General Chemistry (CH101): Chemistry around Us

Department of Chemistry

KAIST

Chapter 8 Energy Storage



- What are the main types of batteries and how do they work?
- What are the differences between galvanic and electrolytic cells?
- How are batteries recycled?
- What are "hybrid" vehicles?
- What are the differences between supercapacitors and batteries?
- Are there benefits to using fuel cells instead of gasoline-fueled vehicles?

Reflect



The Role of Batteries in Your Everyday Life

Watch the chapter opening video above and consider how your life would change without batteries.

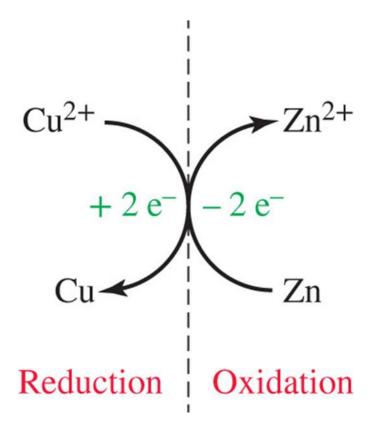
- **a.** List all of your daily activities that involve the use of batteries and include the type of battery used for each of these activities.
- b. Not all batteries are the same. This chapter will describe chemical reactions that occur inside various types of batteries. Among the batteries you listed in part a, which are able to be recharged? For these rechargeable batteries, predict some factors that will influence their usable lifetime (that is, the number of possible charge/discharge cycles until they are no longer able to power a device).

Chapter 8 video

Redox Reactions

A **galvanic cell** is a device that converts the energy released in a spontaneous chemical reaction into electrical energy. This is accomplished by the **transfer of electrons** from one substance to another.

The electron transfer process involves two changes. For instance, zinc is **oxidized** by releasing 2 electrons, and the copper is **reduced** by picking up those 2 electrons.



Applications of Redox Reacions



Ever wonder why the Statue of Liberty is green?

The Statue of Liberty's True Colors? | Reactions Science Videos - American Chemical Society (acs.org)

What Are Half-Reactions?

Each process of reduction-oxidation (redox) is expressed as a half-reaction:

Oxidation half-reaction : $Zn \rightarrow Zn^{2+} + 2e^{-}$

Reduction half-reaction : $Cu^{2+} + 2e^{-} \rightarrow Cu$

Overall cell reaction : $Zn + Cu^{2+} \rightarrow Zn^{2+} + Cu$

The zinc releases two electrons, resulting in a 2+ ion.

The copper ion accepts the two electrons, which results in its charge decreasing from 2+ to 0.

Note: The overall cell reaction does not include electrons, they must cancel when adding up the half-reactions.

Half-Reactions: Practice

Your Turn 8.3 Electrons in Half-Reactions.

Categorize each as an oxidation half-reaction or a reduction half-reaction. Explain your reasoning.

- a. $AI^{3+} + 3e^- \rightarrow AI$
- b. $Zn \rightarrow Zn^{2+} + 2e^{-}$
- $\textbf{C.} \quad \textbf{Mn}^{7+} + 3e^{-} \rightarrow \textbf{Mn}^{4+}$
- **d.** $2H_2O \rightarrow 4H^++O_2+4e^-$
- e. $2H^+ + 2e^- \rightarrow H_2$

Redox Reactions 2

For a redox reaction, reduction means that electrons are added, whereas oxidation implies that electrons are lost.

Some useful mnemonics:

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Oxidation Is Loss; Reduction Is Gain (OIL RIG)
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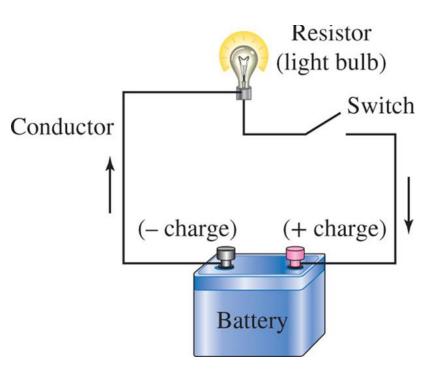
Loss of Electrons Is Oxidation; Gain of Electrons Is Reduction

(LEO the lion says GER)

"Red Cat An Ox", oxidation occurs at the anode and reduction occurs at the cathode.

Electrical Circuits

- The transfer of electrons through an external circuit produces electricity, the flow of electrons from one region to another that is driven by a difference in potential energy.
- To enable this transfer, electrodes (electrical conductors) are placed in the cell as sites for chemical reactions.
- The difference in electrochemical potential between the two electrodes is the **voltage** (units are in **volts**).

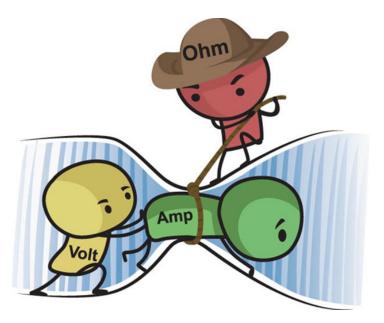


Ohm's Law

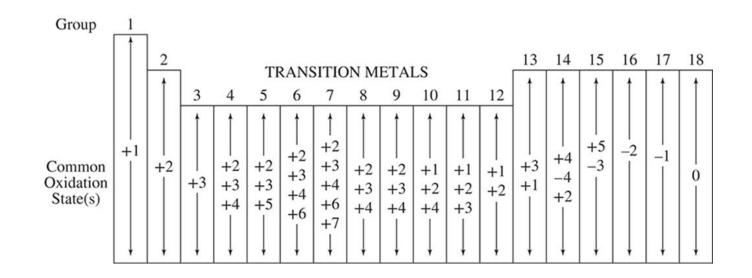
- Alkaline cells each produce 1.5 V, but larger cells can sustain a current through the external circuit for a longer time.
- The current (I) is the rate of electron flow, measured in amperes (amps, A).
 For smaller cells, milliamps, mA, is used.
- Ohm's Law relates voltage, current, and resistance (R,measured in ohms, Ω):

$$V = I \times R$$

Ohm's Law



Preferred Oxidation States



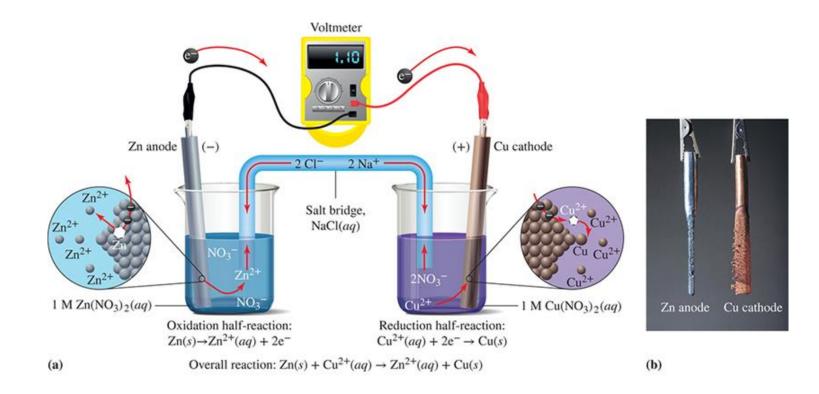
- Electron transfer in a battery takes place within its **electrodes**, electrical conductors that serve as sites for chemical reactions.
- Anode: oxidation takes place.
- Cathode: reduction takes place.
- Depending on their group number, elements have different oxidation states, based on their preference to gain electrons (non-metals) or lose electrons (metals).

Galvanic Cells: "Batteries"

- A **battery** is a system for the direct conversion of chemical energy to electrical energy.
- Batteries are found everywhere in today's society because they are convenient, transportable sources of stored energy.
- The "batteries" shown here are more correctly called **galvanic cells**.
- A series of galvanic cells that are wired together constitutes a true battery like the one in your car.



A Laboratory Model of Galvanic Cells



3D animation: <u>Galvanic Cell.swf (youtube.com)</u>

Video of redox reactions:

Redox Reaction Experiment

Common Galvanic Cells

Table 8.1 Some Common Galvanic Cells.

Туре	Maximum Voltage (V)	Rechargeable?	Examples of Uses
nickel–cadmium (Ni–Cd)	1.25	yes	toys and portable electronic devices, including digital cameras, power tools
nickel–metal hydride (NiMH)	1.25	yes	replacing Ni–Cd for many uses in consumer devices; hybrid vehicles
alkaline	1.5	no	flashlights, small appliances, calculators, audio/video remote controls, toys
lithium (primary)	1.5–3.6	no	LED lighting, smoke alarms, watches, vehicle remotes and key fobs
lead-acid	2.1	yes	automobiles (starting, lighting, and ignition)
lithium-ion, lithium-polymer	3.6	yes	laptop computers, cell phones, portable electronic devices, power tools

Voltage: Independent of Size!

- The voltage of a battery is determined by its chemical composition and is NOT related to the size of the battery.
- All alkaline batteries, from small AAA to large D, produce the same voltage: 1.5
 V. However, larger cells have a greater capacity—they can sustain the flow of electrons longer, since they contain more material.
- **Primary batteries**: not rechargeable (redox reactions only proceed in one direction).
- Secondary batteries: rechargeable (able to run redox reactions either way).

Alkaline Batteries (Primary, Non-Rechargeable)

The half-reactions for an alkaline cell are:

Anode (oxidation):

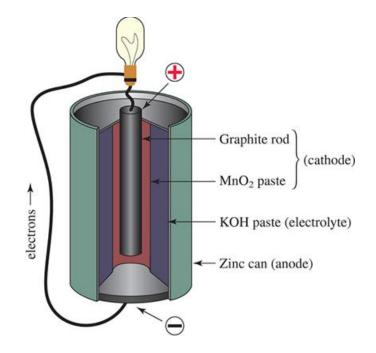
 $\operatorname{Zn}(s) + 2\operatorname{OH}^{-}(aq) \rightarrow \operatorname{Zn}(\operatorname{OH})2(s) + 2e^{-}$

Cathode (reduction):

$$2\operatorname{MnO}_{2}(s) + \operatorname{H}_{2}\operatorname{O}(I) + 2e^{-} \rightarrow \operatorname{Mn}_{2}\operatorname{O}_{3}(s) + 2\operatorname{OH}^{-}(aq)$$

Overall cell reaction:

 $\operatorname{Zn}(s) + 2\operatorname{MnO}_2(s) + \operatorname{H}_2\operatorname{O}(I) \rightarrow \operatorname{Zn}(\operatorname{OH})2(s) + \operatorname{Mn}_2\operatorname{O}_3(s)$



Nickel-Cadmium Batteries (Secondary, Rechargeable)

The half-reactions for the discharge of a Ni-Cd cell are:

Anode (oxidation):

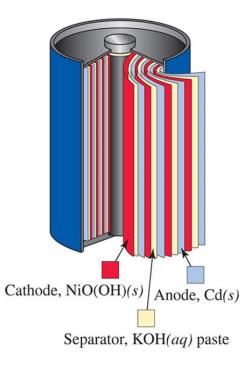
 $\operatorname{Cd}(s) + 2\operatorname{OH}^{-}(aq) \rightarrow \operatorname{Cd}(\operatorname{OH})2(s) + 2e^{-}$

Cathode (reduction):

 $\operatorname{NiO}(\operatorname{OH})(s) + 2\operatorname{H}_{2}\operatorname{O}(I) + 2e^{-} \rightarrow 2\operatorname{Ni}(\operatorname{OH})2(s) + 2\operatorname{OH}^{-}(aq)$

Overall cell reaction (discharge):

 $Cd(s) + 2 \operatorname{NiO}(OH)(s) + 2H_2O(I)$ $\rightarrow Cd(OH)2(s) + 2\operatorname{Ni}(OH)2(s)$



Note: for charging, the above reactions proceed in the opposite direction!

To increase the surface area of electrodes, the components inside batteries are layered.

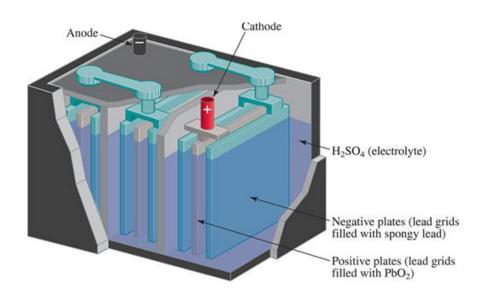
Lead-Acid Storage Batteries

Lead-acid batteries are the workhorse of today's rechargeable batteries. In an automobile, it powers an electric motor that is used to start the car.

The overall chemical reaction (sum of two half-reactions):

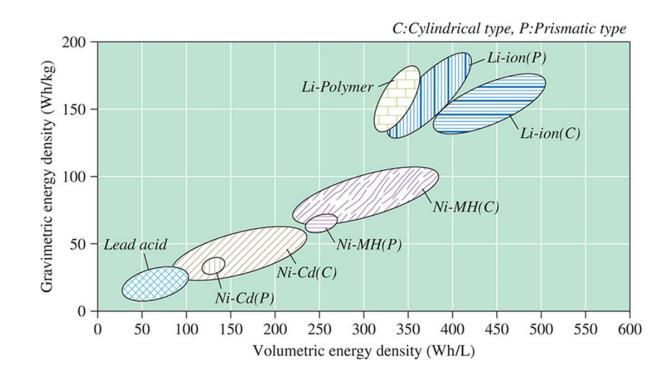
 $Pb(s) + PbO_{2}(s) + 2H_{2}SO_{4}$ $\rightarrow 2PbSO_{4}(s) + 2H_{2}O(I)$

Discharging: left-right direction **Charging**: right-left direction





Energy Density



The **energy density** of a battery relates both to the number of ions stored in the electrode and the weight or volume of the battery:

Energy Density = $\frac{\text{Voltage} \times \text{Number of movable Li ions in electrodes}}{\text{Total battery weight (gravimetric) or volume (volumetric)}}$

Lithium-ion Batteries (Secondary, Rechargeable)

In lithium-ion batteries, lithium ions (Li^{+})

simply shuttle back and forth between the two electrodes during charging and discharging:

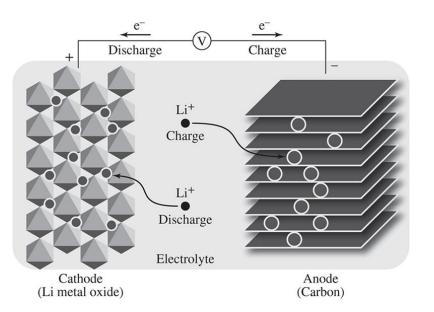
Anode (discharge):

 $\operatorname{Li}_{x}C_{6}(S) \rightarrow 6 C(S) + x \operatorname{Li}^{+} + xe^{-}$

Cathode (discharge):

 $\operatorname{Li}_{1-x \operatorname{CoO2}}(S) + x \operatorname{Li}^{+} + xe^{-} \rightarrow \operatorname{LiCoO}_{2}(s)$

For charging, these reactions run in the opposite direction.



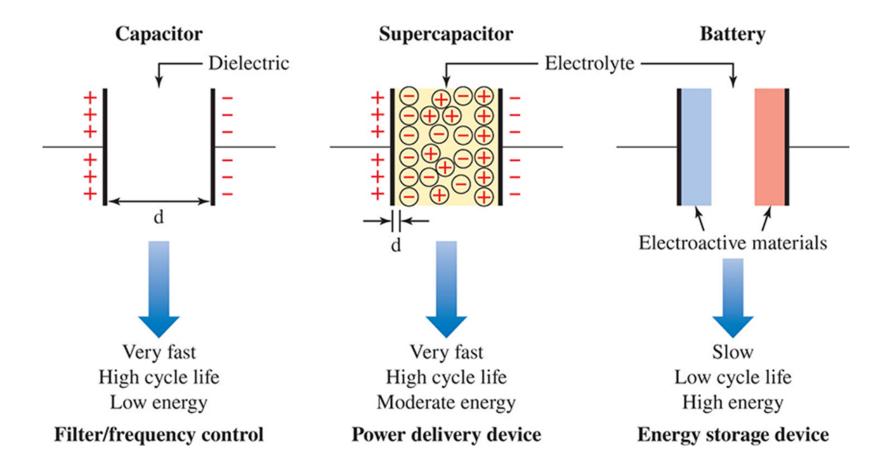


What Causes Battery Fires?

- The metals in Group 1 such as lithium or sodium or dangerously reactive toward oxygen, nitrogen, and water.
- Non-aqueous electrolytes must be used in lithium-ion batteries, and battery packs must be hermetically sealed to prevent exposure to air.
- Fires are initiated if the separator between electrode compartments is broken, which generates a short-circuit and major heat. Also, the circuitry to prevent overcharging may be faulty, which will lead to exothermic reactions.

What Makes Smartphones Explode?

Supercapacitors Versus Batteries



Supercapacitors Versus Batteries: Performance Comparison

Table 8.2 Performance Comparison BetweenSupercapacitors and Li-ion Batteries.

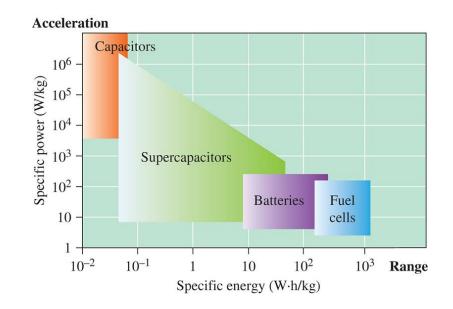
Function	Supercapacitor	Lithium-ion
Charge time	1–10 seconds	10 to 60 minutes
Cycle life	1 million	500 and higher
Cell voltage (V)	2.3 to 2.75	3.6 to 3.7
Specific energy (Wh/kg)	5 to 50	100 to 200
Specific power (W/kg)	10,000 to 50,000	1000 to 3000
Cost per Wh	\$5–\$20	\$0.50-\$1.00 (large systems)
Service life (in vehicle)	10 to 15 years	5 to 10 years
Charge temperature	−40 to 65 °C (−40 to 149 °F)	0–45 °C (32 to 113 °F)
Discharge temperature	-40 to 65 °C (-40 to 149 °F)	-20 to 60 °C (-4 to 140 °F)



Energy Density Versus Power Density

- An analogy for energy and power densities is a water bottle.
- Size of the bottle: energy density (larger for batteries than supercapacitors; electric vehicles with batteries would have longer ranges on a single charge).
- **Size of its opening**: power density (larger for supercapacitors than batteries; electric vehicles with supercapacitors would have very fast acceleration).





Hybrid Electric Vehicles (HEVs)

- Combine the use of gasoline and battery technologies.
- Many hybrids, unlike conventional gasoline-powered cars, deliver better mileage in city driving than at highway speeds.
- The average gasoline-powered vehicle emits 6 to 9 tons of carbon dioxide each year. Each increase of 5 miles per gallon in fuel efficiency can reduce these emissions by 18 tons over a vehicle's lifetime.

Fuel Economy Leaders for the 2019 Model Year

 Table 8.3 Fuel Economy Leaders for the 2019 Model Year.

Rank	Manufacturer/Model	Miles per Gallon (city/highway)
	Electric Vehicles (EVs)	
1	Hyundai Ioniq EV	150/122
2	Tesla Model 3 Standard Range Plus	140/124
3	Hyundai Kona Electric	132/108
4	Chevrolet Bolt EV	128/110
5	Volkswagen e-Golf	126/111

Fuel Economy Leaders for the 2019 Model Year 2

Rank	Manufacturer/Model	Miles per Gallon (city/highway)						
	Plug-in Hybrid Electric Vehicles (PHEVs)							
1	BMW i3s with Range Extender	92/79						
2	Toyota Prius Prime	83/72						
3	Honda Clarity PHEV	82/70						
4	Hyundai Ioniq PHEV	78/74						
5	Kia Niro PHEV	69/62						

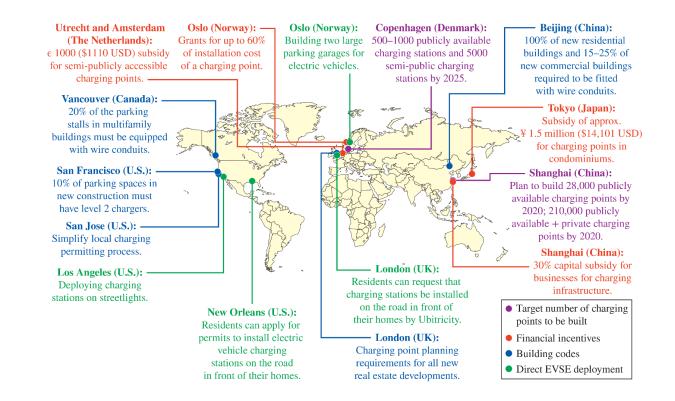
Fuel Economy Leaders for the 2019 Model Year 3

Rank	Manufacturer/Model	Miles per Gallon (city/highway)						
	Hybrid Electric Vehicles (HEVs)							
1	Hyundai Ioniq Blue	57/59						
2	Toyota Prius Eco	58/53						
3	Honda Insight	55/49						
4	Toyota Camry Hybrid LE	51/53						
5	Kia Niro FE	52/49						

This list is taken from the top midsize cars, including plug-in hybrids and allelectric vehicles.

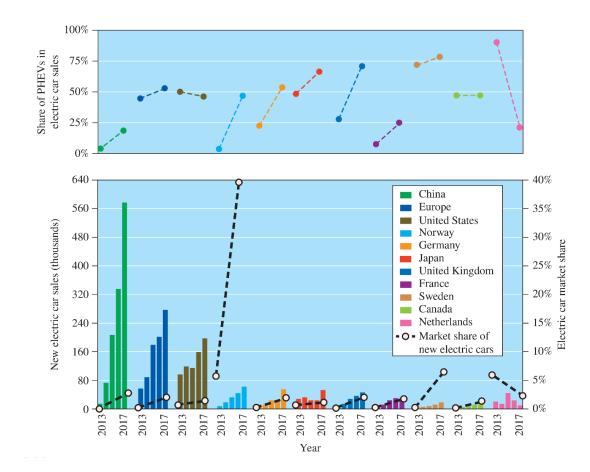
Note: For EVs, fuel economy is given in miles per gallon equivalent (MPGe), where 33.7 kWh = 1 gallon of gasoline.

Worldwide Electric Vehicle (EV) Subsidies



In the U.S. there is a federal tax credit of up to \$7500 toward the purchase of new plug-in hybrids and all-electric vehicles has been offered since 2011. Other policies and incentives have been developed across the world to promote charging infrastructure deployment in major cities.

Worldwide EV Sales & Trends, 2013-17

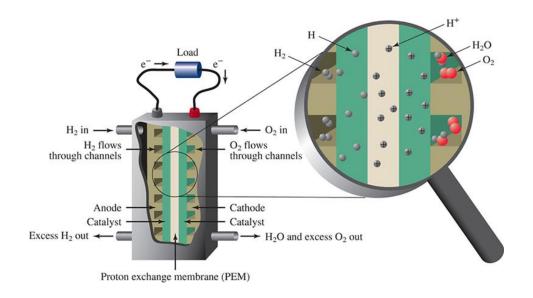


The most significant increases in PHEV sales worldwide were in Norway, Germany, and the United Kingdom.

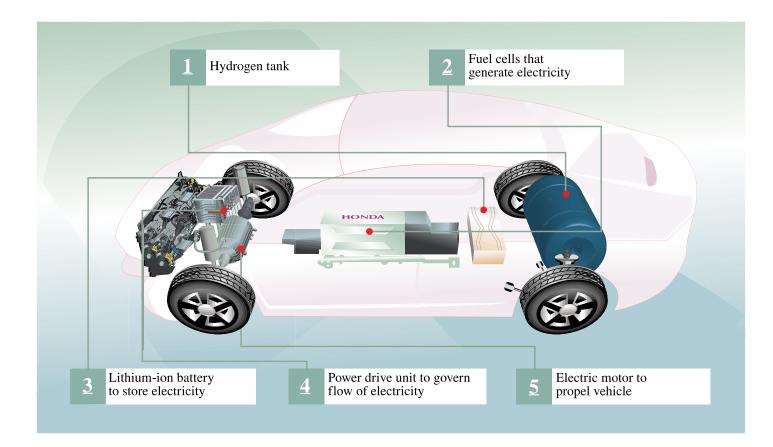
How Do Fuel Cells Work?

A **fuel cell** is a galvanic cell that produces electricity by converting the chemical energy of a fuel directly into electricity without burning the fuel.

Both fuel and oxidizer must constantly flow into the cell to continue the chemical reaction.



How Do Fuel Cells Work? 2



The hydrogen tanks are pressurized up to 5000 lb/in^2 ,

which is equivalent to 34 MPa (340 bar).

Fuel Cell Half-Reactions

Anode reaction (oxidation half-reaction):

 $\mathrm{H}_{2}(g) \rightarrow 2 \mathrm{H}^{+}(aq) + 2e^{-}$

Cathode reaction (reduction half-reaction):

$$\frac{1}{2}O_2(g) + 2 \operatorname{H}^+(aq) + 2e^- \to \operatorname{H}_2O(I)$$

Overall (sum of the half-reactions):

 $\frac{1}{2}O_2(g) + H_2(g) \rightarrow H_2O(I)$



Combustion Versus Hydrogen Fuel Cells

Table 8.4 Combustion versus Hydrogen Fuel Cell Technology.

Process	Fuel	Oxidant	Products	Other Considerations				
combustion	hydrocarbons, alcohols H ₂ , wood, etc.	O ₂ from air	H ₂ O, CO/CO ₂ , heat, light, sound	rapid process, flame present, low efficiency, useful for producing heat				
hydrogen fuel cell	H ₂	O ₂ from air	H ₂ O, electricity, heat	slow process, no flame, quiet, efficient, useful for generating electricity				

Hydrogen Economy

If the "Hydrogen Economy" becomes a reality, where will we get the H₂?

One potential source is fossil fuels.

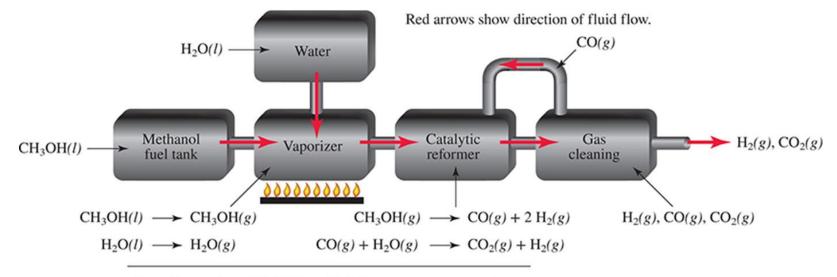
95% of world's supply of H_2 is from methane:

165 kJ + CH₄(g) + 2H₂O(g) \rightarrow 4H₂(g) + CO₂(g) 247 kJ + CO₂(g) + CH₄(g) \rightarrow 2H₂(g) + 2CO(g)

BUT these reactions produce carbon dioxide and carbon monoxide!

Reformed Methanol Fuel Cell

A hydrogen-rich fuel such as methanol (CH₃OH) or methane (CH₄) can be used instead of H₂(g) directly. Because they are liquids under standard conditions, methanol or ethanol could be pumped at conventional gas stations. However, these fuels must be first converted to H₂ by a reformer:

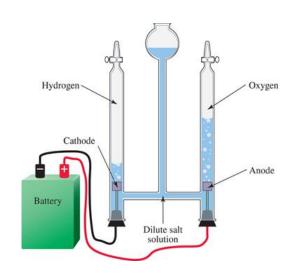


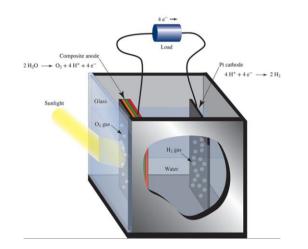
Overall reaction: $CH_3OH(l) + H_2O(l) \longrightarrow 3H_2(g) + CO_2(g)$

Hydrogen Via Water Splitting

Hydrogen (and oxygen) gas produced can be produced by the **electrolysis** of water using battery power or sunlight.

Electrolysis produces no CO or CO₂, but it also requires 237 kJ/mol of energy -supplied by either an electrical source or sunlight (photoelectrochemical light splitting, currently <14% efficient).



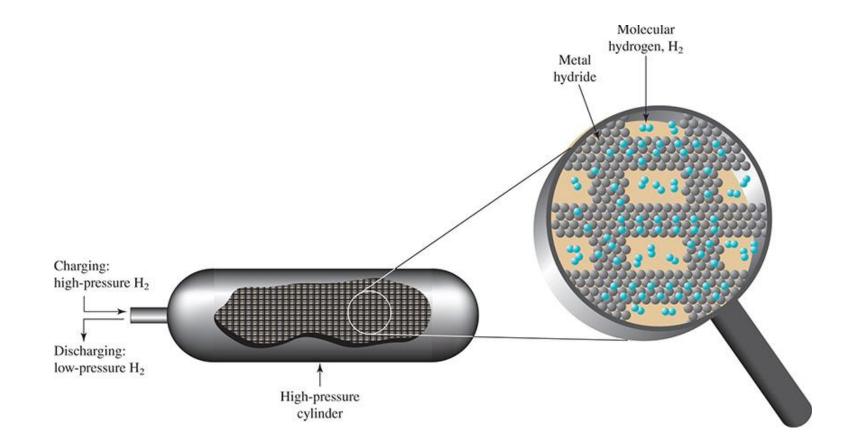




How Do We Safely Store Hydrogen Gas?

- Gaseous H₂ requires a different system for storage and transfer from that used for liquid gasoline.
- As a gas, hydrogen has a very low density & takes up a lot of space. For example, at sea level and room temperature, H₂ occupies a volume of about 11 L (almost 4 gal) per gram. In comparison, 11 L of gasoline has a mass of 8.7 kg!
- Pressurized gas tanks are very dangerous (think of the Hindenberg explosion!).
- It is promising to use a compound such as metal hydrides (for example, LiH) that can reversibly store significant amounts of H₂ per unit mass.

Hydrogen Storage in Metal Hydrides



The safest way to store hydrogen gas is in the structure of some compounds such as **metal hydrides** (M_xH_y) .

Battery Recycling

Your Turn 8.18 Battery Recycling.

What can you do to keep the metals used in batteries from being lost to a landfill? The answer depends on the battery type. Search the Internet to answer the following:

- **a.** Which types of batteries are more commonly recycled: rechargeables (secondary), or nonrechargeables (primary)?
- b. Why is recycling a Ni–Cd battery more critical than recycling an alkaline one?
- **c.** List some reasons why household battery-recycling programs have not been as effective as those for recycling car batteries.

Sustainability of Energy Storage Devices

Your Turn 8.17 Could Metals Become Extinct?

In 2015, the American Chemical Society published this "Periodic Table of Endangered Elements":

1 H 1.008							ious threa next 100										2 He 4.003
3	4	Rising threat from increased use							5	6	7	8	9	10			
Li	Be								B	C	N	0	F	Ne			
6.941	9.012								10.81	12.01	14.01	16.00	19.00	20.18			
11 Na 22.99	12 Mg 24.31		Limited availability, future risk to supply						13 Al 26.98	14 Si 28.09	15 P 30.97	16 S 32.07	17 C1 35.45	18 Ar 39.95			
19	20	21	22	23	24	25	26	27	28	29	30	31	32	33	34	35	36
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr
39.10	40.08	44.96	47.88	50.94	52.00	54.94	55.85	58.47	58.69	63.55	65.38	69,72	72.59	74.97	78.96	79.90	83.80
37	38	39	40	41	42	43	44	45	46	47	48	49	50	51	52	53	54
Rb	Sr	Y	Zr	Nb	Mo	Te	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe
85.47	87.62	88.91	91.22	92.91	95.94	(98)	101.1	102.9	106,4	107.9	112.4	114,8	118.7	121,8	127.6	126.9	131.3
55	56	57	72	73	74	75	76	77	78	79	80	81	82	83	84	85	86
Cs	Ba	La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	TI	РЬ	Bi	Po	At	Rn
132.9	137.3	138.9	178.5	180.9	183.9	186.2	190.2	192.2	195.1	197.0	200.6	204.4	207.2	209,0	(210)	(210)	(222)
87	88	89	104	105	106	107	108	109	110	111	112	113	114	115	116	117	118
Fr	Ra	Ac	Rf	Db	Sg	Bh	Hs	Mt	Ds	Rg	Cn	Nh	Fl	Mc	Lv	Ts	Og
(223)	(226)	(227)	(257)	(260)	(263)	(262)	(265)	(266)	(271)	(272)	(285)	(284)	(289)	(288)	(292)	(294)	(294)
			58 Ce 140.1	59 Pr 140.9	60 Nd 144.2	61 Pm (147)	62 Sm 150.4	63 Eu 152.0	64 Gd 157.3	65 Tb 158.9	66 Dy 162.5	67 Ho 164.9	68 Er 167.3	69 Tm 168.9	70 Yb 173.0	71 Lu 175.0	
			90 Th 232.0	91 Pa (231)	92 U (238)	93 Np (237)	94 Pu (242)	95 Am (243)	96 Cm (247)	97 Bk (247)	98 Cf (249)	99 Es (254)	100 Fm (253)	101 Md (256)	102 No (254)	103 Lr (257)	

Sustainability of Energy Storage Devices 2

- **a.** Is it really possible for a metal to become "extinct"?
- **b.** Which of the highlighted elements above are currently in demand for energy storage devices (batteries, fuel cells, supercapacitors)?
- **c.** Are there any nonhighlighted elements that are currently being used, or tested for future use, in energy storage applications?

Sustainability of Electric Vehicles

Your Turn 8.19 Group Activity: Are Electric Vehicles *Really* Sustainable?

Electric vehicles have the advantage of fewer direct greenhouse gas (GHG) emissions from their use relative to fossil fuel—powered vehicles. However, GHGs are emitted during their production and end-of-life recycling efforts, in addition to emissions from power plants in supplying the electrical grid power needed to recharge the battery in PHEVs and EVs.

As a group, use a variety of sources to answer the following questions, and determine whether gasoline-powered or electric vehicles are more sustainable over their lifetime of use.

- **a.** What is the total global electricity demand of EVs?
- **b.** What is the current power-generation mix in the U.S. (including biomass, renewables, hydroelectric, nuclear, and fossil fuels)? How does this energy distribution differ in other parts of the world? How is this projected to change over the next 10 years?
- **c.** How do the global GHG emissions and other air pollutants compare between EVs and gasoline-powered vehicles? Consider production, use, and end-of-life stages for both types of vehicles.

Example topics that you can delve into further...

- 1. Assess whether nuclear power plants are a viable alternative energy source, supporting your argument with scientific evidence.
- 2. Explore the health impacts of indoor radon exposure, identify its primary sources, and suggest methods to decrease its concentration.
- 3. Investigate if there are any materials that can serve as substitutes for silicon in photovoltaic cells.
- 4. Analyze the reasons behind the significant growth in wind power and its advantages compared to other energy sources.
- 5. Determine the more suitable location for wind power generation: offshore (sea) or mountainous areas.