

Improving Air Quality with Electric Vehicles

Electrochemistry Experiment



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Key Concepts:

- Components of Photochemical Smog
- Why High Levels of Ozone in the Air are Undesirable
 - Antioxidants in the Lungs
 - Ozone as an Oxidizing Agent
- Automobile Emissions Increase Ozone Concentrations
 - Incomplete Combustion of Gasoline Produces Volatile Organic Hydrocarbons (VOC)
 - Combustion at High Temperatures Produces NO
 - VOC, NO and Sunlight Result in Ozone Formation
- Reducing Nitrogen Oxides and VOC Emissions
 - Catalytic Converters
 - Zero Emissions Vehicles (ZEVs): Electric Vehicles
- Current Technology for Electric Vehicles
 - How Lead-Acid Batteries Work
 - Drawbacks to Lead-Acid Batteries
- Vanadium Redox Flow Battery: A Possible Alternative to Lead-Acid Batteries for Electric Vehicles

Related Tutorials:

- [*Nutrients and solubility*](#)

Introduction: Photochemical Smog

Good air quality is important to public health. Several studies have linked high levels of air pollution to increased hospital admissions for respiratory and heart disease. Autopsies reveal more lung and airway damage in people exposed to high levels of air pollution. This tutorial will discuss the harmful components of polluted air, describe the leading sources of air pollution in the United States, and examine several strategies for reducing air pollution. Redox reactions, where electrons are transferred from one compound to another, are the foundation for understanding each of these subjects. Redox reactions are involved in creating the molecules that cause pollution. They are central to understanding why polluted air poses a health threat, and they are at the heart of strategies to reduce air pollution. To understand air pollution and its effects, we must understand redox reactions and electrochemistry, which is the study of the connection between chemical and electrical energy.

In the modern industrial world, photochemical smog is the most common air-quality problem. Smog is a mixture of pollutants including nitrogen oxides, ozone, aldehydes, peroxyacetyl nitrate, particulates and volatile organic hydrocarbons. These small molecules confer a variety of characteristics to the atmosphere. Nitrogen dioxide (NO₂) is a brownish gas, and is responsible for the visible "brown cloud" associated with smog. Many people notice eye irritation when smog is severe because peroxyacetyl nitrate is a lachrymator (irritates the eyes), and some people experience difficulty breathing. In addition, visibility is impaired on smoggy days. Figure 1, below, shows the difference in visibility on high-pollution vs. low-pollution days in St. Louis, Missouri.



Figure 1

On the left is a picture of downtown St. Louis on a low pollution day. On the right is a similar picture on a smoggy day. Notice that it is difficult to see the arch in the figure on the right. These pictures were taken by the [Missouri Department of Natural Resource's Visual Air Pollution Camera](#).

In the United States, the Environmental Protection Agency (EPA) monitors air quality and ensures that air pollution is not allowed to become so severe that it endangers public health. How does the EPA evaluate air quality?

Monitoring Air Quality and Communicating Air-Quality Information to the Public

The EPA sets National Ambient Air Quality Standards (NAAQS). Air-quality data (which include concentrations of nitrogen oxides, ozone, etc.) are collected at monitoring stations, and reported to the EPA. When levels of air pollution exceed legal limits, the state must develop a plan to reduce emissions. St. Louis, Missouri is slightly out of compliance on ozone levels, but has attained NAAQS for the other major outdoor pollutants. [\(Hey! I thought ozone was a good thing! Click here for a discussion of when and where ozone is beneficial.\)](#) Ozone concentrations above the levels set by the EPA are the most prevalent air-quality problem in the U.S. The EPA has set the limit for ozone at 0.12 parts per million (ppm), measured as the average concentration over a one-hour period. This means that in one gram of air, the amount of ozone should not exceed 1.2×10^{-7} grams on average. Why is the acceptable limit for ozone so low?

Why Is Ozone In Our Air a Problem?

Ozone is toxic because it is a powerful oxidant, which means it can easily gain electrons from another substance. [Click here to learn about why ozone is such a strong oxidizing agent.](#) Ozone

can react with cell-membrane lipids or proteins to form peroxide (also a strong oxidizer). These oxidizing agents can damage lung tissue. The body is capable of handling small doses of strong oxidizers. For example, the surface of your lungs is covered with an epithelial lining fluid that contains several antioxidants dissolved in it, including Vitamin C (ascorbic acid) and glutathione (Figure 3).

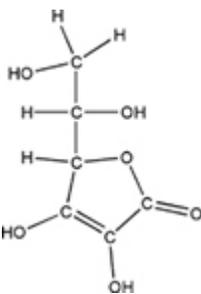
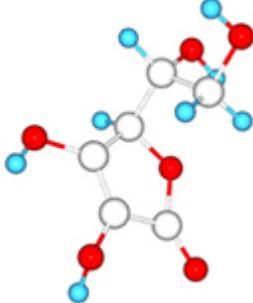
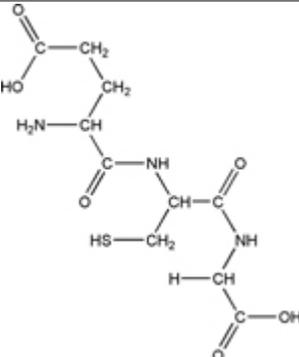
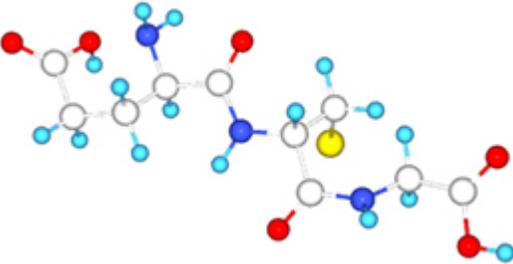
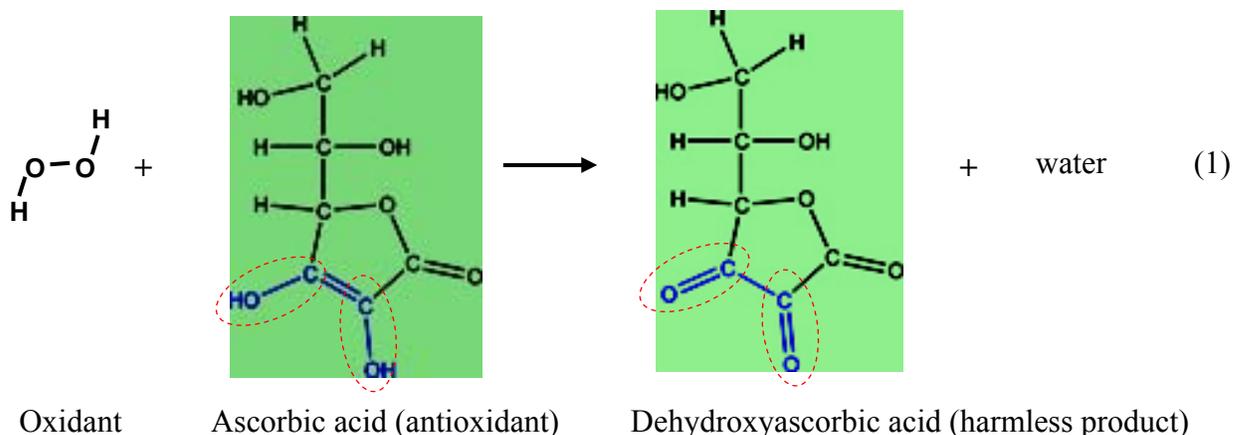
Molecule	2D-Representation	3D- Representation
Ascorbic Acid (Vitamin C)		
Glutathione (a tripeptide composed of three amino acids, glutamic acid, cysteine and glycine).		

Figure 2¹ Molecules of Ascorbic Acid and Glutathione

Antioxidants react with oxidizing agents like peroxide and ozone to form harmless products, as in Equation (1) below. Hydrogen peroxide (H_2O_2), is shown reacting with ascorbic acid (Vitamin C) from the epithelial lining fluid of the lungs. The resulting products are nontoxic, thus the reaction prevents damage to the lung tissue. If the antioxidant solution covering the lung surface were not present, oxidizers would react with the lung tissue itself, damaging the lungs.



Recall that oxidized means the substance is losing electrons (hence the oxidation state of the element being oxidized goes up) and reduced means that it is gaining electrons (hence the oxidation state of the element being reduced goes down). In this example, hydrogen peroxide has gained one

electron (is reduced) as it is converted to water because the oxygen has a (-1) oxidation state in H_2O_2 and a (-2) oxidation state in water. Since hydrogen peroxide is reduced, ascorbic acid must be oxidized. To verify this with oxidation numbers, we need to look at a Lewis structure. (Recall that in order to determine oxidation numbers from Lewis structures, we begin by assigning electrons in bonds to the more electronegative element. Lone-pair electrons are assigned to the atom on which they reside. The oxidation number is equal to the number of valence electrons for that element minus the number of assigned electrons.) Lewis structures for the reduced form of Vitamin C and the oxidized form (dehydroxyascorbic acid) are shown above. The participating atoms are circled. Looking at the circled carbons, we can see that the oxidation number for carbon changes from (+1) in ascorbic acid to (+2) in dehydroxyascorbic acid. If the antioxidant solution covering the lung surface were not present, oxidizers would react with the lung tissue itself, damaging the lungs.

When the concentrations of strong oxidizing agents are high, the antioxidants in the epithelial lining fluid are consumed faster than they can be replaced by the body. Because ozone is a strong oxidizing agent and could be a possible health threat, the EPA has regulated its presence in the atmosphere we breathe. Data show that the combustion of fossil fuels raises ozone concentrations. (That is why we are cautioned to limit driving on poor air-quality days.) But ozone itself is not a product of combustion, so how is ozone formed from the gases released by our automobiles?

Automobile Emissions Increase Ozone Concentrations

Two common emissions products from our automobiles contribute to the formation of ozone: volatile organic hydrocarbons and nitrogen oxides. This section will explore how these ozone precursors are produced and how they lead to the formation of ozone.

Gasoline and other fossil fuels are a mixture of hydrocarbons (compounds containing carbon and hydrogen). Complete combustion of hydrocarbons produces water and carbon dioxide. The balanced equation for combustion of octane (one component of gasoline) is shown in Equation 2.



Incomplete combustion releases volatile organic hydrocarbons (VOCs), because the hydrocarbons are not completely converted to CO_2 . The combustion products we are most concerned with in this tutorial are VOCs and nitrogen oxides. Nitrogen oxides are produced during combustion, even when the nitrogen content of the fuel is zero, because nitrogen is always present in the air (Box 1).

Box 1: Nitrogen Oxide Emissions from Combustion of Fossil Fuels

Since air is about 78% nitrogen and 21% oxygen by volume, nitrogen can react with oxygen to form nitric oxide. Equations 3 and 4 below show the reaction between nitrogen and oxygen in the air, and the equilibrium expression for the reaction.



$$K_{\text{eq}} = \frac{[\text{NO}]^2}{[\text{N}_2][\text{O}_2]} \quad (4)$$

For the reaction in Equation 3, $K_{\text{eq}} = 5 \times 10^{-7}$ at 298 K; hence, the equilibrium lies to the left. However, as temperature increases, the equilibrium shifts to the right. At 675 K (a realistic

temperature for the exhaust manifold in a car), $K_{eq} = 0.01$ and the ratio of NO to O_2 and N_2 , while still small, is no longer negligible. In fact, at 675 K, about 3% of the nitrogen in the air will be converted to NO. Hence, at any time we have nitrogen and oxygen in contact at high temperatures, some NO will be produced as a result. Since nitrogen and oxygen are always present together in the air when we burn gasoline or coal, some NO emissions are inevitable.

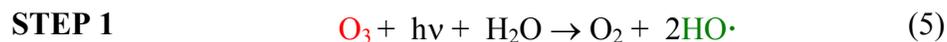
In the U.S., fossil fuels are mostly burned to operate motor vehicles and to produce electricity. As a result, car emissions are a substantial source of VOCs and nitrogen oxides across the nation. Additionally, in parts of the midwest most of the electricity comes from burning coal, which results in high nitrogen-oxide emissions. When concentrations of nitrogen oxides in air are large, noncombustion VOCs can also make a noticeable contribution to total ozone levels. Noncombustion VOCs include gasoline released into the air during refueling and solvents such as paint thinner or charcoal lighter fluid that are allowed to evaporate. Therefore, there are always nitrogen oxides and VOCs present in our atmosphere today. Before strategies can be developed to reduce ozone concentration in the lower atmosphere, we must first understand how VOCs and nitrogen oxides react to form ozone.

How Does Ozone Form?

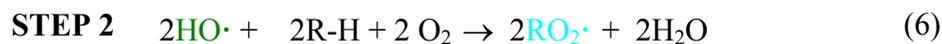
There are many combinations of simple reactions that will form ozone. The series of reactions, or steps, presented below describe one scheme for ozone formation from nitrogen oxides and VOCs. This scheme can be separated into two stages: initiation and nitrogen-oxide cycling.

Initiation

Ironically, the formation of ozone can begin with the destruction of an ozone molecule. When ozone (O_3) is photodissociated by ultraviolet light, it can react with water to form two OH radicals ($HO\cdot$) as shown below in STEP 1 (Equation 5). A radical is a compound with an unpaired electron, which is represented with a dot "." in the chemical formula. Radicals are generally very reactive.



When volatile organic hydrocarbons are present in the air from car exhaust, or other sources, each OH radical reacts with a volatile organic hydrocarbon (represented as R-H) and O_2 to produce peroxy radicals ($RO_2\cdot$, where R represents the rest of the volatile-organic-hydrocarbon molecule). The production of peroxy radicals is shown in STEP 2, Equation 6, below.



Nitrogen-Oxide Cycling and Ozone Production

Car exhaust also contains nitric oxide (as discussed in Box 1). Peroxy radicals react with nitric oxide (NO) to form nitrogen dioxide (NO₂):



Nitrogen dioxide is photodissociated by sunlight, reforming nitric oxide (STEP 4, Equation 8).

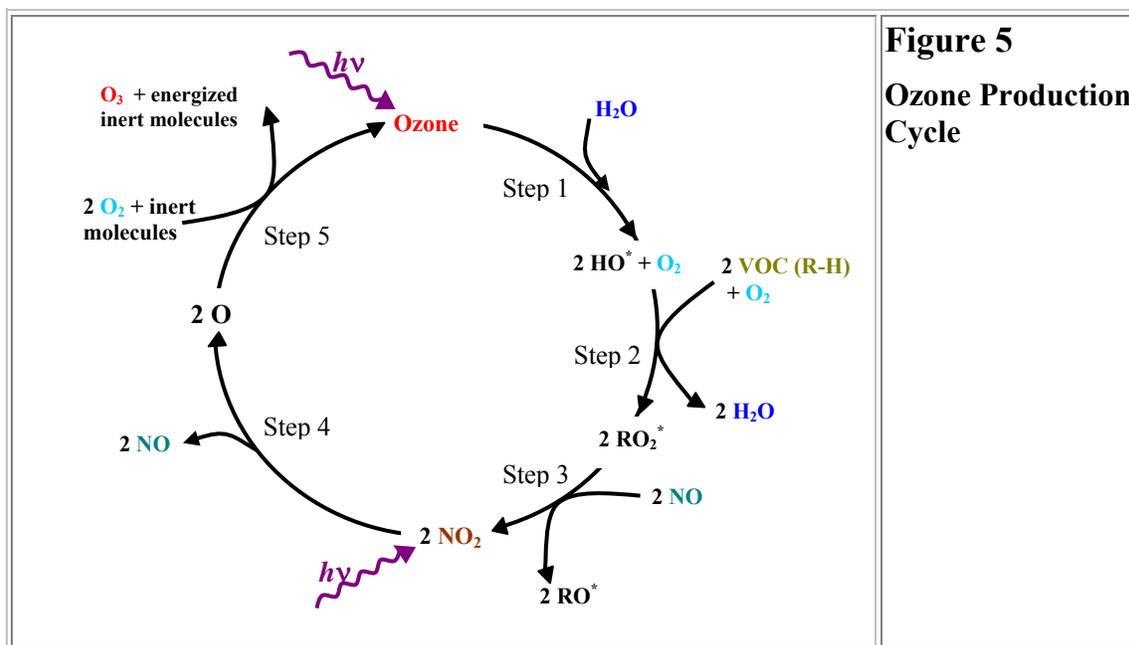


Finally, oxygen atoms formed in Step 4 unload the excess energy to an inert molecule by collision and combine with molecular oxygen to form ozone.

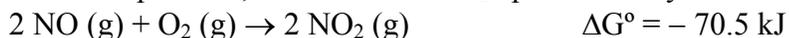


Since NO is produced in Step 4, Steps 3-5 are repeated as long as VOCs are present.

The above ozone production cycle is an example of a chain reaction, which is summarized in Figure 5. Notice that even though STEP 1 uses ozone, there is still a net production of ozone: one molecule of ozone produces two hydroxy radicals which, through a series of reactions, form two molecules of nitrogen dioxide, and eventually produce two molecules of ozone. Therefore, in order to reduce ozone levels, we need to reduce levels of nitrogen oxides and volatile organic hydrocarbons.



* Remarks: At room temperature, NO reacts with O₂ spontaneously to form NO₂.



However, the rate of this reaction is much slower than the reaction of Eq (7). Note that the NO₂ produced may react with water to form nitric acid and terminate the ozone production cycle.

$$2\text{NO}_2 + \text{H}_2\text{O} \rightarrow \text{HNO}_3 + \text{HNO}_2$$

Reducing Nitrogen Oxides and VOC Emissions

Any fossil-fuel combustion will produce some NO and VOC, and in turn increases ozone production in the lower atmosphere. There are essentially two strategies for reducing NO emissions: 1) removing pollutants (such as NO and VOC) from the post-combustion emission gases, and 2) finding alternatives to power cars that do not require the combustion of fossil fuels.

Catalytic Converters

Our main strategy until now for reducing NO emissions (and ozone levels) has been to remove NO from post-combustion emissions gases. Advances in catalytic converter technology have allowed steady progress on this front. The EPA's emissions standards for vehicles manufactured in 1980 are 6 grams/mile of nitrogen oxides and 2 grams/mile of hydrocarbons. Improved catalytic converters have made it possible to lower the maximum level of emissions for cars manufactured after 1996 to 2 grams/mile of nitrogen oxides and 0.8 grams/mile of hydrocarbons. The catalytic converter provides a noble metal (platinum or iridium) catalyst surface that promotes oxidation of VOCs and reduction of nitrogen oxides to yield innocuous products. [For more detail about how catalytic converters work, click here.](#)

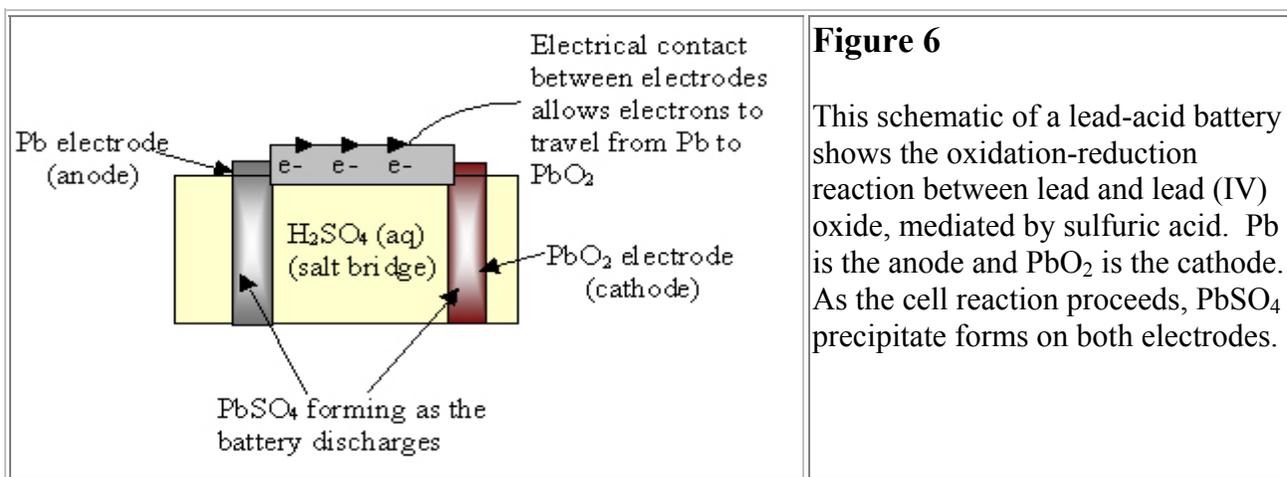
Current Technology for Electric Vehicles

One promising alternative to combustion vehicles is the zero-emission vehicle (ZEV). At this point, the only ZEVs are electric vehicles. Several car manufacturers sell electric vehicles to fleet buyers, and kits are available for individuals who want to convert ordinary cars into electric vehicles. For example, the Honda Insight and the Toyota Prius are hybrid gasoline/electric vehicles that do not require external charging. Although they are superior to ordinary gasoline vehicles in terms of both gas mileage and emissions, they are not ZEVs. Battery technology is the key to making electric vehicles. Some commercially available and most home-built electric vehicles use lead-acid batteries, similar to ordinary car batteries. To understand how to improve electric vehicles, we must first understand how batteries work.

Batteries in Electric Vehicles

Batteries are one of the most common applications of electrochemistry. Batteries harness oxidation-reduction, or redox, reactions to produce energy. All redox reactions can be separated into two half-reactions. When the oxidation half-reaction and reduction half-reaction occur in separated compartments and electrons travel from the oxidation half-cell to the reduction half-cell through a conducting wire, it produces current. This set up is called a galvanic cell (or a battery), where the reaction proceeds spontaneously and the resulting current can be used to do work such as driving an electrical motor.

Figure 6 is a schematic of a lead-acid battery (an ordinary car battery). In the lead-acid battery, Pb is oxidized to Pb^{2+} at the anode (negative battery terminal) as shown in Equation 10 and Pb^{4+} is reduced to Pb^{2+} at the cathode (positive battery terminal) as shown in Equation 11.



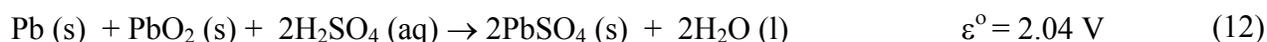
Oxidation half-reaction:



Reduction half-reaction:



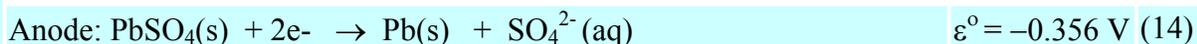
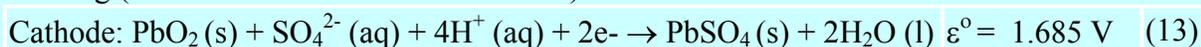
During discharge (when the battery is being used to generate electricity), the sum of the two half-reactions is the following **cell reaction**:



Common car batteries are twelve-volt batteries, because they use six lead-acid cells (each of which has $\epsilon^\circ = 2.04$ volts) connected in series and housed in a single container. Box 2 reviews electrical potentials.

Box 2: Electrical Potentials in Lead-Acid Batteries

Every half-reaction has a standard electrical potential, designated as ϵ° . By convention, we write the half-reactions as reductions; i.e., the addition of electrons to the oxidized form of the substance. The two half reactions that comprise the redox reaction in a lead-acid battery are the following (both written as reduction reactions):



ϵ° is a measure of the tendency of the reactant in the half-reaction (oxidizing agent) to accept electrons relative to $\text{H}^+ + \text{e}^- \rightarrow \frac{1}{2}\text{H}_2$ (every species in its standard state). We obtain the ϵ° for the overall reaction (or the battery) by adding together the standard potentials for the reduction reaction and the oxidation reaction. Note that since the anode half-reaction is written as a reduction reaction in Eq. 14, the sign of its ϵ° is changed when the reaction is reversed.

$$\epsilon_{\text{cell}}^\circ = \epsilon_{\text{reduction}}^\circ + \epsilon_{\text{oxidation}}^\circ = \epsilon_{\text{cathode}}^\circ - \epsilon_{\text{anode}}^\circ \quad (15)$$

Adding together the ϵ° values of the half reactions gives:

$$\epsilon_{\text{cell}}^\circ = 1.685 - (-0.356) = 2.04 \text{ V} \quad (16)$$

Recall, a potential of 2.04 V will only be measured if all the reactants and products are in their standard state, which means a concentration of 1 M for aqueous solutions. The Nernst Equation (Equation 17, below) allows us to calculate the potential when we have conditions other than the standard state.

$$\varepsilon_{\text{non}} = \varepsilon^{\circ} - \frac{RT}{nF} \ln Q \quad (17)$$

Here, R is the gas constant, 8.314 J/mol-K; T is the Kelvin temperature; n is the number of moles of electrons transferred in the cell reaction; F is the value of the Faraday constant, 9.65×10^4 C/mol (i.e., the absolute value of the charge of one mole of electrons); and Q is the reaction quotient, a quantity of the same form as the equilibrium constant but employing activities actually present in the cell rather than those at equilibrium. For the cell reaction in Eq. 12,

$$Q = \frac{1}{[H_2SO_4]^2}$$

Since all the reactants and products other than H_2SO_4 are solids or liquids that do not appear in the equilibrium expression.

To recharge the lead-acid battery, the redox reaction (Equation 12) must be run in reverse. The electrical potential for this reverse reaction is negative ($\varepsilon^{\circ} < 0$); therefore, the reaction is nonspontaneous. This means that energy is needed to drive the reaction (i.e., recharging the battery). Notice that during recharging, the $PbSO_4$ precipitate on the electrodes is oxidized and reduced to PbO_2 and Pb , respectively. Once recharging is complete, the forward reaction can run spontaneously again and create electrical work.

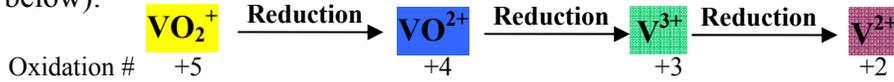
The main drawbacks using lead-acid batteries in electric vehicles are that they are heavy and must be recharged over a period of hours. Depending on the weight of the vehicle and driving conditions, twenty batteries might power the car for only forty miles. The batteries weigh up to eighty pounds each, and they take up quite a bit of space. Although the weight and volume of the internal combustion engine is eliminated, electric vehicles are still heavier than their gasoline counterparts and often sacrifice trunk space for battery storage. In addition, the discharged batteries must be plugged into a battery charger for six or more hours for recharging.

Battery technology is the bottleneck that limits widespread electric vehicle use today. Advances in battery design may yield batteries that are smaller, lighter and can be recharged faster. A large range of possibilities are being explored by researchers in universities, government labs and industrial R&D programs.

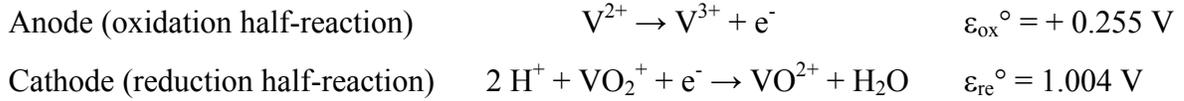
Improving Battery Technology for Electric Vehicles

One interesting approach is the vanadium-redox flow battery developed by Professor Maria Skylas-Kazacos and her team at the University of New South Wales, Australia. Recall from an experiment in Chem 151 about the stepwise reduction of vanadium(V) solution that vanadium has

several stable oxidation states in aqueous solution and each state has a characteristic color (as shown below):



The half-cell reactions in the vanadium flow batteries are:



A schematic diagram of the vanadium-redox flow cell is shown in Figure 7. The electrodes are graphite plates because graphite is chemically inert and conducts electrons well. The cathode solution and the anode solution are stored in reservoirs and pumped into the cell, which is divided by a semipermeable membrane. The membrane allows H^+ ions to pass through and therefore functions as a salt bridge to complete the circuit. When the battery is fully charged, the cathode solution is dioxovanadium(V) sulfate in sulfuric acid. During discharge, VO_2^+ is reduced to VO^{2+} ; hence, the concentration of VO_2^+ decreases gradually while the concentration of VO^{2+} increases gradually in the cathode solution. The anode solution is vanadium(II) sulfate in sulfuric acid when the battery is fully charged. During discharge, the V^{2+} ion is gradually oxidized to V^{3+} . When the electrolyte concentrations and sulfuric acid are 2 M, the cell potential is approximately 1.4 volts at 25°C. In practice, a number of cells are connected in series/parallel to provide the desired voltage/current output. The battery can be recharged if the load is replaced by a dc power source. During the re-charging process, the half-reactions shown above are reversed.

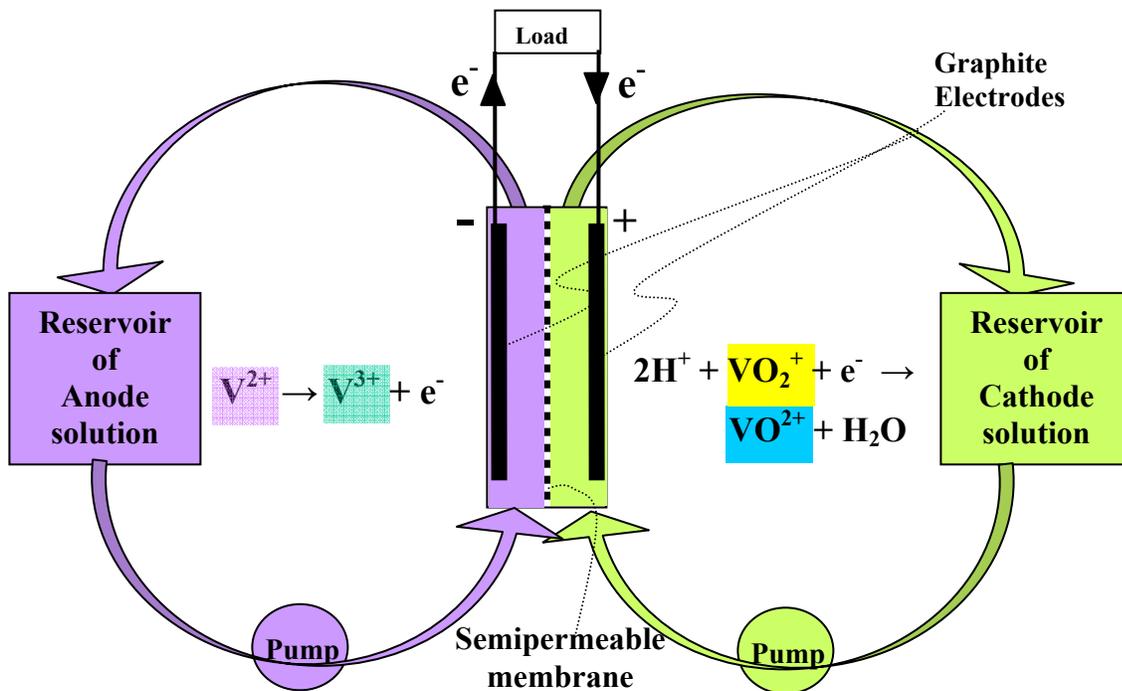


Figure 7 Schematic of a Discharging Vanadium-Redox Flow Battery

The vanadium-redox flow battery may be an excellent alternative to lead-acid batteries for electric vehicles. Since both redox couples are soluble (unlike the lead battery in which both lead, lead oxide, and lead sulfate are solids that have to be part of the electrode or deposited on the

electrode), the battery can be discharged and recharged over thousands of times without damaging the electrode. Vanadium batteries will therefore have a much longer lifetime than lead-acid batteries. Moreover, vanadium compounds are less toxic than lead compounds. The battery's most useful aspect for electric-vehicle applications is that the vanadium-flow cell can be recharged in two ways. Just like lead-acid batteries, a vanadium battery can be plugged into a charger and recharged over a period of hours. However, if one doesn't want to wait several hours for the battery to recharge, the discharged electrolyte solutions can simply be drained and replaced with fully charged electrolyte solutions. This process would not be much more time consuming than refilling a standard car with gasoline.

Although the vanadium-redox flow battery is still in its infancy, there are some wonderful examples of its practical applications around the world. One example of this is an installation at King Island, Australia, in 2003. It stores excess wind turbine power as electric energy when the wind is strong and pumps it out when the wind fades. This installation saves about 2000 tons of carbon dioxide emissions each year when compared to the power generated by diesel generators. Note that the vanadium battery is not the only flow-redox battery known. A flow-redox battery that uses iron and chromium ions was developed by NASA, for instance. However, the all-vanadium battery has a significant advantage over other flow-redox cells because mixing the electrolyte solutions does not damage the battery. If there are cross contamination of the anode solution and the cathode solution, once the battery is recharged, the vanadium ions will return to their charged oxidation states.

Summary

Good air quality is important to public health. Photochemical smog, a mixture of pollutants including ozone, is the most common air-quality problem. Background in electrochemistry and redox reactions can help us understand the causes of air pollution, its effects on our health and strategies to reduce air pollution.

The Environmental Protection Agency (EPA) is responsible for monitoring the air quality around the country. Many urban areas have ozone concentrations that exceed the standards set by the EPA. Ozone is harmful because it is a strong oxidizing agent, which can reduce the antioxidants found on the surface of the lung and can lead to lung damage.

Although ozone is a major component of photochemical smog, it is not directly produced by automobile emissions or by producing electricity (the two main activities that burn fossil fuels). Volatile organic hydrocarbons (VOCs) and nitrogen oxides, which result from the burning of fossil fuels, react in the lower atmosphere to produce ozone. Ozone concentrations are especially difficult to lower, because the mechanism for the formation of ozone contains cyclic steps, which regenerate nitrogen oxides and lead to production of additional ozone.

In the past, the focus for reducing automobile emissions has been on removing the pollutants from the post-combustion emission gases. The main strategy has been the development of more efficient catalytic converters. Catalytic converters provide noble metal surfaces that promote the reaction of nitrogen oxides with other exhaust components to yield innocuous products. However, the goal now is to develop zero-emissions vehicles.

The current ZEV are electric vehicles, and their feasibility depends on battery technology. At the heart of all batteries is an electrochemical cell. Although most electric vehicles use the lead-acid battery (which is the conventional car battery), there are a number of drawbacks such as the weight and the recharging time. Hence, many researchers are studying battery technology. One interesting new design is a vanadium-flow battery, in which the redox reaction consists of solutions instead of solid material. A current is produced through electron transfer from the vanadium (II) ions in solution on one side of the battery to the vanadium (V) ions on the other side. This design looks promising, but it is in its infancy. Battery technology remains an active area of research.

Footnotes: ¹ The 2D representations shown in Figure 3 were drawn using CS ChemDraw Pro. The coordinates for the 3D representations were obtained from molecular-modeling calculations using CS Chem3D Pro, and the images were rendered using SwissPDB Viewer and POV-Ray.

Additional Links:

- Companies like [Corning](#) provide information about their new developments in catalytic converters.
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