

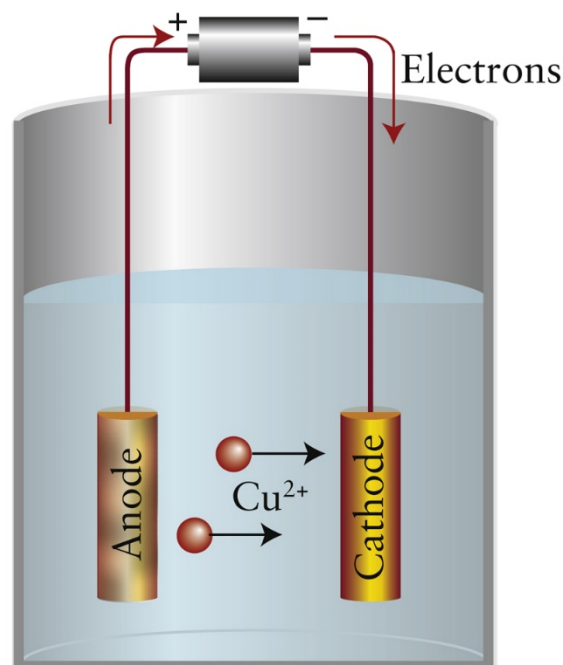
Recap

- ❑ Equilibrium constants and standard potentials
- ❑ Nernst equation → Non-standard potential
- ❑ Electrolysis (overpotential)

Copper is refined electrolytically by using an impure form of copper metal called **blister copper** as the anode in an electrolytic cell. Supplied current drives the oxidation of the blister copper to copper(II) ions, Cu^{2+} , which are then reduced to pure copper metal at the cathode.



Impure copper



Copper is 100% recyclable.

99.99% pure, aqueous!

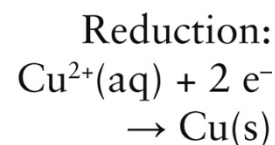
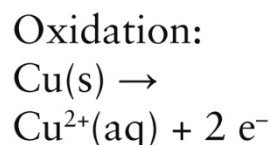


Figure 60.3
Atkins, *Chemical Principles: The Quest for Insight*, 7e
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Example 60.3



What amount of copper (in moles) can be produced by using 4.0 mol e^{-} ?

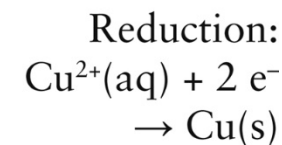
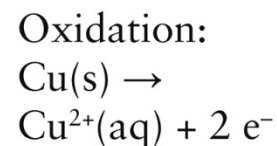
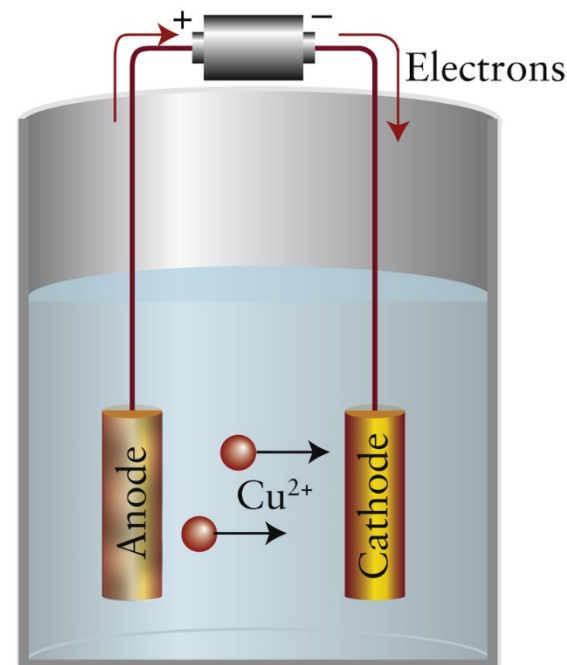


Figure 60.3

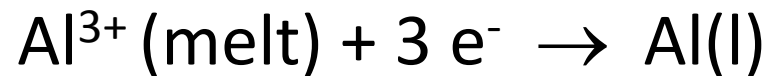
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The stoichiometric ratio is 2 mol $\text{e}^{-} \simeq 1 \text{ mol Cu}(\text{s})$

$$\text{Given } 4.0 \text{ mol e}^{-} \times \frac{1 \text{ mol Cu}(\text{s})}{2 \text{ mol e}^{-}} = 2.0 \text{ mol Cu (s)}$$

Aluminum is produced by electrolysis of its oxide dissolved in molten cryolite (Na_3AlF_6). Find the mass of aluminum that can be produced in 1.00 day (d) in an electrolytic cell operating continuously at 1.00×10^5 A. The cryolite does not react.

The half-reaction we're interested in is



This is $3 \text{ mol e}^- \rightleftharpoons 1 \text{ mol Al}$.

$$F = 96,485 \text{ C} \cdot \text{mol}^{-1}$$

1 coulomb = Amp·sec or more commonly written as:

$$\text{A} = \text{C} \cdot \text{s}^{-1} \quad \text{so} \quad 1.00 \times 10^5 \text{ C} \cdot \text{s}^{-1}$$

$$26.98 \text{ g} \cdot \text{mol}^{-1} \text{ Al}$$

$$3600 \text{ s} = 1 \text{ h}, 24 \text{ h} = 1 \text{ d}$$



Aluminum is produced by electrolysis of its oxide dissolved in molten cryolite (Na_3AlF_6). Find the mass of aluminum that can be produced in 1.00 day (d) in an electrolytic cell operating continuously at $1.00 \times 10^5 \text{ A}$. The cryolite does not react.

Solving for mass

$$\frac{26.98 \text{ g Al}}{\text{mol Al}} \times \frac{1 \text{ mol Al}}{3 \text{ mol e}^-} \times \frac{\text{mol e}^-}{96,485 \text{ C}} \times \frac{1.00 \times 10^5 \text{ C}}{\text{s}} \times \frac{3600 \text{ s}}{1 \text{ h}} \times \frac{24 \text{ h}}{1 \text{ d}} =$$

$$8.05 \times 10^5 \text{ g Al}$$

How many hours are required to plate 12.00 g of chromium metal from a 1 M solution of CrO_3 in dilute sulfuric acid by using a current of 6.20 A?

The reaction is $\text{CrO}_3 + 6 \text{e}^- + 6 \text{H}^+ \rightarrow \text{Cr(s)} + 3 \text{H}_2\text{O}$

This is $6 \text{ mol e}^- \simeq 1 \text{ mol Cr(s)}$.

$$F = 96,485 \text{ C}\cdot\text{mol}^{-1}$$

$$\text{amp} = \text{C}\cdot\text{s}^{-1}, \quad 6.20 \text{ C}\cdot\text{s}^{-1}$$

$$52.00 \text{ g}\cdot\text{mol}^{-1} \text{ Cr}$$

$$3600 \text{ s} = 1 \text{ h}$$

Solving for time (h)

$$\frac{1 \text{ h}}{3600 \text{ s}} \times \frac{\text{s}}{6.20 \text{ C}} \times \frac{96,485 \text{ C}}{\text{mol e}^-} \times \frac{6 \text{ mol e}^-}{1 \text{ mol Cr}} \times \frac{\text{mol Cr}}{52.00 \text{ g Cr}} \times \frac{12.00 \text{ g Cr}}{1} =$$

$$5.99 \text{ hr}$$

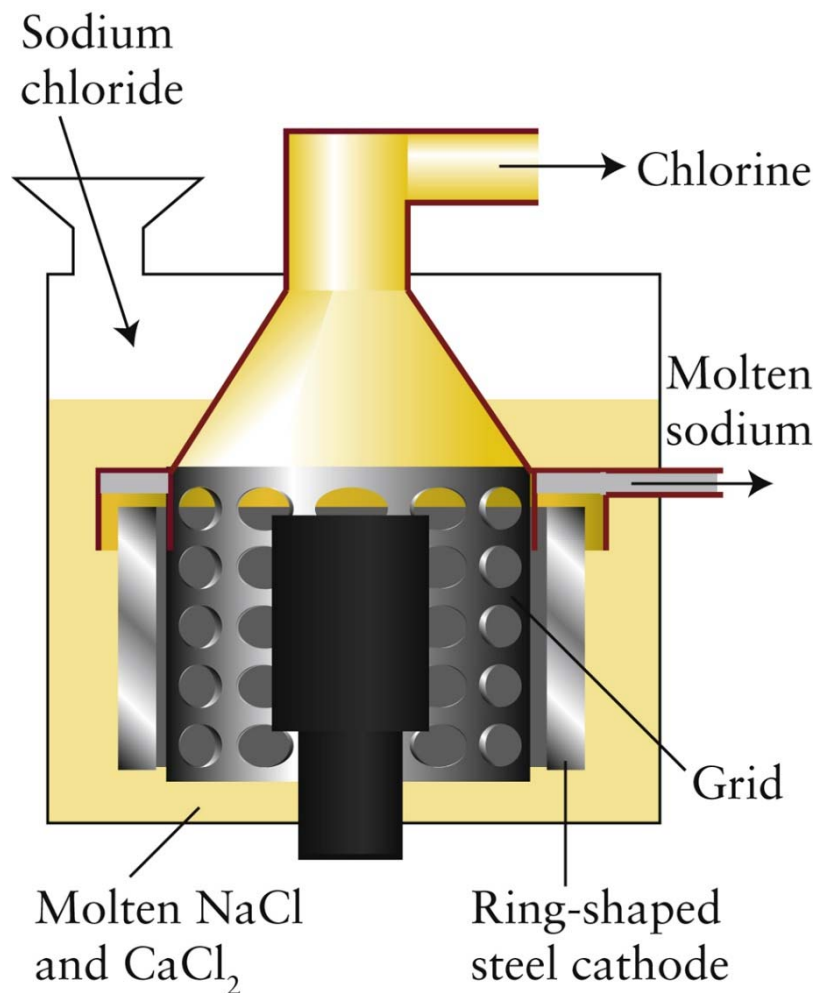
Electrochemical Purification and the Preservation of Metals

In the Downs process, **molten sodium chloride** is electrolyzed with a graphite anode and a steel cathode.

The sodium and chlorine are kept apart by hoods surrounding the electrodes.

Calcium chloride is present to lower the melting point of sodium chloride to an economical temperature.

Electrochemical Purification and the Preservation of Metals



$\text{Na}^+ (\text{melt}) + 1 \text{e}^- \rightarrow \text{Na}(\text{s})$
 Na^+ ions are reduced to sodium.

$2\text{Cl}^- (\text{melt}) \rightarrow \text{Cl}_2(\text{g}) + 2 \text{e}^-$
 Cl^- ions are oxidized to chlorine.

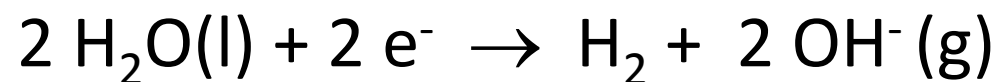
Figure 60.4
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Corrosion with Water and/or Oxygen

Corrosion is the unwanted oxidation of metal in bridges and automobiles.

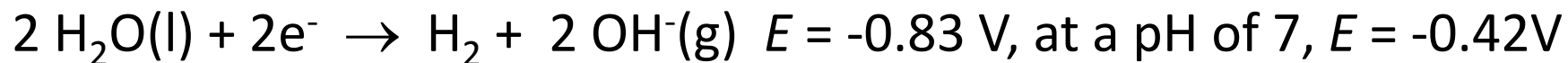
The main culprit in corrosion is water.

One half-reaction that we have to take into account is:



$E = -0.83 \text{ V}$, at a pH of 14, but at a pH of 7, $E = -0.42\text{V}$.

Corrosion with Water and/or Oxygen



Metals with a lower oxidizing ability (more negative) than -0.42 V will get oxidized by water. For example, $\text{Fe}^{2+}(\text{aq}) + 2 \text{e}^- \rightarrow \text{Fe}(\text{s})$, $E = -0.44\text{V}$, so iron will be oxidized by water.



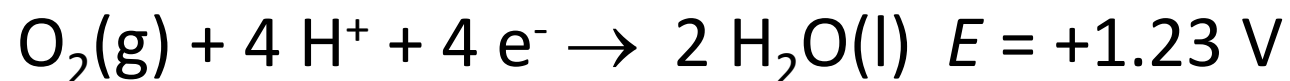
Figure 60.5
Atkins, *Chemical Principles: The Quest for Insight*, 7e
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Hexavalent chrome plating:
Chromium metal has a
positive potential, so
water cannot attack it.

$2 \text{Cr}(\text{s}) + 7 \text{H}_2\text{O}(\text{l}) + 12 \text{e}^- \rightarrow \text{Cr}_2\text{O}_7^{2-}(\text{aq}) + 14 \text{H}^+(\text{aq}) \quad E = +0.59 \text{ V}$. This will not react with water. It has a higher reduction potential (also the reverse of this is not favorable).

Corrosion with Water and/or Oxygen

Another corrosive reaction is with oxygen under acidic conditions.



At pH 7, $E = +0.82 \text{ V}$

O_2 free water
and no reaction.

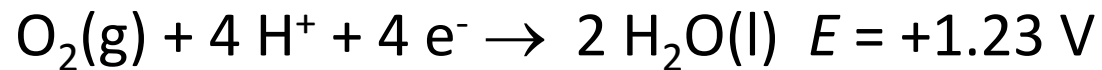


Water with O_2 and
rusting begins.

Figure 6N.2
Atkins, *Chemical Principles: The Quest for Insight*, 7e
W. H. Freeman photo by Ken Karp.

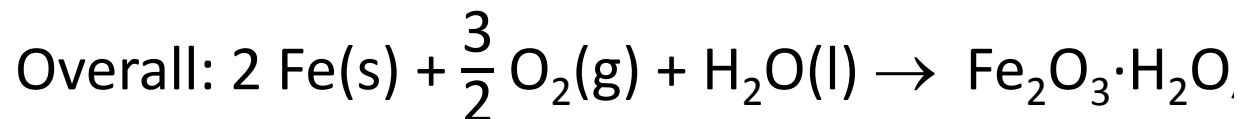
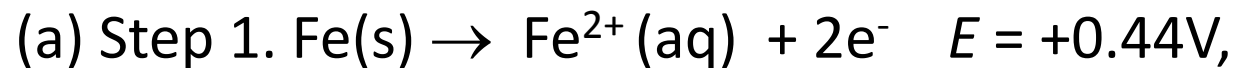
Corrosion with Water and/or Oxygen

Another corrosive reaction is with oxygen under acidic conditions.



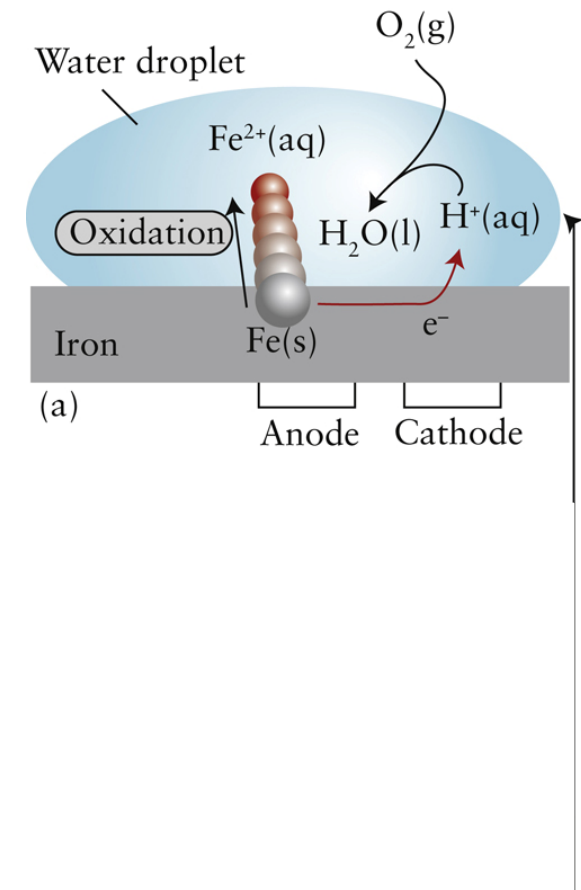
At a pH 7, $P_{\text{O}_2} = 0.21 \text{ bar}$, $E = +0.82 \text{ V}$

When combined with iron:



a voltage exceeding 2 V accounts for this favorable reaction.

The reaction is catalyzed by H^+ .



Protection Against Corrosion

Photo shows **galvanizing metal** with a film of zinc. Zinc lies below iron in the electrochemical series; so, if a scratch exposes the metal beneath, the more strongly reducing zinc releases electrons to the iron.

Large pieces of metal dipped in molten zinc.

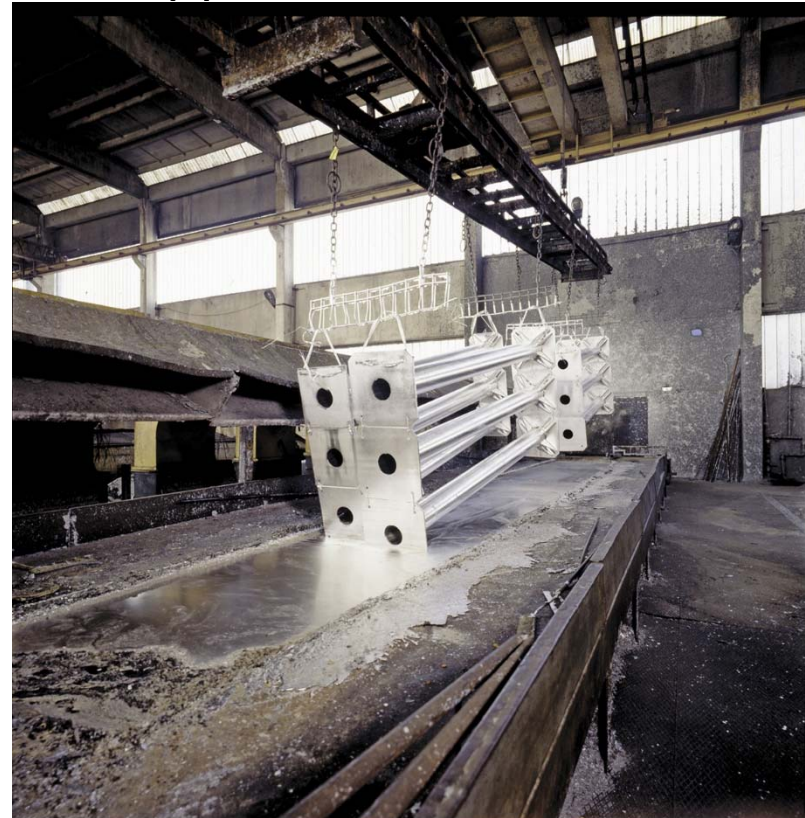


Figure 6N.4
Atkins, *Chemical Principles: The Quest for Insight*, 7e
the palms/ Shutterstock.

As a result, the zinc, not the iron, is oxidized.

Protection Against Corrosion

To protect large metal structures, like ships or underground pipelines (gasoline storage tanks or bridges), cathodic protection is common.

Attached to an iron structure is a block of metal, more strongly reducing metal than iron, typically zinc or magnesium.

These are referred to as **sacrificial anodes** because they are oxidized by oxygen before iron.

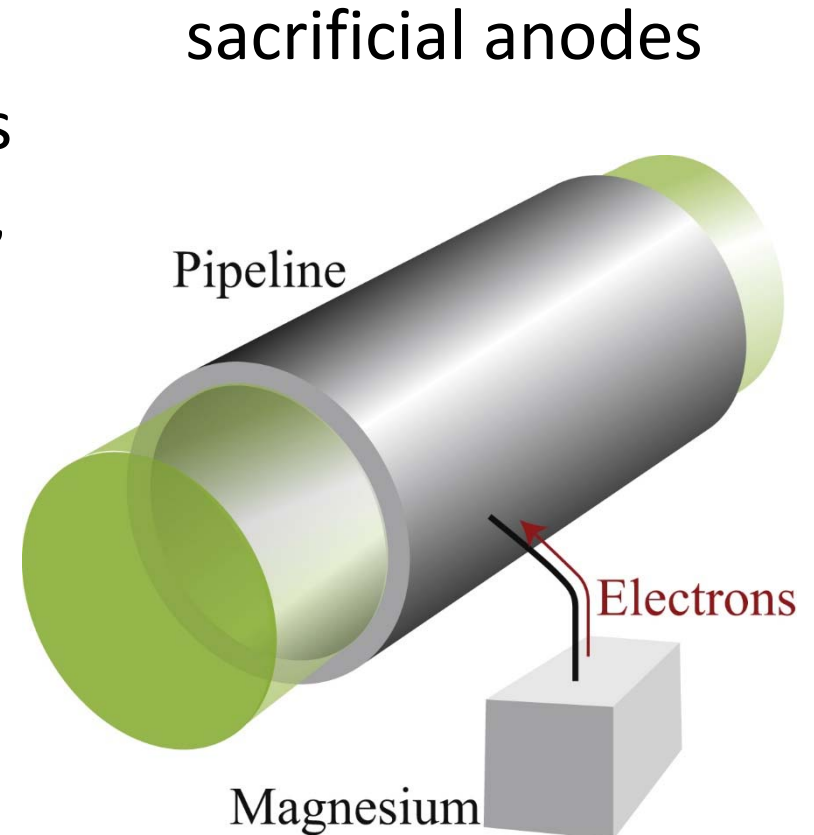
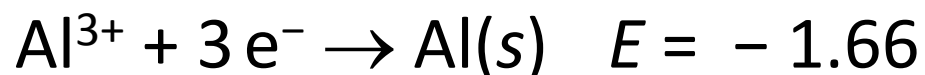
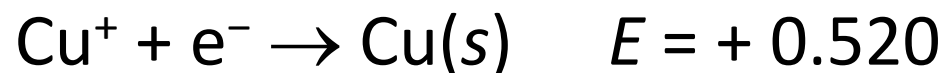


Figure 6N.6
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Which of the following elements can act as a sacrificial anode for iron: (a) copper; (b) aluminum; (c) tin?



Only Al more strongly reduces than Fe.

Practical Cells: Primary and Secondary

All produce 1.5 V.

Galvanic cells are batteries.

The specific energy is measured in kilowatt-hours per kilogram, $\text{kW}\cdot\text{h}\cdot\text{kg}^{-1}$.

A **primary cell is a galvanic cell** with the reactants sealed and are not rechargeable.

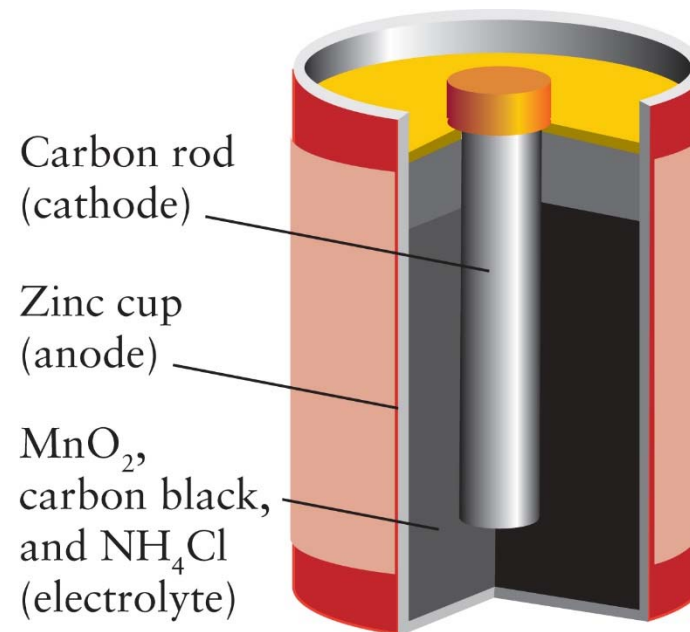
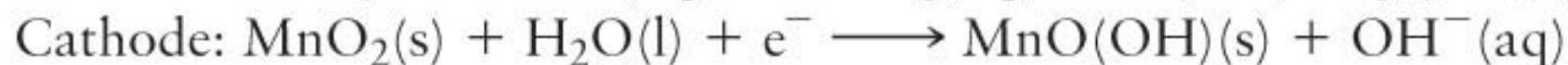


Figure 1
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Practical Cells: Primary and Secondary

Secondary cells are galvanic cells that must be charged before used.

These batteries are found in portable computers, cell phones, and automobiles.

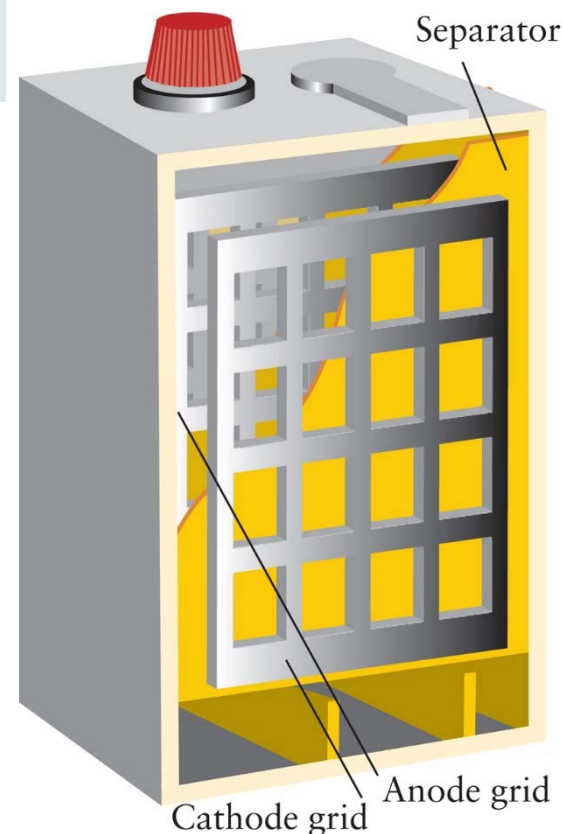


Figure 4
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Pb for a car's battery: each cell is 2 V, so 6 cells = 12 V.

