# Electrochemistry IV

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# Electrochemistry

*Corrosion: A Case of Environmental Electrochemistry*

*Electrolytic Cells: Nonspontaneous Reactions*

*Important Biochemical Oxidation-Reduction Cycles*

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# The Corrosion of Iron

http://antoine.frostburg.edu/chem/senese/101/redox/faq/how-iron-rusts.shtml

~ 25% of the steel in the United States is made to replace steel that has corroded (rusted), which is caused by the oxidation of iron.

1) Iron does not rust in dry air: *moisture must be present*.
2) Iron does not rust in air-free water: *oxygen must be present*.
3) The loss of iron and the deposition of rust often *occur at different places on the same object*.
4) Iron rusts *more quickly at low pH* (high [$H^+$]).
5) Iron rusts *more quickly in contact with ionic solutions*.
6) Iron rusts *more quickly in contact with a less active metal* (such as Cu) and *more slowly in contact with a more active metal* (such as Zn).

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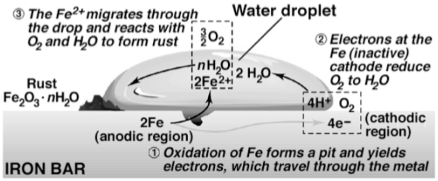
# The Corrosion of Iron

1) Iron does not rust in dry air: *moisture must be present*.
2) Iron does not rust in air-free water: *oxygen must be present*.



$Fe_{(s)} \longrightarrow Fe^{2+}_{(aq)} + 2\ e^-$ [anodic region; oxidation]

$O_{2\,(g)} + 4\ H^+_{(aq)} + 4\ e^- \longrightarrow 2\ H_2O_{(l)}$ [cathodic region; reduction]

$2\ Fe_{(s)} + O_{2\,(g)} + 4\ H^+_{(aq)} \longrightarrow 2\ Fe^{2+}_{(aq)} + 2\ H_2O_{(l)}$

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# The Corrosion of Iron

The loss of iron and the deposition of rust often *occur at different places on the same object (below)*.

Iron rusts *more slowly in contact with a more active metal* such as Zn (*on the left*).

Iron rusts *more quickly in contact with a less active metal* such as Cu (*on the right*).

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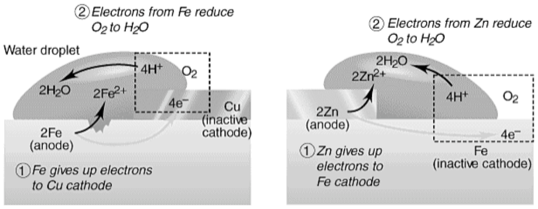
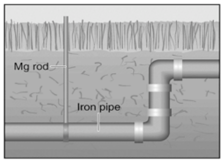
# The Effect of Metal-Metal Contact on the Corrosion of Iron



**A** Enhanced corrosion

**B** Cathodic protection

## The Use of Sacrificial Anodes to Prevent Iron Corrosion in Steel & Iron



*Uses:*
Pipelines, storage tanks, piers, pilings, ships, offshore oil platforms oil well casings and rebar: reinforcement bars in concrete buildings, bridges, and structures.

*Sacrificial anodes use zinc, magnesium and aluminum. The anode must have a lower (more negative) potential than the cathode (the material to be protected).*

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# *QUESTION*

For cathodic protection used to prevent corrosion of iron to be effective which of the following must be true?

A. The anode used must be a better oxidizing agent than iron.
B. The sacrificial anode used must react with oxygen to protect the iron from reacting with oxygen.
C. Iron must have a higher reduction potential than the metal used as the anode.
D. In cathodic protection systems a metal is attached or connected to iron in such a way that electrons flow away from the iron to the ground through the metal.
E. The anode must be free of oxygen and water.

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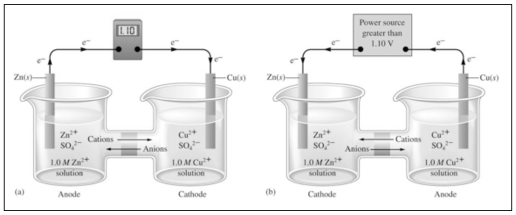
## The Basis of a Voltaic and an Electrolytic Cell



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## Restoration of Corroded Iron Artifacts Using Electrolysis

*http://www.nytimes.com/2011/08/09/science/09monitor.html?_r=2&ref=science*

The New York Times August 9, 2011

Science Times: Aug. 9, 2011

A Brief Dry Spell for the U.S.S. Monitor

By JOHN TIERNEY

Steve Earley/The Virginian-Pilot

**IRONCLAD** The U.S.S. Monitor, designed by John Ericsson, was not just the Union's first ironclad vessel but an entirely new kind of warship. Here, conservators work in the upside-down turret.

Monitor & Merrimack March 9, 1862;
Monitor sinks December 30, 1862; Raised 2002

*http://www.marinersmuseum.org/sites/default/files/electrolyticreduction.swf*

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## Restoration of Silver Artifacts Using Electrolysis

Nuestra Señora de Atocha
1622
Sinks in a hurricane near
Key West, Florida

*Calibrated Peer Review (CPR)*
*Writing Assignment*

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## *Construction and Operation of an Electrolytic Cell*

Let's use the tin-copper voltaic cell:

$$\mathrm{Sn_{(s)}} \longrightarrow \mathrm{Sn^{2+}_{(aq)}} + 2\,\mathrm{e^-} \qquad \text{[anode; oxidation]}$$

$$\mathrm{Cu^{2+}_{(aq)}} + 2\,\mathrm{e^-} \longrightarrow \mathrm{Cu_{(s)}} \qquad \text{[cathode; reduction]}$$

$$\mathrm{Sn_{(s)}} + \mathrm{Cu^{2+}_{(aq)}} \longrightarrow \mathrm{Sn^{2+}_{(aq)}} + \mathrm{Cu_{(s)}} \qquad E^{o}_{\mathrm{cell}} = 0.48\ \mathrm{V} \text{ and } \triangle G^{o} = -93\ \mathrm{kJ}$$

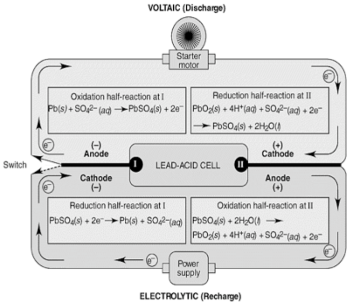
The spontaneous reaction of Sn metal through oxidation to form $Sn^{2+}$ions and the reduction of $Cu^{2+}$ ions to form copper metal will produce a cell voltage of 0.48 volt. Therefore, the reverse reaction is *non*-spontaneous. However, the reverse reaction will occur by supplying power from an external source with an electric potential greater than $E^{o}_{cell}$. The voltaic cell into an electrolytic cell and the reactions are reversed.

$$\mathrm{Cu_{(s)}} \longrightarrow \mathrm{Cu^{2+}_{(aq)}} + 2\mathrm{e^-} \qquad \text{[anode; oxidation]}$$

$$\mathrm{Sn^{2+}_{(aq)}} + 2\,\mathrm{e^-} \longrightarrow \mathrm{Sn_{(s)}} \qquad \text{[cathode; reduction]}$$

$$\mathrm{Sn^{2+}_{(aq)}} + \mathrm{Cu_{(s)}} \longrightarrow \mathrm{Cu^{2+}_{(aq)}} + \mathrm{Sn_{(s)}} \qquad E^{o}_{\mathrm{cell}} = -0.48\ \mathrm{V} \text{ and } \triangle G^{o} = 93\ \mathrm{kJ}$$

# The Processes Occurring During the Discharge and Recharge of a Lead-Acid Battery



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# *Comparison of Voltaic and Electrolytic Cells*

| | | | Electrode | | |
|---|---|---|---|---|---|
| **Cell Type** | **ΔG** | **$E_{cell}$** | **Name** | **Process** | **Sign** |
| Voltaic | < 0 | > 0 | Anode | Oxidation | - |
| Voltaic | < 0 | > 0 | Cathode | Reduction | + |
| Electrolytic | > 0 | < 0 | Anode | Oxidation | + |
| Electrolytic | > 0 | < 0 | Cathode | Reduction | - |

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# *QUESTION*

Voltaic cells and electrolytic cells are based on thermodynamic principles. Which statement about these cells is <u>correct</u>?

A) The mass of the anode increases in a voltaic cell as the cell discharges.

B) Reduction occurs at the anode only in the electrolytic cell.

C) In a voltaic cell, electrons travel from the cathode to the anode in solution.

D) The free energy change ΔG is greater than zero for the electrolytic cell.

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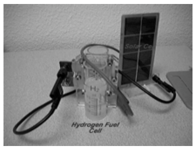
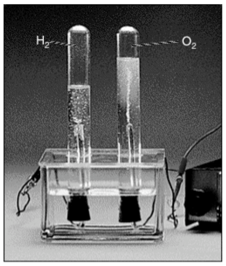
# The Electrolysis of Water





Anode: 1.23 V

Oxidation half-reaction

$2H_2O(l) \rightarrow O_2(g) + 4H^+(aq) + 4e^-$

Cathode: -0.42 V

Reduction half-reaction

$2H_2O(l) + 2e^- \rightarrow H_2(g) + 2OH^-(aq)$

E° cell = -1.65 V

Overall (cell) reaction

$2H_2O(l) \rightarrow 2H_2(g) + O_2(g)$

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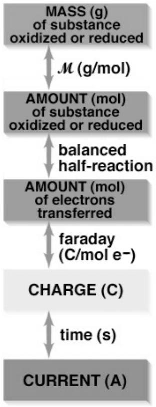
# A Summary Diagram for the Stoichiometry of Electrolysis



MASS (g) of substance oxidized or reduced

$\mathcal{M}$ (g/mol)

AMOUNT (mol) of substance oxidized or reduced

balanced half-reaction

AMOUNT (mol) of electrons transferred

faraday (C/mol e−)

CHARGE (C)

time (s)

CURRENT (A)

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# *Electrolysis: Electroplating*

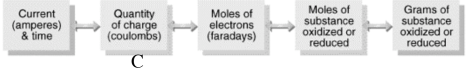
Electroplating

*<u>http://chemconnections.org/general/movies/Electroplating.MOV</u>*

## *Electrolysis*

### Quantitative Aspects of Electrolysis

- We want to know how much material we obtain with electrolysis.
- Consider the reduction of $Cr^{3+}$ to Cr.
  - ❖ $Cr^{3+}(aq) + 3e^- \rightarrow Cr(s)$.
  - ❖ 3 mol of electrons will plate 1 mol of Cr.
  - ❖ The charge of 1 mol of electrons is 96,500 C (1 *F*).
  - ❖ Since C = I x t, the amount of Cu can be calculated from the current (I) and time (t) taken to plate.



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# *QUESTION*

How many grams of Cr would plate out from a solution of $Cr(NO_3)_3$ when $1.93 \times 10^5$ coulombs of charge are passed through the solution? The atomic mass of Cr is 52.0 g/mol, and 1 Faraday is equal to $9.65 \times 10^4$ C/mol $e^-$.

A) 17.3 g B) 34.7 g C) 52.0 g D) 104 g

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## Applying the Relationship Among Current, Time, and Amount of Substance

**Problem:** A technician needs to plate a bathroom fixture with 0.86 g of chromium from an electrolytic bath containing aqueous $Cr_2(SO_4)_3$. If 12.5 min is allowed for the plating, what current is needed?

**Plan:** We write the half-reaction for $Cr^{3+}$ reduction. We then know the number of moles of electrons per mole of Cr, and can calculate the current needed to do the electroplating.

**Solution:** Writing the balanced half-reaction:

$$Cr^{3+}_{(aq)} + 3\ e^- \longrightarrow Cr_{(s)}$$

$$e^- \text{ transferred: } 0.86\text{ g Cr} \times \frac{1\text{ mol Cr}}{52.00\text{ g Cr}} \times \frac{3\text{ mol }e^-}{1\text{ mol Cr}} = 0.050\text{ mol }e^-$$

Calculating charge transfer:

$$\text{Charge (C)} = 0.050\text{ mol }e^- \times \frac{9.65 \times 10^4\text{ C}}{1\text{ mol }e^-} = 4.8 \times 10^3\text{ C}$$

Calculating the current:

$$\text{Current (A)} = \frac{\text{charge (C)}}{\text{time (s)}} = \frac{4.8 \times 10^3\text{ C}}{12.5\text{ min}} \times \frac{1\text{ min}}{60\text{ s}} = 6.4\text{ C/s} = \mathbf{6.4\ A}$$

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# *QUESTION*

Gold (atomic mass = 197) is plated from a solution of chlorauric acid, $HAuCl_4$; it deposits on the cathode. Calculate the time it takes to deposit 0.50 gram of gold, passing a current of 0.10 amperes. (1 faraday = 96,485 coulombs)

A) 41 minutes
B) 2.0 hours
C) 1.0 hour
D) 6.0 hours
E) none of these

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## *Electrolysis: Chrome Plating*

*http://chemconnections.org/general/movies/CHROMEPL.MOV*

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### *QUESTION*

An antique automobile bumper is to be chrome plated. The bumper, which is dipped into an acidic $Cr_2O_7^{2-}$ solution, serves as a cathode of an electrolytic cell. The atomic mass of Cr is 51.996; 1 faraday = 96,485 coulombs. If oxidation of $H_2O$ occurs at the anode, how many moles of oxygen gas will evolve for every $1.00 \times 10^2$ grams of Cr(s) deposited?

A) 2.88
B) 0.48
C) 11.5
D) 7.7
E) 1.44

# *Electrolysis*

Electrical Work

- In an electrolytic cell an external source of energy is required for the reaction to proceed.
- In order to drive the nonspontaneous reaction the external emf must be greater than $E_{\text{cell}}$.
- From physics: work has units watts:

$$1\text{ W} = 1\text{ J/s}.$$

- Electric utilities use units of kilowatt-hours:

$$1\,\text{kWh} = (1000\text{ W})(1\text{ h})\left(\frac{3600\text{ s}}{1\text{ h}}\right)\left(\frac{1\text{ J/s}}{1\text{ W}}\right) = 3.6\times10^{6}\text{ J}.$$

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# *Aluminum Production*

http://chemconnections.org/general/movies/Al-electrolysis.mov

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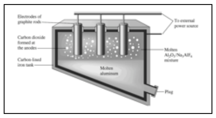
# *QUESTION*



The extraction of aluminum from a mixture of molten $Al_2O_3/Na_3AlF_6$ (cryolite) is superior to the extraction from a solution of aluminum ions in water because…

A. carbon dioxide bubbles can continuously provide agitation that effectively stirs the molten solution.
B. attempts at reducing $Al^{3+}$ from water are hampered because $Al^{3+}$ is a better oxidizing agent than water.
C. the process involves lower temperatures (therefore less energy) due to the ease of oxidation of aluminum in the presence of cryolite.
D. water is easier to oxidize than aluminum, so it would react first at a lower voltage.

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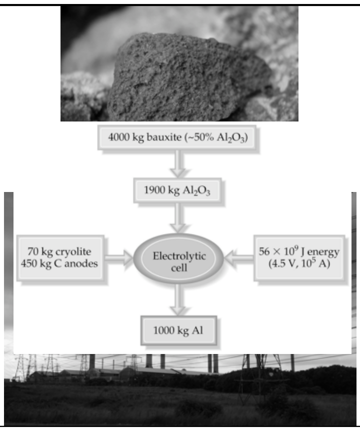
*Aluminum Production*



4000 kg bauxite (~50% $Al_2O_3$)

1900 kg $Al_2O_3$

70 kg cryolite
450 kg C anodes

Electrolytic cell

$56 \times 10^9$ J energy
(4.5 V, $10^5$ A)

1000 kg Al

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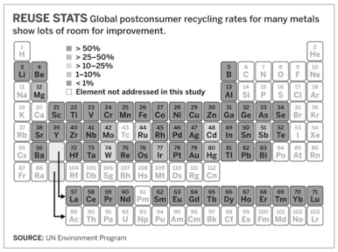
# *Metal Recycling*

http://unep.org/resourcepanel/publications/recyclingratesofmetals/tabid/56073/default.asp



**REUSE STATS** Global postconsumer recycling rates for many metals show lots of room for improvement.

**SOURCE:** UN Environment Program

- •Aluminum, lead, iron, chromium, nickel, and manganese, have recycling rates higher than 50%.
- •34 elements are below 1 per cent recycling.
- •Many of these are crucial to clean technologies such as batteries for hybrid and electric cars.

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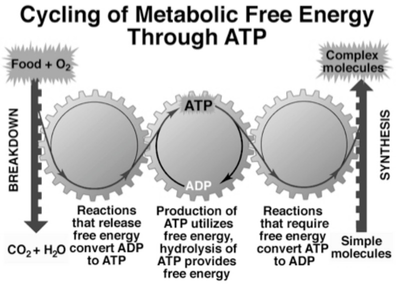
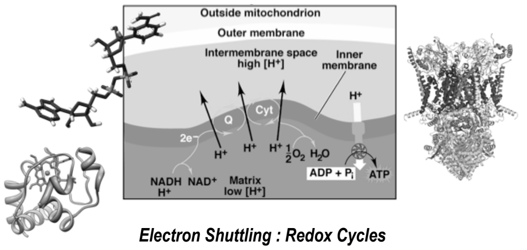
# *Biochemical Production (Synthesis) and Energy Cycles*



# Coupling Electron Transport to Membrane / Proton Transport, ATP, & Synthesis



**Electron Shuttling : Redox Cycles**

NADH || NAD+ = Nicotinamide adenine dinucleotide

Q = Electron Carrier (Ubiquinones, coenzyme Q)

Cyt = Cytochrome, small highly water soluble protein

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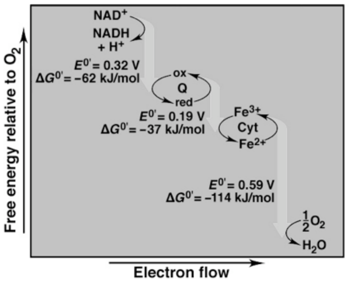
# The Main Energy-Yielding Steps in the Mitochondrial Electron-Transport Cycle



Electrons move from an electron donor NADH to a terminal electron acceptor ($O_2$) via a series of redox reactions.