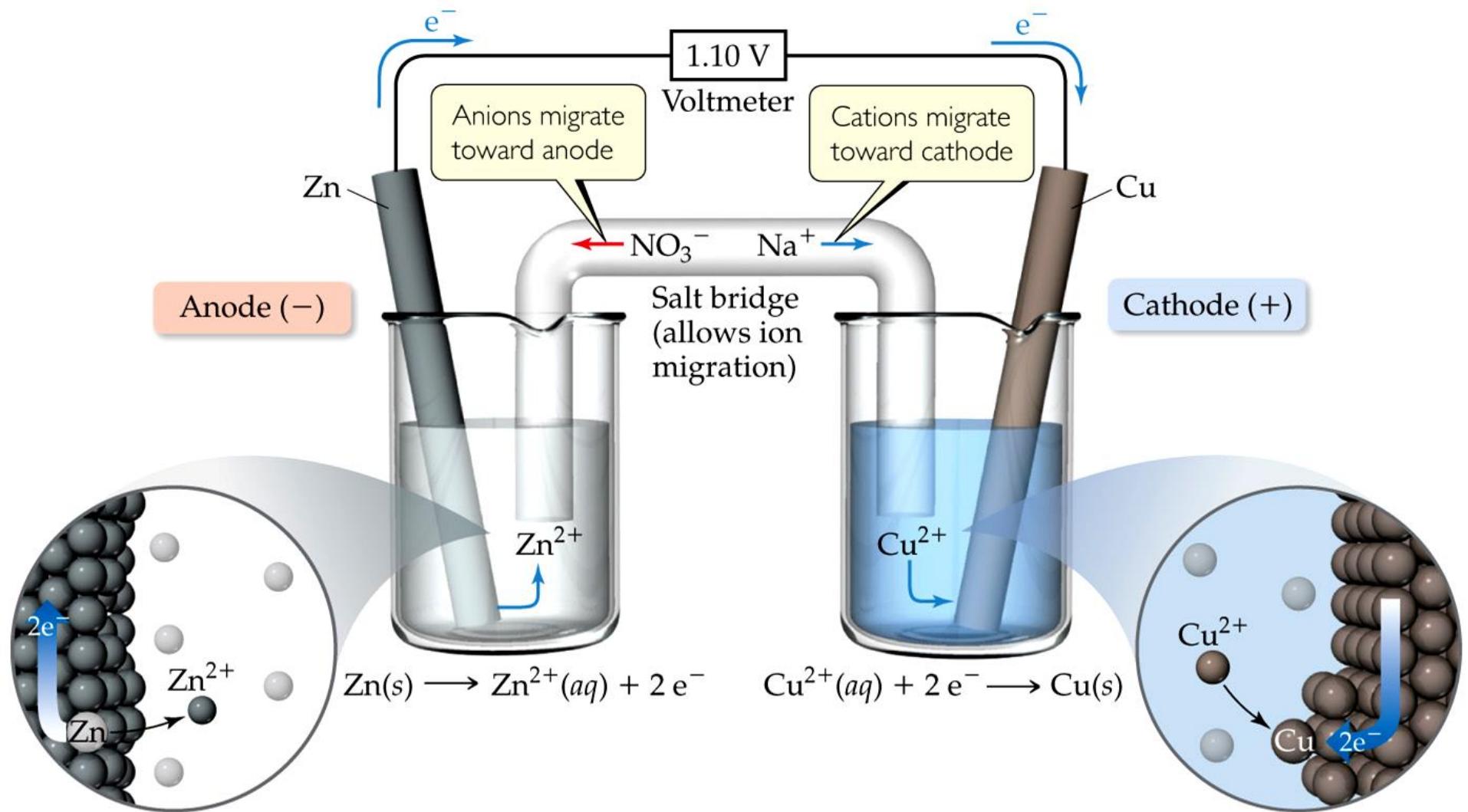


Solutions in contact with each other through porous glass disc

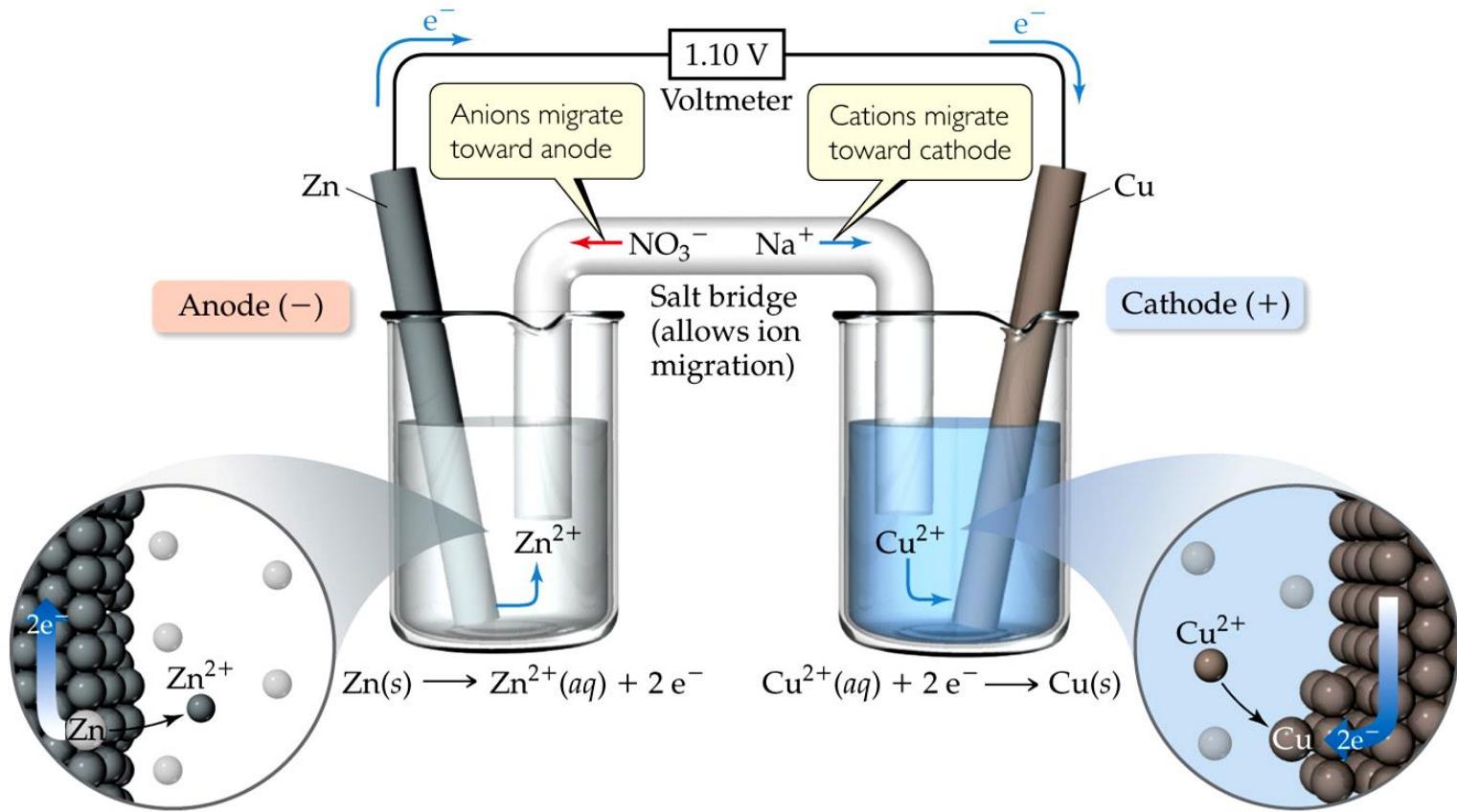


- A typical cell looks like this.
- The **oxidation** occurs at the **anode**.
- The **reduction** occurs at the **cathode**. (**red cat**)





- Once even one **electron flows from the anode to the cathode**, the **charges** in each beaker would **not be balanced** and the flow of electrons would stop.



- Use a **salt bridge**, usually a U-shaped tube that **contains a salt solution**, to **keep the charges balanced**.

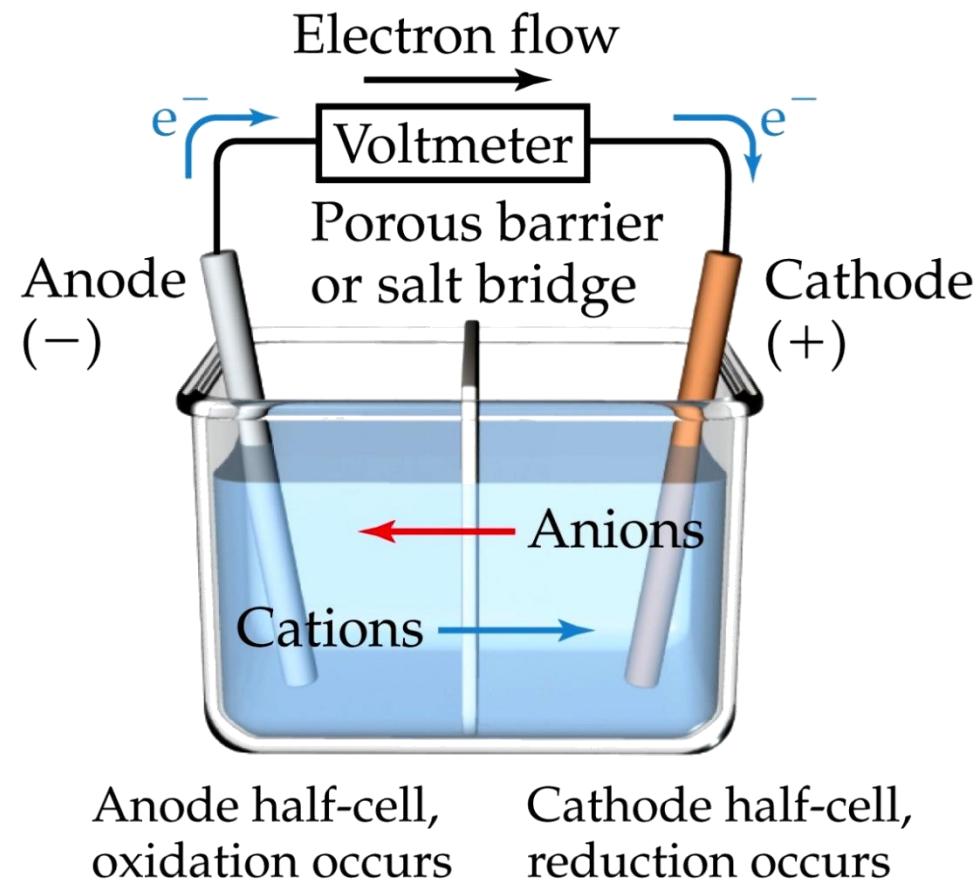
Cations move toward the **cathode**.
Anions move toward the **anode**.

- In the cell, electrons leave the anode and flow through the wire to the cathode.

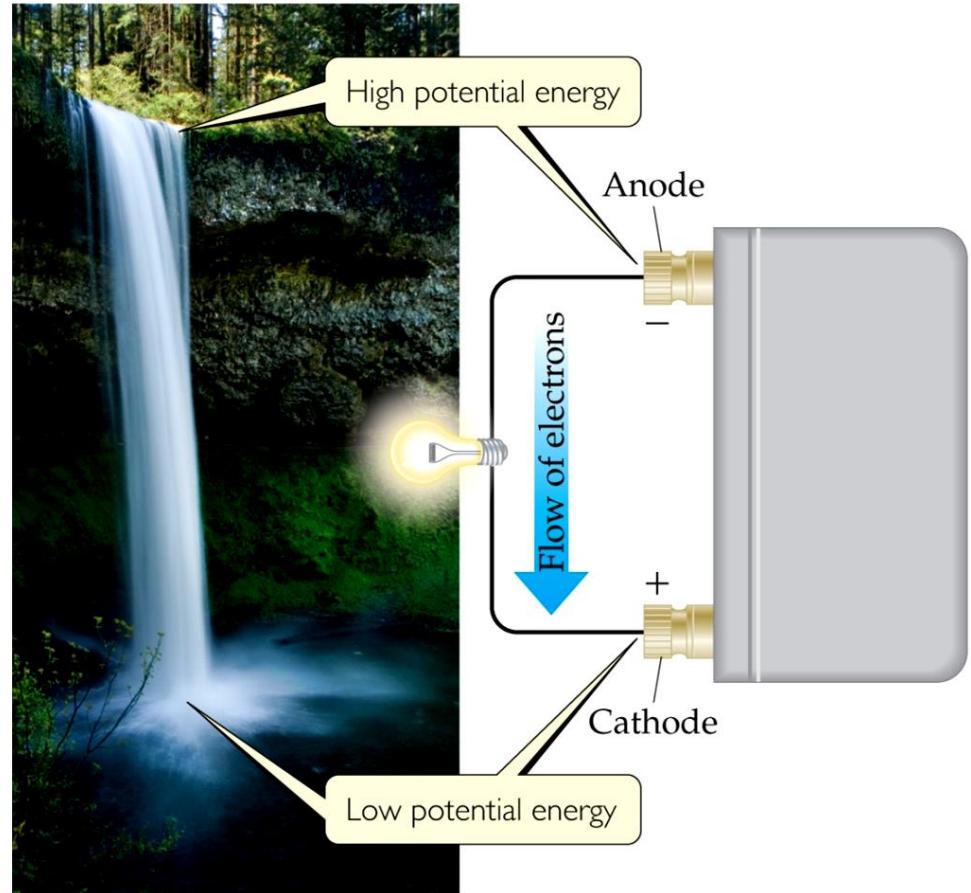
- **Cations are formed** in the **anode** compartment.

- As the electrons reach the cathode, cations in solution are **attracted** to the now **negative cathode**.

- The cations gain electrons and are **deposited as metal** on the cathode.



Electromotive Force (emf) (电动势)



- Water only spontaneously flows one way in a waterfall.
- Likewise, **electrons only spontaneously flow** one way in a redox reaction: **from higher to lower potential energy.**

- The **potential difference** between the anode and cathode in a cell: **electromotive force** & also called the **cell potential (E_{cell} ,** unit: volts (V)).

$$1 \text{ V} = 1 \frac{\text{J}}{\text{C}}$$

Standard Reduction Potentials

- Reduction potentials for many electrodes have been measured.
- The values are compared to the reduction of hydrogen as a standard.

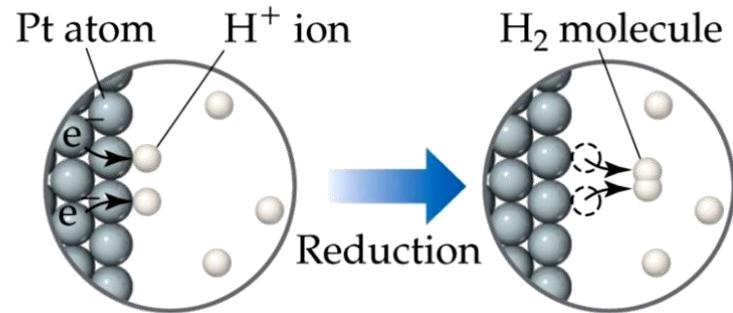
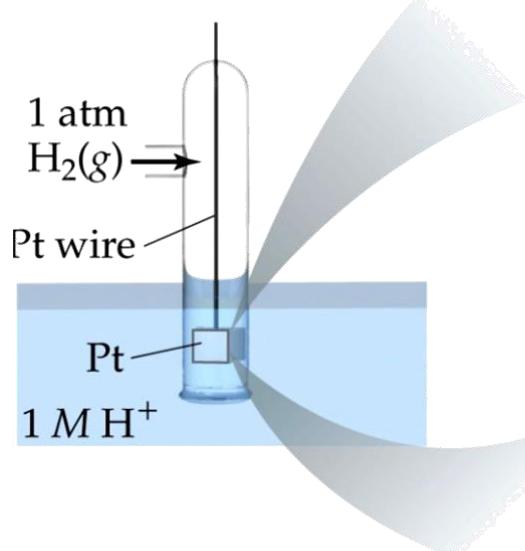
Table 20.1 Standard Reduction Potentials in Water at 25 °C

$E_{\text{red}}^{\circ}(\text{V})$	Reduction Half-Reaction
+2.87	$\text{F}_2(g) + 2 \text{e}^- \longrightarrow 2 \text{F}^-(\text{aq})$
+1.51	$\text{MnO}_4^-(\text{aq}) + 8 \text{H}^+(\text{aq}) + 5 \text{e}^- \longrightarrow \text{Mn}^{2+}(\text{aq}) + 4 \text{H}_2\text{O}(l)$
+1.36	$\text{Cl}_2(g) + 2 \text{e}^- \longrightarrow 2 \text{Cl}^-(\text{aq})$
+1.33	$\text{Cr}_2\text{O}_7^{2-}(\text{aq}) + 14 \text{H}^+(\text{aq}) + 6 \text{e}^- \longrightarrow 2 \text{Cr}^{3+}(\text{aq}) + 7 \text{H}_2\text{O}(l)$
+1.23	$\text{O}_2(g) + 4 \text{H}^+(\text{aq}) + 4 \text{e}^- \longrightarrow 2 \text{H}_2\text{O}(l)$
+1.06	$\text{Br}_2(l) + 2 \text{e}^- \longrightarrow 2 \text{Br}^-(\text{aq})$
+0.96	$\text{NO}_3^-(\text{aq}) + 4 \text{H}^+(\text{aq}) + 3 \text{e}^- \longrightarrow \text{NO}(g) + 2 \text{H}_2\text{O}(l)$
+0.80	$\text{Ag}^+(\text{aq}) + \text{e}^- \longrightarrow \text{Ag}(s)$
+0.77	$\text{Fe}^{3+}(\text{aq}) + \text{e}^- \longrightarrow \text{Fe}^{2+}(\text{aq})$
+0.68	$\text{O}_2(g) + 2 \text{H}^+(\text{aq}) + 2 \text{e}^- \longrightarrow \text{H}_2\text{O}_2(\text{aq})$
+0.59	$\text{MnO}_4^-(\text{aq}) + 2 \text{H}_2\text{O}(l) + 3 \text{e}^- \longrightarrow \text{MnO}_2(s) + 4 \text{OH}^-(\text{aq})$
+0.54	$\text{I}_2(s) + 2 \text{e}^- \longrightarrow 2 \text{I}^-(\text{aq})$
+0.40	$\text{O}_2(g) + 2 \text{H}_2\text{O}(l) + 4 \text{e}^- \longrightarrow 4 \text{OH}^-(\text{aq})$
+0.34	$\text{Cu}^{2+}(\text{aq}) + 2 \text{e}^- \longrightarrow \text{Cu}(s)$
0 [defined]	$2 \text{H}^+(\text{aq}) + 2 \text{e}^- \longrightarrow \text{H}_2(g)$
-0.28	$\text{Ni}^{2+}(\text{aq}) + 2 \text{e}^- \longrightarrow \text{Ni}(s)$
-0.44	$\text{Fe}^{2+}(\text{aq}) + 2 \text{e}^- \longrightarrow \text{Fe}(s)$
-0.76	$\text{Zn}^{2+}(\text{aq}) + 2 \text{e}^- \longrightarrow \text{Zn}(s)$
-0.83	$2 \text{H}_2\text{O}(l) + 2 \text{e}^- \longrightarrow \text{H}_2(g) + 2 \text{OH}^-(\text{aq})$
-1.66	$\text{Al}^{3+}(\text{aq}) + 3 \text{e}^- \longrightarrow \text{Al}(s)$
-2.71	$\text{Na}^+(\text{aq}) + \text{e}^- \longrightarrow \text{Na}(s)$
-3.05	$\text{Li}^+(\text{aq}) + \text{e}^- \longrightarrow \text{Li}(s)$

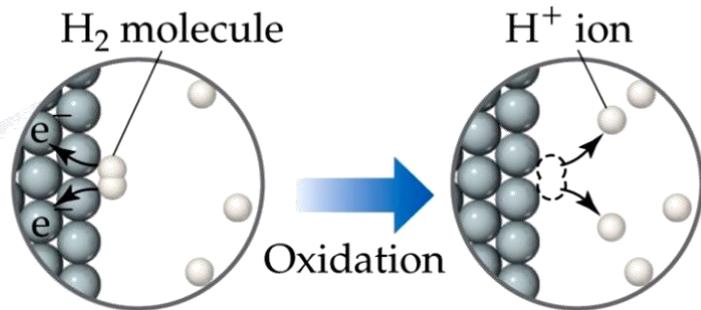
Standard Hydrogen Electrode

- Their values are referenced to a **standard hydrogen electrode (SHE)**.

- By definition, the **reduction potential for hydrogen** is 0 V:



SHE as cathode
(H^+ reduced to H_2)



SHE as anode
(H_2 oxidized to H^+)

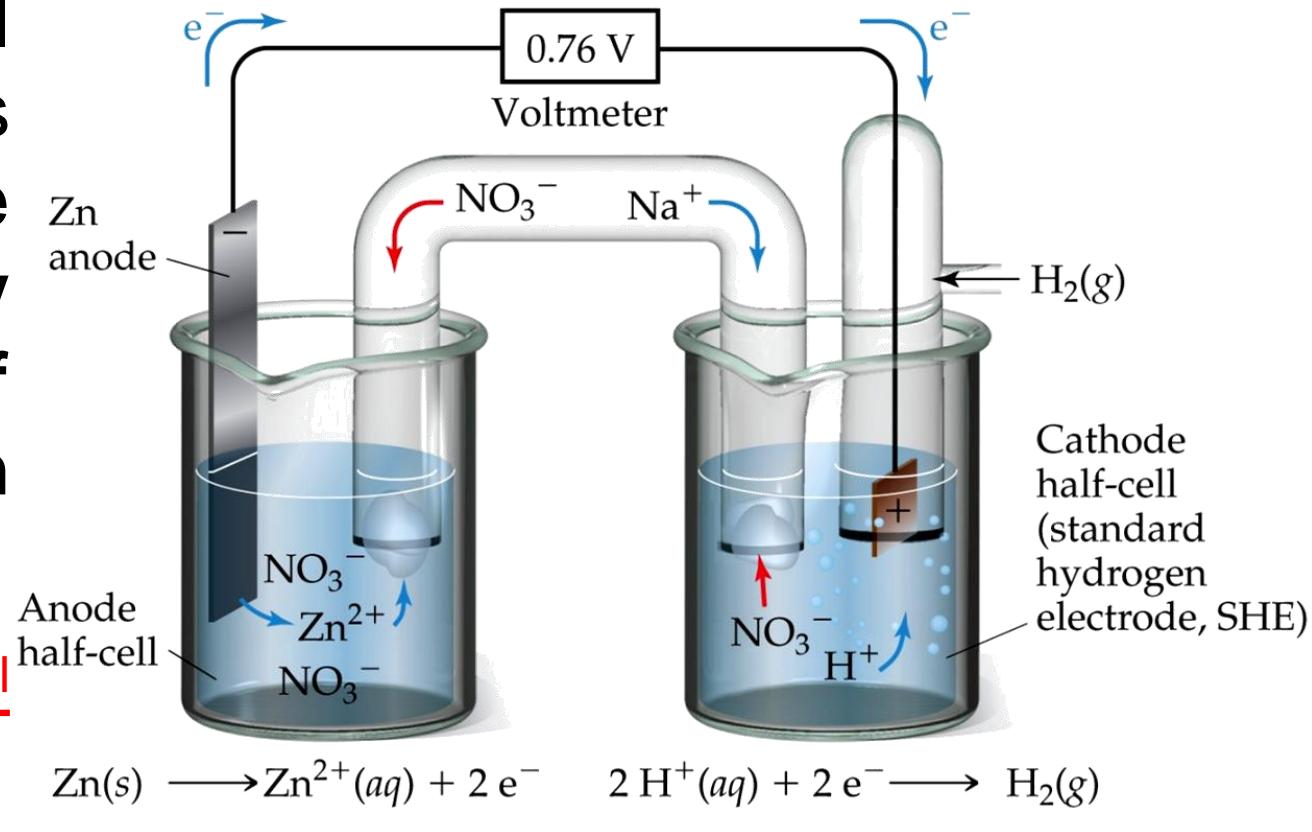


Standard Cell Potentials

- The cell potential at standard conditions can be found through this equation:

$$E_{\text{cell}}^{\circ} = E_{\text{red}}^{\circ}(\text{cathode}) - E_{\text{red}}^{\circ}(\text{anode})$$

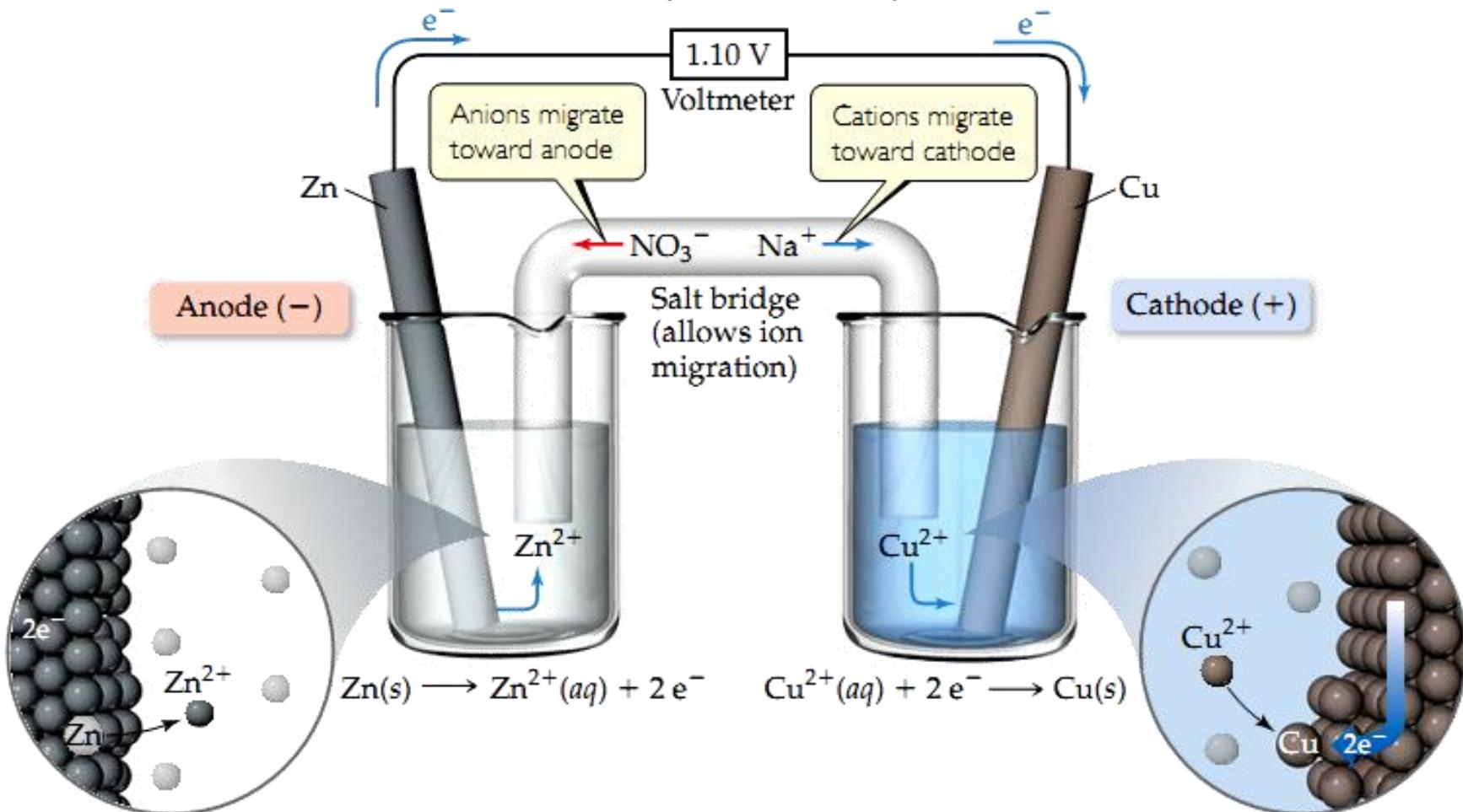
- Because **cell potential** is based on the **potential energy per unit of charge**, it is an **intensive property** → E_{cell} does NOT depend no. of e^- .



Cell Potentials

- For the oxidation, $E_{\text{red}}^{\circ} = -0.76 \text{ V}$
- For the reduction, $E_{\text{red}}^{\circ} = +0.34 \text{ V}$

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

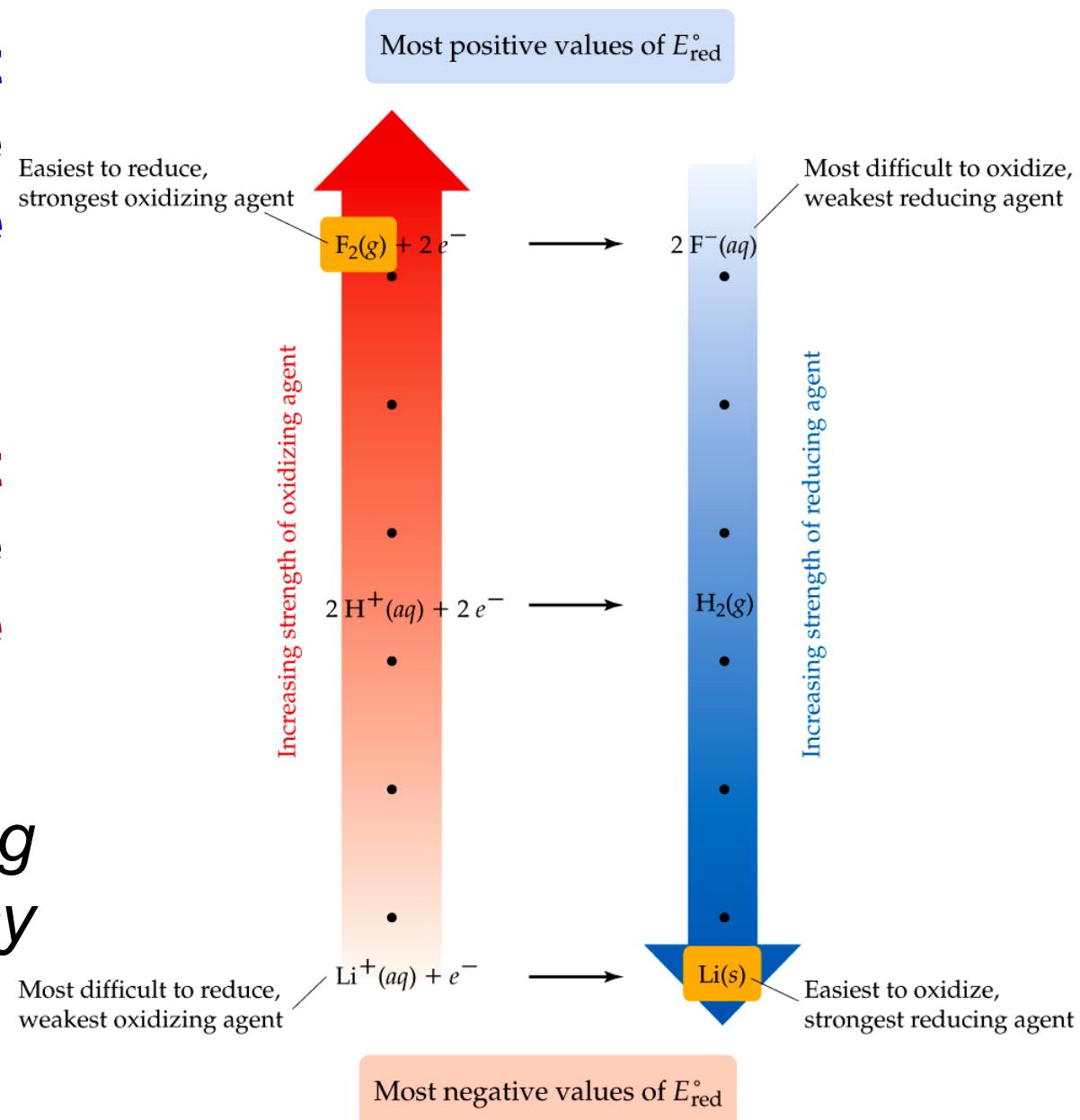


Oxidizing and Reducing Agents

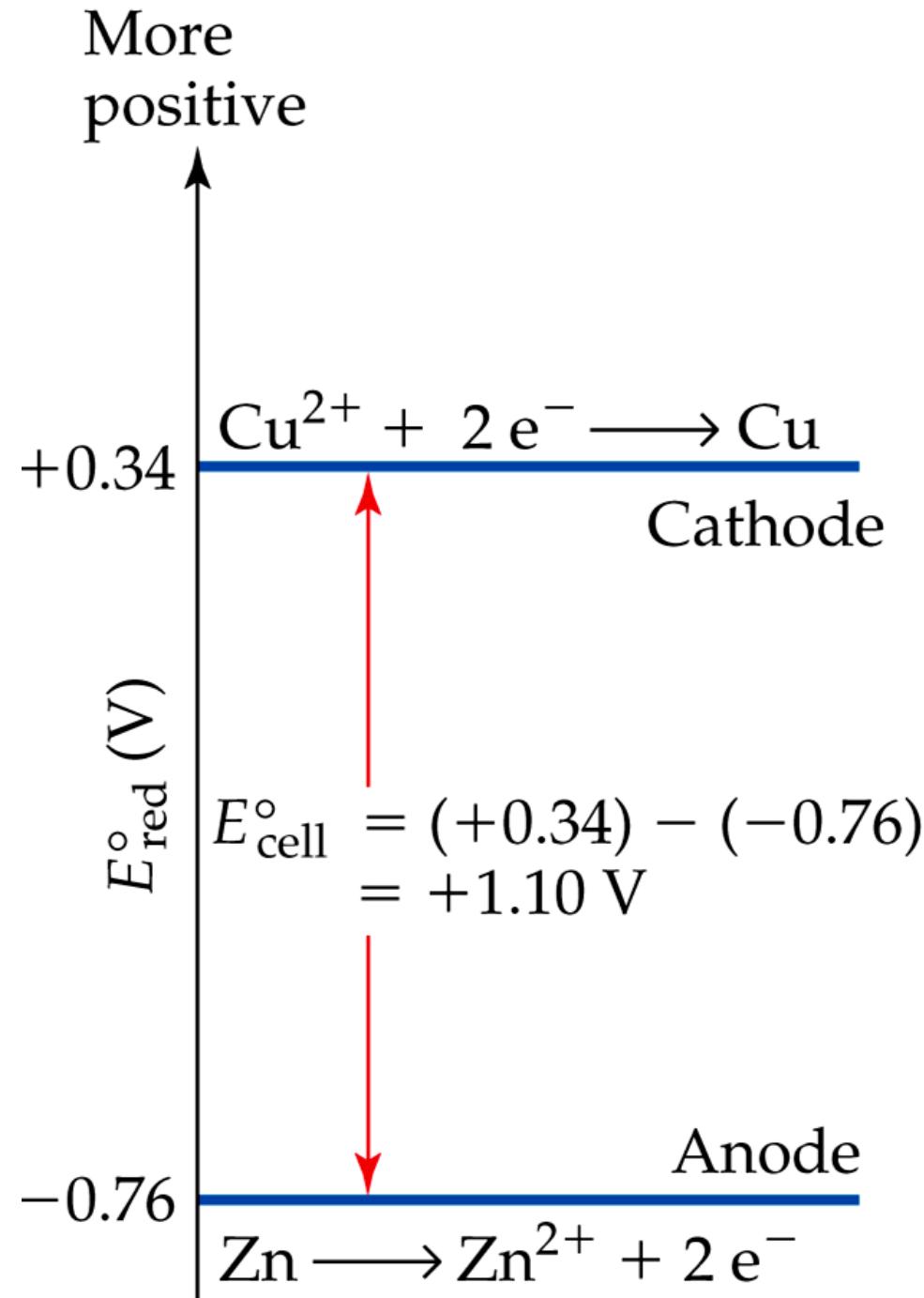
- The **strongest oxidizers** have the **most positive** reduction potentials.

- The **strongest reducers** have the **most negative** reduction potentials.

Why is a strong oxidizing agent easy to reduce?



- The greater the potential difference between the two sides, the **greater the voltage** of the cell.



Free Energy and Redox

- Spontaneous redox reactions produce a positive cell potential, or emf (intensive property).

$$E^\circ = E^\circ_{\text{red}}(\text{reduction}) - E^\circ_{\text{red}}(\text{oxidation})$$

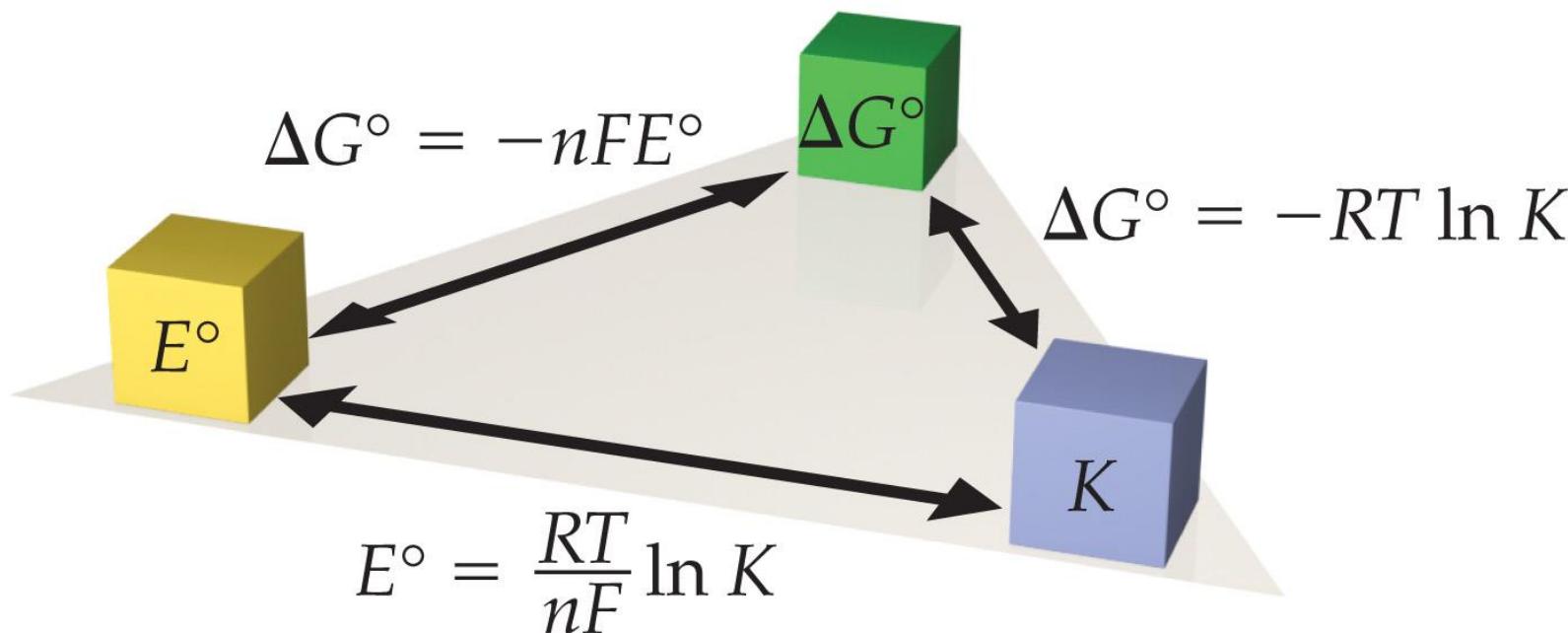
- True for ALL redox reactions, not only for voltaic cells.
- Since Gibbs free energy is the measure of spontaneity, positive emf corresponds to negative ΔG .
- How do they relate?

- ΔG (**extensive** property) for a redox reaction:

$$\Delta G = -nFE$$

where **n** is n. of moles of electrons transferred, & F is a Faraday constant: $1 F = 96,485 \text{ C/mol} = 96,485 \text{ J/V-mol}$

Under standard conditions: $\Delta G^\circ = -nFE^\circ$



$$E_{\text{cell}}^\circ = E_{\text{red}}^\circ(\text{cathode}) - E_{\text{red}}^\circ(\text{anode}) \text{ (NO } n\text{!!)}$$

Nernst Equation

- Remember that

$$\Delta G = \Delta G^\circ + RT \ln Q$$

- Thus,

$$-nFE = -nFE^\circ + RT \ln Q$$

- Dividing both sides by **$-nF$** , Nernst equation:

$$E = E^\circ - \frac{RT}{nF} \ln Q$$

or

$$E = E^\circ - \frac{2.303RT}{nF} \log Q$$

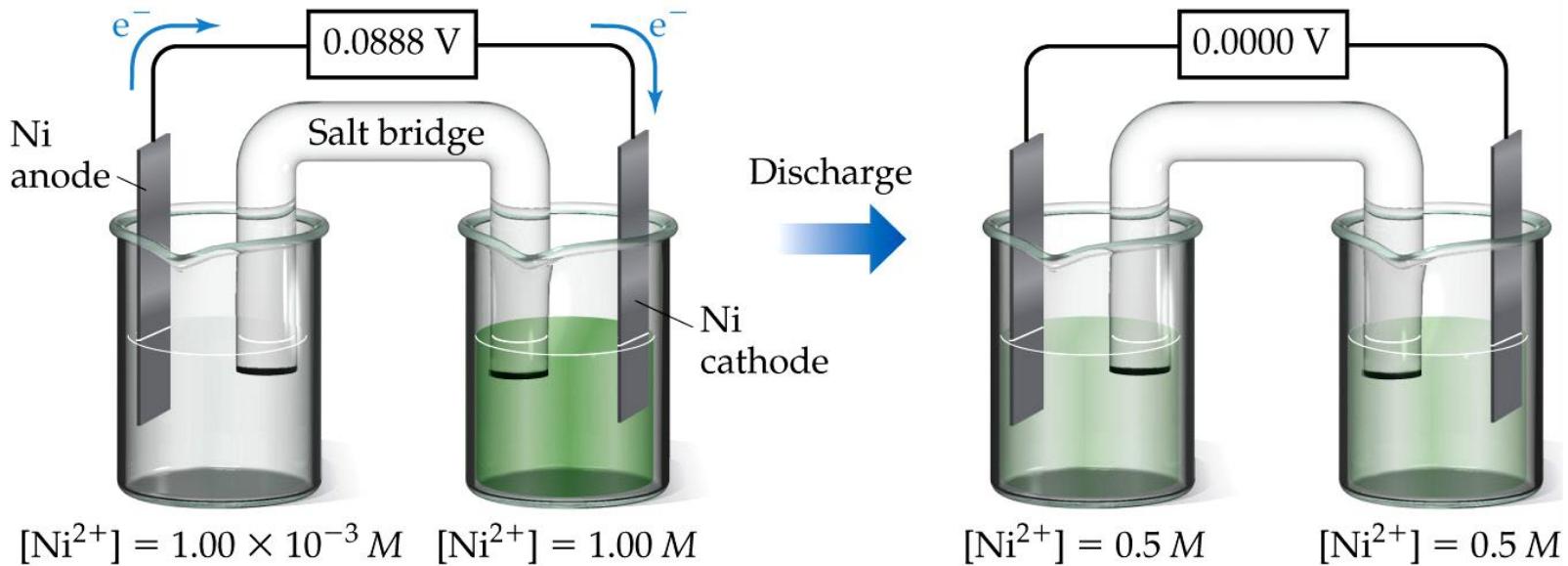
At room temperature (298 K),

$$\frac{2.303RT}{F} = 0.0592 \text{ V}$$

Thus,

$$E = E^\circ - \frac{0.0592}{n} \log Q$$

Concentration Cells



- Nernst equation implies that a **cell** could be **created** that has the **same substance at both electrodes**, called a **concentration cell**.
- For such a cell, E_{cell}° would be 0, but Q would not.
- Therefore, as long as the concentrations are different, $E (= E^{\circ} - RT/nF * \ln Q)$ will not be 0.

The lower-concentrated ones prefer oxidation/reduction?



The reducing agent in the reaction above is _____.

- a. Zn
- b. Cu²⁺
- c. Zn²⁺
- d. Cu



The oxidizing agent in the reaction above is _____.

- a. Zn
- b. Cu²⁺
- c. Zn²⁺
- d. Cu

If the value of the standard cell potential for a reaction is large and positive, then the reaction is

- a. at equilibrium.
- b. spontaneous.
- c. nonspontaneous.
- d. very fast.

The purpose of the salt bridge in a voltaic cell is to

- a. provide H⁺ ions needed to balance charges.
- b. maintain neutrality by allowing the flow of ions.
- c. serve as the site for oxidation to occur.
- d. serve as the site for reduction to occur.



Select the true statement.

- a. Cl_2 will reduce I^- to I_2 .
- b. Cl_2 will oxidize I^- to I_2 .
- c. I_2 will reduce Cl^- to Cl_2 .
- d. I_2 will oxidize Cl_2 to Cl^- .

G = Gibbs free energy. n = moles of electrons. F = Faraday constant. E = cell potential. Change in G = ?

- a. $F + nE$
- b. $F - nE$
- c. $-nFE$
- d. $nF - E$

The Nernst Equation is most useful for determining cell potentials when _____ are nonstandard.

- a. oxidizing agents
- b. reducing agents
- c. ion concentrations
- d. temperatures

In a concentration cell, the half-reactions are

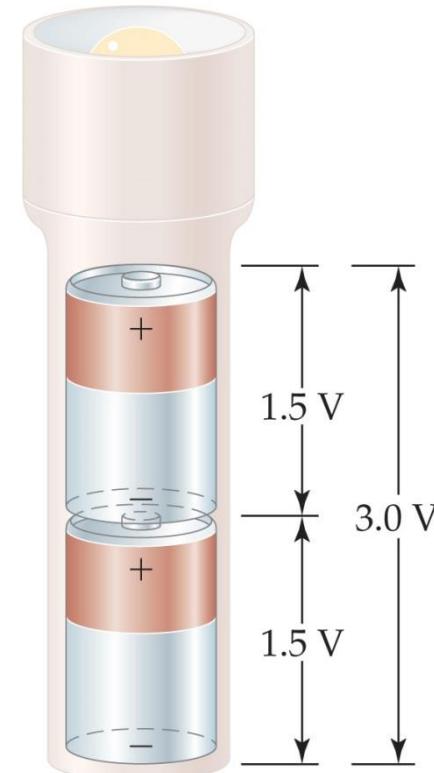
- a. the same.
- b. at equilibrium.
- c. acid–base reactions.
- d. different colors.

Some Applications of Cells

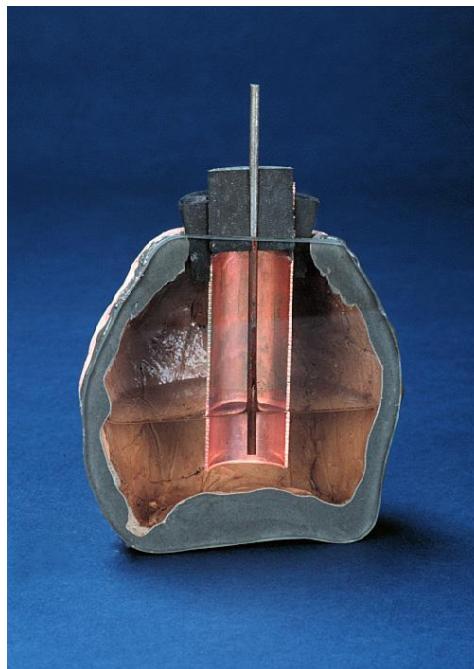
- Electrochemistry can be applied as follows:

❖ **Batteries:** a portable, self-contained electrochemical power source that consists of one or more voltaic cells.

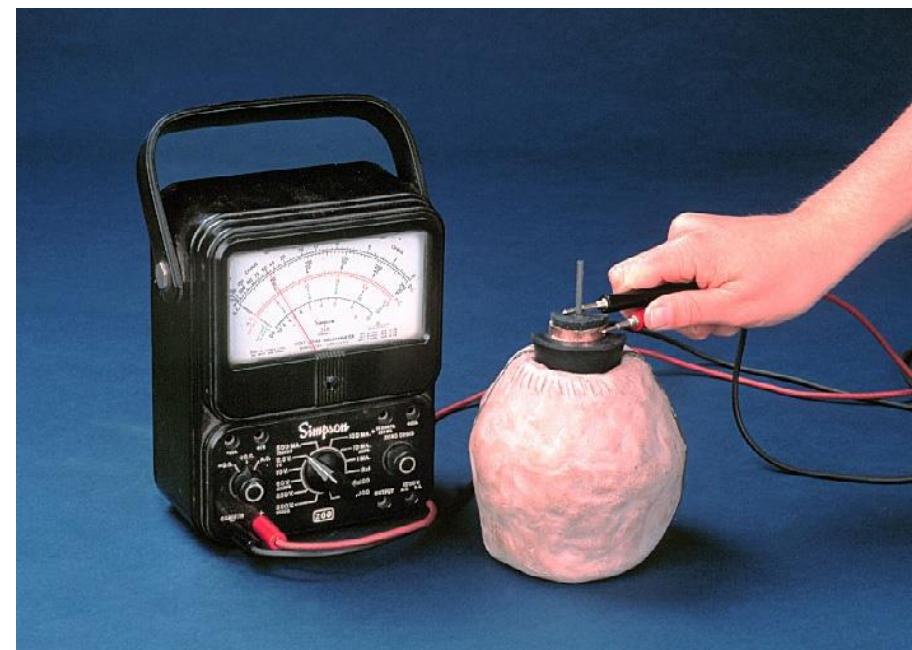
➤ Batteries can be **primary** cells (**cannot** be **recharged** when “dead”—the reaction is complete) or **secondary** cells (can be **recharged**).



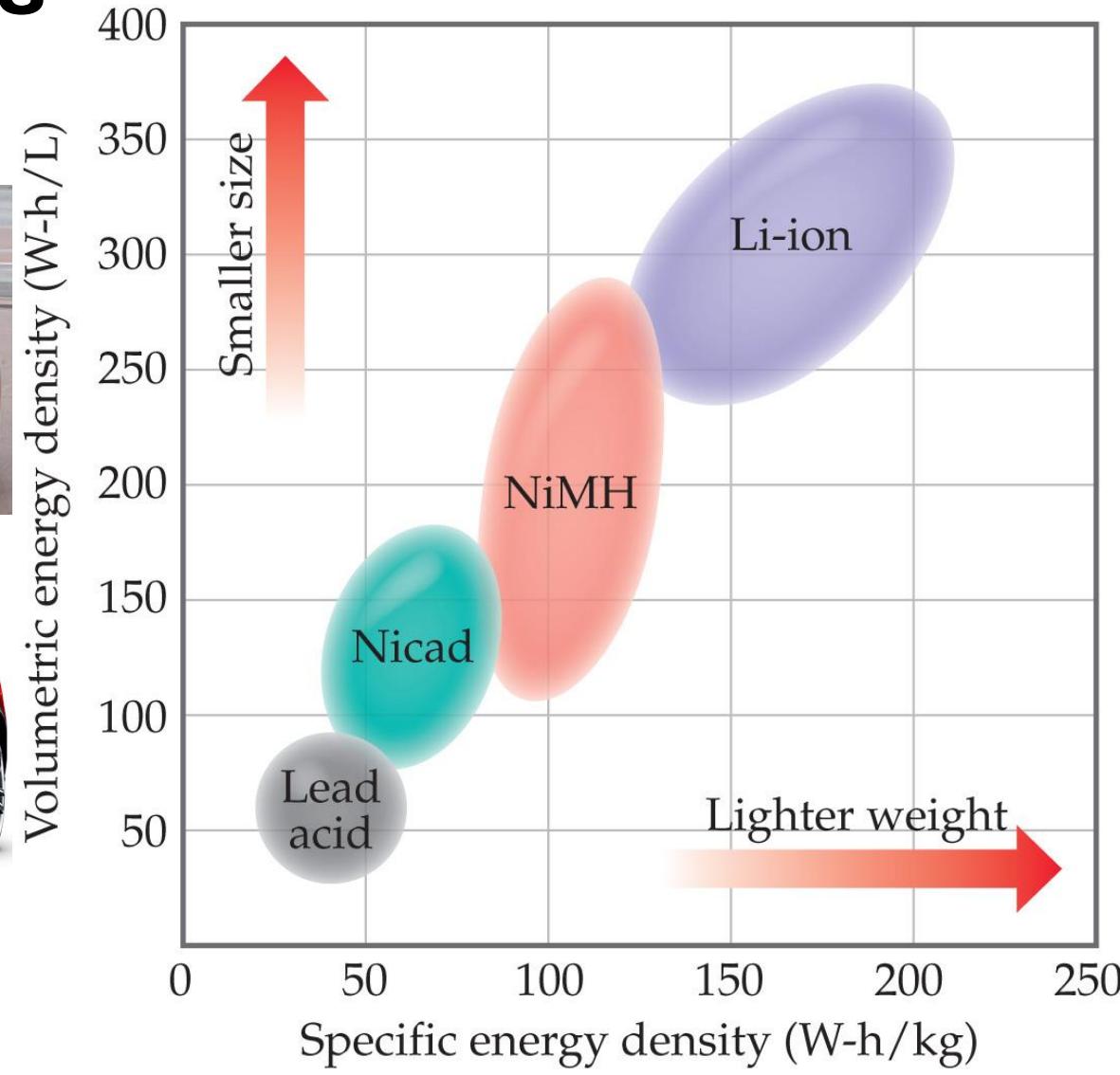
- ❖ **Prevention of corrosion (“rust-proofing”)**
- ❖ **Electrolysis** (电解)



The Baghdad Battery (2000 years before)

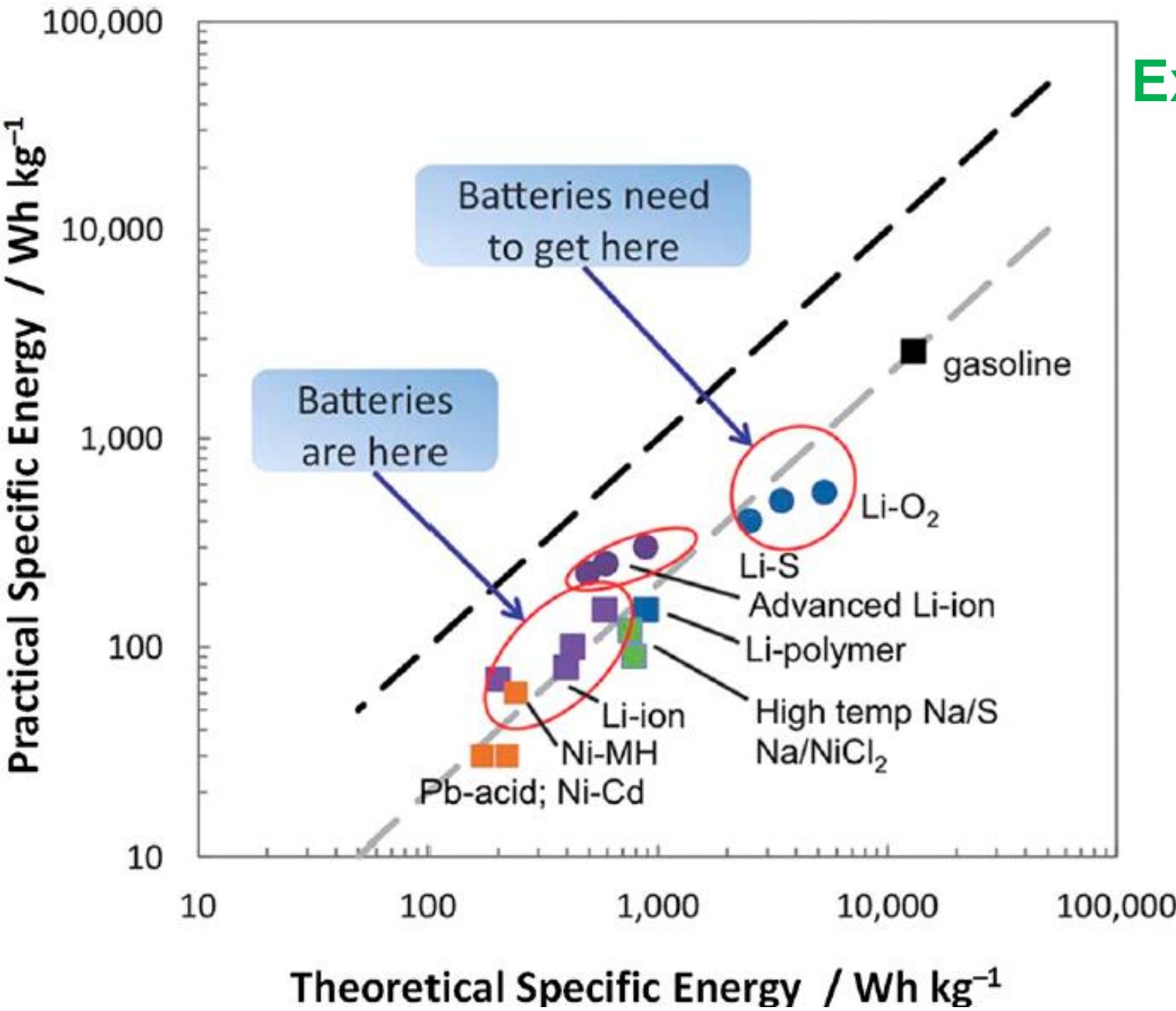


Some Examples of Batteries

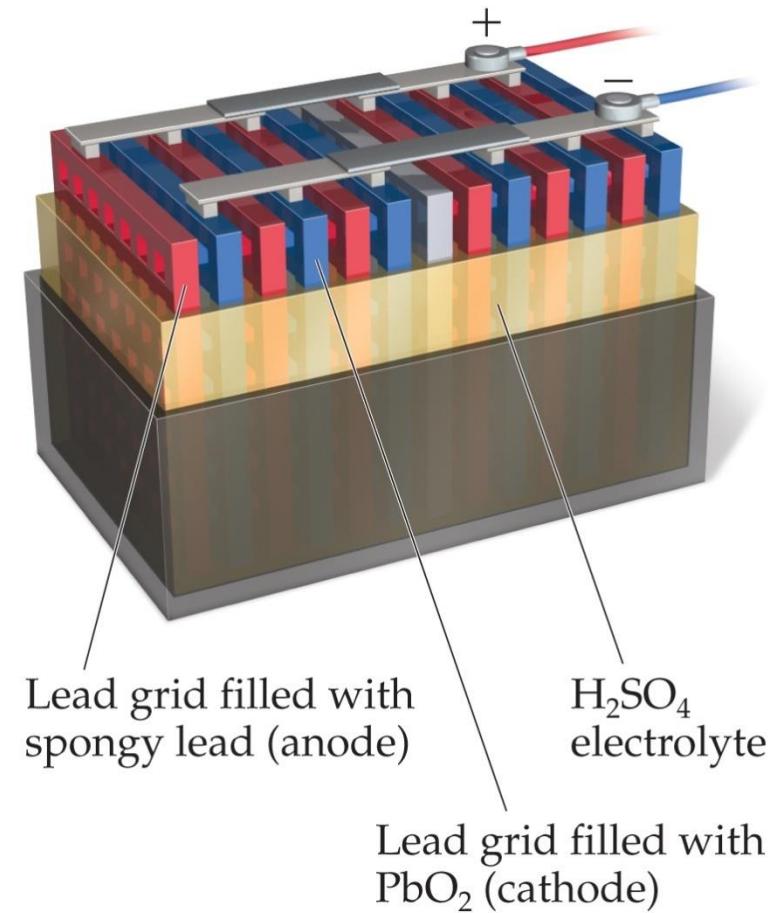


- **Lead-acid battery;**
- **Alkaline battery;**
- **Ni–Cd & Ni–metal hydride batteries;**
- **Lithium-ion batteries.**

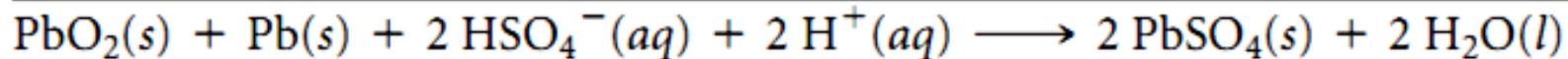
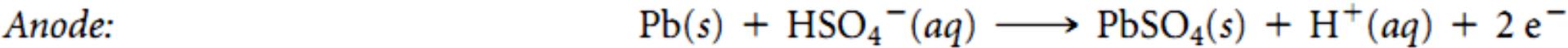
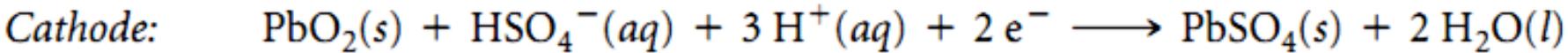
Extra info.



Lead–acid Batteries

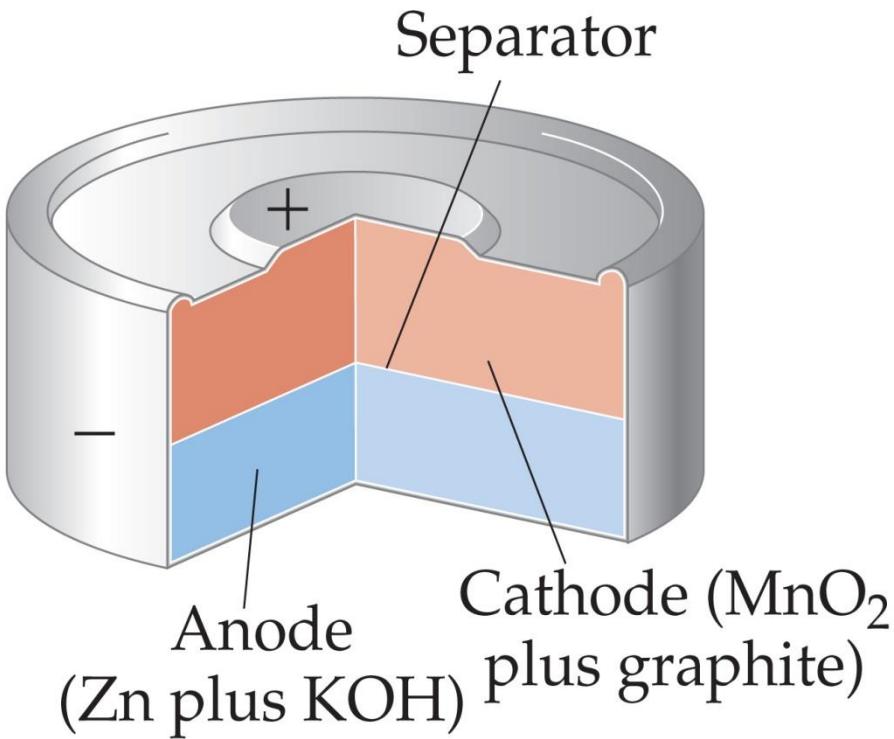


- Reactants and products are solids, so Q is 1 and the potential is independent of concentrations;
- However, made with lead and sulfuric acid (hazards).



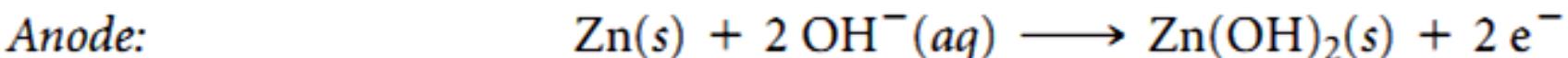
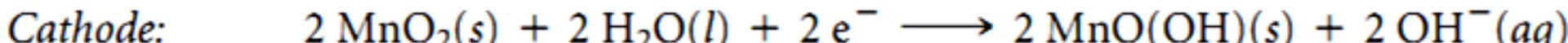
$$E_{\text{cell}}^{\circ} = E_{\text{red}}^{\circ}(\text{cathode}) - E_{\text{red}}^{\circ}(\text{anode}) = (+1.685 \text{ V}) - (-0.356 \text{ V}) = +2.041 \text{ V}$$

Alkaline Batteries



- **Alkaline** battery: most common primary battery.

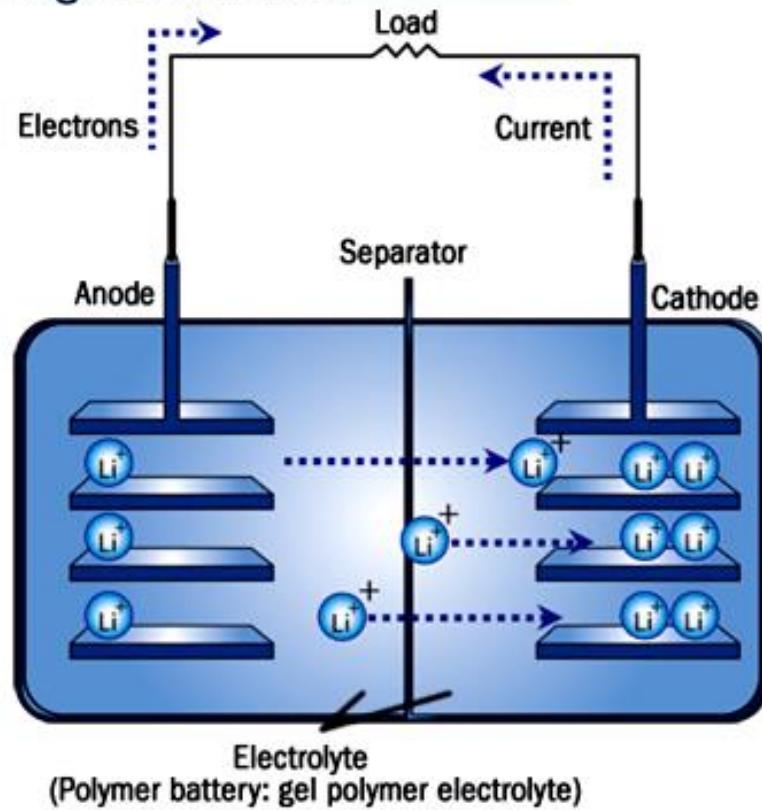
- **Ni–Cd & Ni–metal hydride** batteries: lightweight, rechargeable; Cd is toxic and heavy, so hydrides are replacing it.



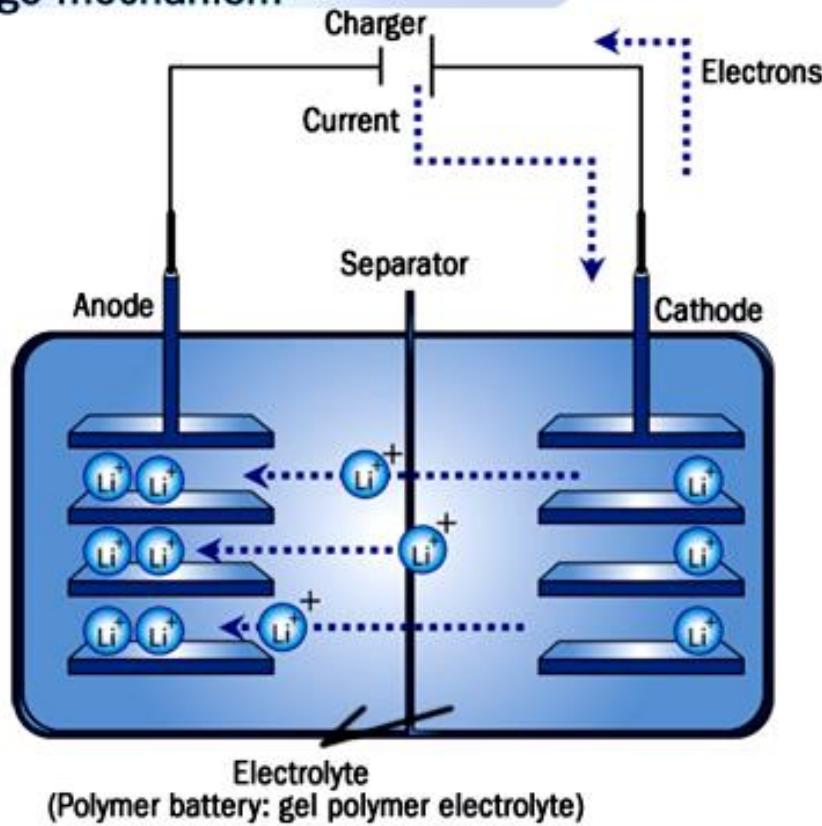
Lithium-Ion Batteries

- A family of rechargeable battery types in which lithium ions move from the anode to the cathode during discharge, and back when charging.

Lithium-ion rechargeable battery
Discharge mechanism

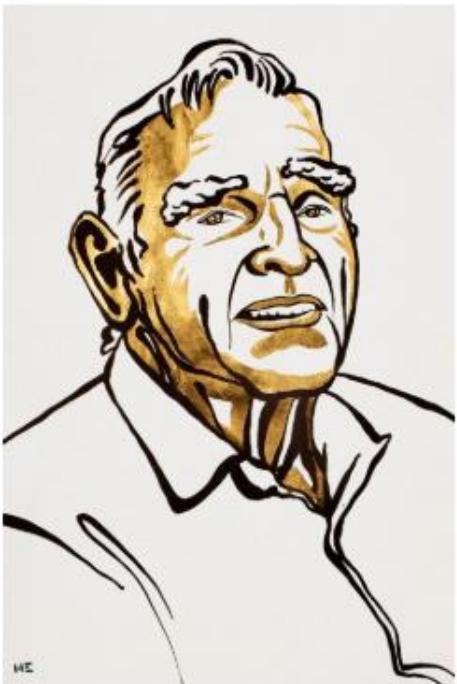


Lithium-ion rechargeable battery
Charge mechanism



The Nobel Prize in Chemistry 2019

Extra info.



III. Niklas Elmehed. ©
Nobel Media.

**John B.
Goodenough**

Prize share: 1/3



III. Niklas Elmehed. ©
Nobel Media.

**M. Stanley
Whittingham**

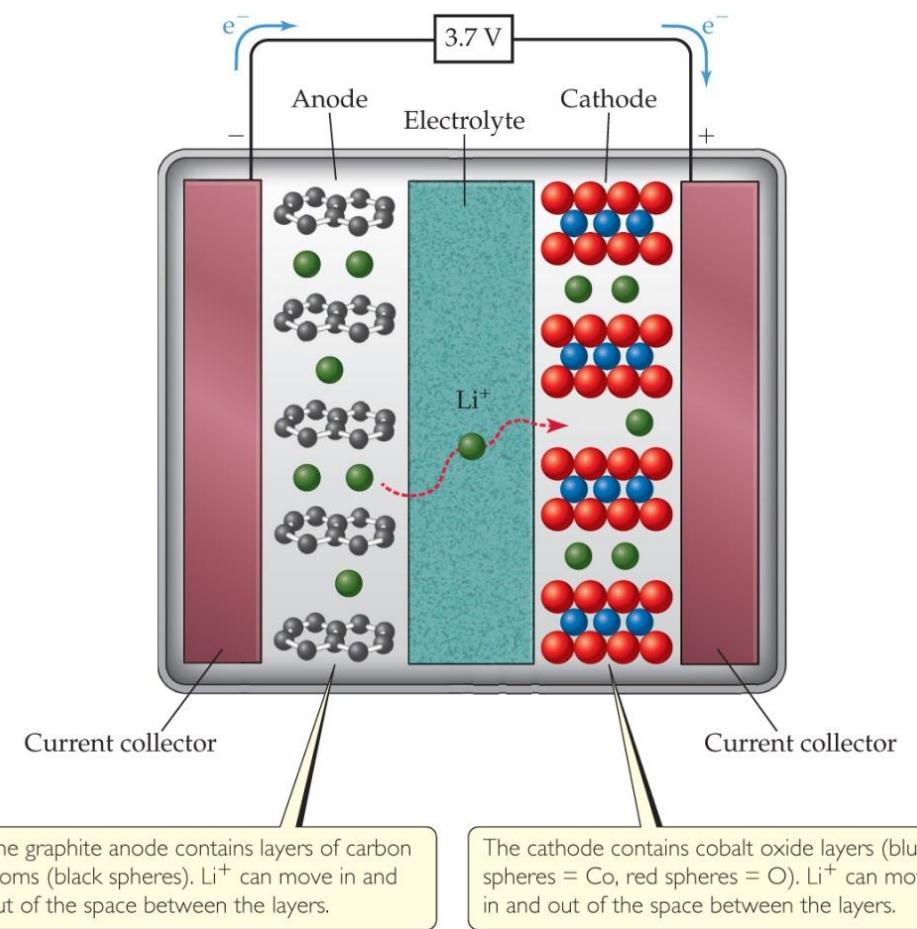
Prize share: 1/3



III. Niklas Elmehed. ©
Nobel Media.

Akira Yoshino
Prize share: 1/3

Extra info.



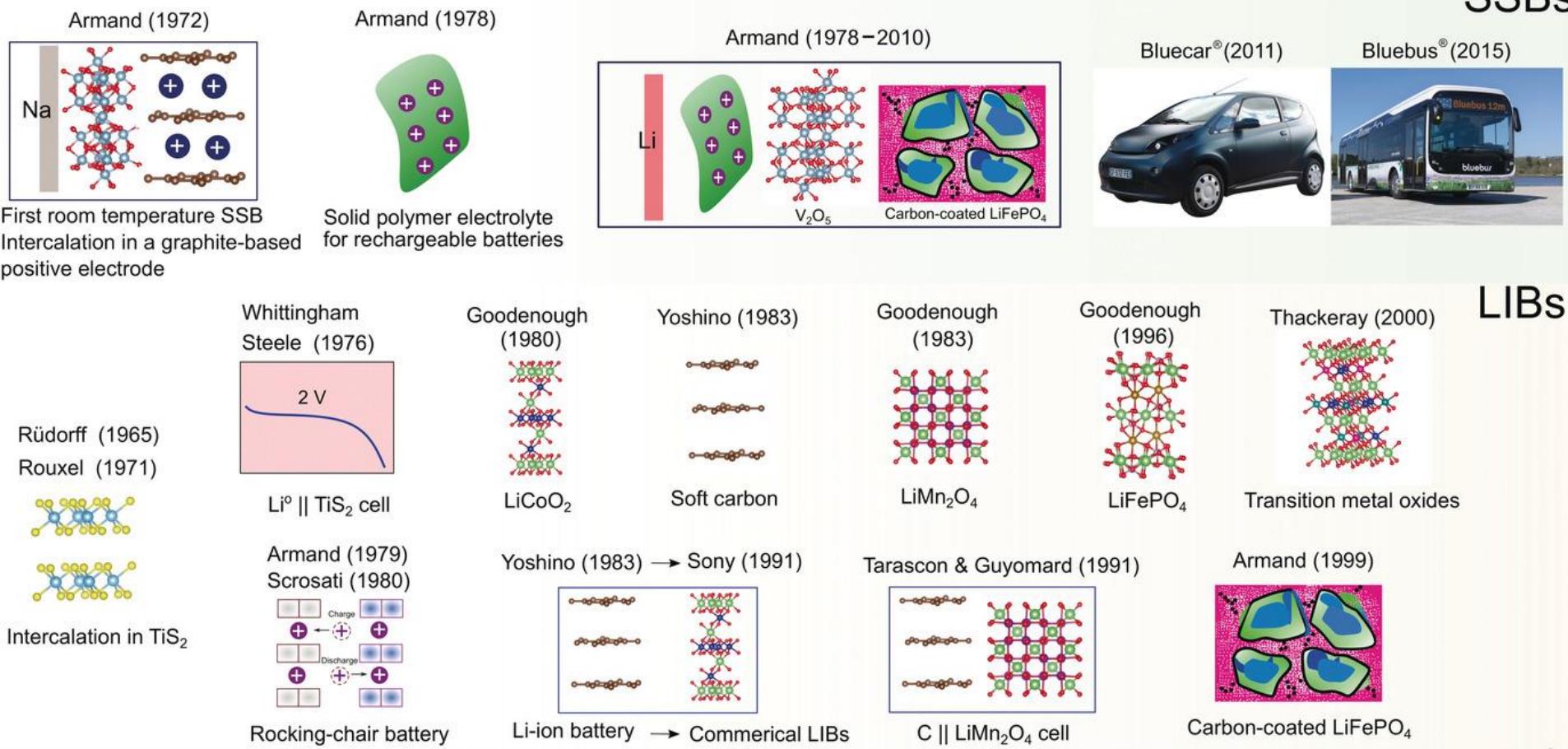
- In 1979, John Goodenough demonstrated a rechargeable cell with high cell voltage in the 4 V range using lithium cobalt oxide (LiCoO_2) as the cathode and lithium metal as the anode.

- In 1981, Bell Labs developed a workable graphite anode to provide an alternative to the lithium metal battery.



From Solid-Solution Electrodes & the Rocking-Chair Concept to Today's Batteries

Extra info.

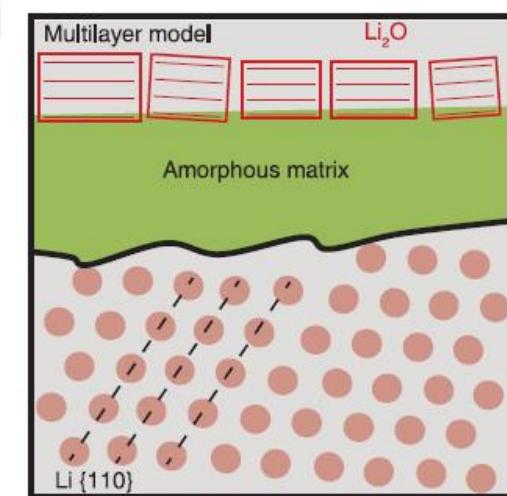
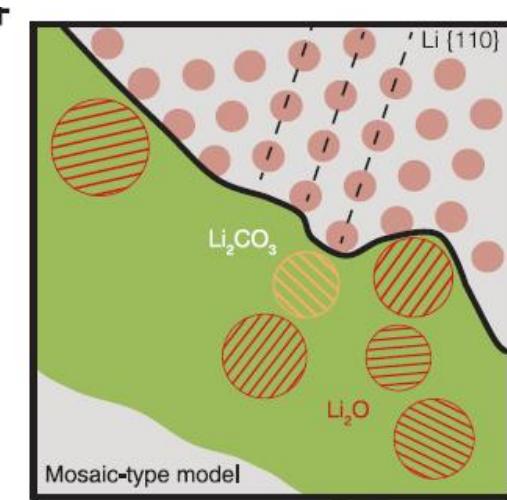
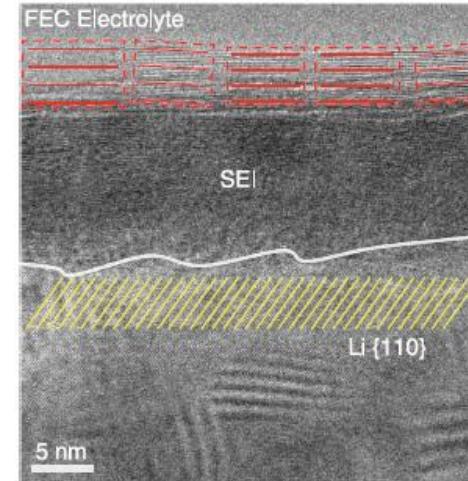
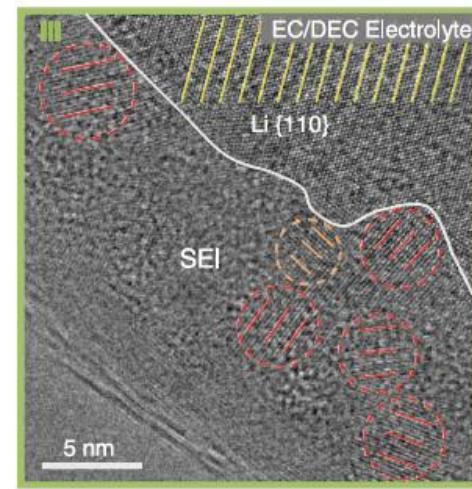
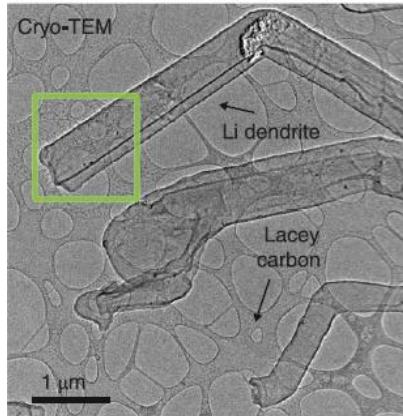


solid-state batteries (SSBs) and lithium-ion batteries (LIBs)

Atomic structure of sensitive battery materials and interfaces revealed by cryo-electron microscopy

Extra info.

Yuzhang Li,^{1*} Yanbin Li,^{1*} Allen Pei,¹ Kai Yan,¹ Yongming Sun,¹ Chun-Lan Wu,¹ Lydia-Marie Joubert,² Richard Chin,³ Ai Leen Koh,³ Yi Yu,⁴ John Perrino,² Benjamin Butz,^{1,5} Steven Chu,^{6,7} Yi Cui^{1,8†}



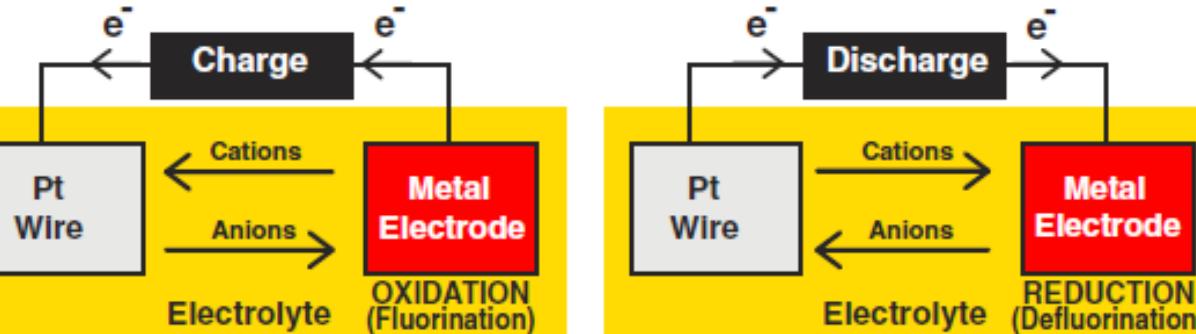
Room-temperature cycling of metal fluoride electrodes: Liquid electrolytes for high-energy fluoride ion cells

Victoria K. Davis^{1*}, Christopher M. Bates^{2†}, Kaoru Omichi^{3‡}, Brett M. Savoie^{2§}, Nebojša Momčilović^{2¶}, Qingmin Xu³, William J. Wolf², Michael A. Webb², Keith J. Billings¹, Nam Hawn Chou³, Selim Alayoglu⁴, Ryan K. McKenney³, Isabelle M. Darolles^{2#}, Nanditha G. Nair², Adrian Hightower², Daniel Rosenberg⁴, Musahid Ahmed⁴, Christopher J. Brooks³, Thomas F. Miller III², Robert H. Grubbs², Simon C. Jones^{1***}

Cathode:



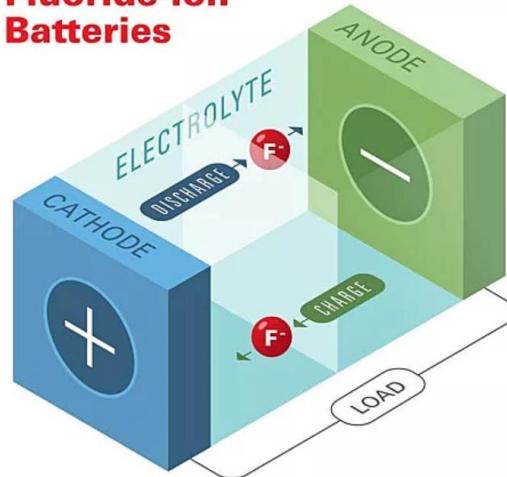
Anode:



Extra info.

Science 362, 1144–1148 (2018)

Fluoride-ion Batteries



$E_{red}^o(V)$	Reduction Half-Reaction
+2.87	$F_2(g) + 2 e^- \longrightarrow 2 F^-$
+1.51	$MnO_4^-(aq) + 8 H^+ + 5 e^- \longrightarrow Mn^{2+}(aq) + 4 H_2O(l)$
+1.36	$Cl_2(g) + 2 e^- \longrightarrow 2 Cl^-$
+1.33	$Cr_2O_7^{2-}(aq) + 14 H^+ + 6 e^- \longrightarrow Cr^{3+}(aq) + 7 H_2O(l)$
+1.23	$O_2(g) + 4 H^+(aq) + 2 e^- \longrightarrow 2 H_2O(l)$
+1.06	$Br_2(l) + 2 e^- \longrightarrow 2 Br^-$
+0.96	$NO_3^-(aq) + 4 H^+(aq) + 3 e^- \longrightarrow NO(g) + H_2O(l)$
+0.80	$Ag^+(aq) + e^- \longrightarrow Ag(s)$
+0.77	$Fe^{3+}(aq) + e^- \longrightarrow Fe^{2+}(aq)$
+0.68	$O_2(g) + 2 H^+(aq) + 2 e^- \longrightarrow H_2O_2(aq)$
+0.59	$MnO_4^-(aq) + 2 H_2O(l) + 3 e^- \longrightarrow Mn^{2+}(aq) + 4 OH^-(aq)$
+0.54	$I_2(s) + 2 e^- \longrightarrow 2 I^-$
+0.40	$O_2(g) + 2 H_2O(l) + 4 e^- \longrightarrow 4 OH^-(aq)$
+0.34	$Cu^{2+}(aq) + 2 e^- \longrightarrow Cu(s)$
0 [defined]	$2 H^+(aq) + 2 e^- \longrightarrow H_2(g)$
-0.28	$Ni^{2+}(aq) + 2 e^- \longrightarrow Ni(s)$
-0.44	$Fe^{2+}(aq) + 2 e^- \longrightarrow Fe(s)$
-0.76	$Zn^{2+}(aq) + 2 e^- \longrightarrow Zn(s)$
-0.83	$2 H_2O(l) + 2 e^- \longrightarrow H_2(g) + 2 OH^-(aq)$
-1.66	$Al^{3+}(aq) + 3 e^- \longrightarrow Al(s)$
-2.71	$Na^+(aq) + e^- \longrightarrow Na(s)$
-3.05	$Li^+(aq) + e^- \longrightarrow Li(s)$

Rechargeable Na/Cl₂ and Li/Cl₂ batteries

Nature | Vol 596 | 26 August 2021 | 525

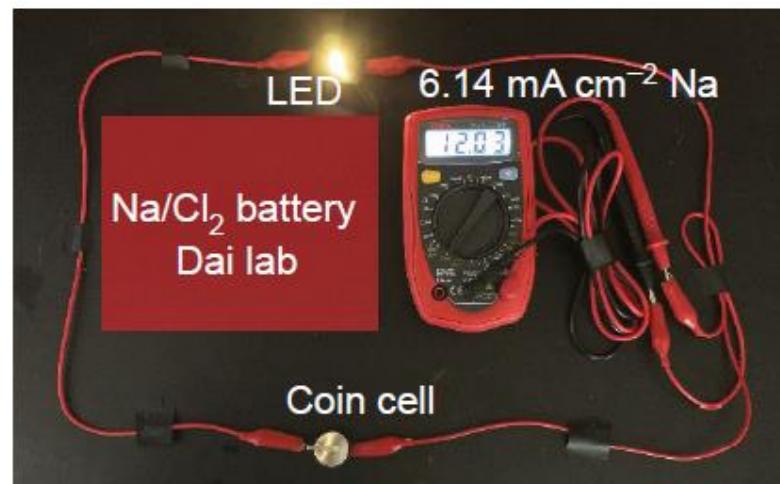
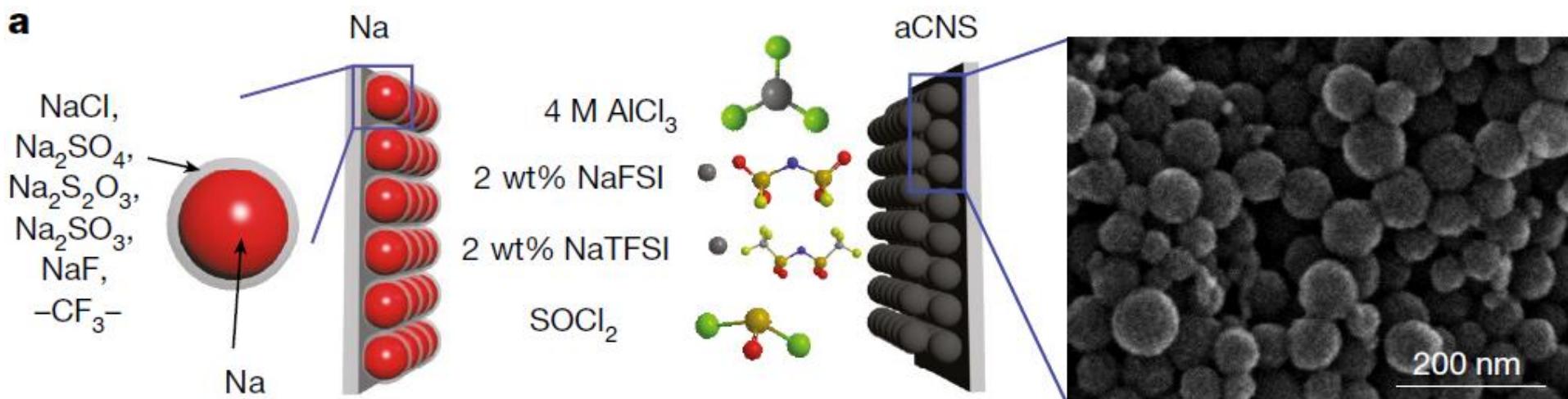
Extra info.

<https://doi.org/10.1038/s41586-021-03757-z>

Received: 24 September 2020

Guanzhou Zhu^{1,7}, Xin Tian^{1,7}, Hung-Chun Tai², Yuan-Yao Li², Jiachen Li¹, Hao Sun¹, Peng Liang¹, Michael Angell¹, Cheng-Liang Huang², Ching-Shun Ku³, Wei-Hsuan Hung⁴, Shi-Kai Jiang⁵, Yongtao Meng¹, Hui Chen⁶, Meng-Chang Lin⁶, Bing-Joe Hwang⁵ & Hongjie Dai¹✉

a



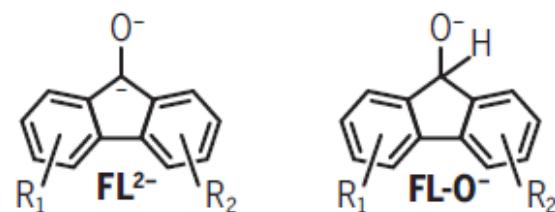
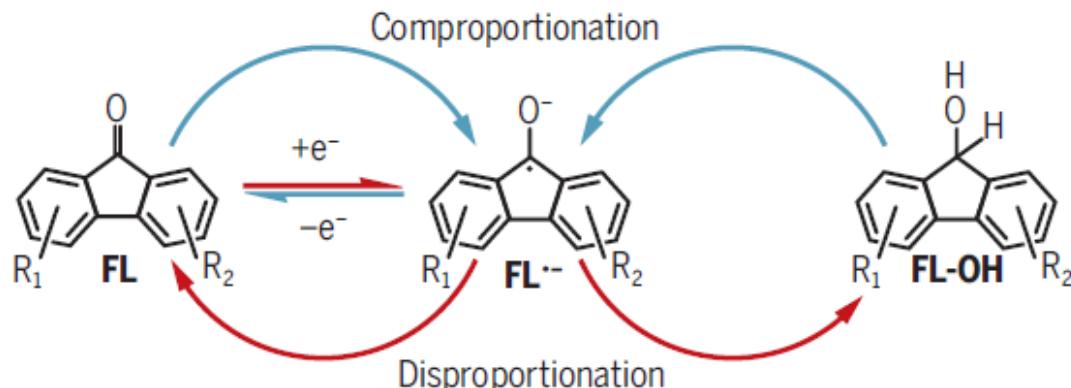
Reversible ketone hydrogenation and dehydrogenation for aqueous organic redox flow batteries

Ruozhu Feng, Xin Zhang*, Vijayakumar Murugesan, Aaron Hollas, Ying Chen, Yuyan Shao, Eric Walter, Nadeesha P. N. Wellala, Litao Yan, Kevin M. Rosso, Wei Wang*
Science **372**, 836–840 (2021)

788 21 MAY 2021 • VOL 372 ISSUE 6544

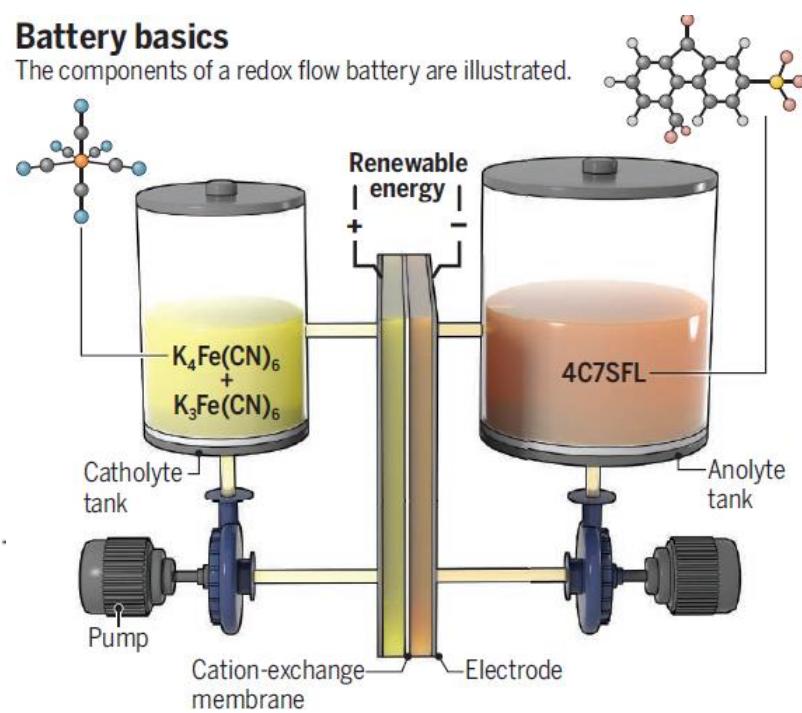
Charging and discharging molecules

Charging (red arrows) and discharging (blue arrows) mechanism of 9-fluorenone (FL) (top) and possibly involved species (bottom) are shown.



Battery basics

The components of a redox flow battery are illustrated.



Polypeptide organic radical batteries

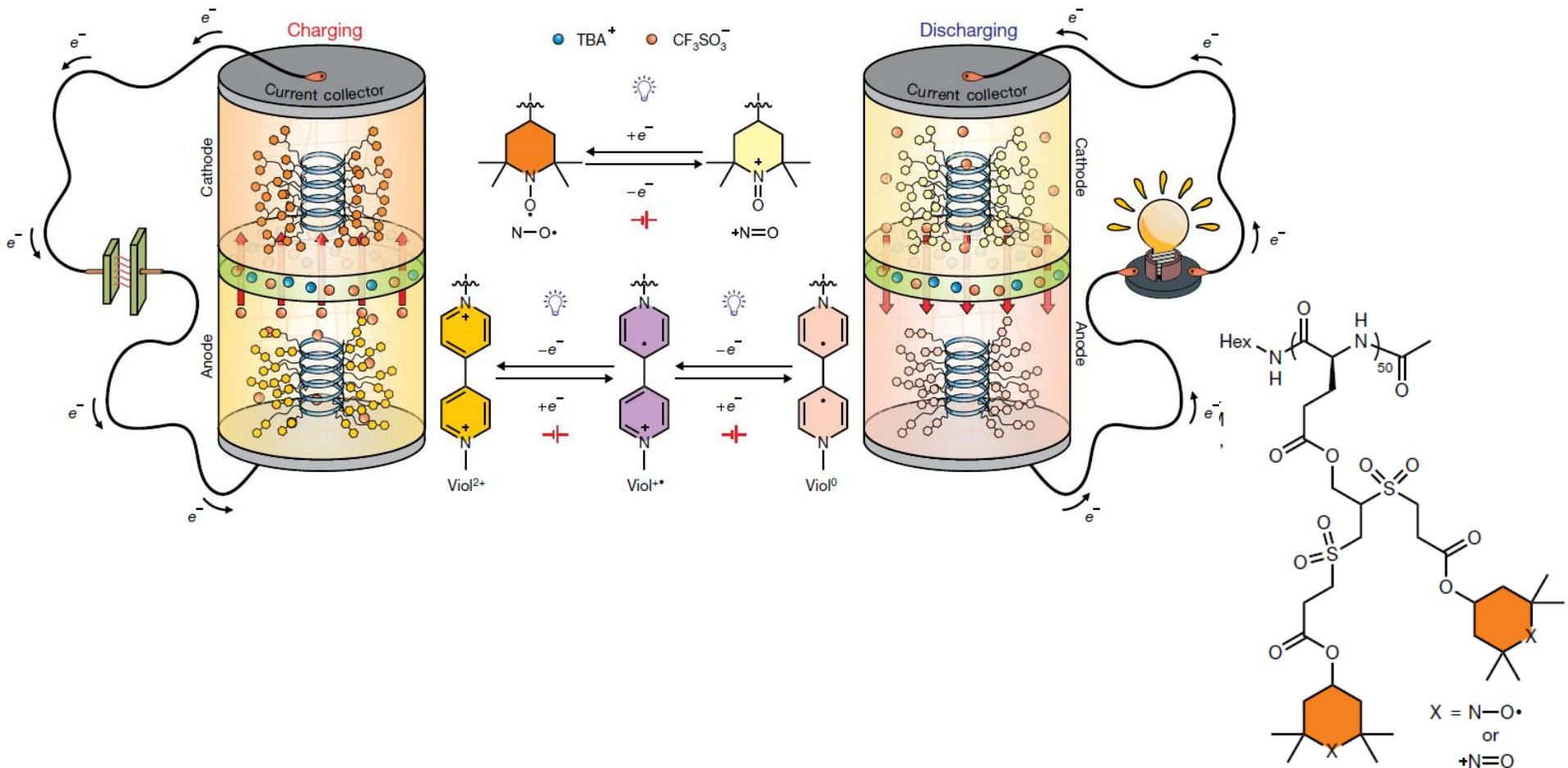
Nature | Vol 593 | 6 May 2021 | 61

Extra info.

<https://doi.org/10.1038/s41586-021-03399-1>

Received: 13 May 2020

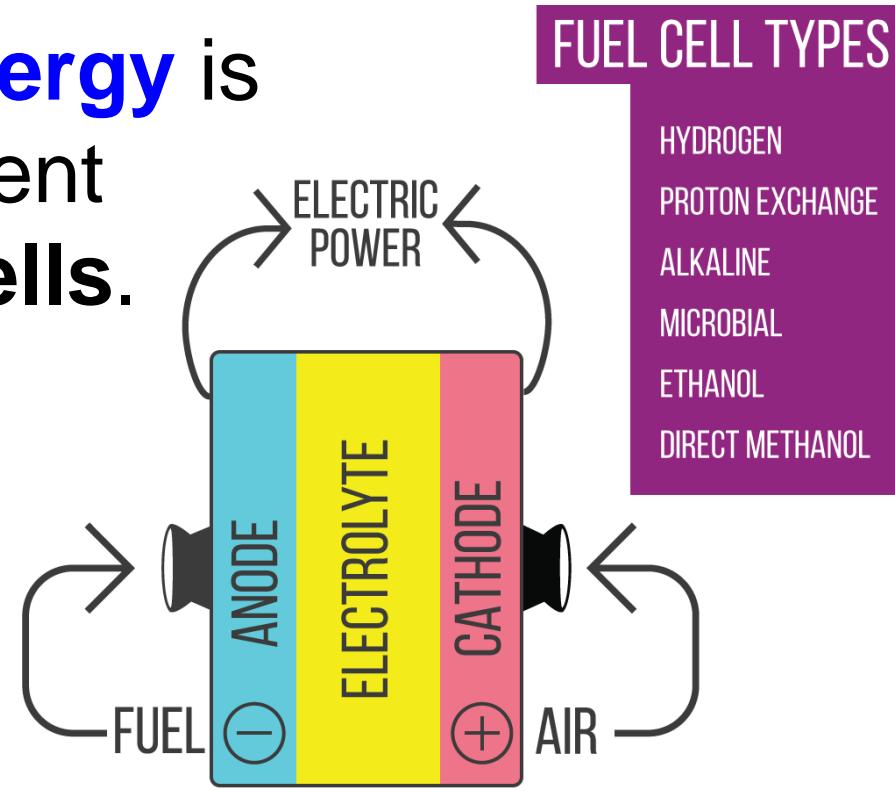
Tan P. Nguyen^{1,4}, Alexandra D. Easley^{2,4}, Nari Kang², Sarosh Khan¹, Soon-Mi Lim¹, Yohannes H. Rezenom¹, Shaoyang Wang³, David K. Tran¹, Jingwei Fan¹, Rachel A. Letteri¹, Xun He¹, Lu Su¹, Cheng-Han Yu¹, Jodie L. Lutkenhaus^{1,3} & Karen L. Wooley^{1,2,3}



$\text{X} = \text{N-O}^\bullet$
or
 $+ \text{N=O}$

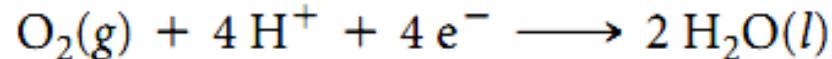
Fuel Cells (燃料电池)

- When a **fuel** is **burned**, the energy created can be **converted to electrical energy**.
- Usually only 40% efficient, with the remainder lost as heat.
- The direct conversion of **chemical to electrical energy** is expected to be more efficient and is the basis for **fuel cells**.
- Fuel cells are **NOT batteries**; the source of energy must be continuously provided.

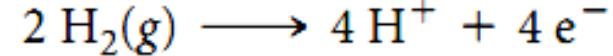


Hydrogen Fuel Cells

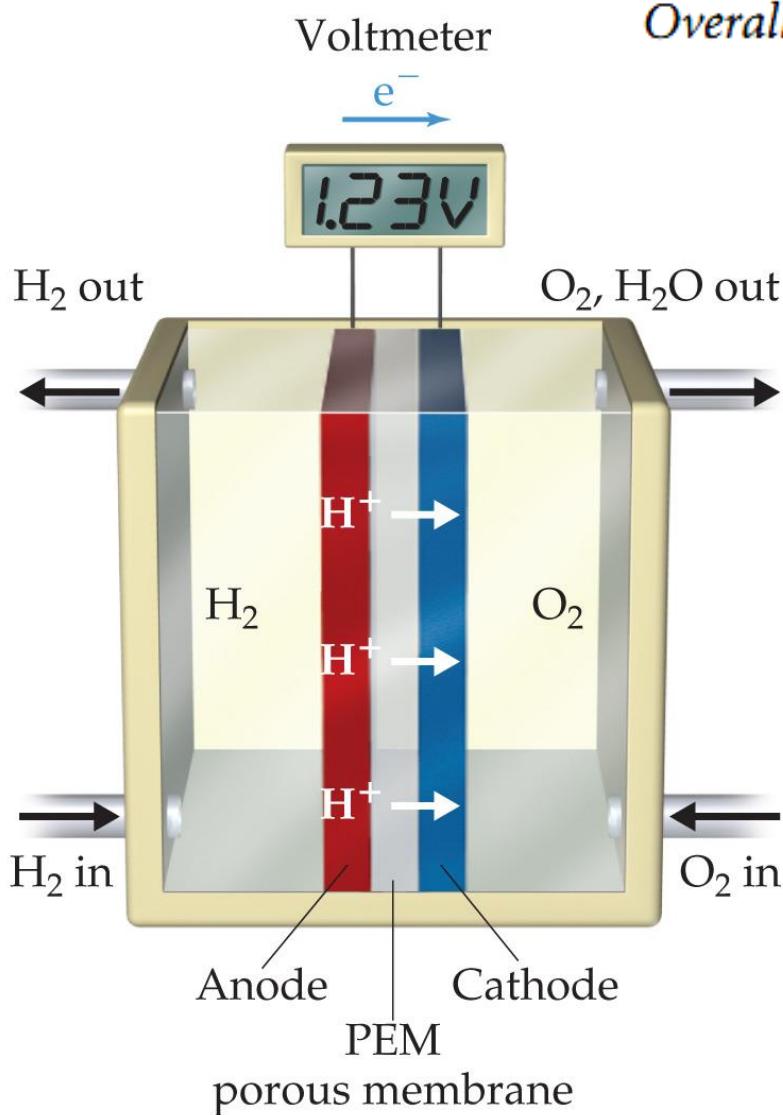
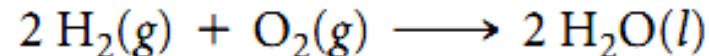
Cathode:



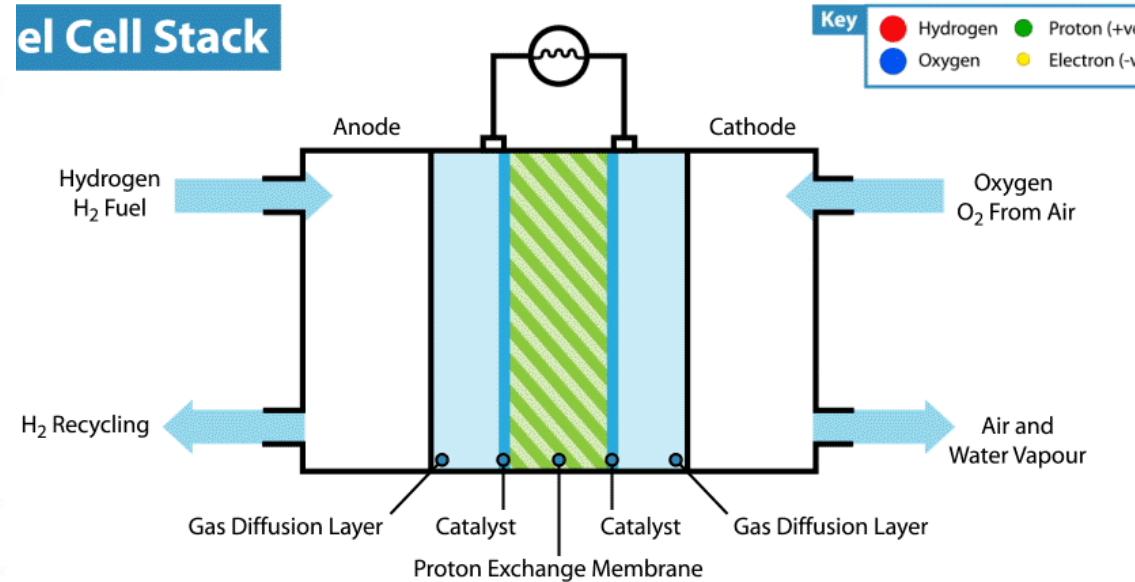
Anode:



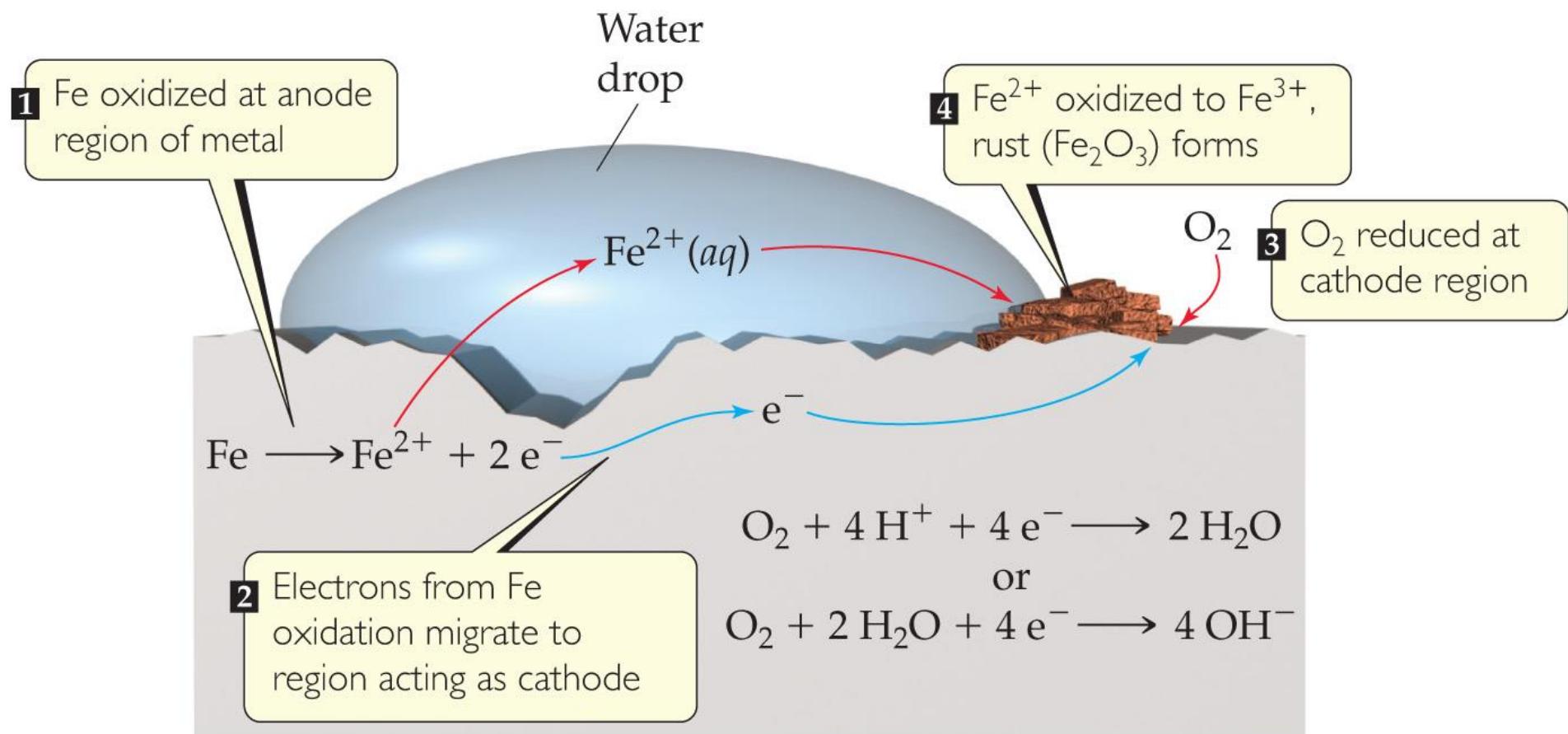
Overall:



el Cell Stack

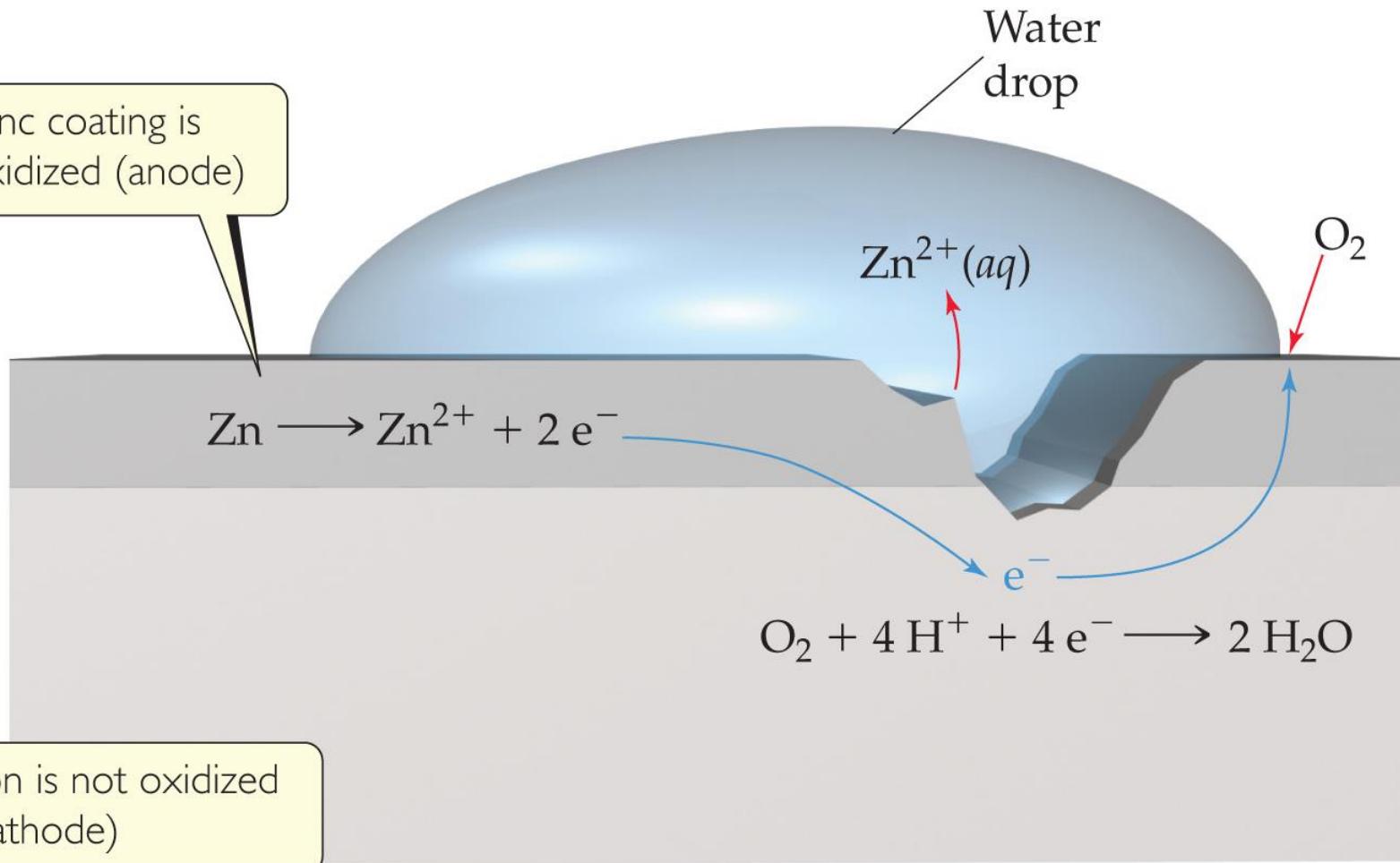


Corrosion and Corrosion Prevention

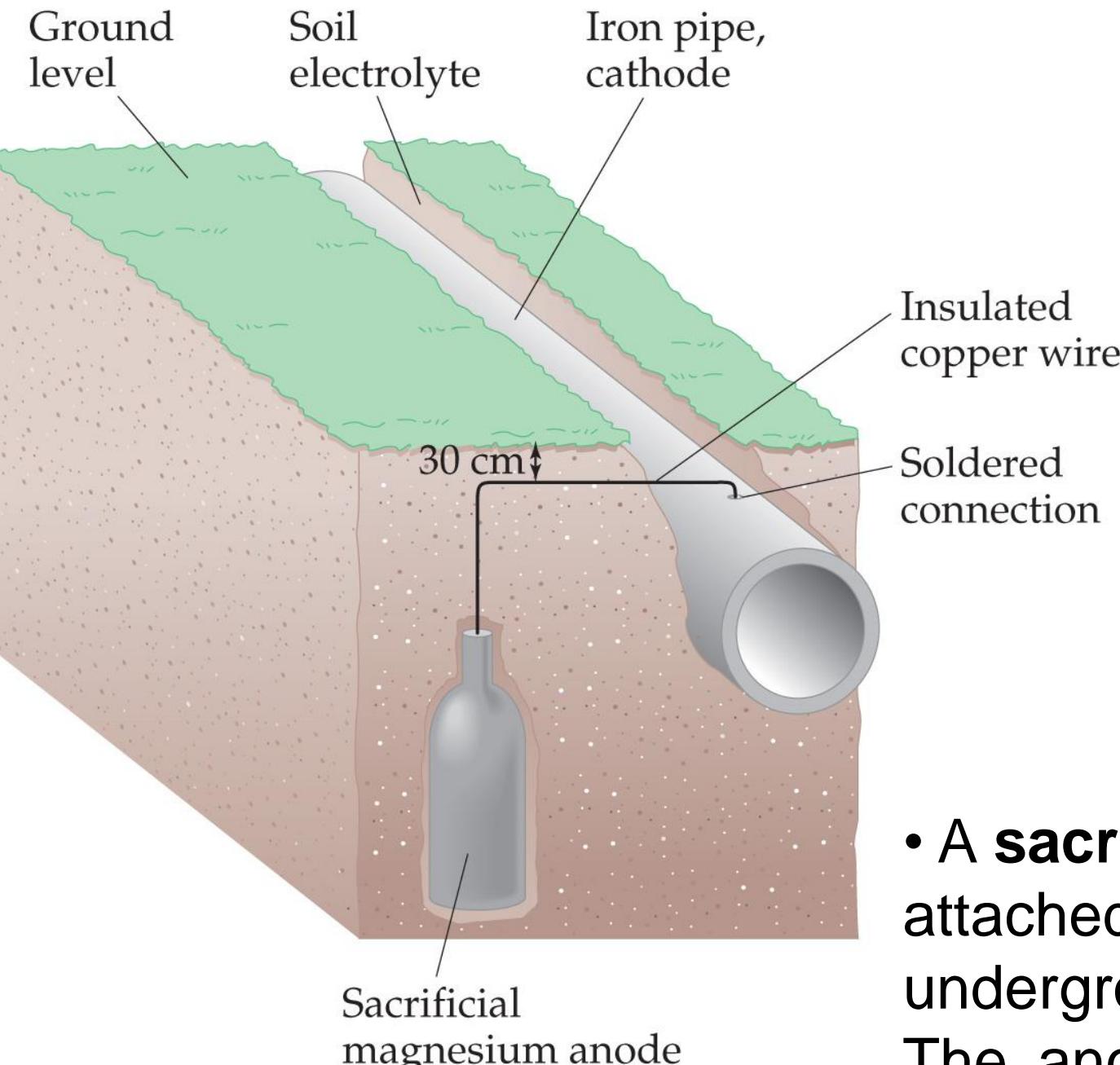


- Corrosion is oxidation.
- Its common name is *rusting*.

What is the oxidizing agent in this corrosion reaction?



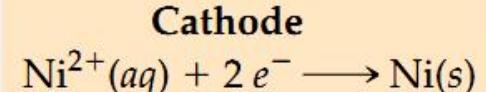
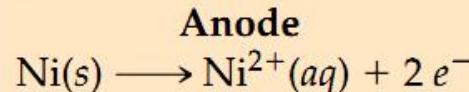
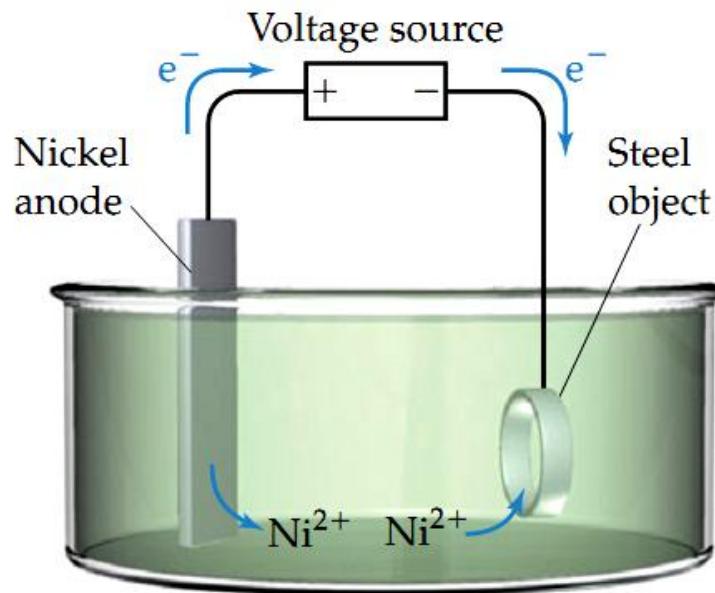
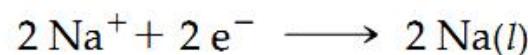
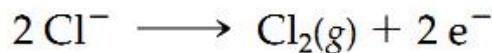
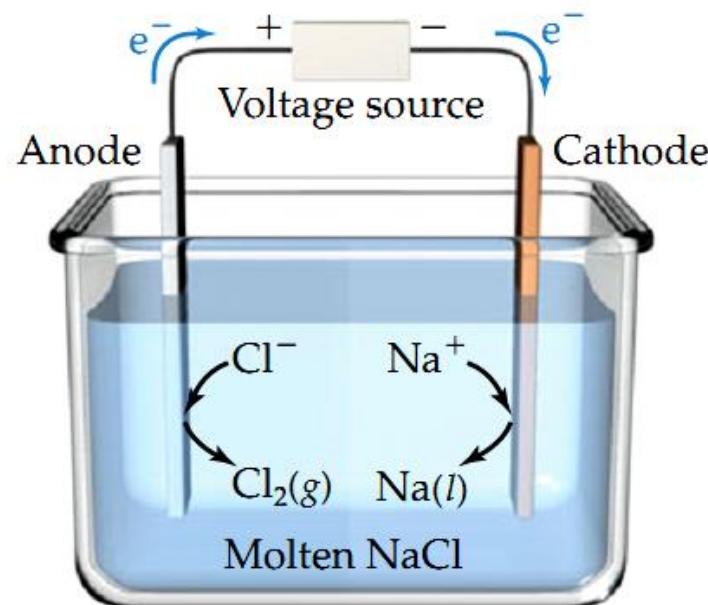
- Corrosion is prevented by coating iron with a metal that is more readily oxidized.
- **Cathodic protection** occurs when zinc is more easily oxidized, so that metal is sacrificed to keep the iron from rusting.



- A **sacrificial anode** is attached to the underground pipes. The anode is oxidized before the pipe.

Electrolysis & Electroplating (电解&电镀)

- Nonspontaneous reactions can occur in electrochemistry if **outside electricity** is used to drive the reaction.
- Use of **electrical energy** to create chemical reactions is called **electrolysis**.



Electrolysis and “Stoichiometry”

- $1 \text{ coulomb} = 1 \text{ ampere} \times 1 \text{ second}$
- $Q = It = nF$
- $Q = \text{charge (C)}$
- $I = \text{current (A)}$
- $t = \text{time (s)}$
- $n = \text{moles of electrons that travel through the wire in the given time}$
- $F = \text{Faraday's constant}$

NOTE: n is different than that for the Nernst equation!

Quantity of charge (coulombs) = current (amperes) \times time (seconds)

Faraday constant

Moles of electrons

Balanced half-reaction

Moles of substance oxidized or reduced

Formula weight

Grams of substance oxidized or reduced

A cell that uses external energy to produce an oxidation-reduction reaction is called _____ cell.

- a. a galvanic
- b. a voltaic
- c. an electrolytic
- d. a prison

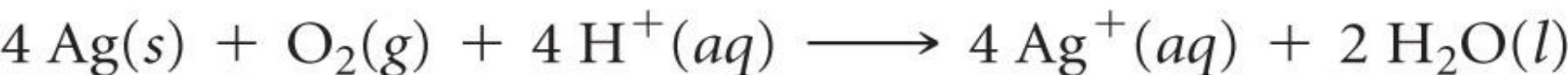
Reduction occurs at the

- a. anode, in both voltaic (galvanic) & electrolytic cells.
- b. cathode, in both voltaic (galvanic) & electrolytic cells.
- c. anode in voltaic (galvanic) cells and cathode in electrolytic cells.
- d. cathode in voltaic (galvanic) cells and anode in electrolytic cells.

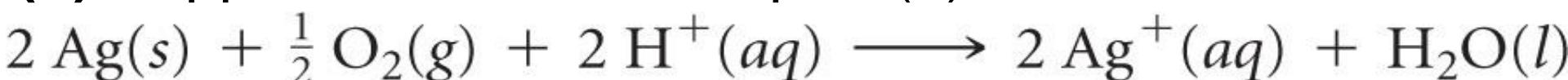
Oxidation occurs at the

- a. anode, in both voltaic (galvanic) and electrolytic cells.
- b. cathode, in both voltaic (galvanic) and electrolytic cells.
- c. anode in voltaic (galvanic) cells and cathode in electrolytic cells.
- d. cathode in voltaic (galvanic) cells and anode in electrolytic cells.

(a) Calculate the standard free-energy change, ΔG° , and the equilibrium constant, K , at 298 K for the reaction



(b) Suppose the reaction in part (a) is written



What are the values of E° , ΔG° , and K when the reaction is written in this way?



$$E^\circ = (1.23 \text{ V}) - (0.80 \text{ V}) = 0.43 \text{ V}$$

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

$$= -(4)(96,485 \text{ J/V-mol})(+0.43 \text{ V})$$

$$= -1.7 \times 10^5 \text{ J/mol} = -170 \text{ kJ/mol}$$

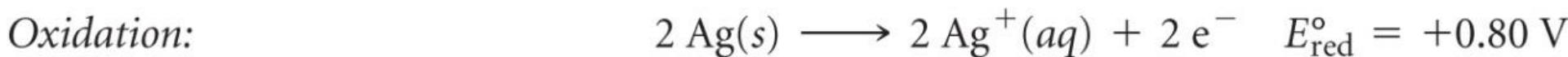
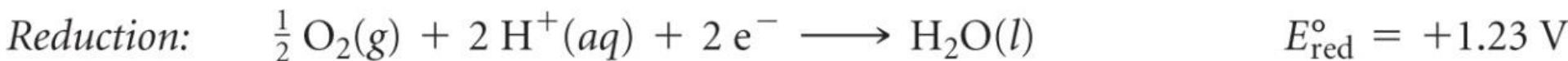
$$\Delta G^\circ = -RT \ln K$$

$$-1.7 \times 10^5 \text{ J/mol} = -(8.314 \text{ J/K mol}) (298 \text{ K}) \ln K$$

$$\ln K = \frac{-1.7 \times 10^5 \text{ J/mol}}{-(8.314 \text{ J/K mol})(298 \text{ K})}$$

$$\ln K = 69$$

$$K = 9 \times 10^{29}$$

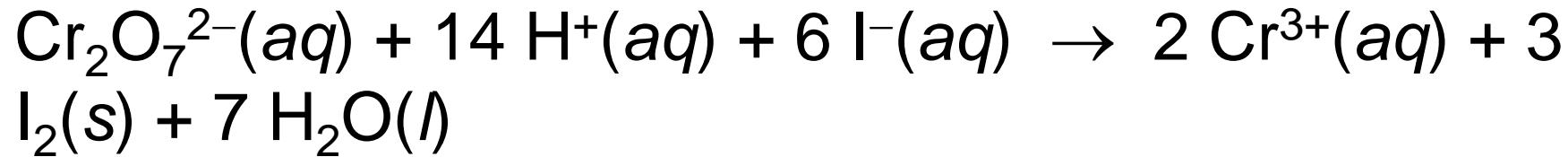


$$E^\circ = +0.43 \text{ V}$$

$$\Delta G^\circ = -(2)(96,485 \text{ J/V-mol})(+0.43 \text{ V}) = -83 \text{ kJ/mol}$$

$$-8.3 \times 10^4 \text{ J/mol} = -(8.314 \text{ J/K mol})(298 \text{ K}) \ln K$$
$$K = 4 \times 10^{14}$$

Calculate the emf at 298 K generated by a voltaic cell in which the reaction is



when $[\text{Cr}_2\text{O}_7^{2-}] = 2.0 \text{ M}$, $[\text{H}^+] = 1.0 \text{ M}$, $[\text{I}^-] = 1.0 \text{ M}$, and $[\text{Cr}^{3+}] = 1.0 \times 10^{-5} \text{ M}$.

$$E = E^\circ - \frac{0.0592 \text{ V}}{n} \log Q \quad (T = 298 \text{ K})$$

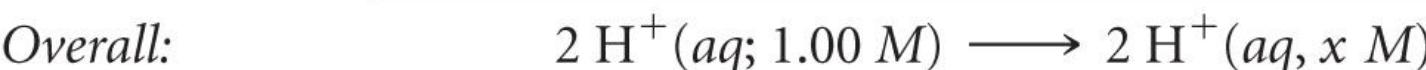
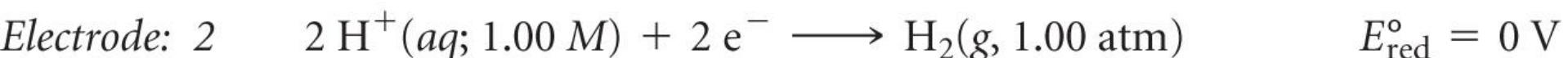
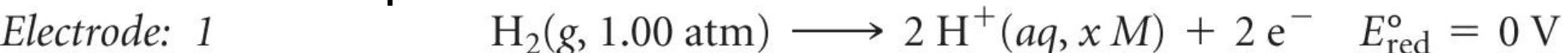
$$Q = \frac{[\text{Cr}^{3+}]^2}{[\text{Cr}_2\text{O}_7^{2-}][\text{H}^+]^{14} [\text{I}^-]^6} = \frac{(1.0 \times 10^{-5})^2}{(2.0)(1.0)^{14} (1.0)^6} = 5.0 \times 10^{-11}$$

$$E = 0.79 \text{ V} - \left(\frac{0.0592 \text{ V}}{6} \right) \log(5.0 \times 10^{-11})$$

$$= 0.79 \text{ V} - \left(\frac{0.0592 \text{ V}}{6} \right) (-10.30)$$

$$= 0.79 \text{ V} + 0.10 \text{ V} = 0.89 \text{ V}$$

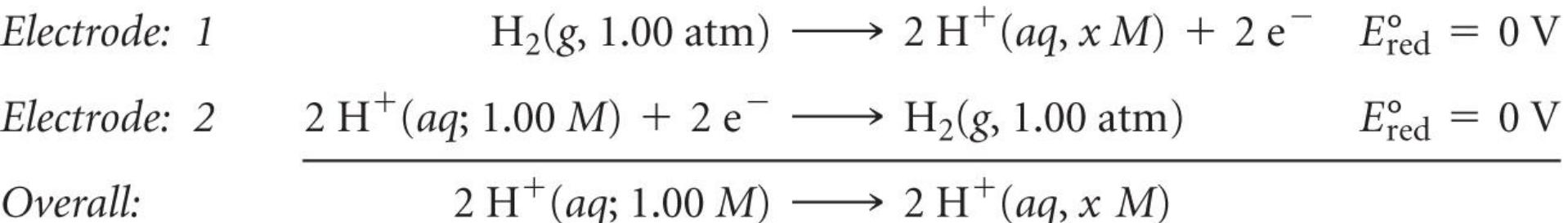
A voltaic cell is constructed with two hydrogen electrodes. Electrode 1 has $P_{H_2} = 1.00$ atm and an unknown concentration of $H^+(aq)$. Electrode 2 is a standard hydrogen electrode ($P_{H_2} = 1.00$ atm, $[H^+] = 1.00\text{ M}$). At 298 K the measured cell potential is 0.211 V, and the electron is observed to flow from electrode 1 through the external circuit to electrode 2. Calculate for the solution at electrode 1. What is the pH of the solution?



$$0.211\text{ V} = 0 - \frac{0.0592\text{ V}}{2} \log Q$$

$$\log Q = -(0.211\text{ V}) \left(\frac{2}{0.0592\text{ V}} \right) = -7.13$$

$$Q = 10^{-7.13} = 7.4 \times 10^{-8}$$



$$Q = \frac{[\text{H}^+(\text{aq}, x \text{ M})]^2}{[\text{H}^+(\text{aq}, 1.00 \text{ M})]^2}$$

$$= \frac{x^2}{(1.00)^2} = x^2 = 7.4 \times 10^{-8}$$

$$x = [\text{H}^+] = \sqrt{7.4 \times 10^{-8}} = 2.7 \times 10^{-4}$$

$$\text{pH} = -\log[\text{H}^+] = -\log(2.7 \times 10^{-4}) = 3.57$$

Key Summary

Relationships between electricity & chemical (redox) reactions; Half-reaction method

Voltaic Cells: oxidation (anode); reduction (cathode); salt bridge

Electromotive force (emf), cell potential, standard reduction potentials, standard hydrogen electrode, standard cell potentials

Free energy and redox/emf; Nernst Equation

Applications: batteries, fuel cells, corrosion prevention, electrolysis

**Thank You for Your
Attention!
Any Questions?**