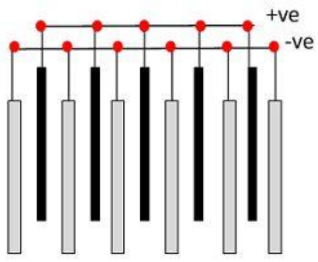
Lead Acid Battery



Arrangements of Plates in a Lead-acid-Battery

Circuit GLobe

Definition: The battery which uses sponge lead and lead peroxide for the conversion of the chemical energy into electrical power, such type of battery is called a lead acid battery. The lead acid battery is most commonly used in the power stations and substations because it has higher cell voltage and lower cost

Construction of Lead Acid Battery

The various parts of the lead acid battery are shown below. The container and the plates are the main part of the lead acid battery. The container stores chemical energy which is converted into electrical energy by the help of the plates.

1. Container – The container of the lead acid battery is made of glass, lead lined wood, ebonite, the hard rubber of bituminous compound, ceramic materials or moulded plastics and are seated at the top to avoid the discharge of electrolyte. At the bottom of the container, there are four ribs, on two of them rest the positive plate and the others support the negative plates.

The prism serves as the support for the plates and at the same time protect them from a short-circuit.The material of which the battery containers are made should be resistant to sulfuric acid, should not deform or porous, or contain impurities which damage the electrolyte.

2. Plate – The plate of the lead-acid cell is of diverse design and they all consist some form of a grid which is made up of lead and the active material. The grid is essential for conducting the electric current and for distributing the current equally on the active material. If the current is not uniformly distributed, then the active material will loosen and fall out.

The grids are made up of an alloy of lead and antimony. These are usually made with the transverse rib that crosses the places at a right angle or diagonally. The grid for the positive and negative plates are of the same design, but the grids for the negative plates are made lighter because they are not as essential for the uniform conduction of the current.

The plates of the battery are of two types. They are the formed plates or plante plates and pasted or faure plates.

Plante's plates are used largely for stationary batteries as these are heavier in weight and more costly than the pasted plates. But the plates are more durable and less liable to lose active material by rapid charging and discharging. The plantes plate has low capacity weight-ratio.
Faure process is much suitable for manufacturing of negative plates rather than positive plates. The negative active material is quite tough, and it undergoes a comparatively low change from charging and discharging.

3. Active Material – The material in a cell which takes active participation in a chemical reaction (absorption or evolution of electrical energy) during charging or discharging is called the active material of the cell. The active elements of the lead acid are

1. **Lead peroxide (PbO_2)** – It forms the positive active material. The PbO_2 are dark chocolate broom in colour.
2. **Sponge lead** – Its form the negative active material. It is grey in colour.
3. **Dilute Sulfuric Acid (H_2SO_4)** – It is used as an electrolyte. It contains 31% of sulfuric acid.

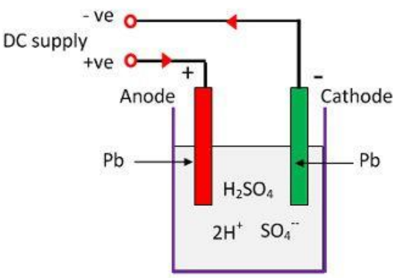
The lead peroxide and sponge lead, which form the negative and positive active materials have the little mechanical strength and therefore can be used alone.

4. Separators – The separators are thin sheets of non-conducting material made up of chemically treated leadwood, porous rubbers, or mats of glass fibre and are placed between the positive and negative to insulate them from each other. Separators are grooved vertically on one side and are smooth on the other side.

5. Battery Terminals – A battery has two terminals the positive and the negative. The positive terminal with a diameter of 17.5 mm at the top is slightly larger than the negative terminal which is 16 mm in diameter.

Working Principle of Lead Acid Battery

When the sulfuric acid dissolves, its molecules break up into positive hydrogen ions ($2H^+$) and sulphate negative ions (SO_4^{--}) and move freely. If the two electrodes are immersed in solutions and connected to DC supply then the hydrogen ions being positively charged and moved towards the electrodes and connected to the negative terminal of the supply. The SO_4^{--} ions being negatively charged moved towards the electrodes connected to the positive terminal of the supply main (i.e., anode).



Charging of Lead Acid Cells

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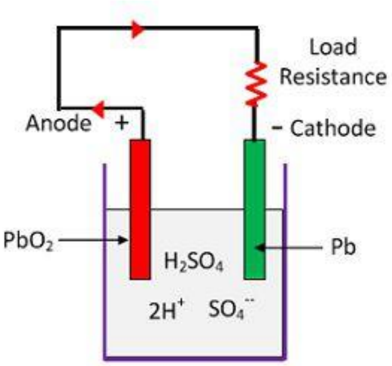
Each hydrogen ion takes one electron from the cathode, and each sulphates ions takes the two negative ions from the anodes and react with water and form sulfuric and hydrogen acid.

The oxygen, which produced from the above equation react with lead oxide and form lead peroxide (PbO_2.) Thus, during charging the lead cathode remain as lead, but lead anode gets converted into lead peroxide, chocolate in colour.
If the DC source of supply is disconnected and if the voltmeter connects between the electrodes, it will show the potential difference between them. If wire connects the electrodes, then current will flow from the positive plate to the negative plate through external circuit i.e. the cell is capable of supplying electrical energy.

Chemical Action During Discharging

When the cell is full discharge, then the anode is of lead peroxide (PbO_2) and a cathode is of metallic sponge lead (Pb). When the electrodes are connected through a resistance, the cell discharge and electrons flow in a direction opposite to that during charging.
The hydrogen ions move to the anode and reaching the anodes receive one electron from the anode and become hydrogen atom. The hydrogen atom comes in contacts with a PbO_2, so it attacks and forms lead sulphate ($PbSO_4$), whitish in colour and water according to the chemical equation.

$$\begin{array}{c} PbSO_4 + 2H = PbO + H_2O \\ PbO + H_2SO_4 = PbSO_4 + 2H_2O \\ \hline PbO_2 + H_2SO_4 + 2H = PbSO_4 + 2H_2O \end{array}$$



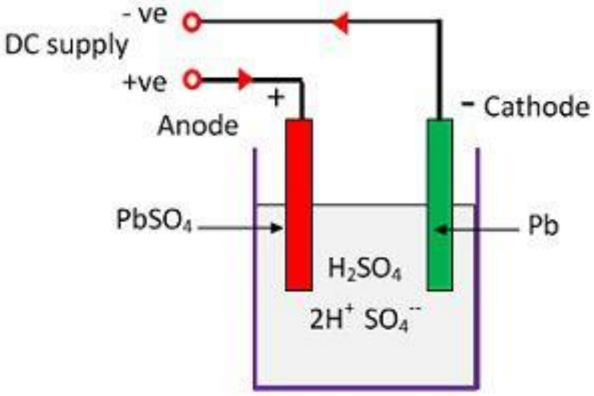
Discharging of Lead Acid Cells
Circuit Globe

The each sulphate ion (SO_4^{--}) moves towards the cathode and reaching there gives up two electrons becomes radical SO_4, attack the metallic lead cathode and form lead sulphate whitish in colour according to the chemical equation.

Chemical Action During Recharging

For recharging, the anode and cathode are connected to the positive and the negative terminal of the DC supply mains. The molecules of the sulfuric acid break up into ions of $2H^+$ and SO_4^{--}. The hydrogen ions being positively charged moved towards the cathodes and receive two electrons from there and form a hydrogen atom. The hydrogen atom reacts with lead sulphate cathode forming lead and sulfuric acid according to the chemical equation.

$$PbSO_4 + 2H_2O + 2H = PbSO_4 + 2H_2SO_4$$



Recharging of Lead Acid Cell

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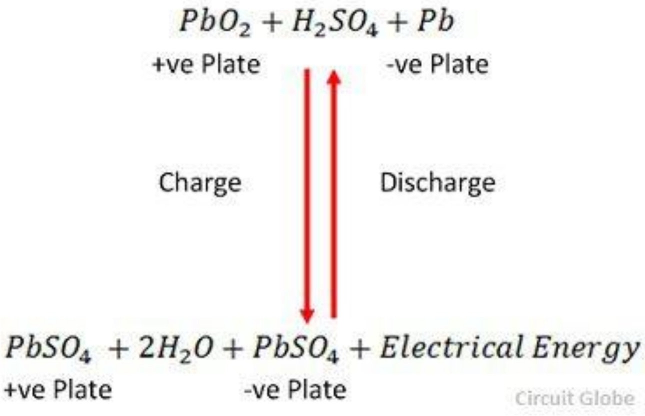
SO_4^{--} ion moves to the anode, gives up its two additional electrons becomes radical SO_4, react with the lead sulphate anode and form leads peroxide and lead sulphuric according to the chemical equation.

$$PbSO_4 + 2H = H_2SO_4 + Pb$$

The charging and discharging are represented by a single reversible equation given below.



The equation should read downward for discharge and upward for recharge.

Li ion battery

They give us all the convenience of electricity in a handy, portable form

The only trouble is, most batteries run flat very quickly and, unless one use a specialized charger, you then have to throw them away. It's hard on the pocket and bad for the environment as well: worldwide, we throw away billions of disposable batteries every single year. Rechargeable batteries help to solve this problem and the best kind use a technology called **lithium ion**. cellphone, laptop computer, and MP3 player probably all use lithium-ion batteries. They've been in widespread use since about 1991, but the basic chemistry was first discovered by American chemist Gilbert Lewis (1875–1946) way back in 1912.

The trouble with ordinary batteries

If you've read our main article on batteries, you'll know a battery is essentially a chemical experiment happening in a small metal canister. Connect the two ends of a battery to something like a flashlight and chemical reactions begin: chemicals inside the battery slowly but systematically break apart and join themselves together to make other chemicals, producing a stream of positively charged particles called **ions** and negatively charged **electrons**. The ions move through the battery; the electrons go through the circuit to which the battery's connected, providing electrical energy that drives the flashlight. The only trouble is, this chemical reaction can happen only once and in only one direction: that's why ordinary batteries usually can't be recharged.

Rechargeable batteries = reversible reactions

Different chemicals are used in rechargeable batteries and they split apart through entirely different reactions. The big difference is that the chemical reactions in a rechargeable battery are **reversible**: when the battery is discharging the reactions go one way and the battery gives out power; when the battery is charging, the reactions go in the opposite direction and the battery absorbs power. These chemical reactions can happen hundreds of times in both directions, so a rechargeable battery will typically give you anything from two or three to as much as 10 years of useful life (depending on how often you use it and how well you look after it).

How lithium-ion batteries work

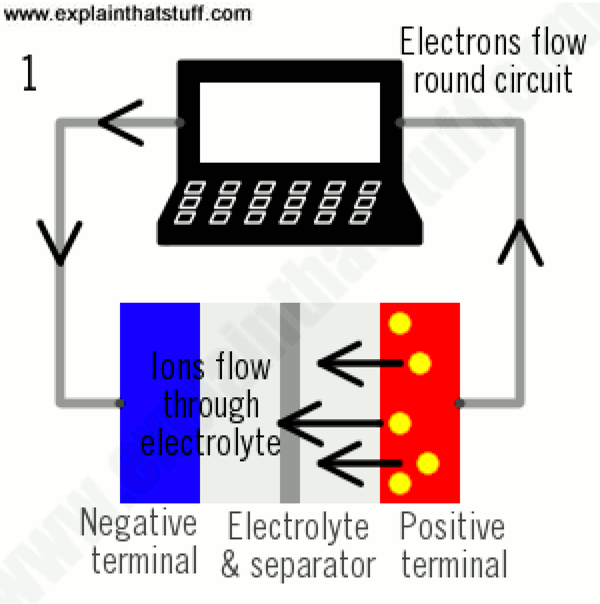
Like any other battery, a rechargeable lithium-ion battery is made of one or more power-generating compartments called **cells**. Each cell has essentially three components: a **positive electrode** (connected to the battery's positive or + terminal), a **negative electrode** (connected to the negative or − terminal), and a chemical called an **electrolyte** in between them. The positive electrode is typically made from a chemical compound called lithium-cobalt oxide ($LiCoO2$) or, in newer batteries, from lithium iron phosphate ($LiFePO4$). The negative electrode is generally made from carbon (graphite) and the electrolyte varies from one type of battery to another—but isn't too important in understanding the basic idea of how the battery works.

All lithium-ion batteries work in broadly the same way. When the battery is charging up, the lithium-cobalt oxide, positive electrode gives up some of its lithium ions, which move through the electrolyte to the negative, graphite electrode and remain there. The battery takes in and stores energy during this process. When the battery is discharging, the lithium ions move back across the electrolyte to the positive electrode, producing the energy that powers the battery. In both cases, electrons flow in the opposite direction to the ions around the outer circuit. Electrons do not flow through the electrolyte: it's effectively an insulating barrier, so far as electrons are concerned.

The movement of ions (through the electrolyte) and electrons (around the external circuit, in the opposite direction) are interconnected processes, and if either stops so does the other. If ions stop moving through the electrolyte because the battery completely discharges, electrons can't move through the outer circuit either—so you lose your power. Similarly, if you switch off whatever the battery is powering, the flow of electrons stops and so does the flow of ions. The battery essentially stops discharging at a high rate (but it does keep on discharging, at a very slow rate, even with the appliance disconnected).

Unlike simpler batteries, lithium-ion ones have built in electronic controllers that regulate how they charge and discharge. They prevent the overcharging and overheating that can cause lithium-ion batteries to explode in some circumstances

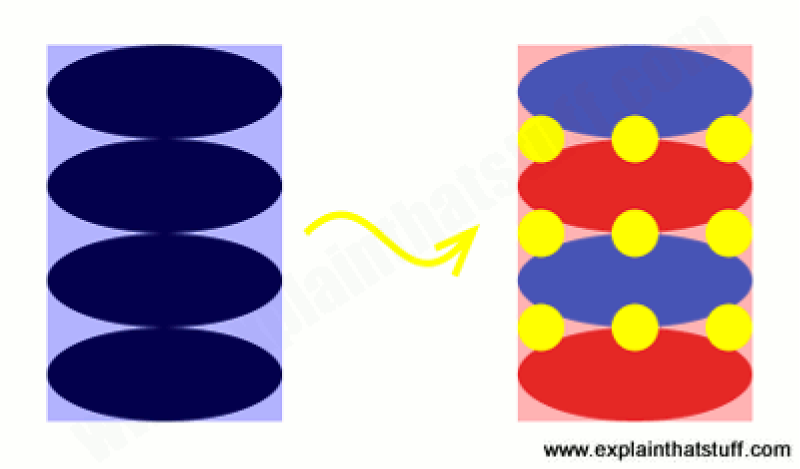
How a lithium-ion battery charges and discharges



As their name suggests, lithium-ion batteries are all about the movement of lithium ions: the ions move one way when the battery charges (when it's absorbing power); they move the opposite way when the battery discharges (when it's supplying power):

1. During charging, lithium ions (yellow circles) flow from the positive electrode (red) to the negative electrode (blue) through the electrolyte (gray). Electrons also flow from the positive electrode to the negative electrode, but take the longer path around the outer circuit. The electrons and ions combine at the negative electrode and deposit lithium there.
2. When no more ions will flow, the battery is fully charged and ready to use.
3. During discharging, the ions flow back through the electrolyte from the negative electrode to the positive electrode. Electrons flow from the negative electrode to the positive electrode through the outer circuit, powering your laptop. When the ions and electrons combine at the positive electrode, lithium is deposited there.
4. When all the ions have moved back, the battery is fully discharged and needs charging up again.

How are the lithium ions stored?



lithium ions are stored in the negative graphite electrode (left) and positive cobalt-oxide electrode (right).

This figure shows what's going on in the battery in a bit more detail. Again, the negative graphite electrode (blue) is shown on the left, the positive cobalt-oxide electrode (red) on the right, and the lithium ions are represented by yellow circles. When the battery is fully charged, all the lithium ions are stored between layers of graphene (sheets of carbon one atom thick) in the graphite electrode (they have all moved over to the left). In this charged-up state, the battery is effectively a multi-layer sandwich: graphene layers alternate with lithium ion layers. As the battery discharges, the ions migrate from the graphite electrode to the cobalt-oxide electrode (from left to right). When it's fully discharged, all the lithium ions have moved over to the cobalt-oxide electrode on the right. Once again, the lithium ions sit in layers, in between layers of cobalt ions (red) and oxide ions (blue). As the battery charges and discharges, the lithium ions shunt back and forth from one electrode to the other.

Advantages of lithium-ion batteries

Generally, lithium ion batteries are more reliable than older technologies such as nickel-cadmium (NiCd, pronounced "nicad") and don't suffer from a problem known as the "memory effect" (where nicad batteries *appear* to become harder to charge unless they're discharged fully first). Since lithium-ion batteries don't contain cadmium (a toxic, heavy metal), they are also (in theory, at least) better for the environment—although dumping any batteries (full of metals, plastics, and other assorted chemicals) into landfills is never a good thing. Compared to heavy-duty rechargeable batteries (such as the lead-acid ones used to start cars), lithium-ion batteries are relatively light for the amount of energy they store.

Disadvantages of lithium-ion batteries

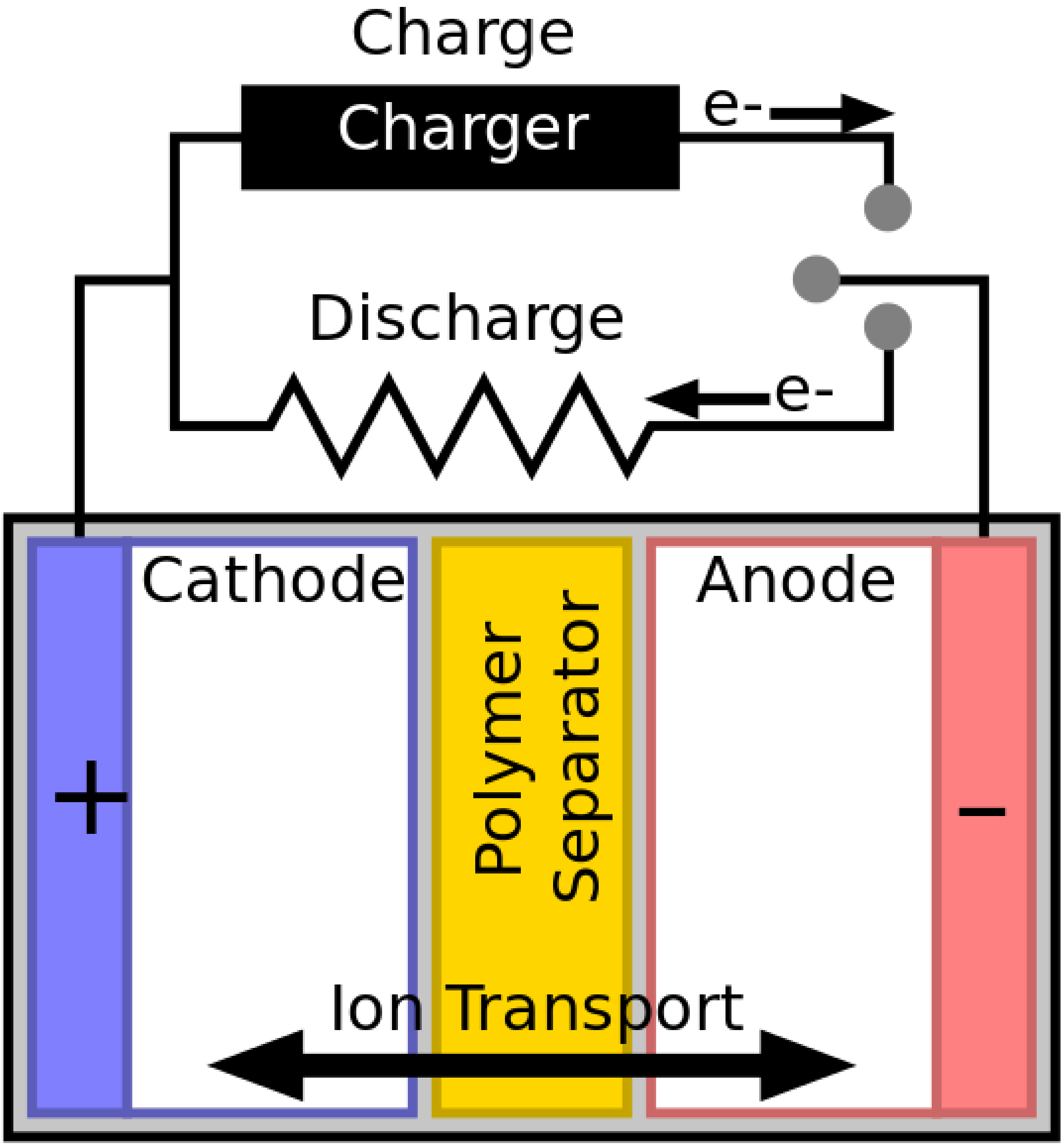
If we're interested in the drawbacks of lithium-ion batteries, it's important to bear in mind what we're comparing them with. As a power source for automobiles, we really need to compare them not with other types of batteries but with *gasoline*. Despite considerable advances over the years, kilo for kilo, rechargeable batteries still store only a fraction as much energy as ordinary gas; in more scientific words, they have a much lower energy density (they store less energy per unit of weight). That also explains why you can fully "recharge" (refuel) a gas-powered automobile in a couple of minutes, whereas it'll generally take you *hours* to recharge the batteries in an electric car. Then again, you have to bear in mind that these disadvantages are balanced by other advantages, such as the greater fuel economy of electric cars and their relative lack of air pollution (zero tailpipe/exhaust emissions from the vehicle itself).

The big difference between solid-state batteries and other types of batteries is the use of solid electrolytes, rather than the liquid electrolytes used in other batteries. Lithium-ion batteries have seen technological advances, but experts widely believe that lithium-ion technology has reached the limits of its efficiency. The next step into the future requires a different type of battery, and that’s where solid-state batteries come into the picture.

Solid-state batteries are smaller, lighter, and provide greater power density than lithium-ion batteries based on liquid electrolytes. The main challenge to their widespread adoption has been the search for a solid electrolyte with sufficient conductive capacity for large batteries, as well as a manufacturing method that allows for economies of scale.

How Does a Battery Work?

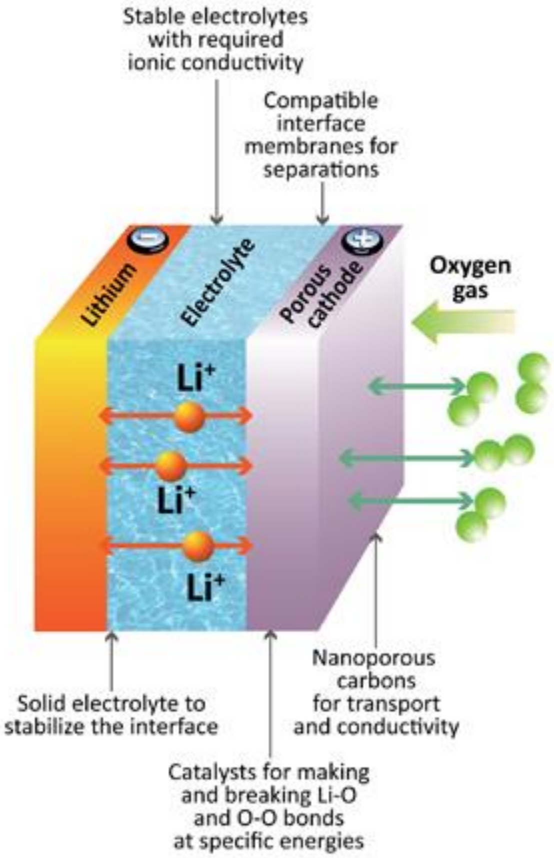
All batteries have three primary parts: the anode, the cathode, and the electrolyte. A battery works because charged ions want to travel from the cathode to the anode through the electrolyte. This happens because the carefully-chosen battery components create a chemical reaction that produces free electrons. As a result, a positive charge builds up on the battery’s cathode. This attracts the negatively charged free electrons from the anode. Those free electrons want to travel from anode to cathode. As they do, they power your device.



Keep in mind that electrical and chemical forces always want to equalize. Picture a charged battery like a seesaw tilted in one direction. The charges want to slide down this plane until the reaction is equalized. Recharging moves all the ions back into their starting positions. Imagine charging as cranking up our unbalanced seesaw from the previous metaphor.

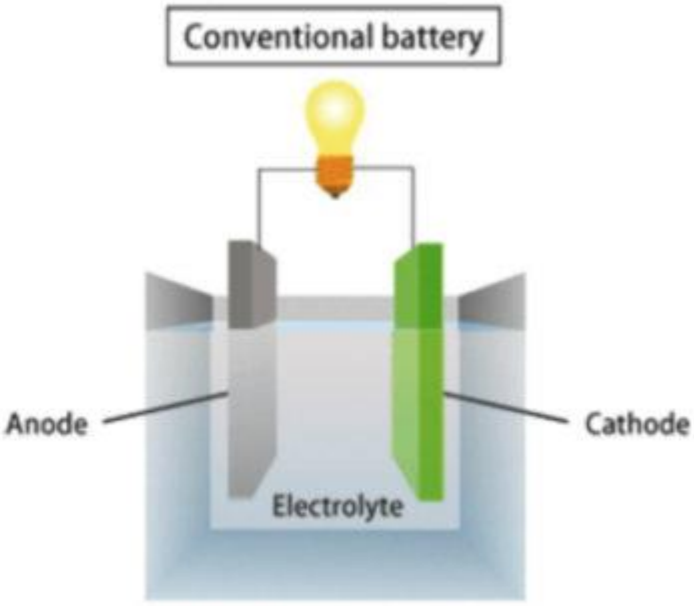
How Are Modern Batteries Better?

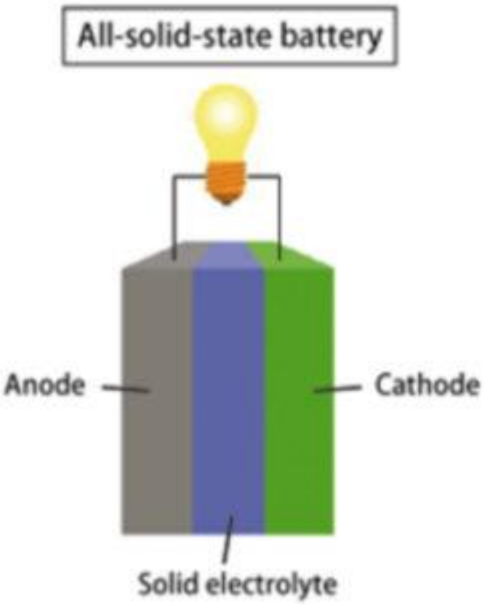
Only some materials are capable of working as batteries, so components have to be chosen very carefully based on their chemical properties. As a result, advancing battery tech either involves improving the efficiency of an existing battery material or discovering new materials that work better. And since we've looked in all the obvious places for battery improvements, now we have to start looking under the rocks of nanotechnology and material science. Solid-state batteries are one of the discoveries to come out of that process, using different electrolytes to achieve the same goal as any other type of battery, but faster, cheaper, and less prone to exploding.



The electrolyte best poised to replace lithium-ion batteries is a sodium-based glass electrolyte. According to researchers, a glass electrolyte produces a battery with three times the energy density of a lithium-ion battery. The sodium required for manufacturing these batteries is plentiful. This dramatically reduces the ecological impact of battery production.

How Are Solid-State Batteries Better?



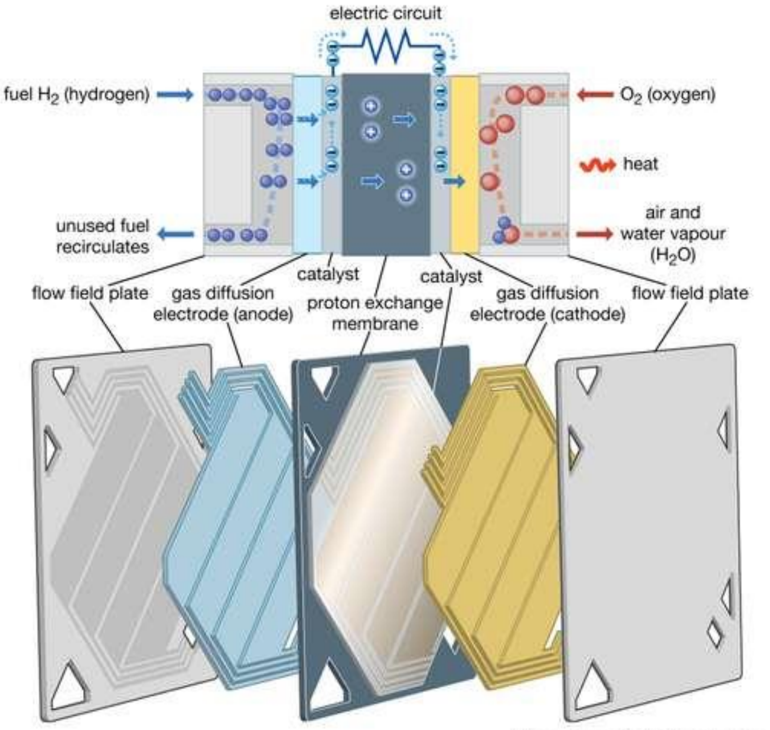


Solid-state batteries improve lithium-ion batteries by using a solid electrolyte in place of a liquid or polymer electrolyte. It just so happens that this change improves nearly all the battery’s characteristics. Solid-state batteries tick all the boxes of our fantasy battery tech. They’re lightweight, have a low environmental impact, use plentiful components, are less likely to catch fire, and offer more power.

The one problem is the manufacturing process. We’re still figuring out how to make these batteries cheaply and at scale. Right now, solid-state batteries are too expensive for widespread adoption. Fortunately, we’re very good at finding novel ways to make things more efficiently. Solid-state batteries should eventually yield to economies of scale and see broad adoption.

Fuel Cell

Fuel cell, any of a class of devices that convert the chemical energy of a fuel directly into electricity by electrochemical reactions. A fuel cell resembles a battery in many respects, but it can supply electrical energy over a much longer period of time. This is because a fuel cell is continuously supplied with fuel and air (or oxygen) from an external source, whereas a battery contains only a limited amount of fuel material and oxidant that are depleted with use. For this reason fuel cells have been used for decades in space probes, satellites, and manned spacecraft. Around the world thousands of stationary fuel cell systems have been installed in utility power plants, hospitals, schools, hotels, and office buildings for both primary and backup power; many waste-treatment plants use fuel cell technology to generate power from the methane gas produced by decomposing garbage.



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Proton exchange membrane (PEM) fuel cell. The proton exchange membrane is one of the most advanced fuel cell designs. Hydrogen gas under pressure is forced through a catalyst, typically made of platinum, on the anode (negative) side of the fuel cell. At this catalyst, electrons are stripped from the hydrogen atoms and carried by an external electric circuit to the cathode (positive) side. The positively charged hydrogen ions (protons) then pass through the proton exchange membrane to the catalyst on the cathode side, where they react with oxygen and the electrons from the electric circuit to form water vapour (H_2O) and heat. The electric circuit is used to do work, such as power a motor.

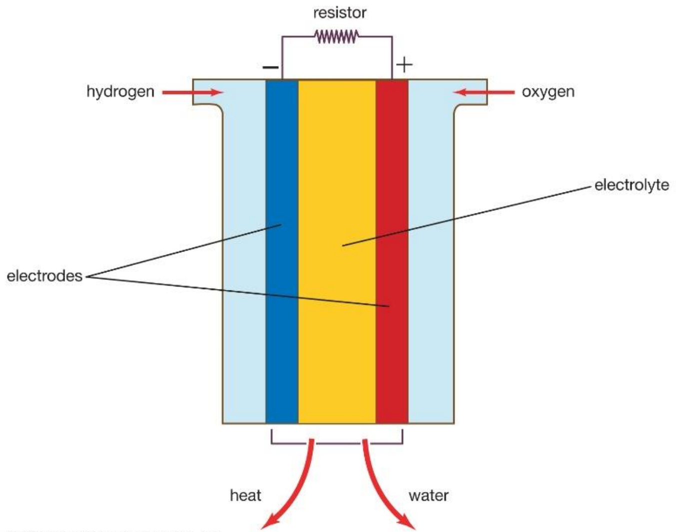
The United States government and several state governments, most notably California, have launched programs to encourage the development and use of hydrogen fuel cells in transportation and other applications. While the technology has proven to be workable, efforts to make it commercially competitive have been less successful because of concern with the explosive power of hydrogen, the relatively low energy density of hydrogen, and the high cost of platinum catalysts used to create an electric current by separating electrons from hydrogen atoms.

Principles of operation

From chemical energy to electrical energy

A fuel cell (actually a group of cells) has essentially the same kinds of components as a battery. As in the latter, each cell of a fuel cell system has a matching pair of electrodes.

These are the anode, which supplies electrons, and the cathode, which absorbs electrons. Both electrodes must be immersed in and separated by an electrolyte, which may be a liquid or a solid but which must in either case conduct ions between the electrodes in order to complete the chemistry of the system. A fuel, such as hydrogen, is supplied to the anode, where it is oxidized, producing hydrogen ions and electrons. An oxidizer, such as oxygen, is supplied to the cathode, where the hydrogen ions from the anode absorb electrons from the latter and react with the oxygen to produce water. The difference between the respective energy levels at the electrodes (electromotive force) is the voltage per unit cell. The amount of electric current available to the external circuit depends on the chemical activity and amount of the substances supplied as fuels. The current-producing process continues for as long as there is a supply of reactants, for the electrodes and electrolyte of a fuel cell, unlike those in a regular battery, are designed to remain unchanged by chemical reaction.



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A practical fuel cell is necessarily a complex system. It must have features to boost the activity of the fuel, pumps and blowers, fuel-storage containers, and a variety of sophisticated sensors and controls with which to monitor and adjust the operation of the system. The operating capability and lifetime of each of these system design features may limit the performance of the fuel cell.

As in the case of other electrochemical systems, fuel cell operation is dependent on temperature. The chemical activity of the fuels and the value of the activity promoters, or catalysts, are reduced by low temperatures (e.g., 0 °C, or 32 °F). Very high temperatures, on the other hand, improve the activity factors but may reduce the functioning lifetime of the electrodes, blowers, construction materials, and sensors. Each type of fuel cell thus has an operating-temperature design range, and a significant departure from this range is likely to diminish both capacity and lifetime.

A fuel cell, like a battery, is inherently a high-efficiency device. Unlike internal-combustion machines, in which a fuel is burned and gas is expanded to do work, the fuel cell converts chemical energy directly into electrical energy. Because of this fundamental characteristic, fuel cells may convert fuels to useful energy at an efficiency as high as 60 percent, whereas the internal-combustion engine is limited to efficiencies near 40 percent or less. The high efficiency means that much less fuel and a smaller storage container are needed for a fixed energy requirement. For this reason, fuel cells are an attractive power supply for space missions of limited duration and for other situations where fuel is very expensive and difficult to supply. They also emit no noxious gases such as nitrogen dioxide and produce virtually no noise during operation, making them contenders for local municipal power-generation stations.

A fuel cell can be designed to operate reversibly. In other words, a hydrogen-oxygen cell that produces water as a product can be made to regenerate hydrogen and oxygen. Such a regenerative fuel cell entails not only a revision of electrode design but also the introduction of special means for separating the product gases. Eventually, power modules comprising this type of high-efficiency fuel cell, used in conjunction with large arrays of thermal collectors for solar heating or other solar energy systems, may be utilized to keep energy-cycle costs lower in longer-lived equipment. Major automobile companies and electrical-machinery manufacturing companies worldwide have announced their intention to produce or use fuel cells commercially in the next few years.

Designing fuel cell systems

Because a fuel cell produces electricity continuously from fuel, it has many output characteristics similar to those of any other direct-current (DC) generator system. A DC generator system can be operated in either of two ways from a planning viewpoint: (1) fuel may be burned in a heat engine to drive an electric generator, which makes power available and current flow, or (2) fuel may be converted to a form suitable for a fuel cell, which then generates power directly.

A wide range of liquid and solid fuels may be used for a heat-engine system, while hydrogen, reformed natural gas (i.e., methane that has been converted to hydrogen-rich gas), and methanol are the primary fuels available for current fuel cells. If fuels such as natural gas must be altered in composition for a fuel cell, the net efficiency of the fuel cell system is reduced, and much of its efficiency advantage is lost. Such an “indirect” fuel cell system would still display an efficiency advantage as high as 20 percent. Nonetheless, to be competitive with modern thermal generating plants, a fuel cell system must attain a good design balance with low internal electrical losses, corrosion-resistant electrodes, an electrolyte of constant composition, low catalyst costs, and ecologically acceptable fuels.

The first technical challenge that must be overcome in developing practical fuel cells is to design and assemble an electrode that allows the gaseous or liquid fuel to contact a catalyst and an electrolyte at a group of solid sites that do not change very rapidly. Thus, a three-phase reaction situation is typical on an electrode that must also serve as an electrical conductor. Such can be provided by thin sheets that have (1) a waterproof layer usually with polytetrafluoroethylene (Teflon), (2) an active layer of a catalyst (e.g., platinum, gold, or a complex organometallic compound on a carbon base), and (3) a conducting layer to carry the current generated in or out of the electrode. If the electrode floods with electrolyte, the operation rate will become very slow at best. If the fuel breaks through to the electrolyte side of the electrode, the electrolyte compartment may become filled with gas or vapour, inviting an explosion should the oxidizing gas also reach the electrolyte compartment or the fuel gas enter the oxidizing gas compartment. In short, to maintain stable operation in a working fuel cell, careful design, construction, and pressure control are essential. Because fuel cells have been used on Apollo lunar flights as well as on all other U.S. orbital manned space missions (e.g., those of Gemini and the space shuttle), it is evident that all three requirements can be met reliably.

Providing a fuel cell support system of pumps, blowers, sensors, and controls for maintaining fuel rates, electric current load, gas and liquid pressures, and fuel cell temperature remains a major engineering design challenge. Significant improvements in the service life of these components under adverse conditions would contribute to the wider use of fuel cells.

Types of fuel cells

Various types of fuel cells have been developed. They are generally classified on the basis of the electrolyte used, because the electrolyte determines the operating temperature of a system and in part the kind of fuel that can be employed.

Alkaline fuel cells

These are devices that, by definition, have an aqueous solution of sodium hydroxide or potassium hydroxide as the electrolyte. The fuel is almost always hydrogen gas, with oxygen (or oxygen in air) as the oxidizer. However, zinc or aluminum could be used as an anode if the by-product oxides were efficiently removed and the metal fed continuously as a strip or as a powder. Fuel cells generally operate at less than 100 °C (212 °F) and are constructed of metal and certain plastics. Electrodes are made of carbon and a metal such as nickel. Water, as a reaction product, must be removed from the system, usually by evaporation from the electrolyte either through the electrodes or in a separate evaporator. The operating support system presents a significant design problem. The strong, hot alkaline electrolyte attacks most plastics and tends to penetrate structural seams and joints. This problem has been overcome, however, and alkaline fuel cells are used on the U.S. space shuttle orbiters. Overall efficiencies range from 30 to 80 percent, depending on the fuel and oxidizer and on the basis for the calculation.

Phosphoric acid fuel cells

Such cells have an orthophosphoric acid electrolyte that allows operation up to about 200 °C (400 °F). They can use a hydrogen fuel contaminated with carbon dioxide and an oxidizer of air or oxygen. The electrodes consist of catalyzed carbon and are arranged in pairs set back-to-back to create a series generation circuit. The framing structure for this assembly of cells is made of graphite, which markedly raises the cost. The higher temperature and aggressive hot phosphate create structural design problems, particularly for joints, supporting pumps, and sensors. Phosphoric acid fuel cells have been proposed and tested on a limited scale for local municipal power stations and for remote-site generators.

Molten carbonate fuel cells

Fuel cells of this type operate quite differently from those so far discussed. The fuel consists of a mixture of hydrogen and carbon monoxide generated from water and a fossil fuel. The electrolyte is molten potassium lithium carbonate, which requires an operating temperature of about 650 °C (1,200 °F). Warming up to operational temperatures may take several hours, making these cells unsuitable for vehicles. In most cases, the electrodes are metallic-based, and the containment system is made of metals and special engineering plastics. Such combinations of materials are anticipated to be relatively inexpensive, perhaps only three times that of the alkaline fuel cell and less than that of the phosphoric acid variety. The cells combine the hydrogen and carbon monoxide first with the carbonate electrolyte and then with oxidizing oxygen to produce a reaction product of water vapour and carbon dioxide.

Molten carbonate fuel cells are expected to be useful in both local and larger power stations. Efficiencies of 45 percent may be attained where fossil fuels are already used. Operation at high temperatures creates a design problem for long-lived system parts and joints, especially if the cells must be heated and cooled frequently. The toxic fuel and high temperature together make power plant safety an area of special concern in engineering design and testing as well as in commercial operation.

Solid oxide fuel cells

In some ways solid oxide fuel cells are similar to molten carbonate devices. Most of the cell materials, however, are special ceramics with some nickel. The electrolyte is an ion-conducting oxide such as zirconia treated with yttria. The fuel for these experimental cells is expected to be hydrogen combined with carbon monoxide, just as for molten carbonate cells. While internal reactions would be different in terms of path, the cell products would be water vapour and carbon dioxide. Because of the high operating temperatures (900 to 1,000 °C, or 1,600 to 1,800 °F), the electrode reactions proceed very readily. As in the case of the molten carbonate fuel cell, there are many engineering challenges involved in creating a long-lived containment system for cells that operate at such a high-temperature range.

Solid oxide fuel cells would be designed for use in central power-generation stations where temperature variation could be controlled efficiently and where fossil fuels would be available. The system would in most cases be associated with the so-called bottoming steam (turbine) cycle—i.e., the hot gas product (at 1,000 °C) of the fuel cell could be used to generate steam to run a turbine and extract more power from heat energy. Overall efficiencies of 60 percent might be possible.

Solid polymer electrolyte fuel cells

A cell of this sort is built around an ion-conducting membrane such as Nafion (trademark for a perfluorosulfonic acid membrane). The electrodes are catalyzed carbon, and several construction alignments are feasible. Solid polymer electrolyte cells function well (as attested to by their performance in Gemini spacecraft), but cost estimates are high for the total system compared with the types described above. Engineering or electrode design improvements could change this disadvantage.

Development of fuel cells

The general concept of a fuel battery, or fuel cell, dates back to the early days of electrochemistry. British physicist William Grove used hydrogen and oxygen as fuels catalyzed on platinum electrodes in 1839. During the late 1880s two British chemists—Carl Langer and German-born Ludwig Mond—developed a fuel cell with a longer service life by employing a porous nonconductor to hold the electrolyte. It was subsequently found that a carbon base permitted the use of much less platinum, and the German chemist Wilhelm Ostwald proposed, as a substitute for heat-engine generators, electrochemical cells in which carbon would be oxidized to carbon dioxide by oxygen. During the early years of the 20th century, Fritz Haber and Walther H. Nernst in Germany and Edmond Bauer in France experimented with cells using a solid electrolyte. Limited success and high costs, however, suppressed interest in continuing developmental efforts.

From 1932 until well after World War II, British engineer Francis Thomas Bacon and his coworkers at the University of Cambridge worked on creating practical hydrogen-oxygen fuel cells with an alkaline electrolyte. Research resulted in the invention of gas-diffusion electrodes in which the fuel gas on one side is effectively kept in controlled contact with an aqueous electrolyte on the other side. By mid-century O.K. Davtyan of the Soviet Union had published the results of experimental work on solid electrolytes for high-temperature fuel cells and for both high- and low-temperature alkaline electrolyte hydrogen-oxygen cells.

The need for highly efficient and stable power supplies for space satellites and manned spacecraft created exciting new opportunities for fuel cell development during the 1950s and ’60s. Molten carbonate cells with magnesium oxide pressed against the electrodes were demonstrated by J.A.A. Ketelaar and G.H.J. Broers of the Netherlands, while the very thin Teflon-bonded, carbon-metal hybrid electrode was devised by other researchers. Many other technological advances, including the development of new materials, played a crucial role in the emergence of today’s practical fuel cells. Further improvements in electrode materials and construction, combined with the rising costs of fossil fuels, are expected to make fuel cells an increasingly attractive alternative power source, especially in Japan and other countries that have meagre nonrenewable energy resources. At the beginning of the 21st century, many electrical-equipment manufacturers were developing power-generation equipment based on fuel cell technology.

The American military is funding development of small fuel cells for soldiers to carry in their backpacks in order to power various electronic devices, for powering small pilotless reconnaissance aircraft, and for powering robots to clear minefields.

What are solar cells?

A **solar cell** is an electronic device that catches sunlight and turns it directly into electricity. It's about the size of an adult's palm, octagonal in shape, and colored bluish black. Solar cells are often bundled together to make larger units called **solar modules**, themselves coupled into even bigger units known as **solar panels** (the black- or blue-tinted slabs you see on people's homes—typically with several hundred individual solar cells per roof) or chopped into chips (to provide power for small gadgets like pocket calculators and digital watches).

Just like the cells in a battery, the cells in a solar panel are designed to generate electricity; but where a battery's cells make electricity from chemicals, a solar panel's cells generate power by capturing sunlight instead. They are sometimes called photovoltaic (PV) cells

because they use sunlight ("photo" comes from the Greek word for light) to make electricity (the word "voltaic" is a reference to Italian electricity pioneer Alessandro Volta, 1745–1827).

We can think of light as being made of tiny particles called **photons**, so a beam of sunlight is like a bright yellow fire hose shooting trillions upon trillions of photons our way. Stick a solar cell in its path and it catches these energetic photons and converts them into a flow of electrons—an electric current. Each cell generates a few volts of electricity, so a solar panel's job is to combine the energy produced by many cells to make a useful amount of electric current and voltage. Virtually all of today's solar cells are made from slices of silicon (one of the most common chemical elements on Earth, found in sand), although as we'll see shortly, a variety of other materials can be used as well (or instead). When sunlight shines on a solar cell, the energy it carries blasts electrons out of the silicon. These can be forced to flow around an electric circuit and power anything that runs on electricity. That's a pretty simplified explanation! Now let's take a closer look...

How are solar cells made?

Photo: A single solar cell. Picture by Rick Mitchell, courtesy of US Department of Energy/National Renewable Energy Laboratory (DOE/NREL).

Silicon is the stuff from which the transistors (tiny switches) in microchips are made—and solar cells work in a similar way. Silicon is a type of material called a semiconductor. Some materials, notably metals, allow electricity to flow through them very easily; they are called conductors. Other materials, such as plastics and wood, don't really let electricity flow through them at all; they are called insulators. Semiconductors like silicon are neither conductors nor insulators: they don't normally conduct electricity, but under certain circumstances we can make them do so.

A solar cell is a sandwich of two different layers of silicon that have been specially treated or doped so they will let electricity flow through them in a particular way. The lower layer is doped so it has slightly too few electrons. It's called p-type or positive-type silicon (because electrons are negatively charged and this layer has too few of them). The upper layer is doped the opposite way to give it slightly too many electrons. It's called n-type or negative-type silicon. (You can read more about semiconductors and doping in our articles on transistors and integrated circuits.)

When we place a layer of n-type silicon on a layer of p-type silicon, a barrier is created at the **junction** of the two materials (the all-important border where the two kinds of silicon meet up). No electrons can cross the barrier so, even if we connect this silicon sandwich to a flashlight, no current will flow: the bulb will not light up. But if we shine light onto the sandwich, something remarkable happens. We can think of the light as a stream of energetic "light particles" called photons. As photons enter our sandwich, they give up their energy to the atoms in the silicon. The incoming energy knocks electrons out of the lower, p-type layer so they jump across the barrier to the n-type layer above and flow out around the circuit. The more light that shines, the more electrons jump up and the more current flows.

This is what we mean by photovoltaic—light making voltage—and it's one kind of what scientists call the photoelectric effect.

How do solar cells work?

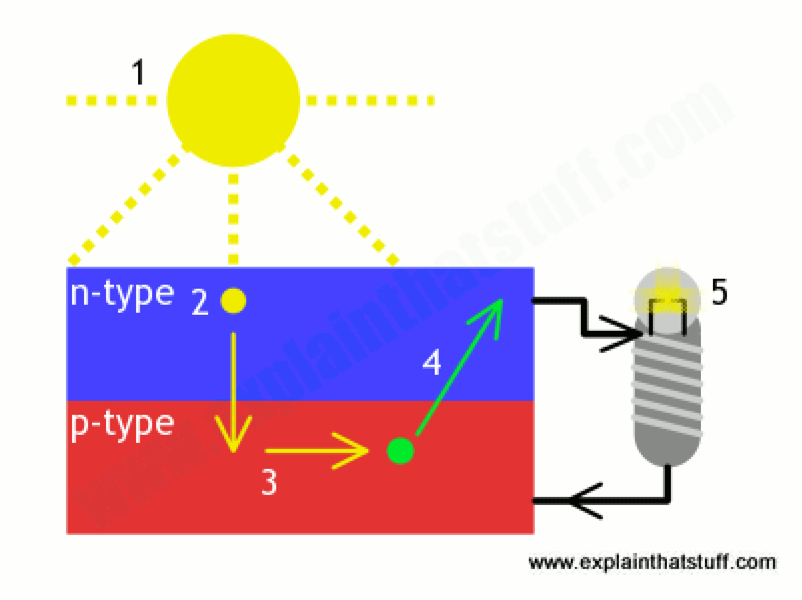


Figure: How a simple, single-junction solar cell works.

A solar cell is a sandwich of n-type silicon (blue) and p-type silicon (red). It generates electricity by using sunlight to make electrons hop across the junction between the different flavors of silicon:

1. When sunlight shines on the cell, photons (light particles) bombard the upper surface.
2. The photons (yellow blobs) carry their energy down through the cell.
3. The photons give up their energy to electrons (green blobs) in the lower, p-type layer.
4. The electrons use this energy to jump across the barrier into the upper, n-type layer and escape out into the circuit.
5. Flowing around the circuit, the electrons make the lamp light up.

How efficient are solar cells?

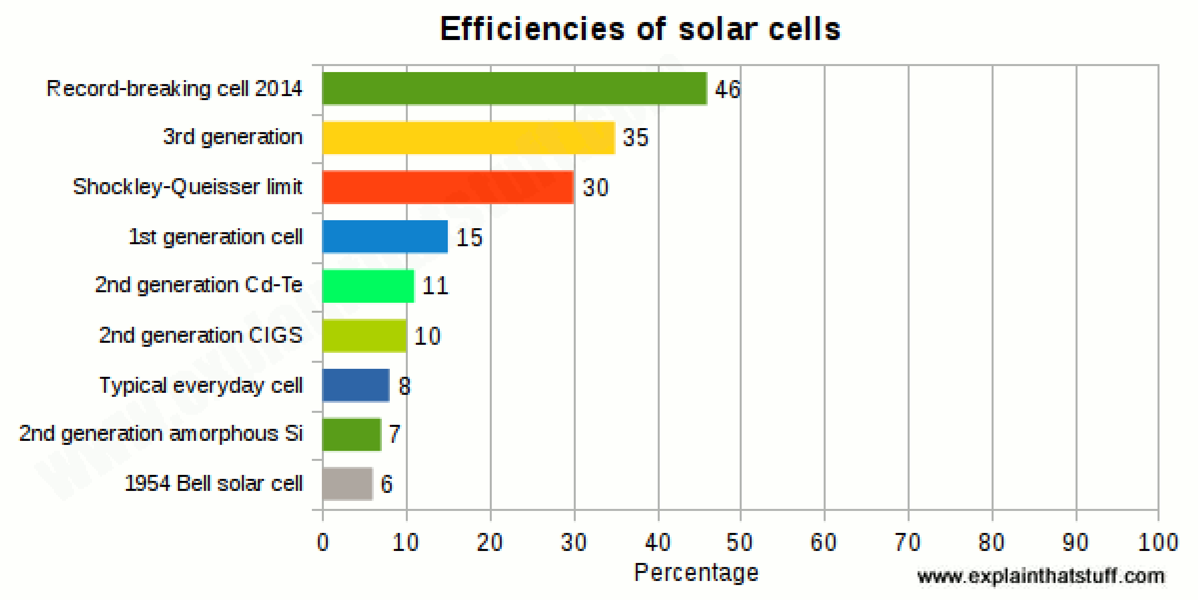


Chart: Efficiencies of solar cells compared: The very first solar cell scraped in at a mere 6 percent efficiency; the most efficient one that's been produced to date managed 46 percent in laboratory conditions. Most cells are first-generation types that can manage about 15 percent in theory and probably 8 percent in practice.

A basic rule of physics called the law of conservation of energy says that we can't magically create energy or make it vanish into thin air; all we can do is convert it from one form to another. That means a solar cell can't produce any more electrical energy than it receives each second as light. In practice, as we'll see shortly, most cells convert about 10–20 percent of the energy they receive into electricity. A typical, single-junction silicon solar cell has a theoretical maximum efficiency of about 30 percent, known as the **Shockley-Queisser limit**. That's essentially because sunlight contains a broad mixture of photons of different wavelengths and energies and any single-junction solar cell will be optimized to catch photons only within a certain frequency band, wasting the rest. Some of the photons striking a solar cell don't have *enough* energy to knock out electrons, so they're effectively wasted, while some have too much energy, and the excess is also wasted. The very best, cutting-edge laboratory cells can manage 46 percent efficiency in absolutely perfect conditions using multiple junctions to catch photons of different energies.

Real-world domestic solar panels might achieve an efficiency of about 15 percent, give a percentage point here or there, and that's unlikely to get much better. First-generation, single-junction solar cells aren't going to approach the 30 percent efficiency of the Shockley-Queisser limit, never mind the lab record of 46 percent. All kinds of pesky real-world factors will eat into the nominal efficiency, including the construction of the panels, how they are positioned and angled, whether they're ever in shadow, how clean you keep them, how hot they get (increasing temperatures tend to lower their efficiency), and whether they're ventilated (allowing air to circulate underneath) to keep them cool.

Types of photovoltaic solar cells

Most of the solar cells you'll see on people's roofs today are essentially just silicon sandwiches, specially treated ("doped") to make them better electrical conductors. Scientists refer to these classic solar cells as first-generation, largely to differentiate them from two different, more modern technologies known as second- and third-generation. So what's the difference?

First-generation

Photo: A colorful collection of first-generation solar cells. Picture courtesy of NASA Glenn Research Center (NASA-GRC).

About 90 percent of the world's solar cells are made from wafers of crystalline silicon (abbreviated c-Si), sliced from large ingots, which are grown in super-clean laboratories in a process that can take up to a month to complete. The ingots either take the form of single crystals (**monocrystalline** or mono-Si) or contain multiple crystals (**polycrystalline**, multi-Si or poly c-Si). First-generation solar cells work like we've shown in the box up above: they use a single, simple junction between n-type and p-type silicon layers, which are sliced from separate ingots. So an n-type ingot would be made by heating chunks of silicon with small amounts of phosphorus, antimony, or arsenic as the dopant, while a p-type ingot would use boron as the dopant. Slices of n-type and p-type silicon are then fused to make the junction. A few more bells and whistles are added (like an antireflective coating, which improves light absorption and gives photovoltaic cells their characteristic blue color, protective glass on front and a plastic backing, and metal connections so the cell can be wired into a circuit), but a simple p-n junction is the essence of most solar cells. It's pretty much how all photovoltaic silicon solar cells have worked since 1954, which was when scientists at Bell Labs pioneered the technology: shining sunlight on silicon extracted from sand, they generated electricity.

Second-generation

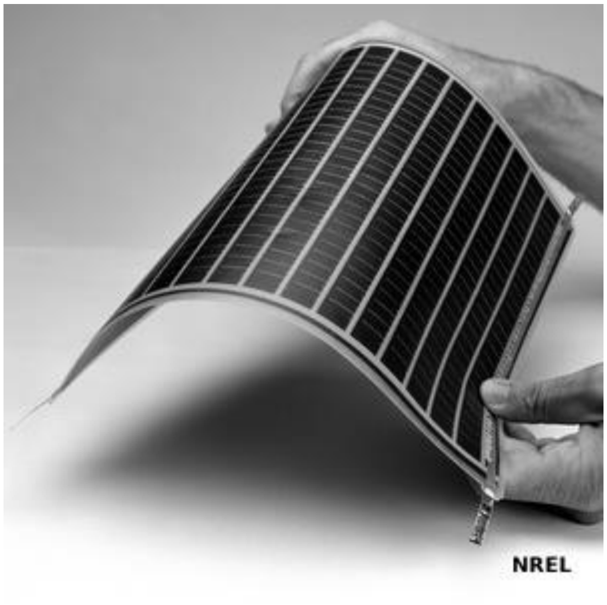


Photo: A thin-film, second-generation solar "panel." The power-generating film is made from amorphous silicon, fastened to a thin, flexible, and relatively inexpensive plastic backing (the "substrate"). Photo by Warren Gretz courtesy of NREL (image id #6321083).

Classic solar cells are relatively thin wafers—usually a fraction of a millimeter deep (about 200 micrometers, 200µm, or so). But they're absolute *slabs* compared to second-generation cells, popularly known as **thin-film solar cells** (TPSC) or thin-film photovoltaics (TFPV), which are about 100 times thinner again (several micrometers or millionths of a meter deep). Although most are still made from silicon (a different form known as amorphous silicon, a-Si, in which atoms are arranged randomly instead of precisely ordered in a regular crystalline structure), some are made from other materials, notably cadmium-telluride (Cd-Te) and copper indium gallium diselenide (CIGS). Because they're extremely thin, light, and flexible, second-generation solar cells can be laminated onto windows, skylights, roof tiles, and all kinds of "substrates" (backing materials) including metals, glass, and polymers (plastics). What second-generation cells gain in flexibility, they sacrifice in efficiency: classic, first-generation solar cells still outperform them. So while a top-notch first-generation cell might achieve an efficiency of 15–20 percent, amorphous silicon struggles to get above 7 percent, the best thin-film Cd-Te cells only manage about 11 percent, and CIGS cells do no better than 7–12 percent. That's one reason why, despite their practical advantages, second-generation cells have so far made relatively little impact on the solar market.

Third-generation

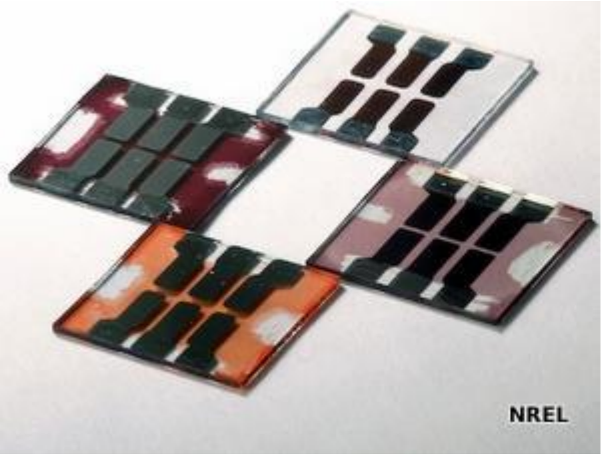


Photo: Third-generation plastic solar cells produced by researchers at the National Renewable Energy Laboratory. Photo by Jack Dempsey courtesy of NREL (image id #6322357).

The latest technologies combine the best features of first and second generation cells. Like first-generation cells, they promise relatively high efficiencies (30 percent or more). Like second-generation cells, they're more likely to be made from materials other than "simple" silicon, such as amorphous silicon, organic polymers (making organic photovoltaics, OPVs), perovskite crystals, and feature multiple junctions (made from multiple layers of different semiconducting materials). Ideally, that would make them cheaper, more efficient, and more practical than either first- or second-generation cells.

How much power can we make with solar cells?

"The total solar energy that reaches the Earth's surface could meet existing global energy needs 10,000 times over."

European Photovoltaic Industry Association/Greenpeace, 2011.

In theory, a huge amount. Let's forget solar cells for the moment and just consider pure sunlight. Up to 1000 watts of raw solar power hits each square meter of Earth pointing directly at the Sun (that's the theoretical power of direct midday sunlight on a cloudless day—with the solar rays firing perpendicular to Earth's surface and giving maximum illumination or **insolation**, as it's technically known). In practice, after we've corrected for the tilt of the planet and the time of day, the best we're likely to get is maybe 100–250 watts per square meter in typical northern latitudes (even on a cloudless day). That translates into about 2–6 kWh per day (depending on whether you're in a northern region like Canada or Scotland or somewhere more obliging such as Arizona or Mexico). Multiplying up for a whole year's production gives us somewhere between 700 and 2500 kWh per square meter (700–2500 units of electricity). Hotter regions clearly have much greater solar potential: the Middle East, for example, receives around 50–100 percent more useful solar energy each year than Europe.

Unfortunately, typical solar cells are only about 15 percent efficient, so we can only capture a fraction of this theoretical energy. That's why solar panels need to be so big: the amount of power you can make is obviously directly related to how much area you can afford to cover with cells. A single solar cell (roughly the size of a compact disc) can generate about 3–4.5 watts; a typical solar module made from an array of about 40 cells (5 rows of 8 cells) could make about 100–300 watts; several solar panels, each made from about 3–4 modules, could therefore generate an absolute maximum of several kilowatts (probably just enough to meet a home's peak power needs).

A brief history of solar cells

- 1839: French physicist **Alexandre-Edmond Becquerel** (father of radioactivity pioneer Henri Becquerel) discovers some metals are photoelectric: they produce electricity when exposed to light.
- 1873: English engineer **Willoughby Smith** discovers that selenium is a particularly effective photoconductor (it's later used by Chester Carlson in his invention of the photocopier).
- 1905: German-born physicist **Albert Einstein** figures out the physics of the photoelectric effect, a discovery that eventually earns him a Nobel Prize.
- 1916: American physicist **Robert Millikan** proves Einstein's theory experimentally.
- 1940: **Russell Ohl** of Bell Labs accidentally discovers that a doped junction semiconductor will produce an electric current when exposed to light.
- 1954: Bell Labs researchers **Daryl Chapin**, **Calvin Fuller**, and **Gerald Pearson** make the first practical photovoltaic silicon solar cell, which is about 6 percent efficient (a later version manages 11 percent). They announce their invention—initially called the "solar battery"—on April 25.
- 1958: Vanguard, Explorer, and Sputnik space satellites begin using solar cells.
- 1962: 3600 of the Bell solar batteries are used to power Telstar, the pioneering telecommunications satellite.
- 1997: US Federal government announces its Million Solar Roofs initiative—to construct a million solar-powered roofs by 2010.
- 2002: NASA launches its Pathfinder Plus solar plane.
- 2009: Scientists discover that perovskite crystals have great potential as third-generation photovoltaic materials.
- 2014: A collaboration between German and French scientists produces a new record of 46 percent efficiency for a four-junction solar cell.
- 2020: Solar cells are predicted to achieve grid parity (solar-generated electricity you make yourself will be as cheap as power you buy from the grid).

Polymer Cell

What is polymer cell?

A lithium **polymer battery**, or more correctly lithium-ion **polymer battery** (abbreviated as LiPo, LIP, Li-poly, lithium-poly and others), is a rechargeable **battery** of lithium-ion

technology using a **polymer** electrolyte instead of a liquid electrolyte. High conductivity semisolid (gel) **polymers** form this electrolyte.
The term polymer is commonly used to describe certain type of lithium-based battery that may or may not be polymer based. These typically include pouch and prismatic cells. While the word “polymer” is perceived as a plastic, polymers range from synthetic plastics to natural biopolymers and proteins that form fundamental biological structures.

Lithium-polymer differs from other battery systems in the type of electrolyte used. The original polymer design dating back to the 1970s used a solid (dry) polymer electrolyte that resembles a plastic-like film. This insulator allows the exchange of ions (electrically charged atoms) and replaces the traditional porous separator that is soaked with electrolyte.

A solid polymer has poor conductivity at room temperature, and the battery must be heated to 60°C (140°F) and higher to enable current flow. Large polymer batteries for stationary applications were installed that needed heating, but these have since disappeared. The much anticipated hype of the “true plastic battery” promised in the early 2000s did not materialize as conductivity could not be attained at ambient temperature.

To make the modern Li-polymer battery conductive at room temperature, gelled electrolyte has been added. Most Li-ion polymer cells today incorporate a micro porous separator with some moisture. Li-polymer can be built on many systems, the likes of Li-cobalt, NMC, Li-phosphate and Li-manganese, and is not considered a unique battery chemistry. The majority of Li-polymer packs are cobalt based; other active material may also be added.

With gelled electrolyte added, what is the difference between a normal Li ion and Li ion polymer? As far as the user is concerned, lithium polymer is essentially the same as lithium-ion. Both systems use identical cathode and anode material and contain a similar amount of electrolyte.

Li-polymer is unique in that a micro porous electrolyte replaces the traditional porous separator. Li-polymer offers slightly higher specific energy and can be made thinner than conventional Li-ion, but the manufacturing cost is said to be higher than cylindrical design. For the purpose of discussion, pouch cells are often identified as being Li-polymer.

Li-polymer cells also come in a flexible foil-type case that resembles a food package. While a standard Li-ion needs a rigid case to press the electrodes together, Li-polymer uses laminated sheets that do not need compression. A foil-type enclosure reduces the weight by more than 20 percent over the classic hard shell. Thin film technology liberates the design as the battery can be made into any shape, fitting neatly into stylish mobile phones and tablet. Li-polymer can also be made very slim to resemble a credit card (See Pouch Cell.) Light weight and high specific power make Li-polymer the preferred choice for hobbyists.

Charge and discharge characteristics of Li-polymer are identical to other Li-ion systems and do not require a dedicated charger. Safety issues are also similar in that protection circuits are needed. Gas buildup during charge can cause some prismatic and pouch cells to swell, and equipment manufacturers must make allowances for expansion. Li-polymer in a foil package may be less durable than Li-ion in the cylindrical package.

How long does lithium polymer battery last?

If the voltage of a **lithium**-ion cell drops below a certain level, it's ruined. **Lithium**-ion **batteries** age. They only **last** two to three years, even if they are sitting on a shelf unused. So **do** not "avoid using" the **battery** with the thought that the **battery** pack **will last** five years.

Are lithium polymer batteries safe?

Devices on the market that heat up **lithium polymer batteries** can increase the risk of a fire. **Lithium polymer** cell manufacturers suggest that exceeding 140 degrees is NOT a **safe** temperature for a **lithium polymer** cell. At 140 degrees, the pack can become unstable and very dangerous.

Can lithium polymer batteries explode?

The very thing that makes **lithium-ion batteries** so useful is what also gives them the capacity to catch fire or **explode**. **Lithium** is really great at storing energy. When it's released as a trickle, it powers your phone all day. When it's released all in one go, the **battery can explode**

Are lithium batteries better than alkaline?

Lithium batteries supply more energy **than alkaline batteries** and are lighter weight. **Lithium batteries** perform well in extreme weather environments. Very long shelf life even compared to **alkaline batteries** which often last for 5 to 7 yerars.

Difference between lithium ion and lithium polymer battery

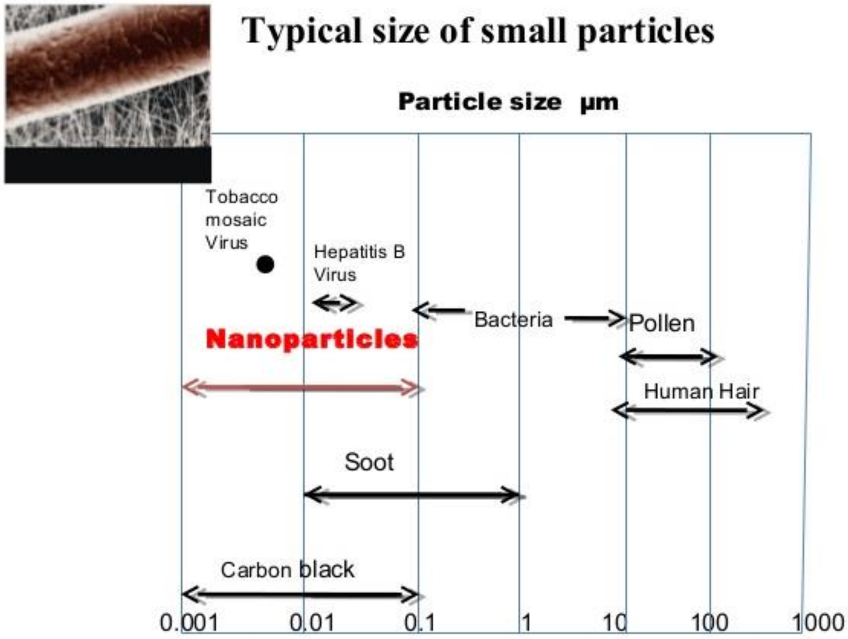
The most significant difference between **lithium-ion and lithium-polymer batteries** is the **chemical electrolyte** between their **positive and negative electrodes.**

1. **Lithium ion batteries:** They have **high energy density** and **cost less** than **lithium polymer**. They are essentially a group of very rigid electricity generating compartments, which consists of three pieces: a positive electrode; a negative electrode; and an electrolyte, or liquid chemical compound between them. Most lithium-ion batteries, unlike more traditional ones, also include an electronic controller, which regulates power and discharge flows so your battery doesn’t overheat or explode.
2. **Lithium polymer batteries:** They are **light weight** and have **improved safety**. However their cost is high (30% average) as compared to **lithium ion**. Also the the

energy density of **Li-Polymer battery** compared to **Li-Ion Batteries** is quite less. In Li-Po batteries it isn't a liquid. Instead, Li-Po technology uses one of three forms: a dry solid, which was largely phased out during the prototype years of lithium polymer batteries; a porous chemical compound; or, a gel-like electrolyte. The most popular among these is the last one, which is the type of battery you'll find in newer laptop computers and electric cars. The catch is that plenty of companies are not actually selling you a true Li-Po battery, instead it's a lithium-ion polymer battery, or a Li-ion in a more flexible casing. Lithium-polymer batteries are generally **robust and flexible**, especially when it comes to the size and shape of their build. They **have an extremely low profile, and have a lower chance of suffering from leaking electrolyte**. But they are significantly more costly to manufacture, and they do not they have the same energy density nor lifespan as a lithium-ion.

Nanomaterials:

Nanomaterials describe materials of which a single unit is sized (in at least one dimension) between 1 and 1000 nanometers, but is usually 1—100 nm. Nanomaterials research takes a materials science-based approach to nanotechnology, leveraging advances in materials metrology and synthesis which have been developed in support of microfabrication research. Materials with structure at the nanoscale often have unique optical, electronic, or mechanical properties.



- Conventional material have grain size anywhere from 100 µm to 1mm and more
- Particles with size between 1-100 nm are normally regarded as Nanomaterials
- The average size of an atom is in the order of 1-2 Angstroms in radius.
- 1 nanometer =10 Angstroms
- 1 nm there may be 3-5 atoms

- Two principal factors cause the properties of nanomaterials to differ significantly from Bulk materials:
- Increased relative surface area
- Quantum effects.

These factors can change or enhance properties such as reactivity, strength and electrical characteristics.

Surface Effects

- As a particle decreases in size, a greater proportion of atoms are found at the surface compared to those inside. For example, a particle of
- Size-30 nm-> 5% of its atoms on its surface
- Size-10 nm->20% of its atoms on its surface
- Size-3 nm-> 50% of its atoms on its surface
- Nanoparticals are more reactive than large particles (Catalyst)

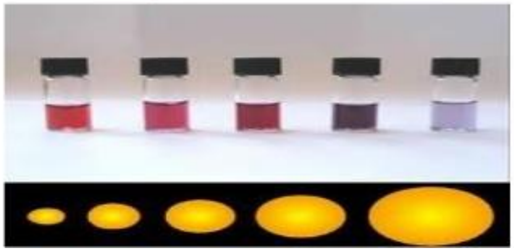
Quantum Effects

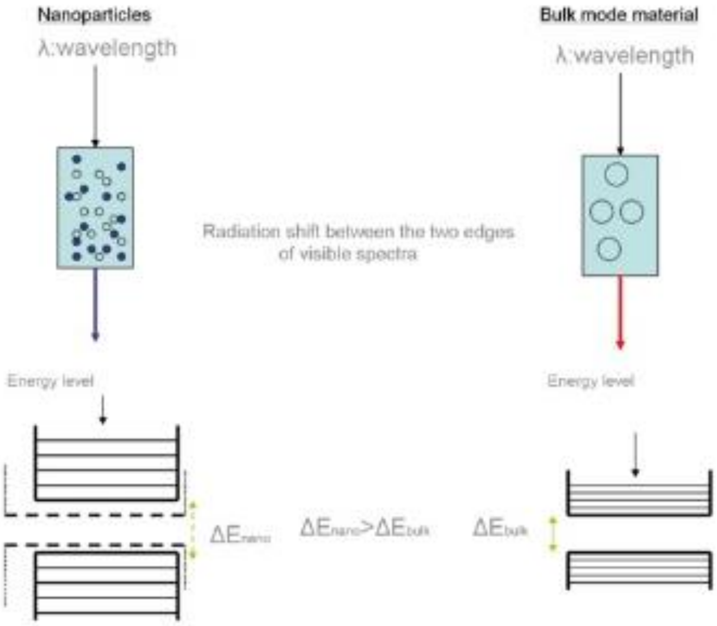
Quantum confinement

The quantum confinement effect can be observed once the diameter of the particle is of the same magnitude as the wavelength of the electron Wave function.

Quantum confinement is responsible for the increase of energy difference between energy states and band gap. A phenomenon tightly related with the optical and electronic properties of the materials.

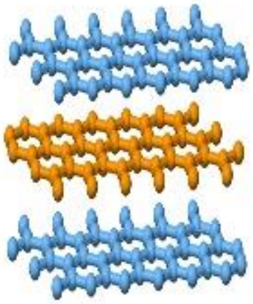
When materials are this small, their electronic and optical properties deviate substantially from those of bulk materials.(GOLD)

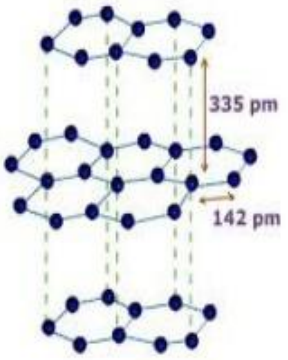




Classification of Nanomaterials

- **Nanomaterials as those which have structured components with atleast one dimension less than 100nm.**
- **One dimension in nanoscale (Other two dimensions are extended)**
  - **Thin films**
  - **Surface Coatings**
  - **Computer chips**
- **Two dimensions in nanoscale (Other one dimension is extended)**
  - **Nanowires**
  - **Nanotubes**
- **Three dimensions in nanoscale**
  - **Nanoparticles**
  - **Precipitates**
  - **Colloids**
  - **Quantum dots (tiny particles of semiconductor material)**





Graphite

It is also a crystalline form of carbon.

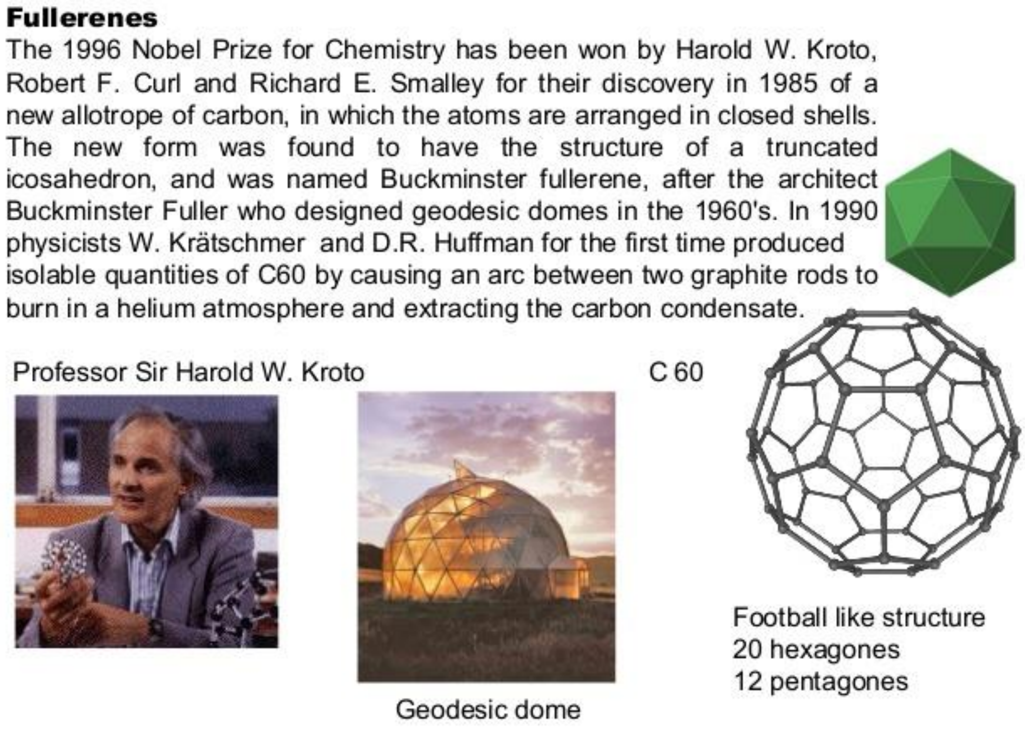
STRUCTURE OF GRAPHITE

In graphite each carbon atom is covalently bonded to three carbon atoms to give trigonal geometry. Bond angle in graphite is 120°C. Each carbon atom in graphite is sp2 hybridized. Three out of four valence electrons of each carbon atom are used in bond formation with three other carbon atoms while the fourth electron is free to move in the structure of graphite.

Basic trigonal units unite together to give basic hexagonal ring. In hexagonal ring C-C bond length is 1.42A°.In graphite these rings form flat layers. These layers are arranged in parallel, one above the other. These layers are 3.35Ao apart and are held together by weak van der waals forces only. These layers can slide over one another. Thus it is very soft. Fourth electron of each carbon atom forms delocalized p-bonds which spreads uniformly over all carbon atoms. Due to this reason graphite conducts electricity parallel to the of its plane.

Uses

Solid lubricants
Electrodes
Moderator in nuclear reactors
Pencil lead



Fullerenes

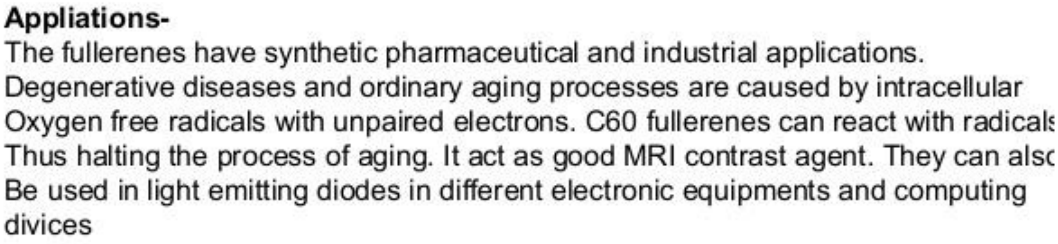
The 1996 Nobel Prize for Chemistry has been won by Harold W. Kroto, Robert F. Curl and Richard E. Smalley for their discovery in 1985 of a new allotrope of carbon, in which the atoms are arranged in closed shells. The new form was found to have the structure of a truncated icosahedron, and was named Buckminster fullerene, after the architect Buckminster Fuller who designed geodesic domes in the 1960's. In 1990 physicists W. Krätschmer and D.R. Huffman for the first time produced isolable quantities of C60 by causing an arc between two graphite rods to burn in a helium atmosphere and extracting the carbon condensate.

Professor Sir Harold W. Kroto

C 60

Football like structure
20 hexagones
12 pentagones

Geodesic dome

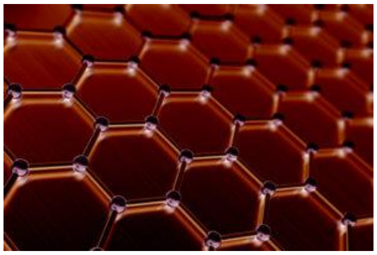


Appliations-

The fullerenes have synthetic pharmaceutical and industrial applications. Degenerative diseases and ordinary aging processes are caused by intracellular Oxygen free radicals with unpaired electrons. C60 fullerenes can react with radicals Thus halting the process of aging. It act as good MRI contrast agent. They can also Be used in light emitting diodes in different electronic equipments and computing divices

Graphene Synthesis, Properties, And Applications

Introduction To Graphene



Graphene-atomic-structure-3d-illustration

This introduction to graphene has been created to impart a general understanding of what graphene is, the types of graphene available, as well as synthesis methods and applications of graphene.

Graphene is quickly finding it’s way into a variety of applications and there are many advantages to using graphene to develop new products as well as to enhance specific properties in existing products.

What is Graphene?

Graphene is an allotrope of carbon that exists as a two-dimensional planar sheet. One way to think of graphene is as a single atomic graphite layer.

Graphene is technically a non-metal but is often referred to as a quasi-metal due to its properties being like that of a semi-conducting metal. As such, it has many unique properties that you don’t find with other non-metallic materials. Each carbon atom is covalently bonded (sp^2 hybridized) to three other carbon atoms in a hexagonal array, leaving one free electron per each carbon atom.

This free electron exists in a p-orbital that sits above the plane of the material. Each hexagon in the graphene sheet exhibits two pi-electrons, which are delocalized, allowing for an efficient conduction of electricity.

The holes in the structure also allow phonons to pass through unimpeded, which gives rise to a high thermal conductivity.

Graphene has many unique properties, making it an ideal material for use in electronic applications when compared to conventional materials.

Electrical conductivity the most prevalent and important property of graphene. Graphene doesn’t have an electronic band-gap (meaning that it can’t be switched on or off) as the valence and conduction bands have a small overlap and the electrons act as massless relativistic particles.

At room temperature, graphene can exhibit a concentration of charge carriers up to 10^{13} cm^{-2}, with a mobility of $1 X 10^4$ $cm^2 V^{-1} s^{-1}$. At low temperatures, this can increase to $2 X 10^5$ $cm^2 V^{-1} s^{-1}$.

Because the charge carriers act as quasi-particles, otherwise known as massless Dirac Fermions, graphene also exhibits a half-integer Quantum Hall Effect (QHE).

The QHE is the relationship of the charge, density and velocity of the charge carriers. It occurs when a magnetic field is applied along the axis perpendicular to the plane of the conducting material.

Under these conditions, the path of the carriers becomes curved, leading to an accumulation of opposite charges at either end of the material. Due to the two-dimensional nature of graphene, the electron confinement produces discrete band levels known as Landau levels, which are filled by the charge carriers.

Unlike other materials, the charge carriers in graphene only half-fill these levels, leading to a quantization of the Landau levels, and in effect the energy levels of graphene.

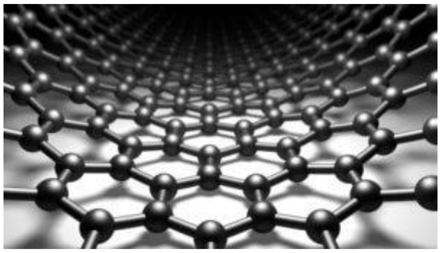
Graphene also has great optical, thermal and mechanical properties. Single sheet graphene is a highly transparent material but each layer in thickness absorbs up to 2.3% of white light, with less than 0.1% reflectance.

There is also a linear absorbance increase with respect to the number of layers stacked on top of each other. A suspended graphene sheet can exhibit a thermal conductivity of 3000-5000 W m^{-1} K^{-1} at room temperature. However, this can drop to as low as 600 W m^{-1} K^{-1} when it is attached to another substrate.

The drop is caused by a scattering of phonons at the interface which impedes their movement, whereas in free standing graphene the phonon path is uninterrupted. Even at this lower conductivity, the thermal conductivity is still twice as high as copper.

Graphene is also known to be one of the strongest materials ever made and a single-layer graphene sheet can withstand up to 42 N m^{-1} of stress, with a Young's modulus of 1.0 Tpa.

Types Of Graphene



Graphene-molecular-structure

There are many types of graphene. True Graphene is only one atomic layer thick (often called a monolayer) and it typically exists as a film but it can be floated off the substrate and can be redeposited onto another substrate or used in it's isolated form.

There are, however, several types of graphene containing powder form materials such as graphene oxide, graphene nanoplatelets, graphene nanoribbons, and graphene quantum dots as well as graphene enabled products such as graphene ink or graphene masterbatches.

There are 3 main ways to synthesize graphene, they are:

- Chemical Vapor Deposition
- Chemical or Plasma Exfoliation from natural Graphite

- Mechanical cleavage from natural Graphite

Graphene can also be fully synthetic but those methods haven't proven to be commercially viable.

Chemical Vapor Deposition (CVD) Graphene Films

Monolayer Graphene Film On Wafer

Graphene films can be produced by varying methods, which include mechanical and thermal exfoliation, chemical reduction and epitaxial growth; but the most common method used in production today is by chemical vapor deposition (CVD).

CVD works by combining and depositing volatile gas molecules onto a substrate. The process takes place in a reaction chamber, where the material is formed on the surface of the substrate and the waste gases are pumped out.

Temperature dependence plays a vital role and can affect the type of reaction that occurs. CVD produces graphene films of high quality and purity, but the by-products produced during the reaction can be toxic due to the volatile nature of the precursor gases.

The graphene film is created by CVD in two steps. The first involves the pyrolysis of a precursor material to form carbon atoms on a substrate material.

By pyrolyzing the material on the substrate, carbon clusters are prevented from forming. Due to the amount of energy required to break the carbon bonds ($C-C = 347\ kjmol^{-1}$, $C=C = 614\ kjmol^{-1}$, $C\equiv C = 839\ kjmol^{-1}$, $C-H = 413\ kjmol^{-1}$), a high heat is required, and therefore a metal catalyst is required during the process.

The second step is a heat intensive step which assembles the dissociated carbon atoms onto a substrate (in the presence of a catalyst), which forms a single layer structure.

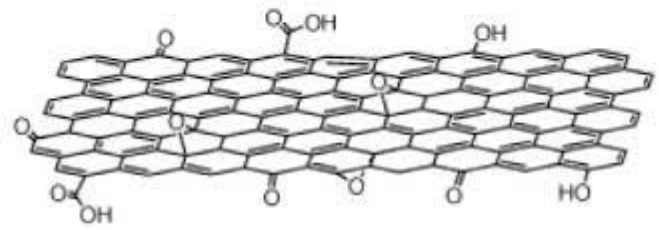
CVD graphene films are predicted to have strong chemical, electronic, mechanical and magnetic properties depending on the arrangement of the atoms in the film. Due to the five-order-of-magnitude difference between the grains and atoms at grain boundaries, only a few experiments have been produced to study these interactions.

One substrate that is known to produce high-quality graphene is copper. Copper acts as both a catalyst and the substrate.

The copper bonds to the carbon atoms, which provides strong carbon-substrate interactions, allowing for a single graphene layer to be easily formed on the surface. Copper oxide can also be inserted between layers of graphene, making it an easy process to remove a single layer.

Treating the copper substrate can also rearrange the surface morphology of the substrate-catalyst and is known to produce graphene with fewer defects.

Graphene Oxide (GO)



Single Layer Graphene Oxide Molecular Structure

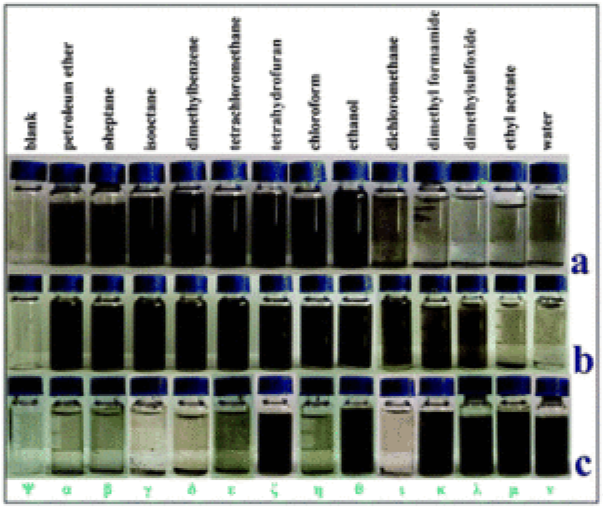
Graphene oxide (GO) is most commonly produced by the oxidation of graphite oxide. The oxidation process is beneficial, as it functionalizes the surface of the graphene layers with multiple species of oxygenated functional groups.

The multiple functional groups provide an enhanced layer separation and improved hydrophilicity. The hydrophilicity allows the graphene oxide to undergo ultrasonic irradiation, which produces a single/a few graphene layers that are highly stable when dispersed in DI Water and other solvents.

GO has many desirable properties. It disperses very easily in various mediums including aqueous solvents, organic solvents and various matrices.

The presence of both electron rich oxygen species and an electron rich graphene backbone allow for further surface functionalization, which gives rise to an adaptable material for multiple applications.

Graphene oxide does however suffer from a low electrical conductivity and is an electrical insulator. Graphene oxide is also soluble in many solvents, both aqueous and organic.



Graphene Oxide Solubility

Graphene Oxide Is Highly Soluble

To gain the benefits of graphene oxide, it is typically dispersed, added into a formulation, made into a film or other nano-enabled product and then reduced to restore the graphene structure.

<u>Reduced Graphene Oxide (rGO)</u>

There are many methods to reduce graphene oxide (GO) into reduced graphene oxide (rGO), but most fall into three main categories: chemical reduction, thermal reduction and electrochemical reduction.

The other methods include hydrazine vapor treatment, annealing, laser and microwave reduction. The reduction process is vital to producing rGO, as it determines how consistent the rGO structure is with the GO precursor.

Many commercial producers of Graphene Nanoplatelets are in fact providing a product similar to industrial scale rGO as their GNP product. However this method differs from the rGO most people refer to which is a higher quality research product used for nano enabled devices.

Chemical reduction is a scalable method but can often result in poor yields and utilizes highly toxic materials such as hydrazine. rGO produced by this method generally exhibits a low surface area and has a low conductivity compared to the GO precursor.

Thermal reduction produces rGO with a high surface area that is close to the surface area of pristine graphene. However, the intense heating process causes a high-pressure build-up of carbon dioxide which causes structural damage to the graphene layers.

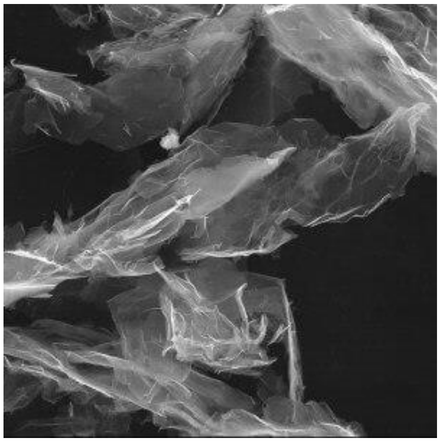
The structural imperfections can then give rise to a reduction in the overall mass (and yield against the theoretical output), vacancies, voids and it can hinder the mechanical strength of the material.

Electrochemical reduction shows the best results in terms of production and quality. The rGO produced is consistent with that of pristine graphene.

During the electrochemical process, the substrates (generally ITO or glass) are coated with a layer of GO and a current is passed through the material (via electrodes at either end of the substrate). rGO produced by this method have shown to have a high carbon to oxygen ratio and have exhibited conductivity comparable to that of silver.

The process also benefits from no toxic waste. This process does however suffer from issues regarding the feasibility of the scalability of the method.

Graphene Nanoplatelets (GNPs)



Graphene Nanoplatelets SEM Image

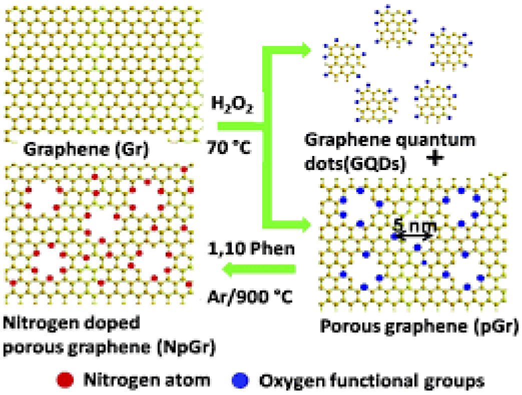
Graphene Nanoplatelets are typically synthesized by micromechanical cleavage of bulk graphite and can only produce graphene flakes in limited quantities which are mixed in with graphitic stacks. Large scale GNP production often uses mechanical cleavage followed by chemical reduction to produce the final GNP product.

Another method to make GNPs in bulk is by plasma exfoliation. A unique benefit of plasma exfoliation is the ability to synthesize and functionalize the GNPs to promote dispersion in the host matrix in a single, dry, processing step.

The RF or Microwave Plasma Reactor has a vacuum applied to remove atmospheric contaminants as well as residual contaminants which are liberated during the plasma milling process. These benefits make the material an excellent choice for large scale industrial applications with a wide variety of available functional groups such as OH, COOH, NH2, N2, & F.

Due to the lower cost of input materials, capital equipment, and plasma purification and/or functionalization, the GNPs can ultimately be a cheaper material than CNTs on a ton level thus paving the way for increased industrial applications with early adopters.

Graphene And Graphene Oxide Quantum Dots



Graphene Quantum Dots with Nitrogen Atoms

Graphene and graphene oxide quantum dots (GQDs) can be synthesized into various forms, from single-layer to tens of layers, but are generally less than 30 nm. GQDs also show similar properties to other types of quantum dots.

Like many graphene-based materials, GQDs exhibit a large surface area, a good linear dispersibilty and a high charge carrier mobility. GQDs also exhibit an efficient hole transporting ability, making them efficient materials for hole-transport layers.

They are useful materials for both electronic and opto-electronic applications.

GQDs can now be produced by a multitude of methods which includes both top-down and bottom-up approaches. Production by bottom-up methods can produce GQDs with a controlled size (due to the ability to control the band gap), but the synthesis itself can be complex which requires stringent conditions.

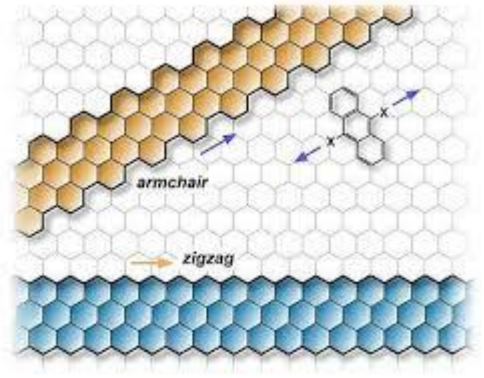
Top-down methods are in their infancy, but do provide a much simpler and cheaper approach. The breakdown of graphite oxide can produce single layered GQDs, but the yields aren’t high and the size distribution cannot be easily controlled. GQDs can also be synthesized by the breakdown of range of carbon allotropes including CNTs, fullerenes and carbon fibers.

Other methods include ultrasonication, microwave irradiation, radical methods and hydro-thermal or solvo-thermal methods.The main challenge that faces GQD production today is finding an efficient process that can take the production to industrial levels, as they have potential for many applications.

The applications of GQDs include lithium-ion batteries, supercapacitors and solar cells. But one area in which they are particularly useful is in LED displays. GQD-LEDs are a growing area and have been produced by etching CVD-grown graphene with block copolymers, followed by fabrication with graphite intercalating compounds.

The process produces graphene flakes that are low in oxygenated functional groups, of low toxicity and environmentally safe. It is also both a cheap and scalable process. GQDs emit light upon excitation, so are now being tested as emitters in organic light-emitting diodes (OLEDS). So far, they have exhibited a luminescence of 1000 cdm^{-2}. The thin nature of GQDs may also open up future opportunities to create and perfect fold-able displays.

Graphene Nanoribbons



Graphene Nanoribbons

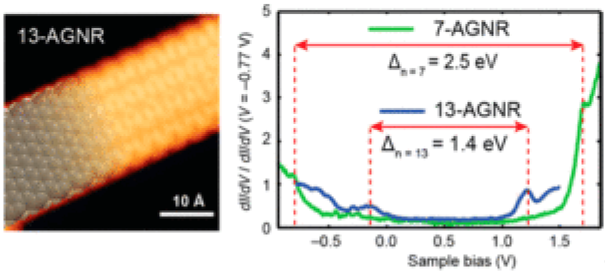
Unlike many other forms of graphene which are two-dimensional, graphene nanoribbons (GNRs) are quasi-one-dimensional materials with an ultra-thin width.

The electrical properties that GNRs exhibit are highly tunable and can be manipulated by dimension confinement, edge morphology and functionalization of the GNR.

GNRs also exhibit large aspect ratios, a high surface area, a conductive matrix and good mechanical flexibility. The combination of these properties has given GNRs a strong footing in composite materials for electronic applications. GNR anode composites have been shown to exhibit a specific reversible capacity of 1130 mAh g^{-1}, with a coulombic efficiency >98%.

GNRs are produced by various methods. One of the most common methods involves unzipping the walls of MWCNTs with sodium and potassium-based compounds, sonicating and drying under vacuum.

They can also be produced by plasma etching of nanotubes onto polymer films, epitaxial growth and annealing on silicon carbide and CVD.



Graphene Nanoribbon Band Gaps Are Contollable

GNRs can enhance the performance of lithium-ion batteries through edge chirality effects. GNRs have a band gap that is inversely proportion to their width, which is dependent upon their edge chirality.

Chirality occurs at the edges because the electron confinement potential deforms the wave-function and causes the electrons move in a single direction, with more weight in the ‘positive x’ direction. This leads to a current in the ‘positive y’ direction.

For electronic applications, the edges in GNRs have shown the best results when armchair and metallic edges are present due to their semi-conducting abilities. Armchair edges also reduce the band gap energy when there is a defined width.

The energy at the edges of GNRs is proportional to their density and armchair edges are more tightly packed at the graphene interface, so the energy is higher than that of zig-zag edges. Such edges can be produced on GNRs by electron beam irradiation and electron beam lithography.

A GNR with a high concentration and purity of armchair edges has been found to provide highly efficient p-n junctions in electronic devices.

Graphene Aerogels

A Graphene Aerogel Foam Sits On A Flower

Carbon aerogels are derived by sol-gel synthesis methods and are a unique class of high-surface-area materials. Their high mass-specific surface area, electrical conductivity, environmental compatibility, and chemical inertness make them very promising materials for many energy related applications.

Recent developments in controlling their morphology make them especially well suited to super capacitor applications.

Aerogels are a special class of open-cell foams that exhibit many unique and interesting properties, such as low mass density, continuous porosity and high surface areas. These properties are derived from the aerogel microstructure, which consists of three-dimensional networks of interconnected nanometer-sized particles.

Aerogels are typically prepared by sol–gel methods, a process that transforms molecular precursors into highly cross-linked inorganic or organic gels that can then be dried using techniques such as supercritical drying, freeze drying, ect to preserve the insubstantial solid network.

For organic and carbon aerogels, the transformation involves the polymerization of multi-functional organic species into three-dimensional polymer networks.

Graphene Masterbatches

Graphene Masterbatches

Graphene masterbatches are composite materials that contain a graphene-based compound (most commonly GO) and a polymer.

The graphene is used to enhance the properties of various common polymeric materials. Many polymers exhibit desirable properties such as low cost, low toxicity, bio-compatibility and chemical resistance, but they lack desirable mechanical properties.

By incorporating graphene nanoplatelets into polymer matrices, the polymers retain their original properties but benefit from enhanced rigidity and stiffness, while still being lightweight.

Using graphene as a filler compound rather than conventional inorganic materials can bring an enhanced electrical conductivity to the polymer, but it does have some issues.

In many graphene-based composites, graphene oxide acts as the dispersing support for other ions and molecules.

In polymer masterbatches, this can lead to problems as graphene doesn't always disperse well in polymer phases (especially polyolefins) due to a lack of positive interactions at the grpahene polymer interface.

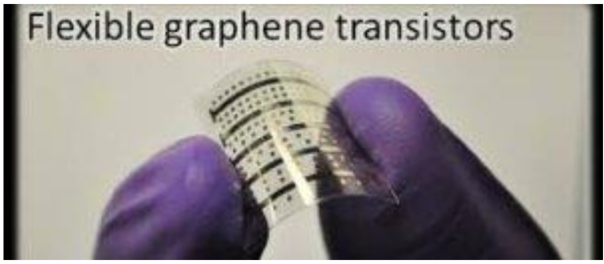
However, this can be overcome by the use of a surfactant, or by tailoring surface functionality of the graphene surface. The surfactant increases the surface interaction between the polymer and graphene.

If functionalized, the functional groups promote interaction between itself and the polymer molecules. If the functional groups aren't compatible, you may observe what we call "islands of masterbatch" with easily observed islands of polymer in between well dispersed graphene-polymer masterbatches.

Properties Of Graphene

The properties of graphene are unique due to its all carbon structure and nanoscale geometry.

<u>Electronic Properties</u>



Flexible Graphene Transistors

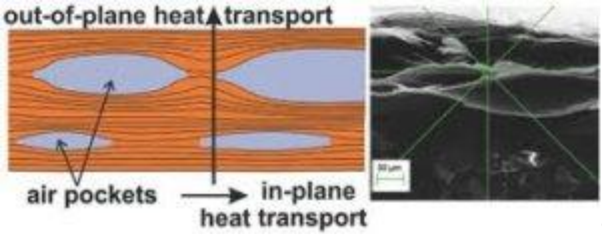
Because graphene has a delocalized pi-electron system across the entirety of its surface, the movement of electrons is very fluid.

The graphene system also exhibits no band gap, due to overlapped pi-electrons, allowing for an easy movement of electrons without the need to input energy into the system.

The electronic mobility of graphene is very high and the electrons act like photons, with respect to their movement capabilities.

The electrons are also able to move sub-micrometer distances without scattering. From tests done to date the electron mobility has found to be in excess of 15,000 $cm^2V^{-1}s^{-1}$, with the potential of producing up to 200,000 $cm^2V^{-1}s^{-1}$.

Thermal Properties



Graphene Thermal Properties

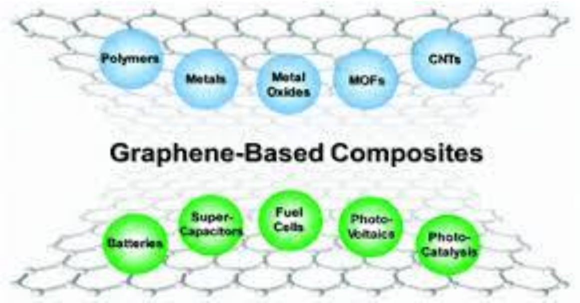
The repeating structure of graphene makes it an ideal material to conduct heat in plane. Interplane conductivity is problematic and typically other nanomaterials such as CNTs are added to boost interplane conductivity.

The regular structure allows the movement of phonons through the material without impediment at any point along the surface. Graphene can exhibit two types of thermal conductivity- in-plane and inter-plane.

The in-plane conductivity of a single-layered sheet is 3000-5000 W m^{-1} K^{-1}, but the cross-plane conductivity can be as low as 6 W m^{-1} K^{-1}, due to the weak inter-plane van der Waals forces.

The specific heat capacity for graphene has never been directly measured, but the specific heat of the electronic gas in graphene has been estimated to be around 2.6 μ J g^{-1} K^{-1} at 5 K.

Mechanical Strength



Graphene Composites Applications

Graphene is one of the strongest materials ever discovered with a tensile strength of 1.3 x 10^{11} Pa. In addition to having an unrivaled strength, it is also very lightweight (0.77 mgm^{-2}).

The mechanical strength of graphene is unmatched and as such can significantly enhance strength in many composite materials.

Flexibility/Elasticity

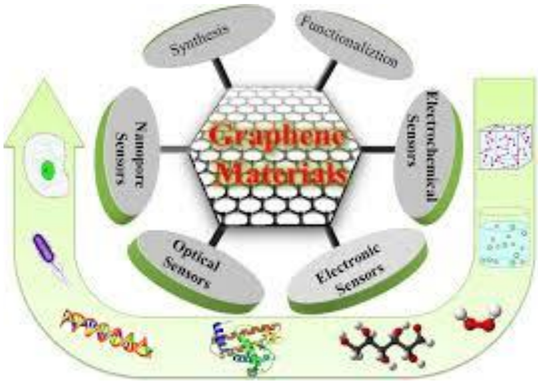
The repeating sp^2 hybridized backbone of graphene molecules allow for flexibility, as there is rotation around some of the bonds, whilst still providing enough rigidity and stability that the molecule can withstand changes in conformation and support other ions.

This is a very desirable property as there are not many molecules that can be flexible and supportive at the same time. In terms of its elasticity, graphene has found to have a spring constant between 1-5 Nm^{-1}, with a Young's modulus of 0.5 TPa.

Applications of Graphene

There are many applications of graphene because it's a revolutionary material. It has many applications replacing conventional materials as well as the ability to support applications previously not possible before the advent of 2D materials. The applications of Graphene are truly endless and many are yet to be conceived of yet.

Sensors



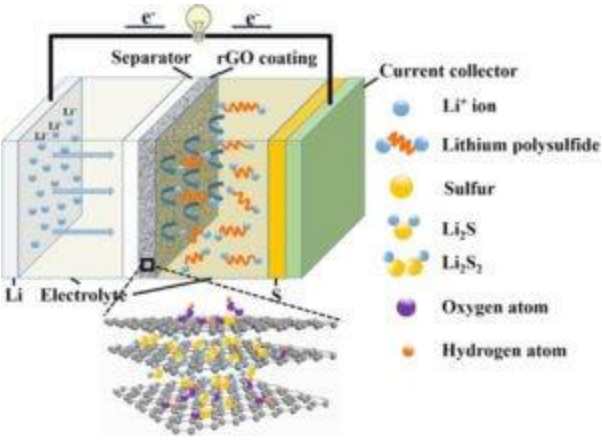
Graphene Sensors

The ideal sensor is able to detect minute changes in its surrounding environment. Due to the planar and consitent arrangement of atoms in a graphene sheet, every atom within the sheet is exposed to the surrounding environment.

This allows graphene to effectively detect changes in its surroundings at micrometer dimensions, providing a high degree of sensitivity.

Graphene is also able to detect individual events on a molecular level. Many of graphenes properties are beneficial in sensor applications; as such, graphene could be used in sensors in various fields including bio-sensors, diagnostics, field effect transistors, DNA sensors and gas sensors, to name a few.

Batteries



Lithium Reduced Graphene Oxide Battery

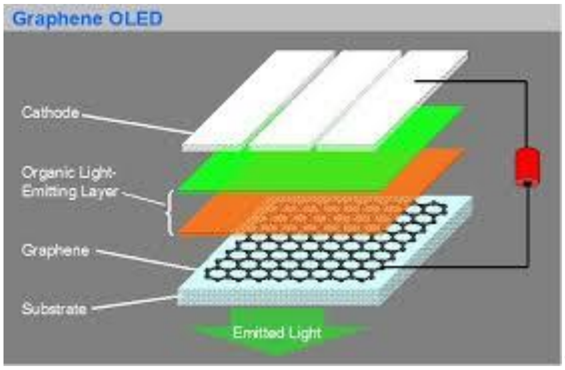
Graphene can be incorporated into both the anode or the cathode in various battery systems to increase the efficiency of the battery and improve the charge/discharge cycle rate.

The excellent electrical conductivity, surface area and dispersibility of graphene enhances the beneficial properties present in many traditional inorganic-based electrodes, whilst simultaneously relieving the electrodes of their limitations.

Due to its versatile nature, graphene has been incorporated into lithium-ion batteries, lithium-sulphur batteries, supercapacitors and fuel cells, of which there are multiple variations of each available on the market today.

Check out our detailed Graphene Batteries User’s Guide here.

Electron Emission Displays



Graphene Displays

Graphene is an ideal material for use in electron emission displays as it exhibits a high aspect ratio and the dangling bonds at either end of the sheet allow for efficient electron tunneling.

The linear disperisty that the graphene surface provides produces massless Dirac Fermions. When exposed to an electric field, the field emission liberated electrons avoid all back-scattering because their escape velocity is independent to their energy.

Graphene can turn-on an electric field at 0.1 V µm^{-2}, with a field enhancement factor of up to 3700. This can increase up to 4500 in screen printed graphene films.

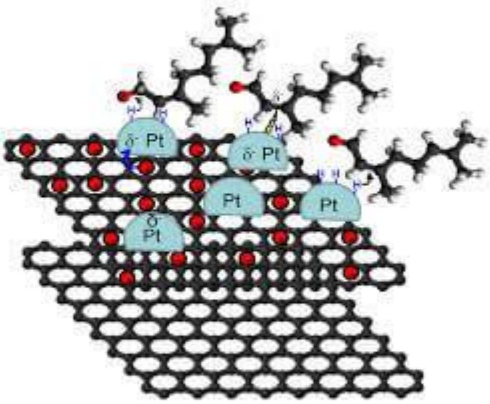
Structural Composites

Graphene is incorporated into various composites for applications where strength and weight are limiting factors, for example in the aerospace industry.

Graphene is being incorporated into many materials to make the existing material stronger and more lightweight. For the aviation industry, a composite material which is much lighter than steel but will still provide the necessary strength will save a lot of money on fuel consumption, which is why graphene has started to be incorporated into such materials.

Graphene-based structural composites have a huge potential to become a widely used alternative to many materials used today.

Catalyst Supports



Graphene Catalyst Supports

Even though the surface of graphene is planar and uniform, like any other material in existence it is subject to intrinsic defects.

Catalysts in the form of metal ions can sit in these cavities and be supported. In addition to providing mechanical support, the excellent charge carrier ability of graphene assists the charge transfer reactions involving the catalyst.

Graphene is also inert and does not interfere (in a negative way) with the interaction between the catalyst and the substrate materials. Graphene also provides an even dispersion of catalyst particles, so the catalyst-substate reaction is consistent across the whole support.

Polymer Masterbatches

Graphene can be incorporated into polymeric materials to form graphene-polymer composite materials.

As many polymeric materials suffer from strength-related problems, the incorporation of graphene can help to increase the tensile strength of the polymers, increasing the shelf life of the polymeric material in commercial applications.

Incorporating graphene into polymers can also give polymers electrical conductivity properties.

Functional Inks

Graphene can be used in functional inks for electronic, heat resistant and anti-corrosion purposes. By incorporating graphene into ink formulations, the conductivity properties associated with graphene influence the ink, causing it to become conductive.

The inks can then be used to coat electronics. Compared to other conducting inks, graphene is non-toxic, environmentally friendly, cheaper, quick-drying and recyclable. Graphene also has a high thermal stability, making it an ideal for heat resistant ink coating in electronic applications that produce large amounts of heat.

It is also an ink of choice when processing temperatures need to be high, as the graphene won't break down during the manufacturing process. Graphene also exhibits excellent chemical stability and is inert.

For applications where environmental factors are an issue, graphene inks can provide a stable barrier to protect materials from chemicals and corrosion.

plasmonic material

it is a metamaterial that uses surface plasmons to achieve optical properties not seen in nature. Plasmons are produced from the interaction of light with metal-dielectric materials. Under specific conditions, the incident light couples with the surface plasmons to create self-sustaining, propagating electromagnetic waves known as surface plasmon polaritons (SPPs). Once launched, the SPPs ripple along the metal-dielectric interface. Compared with the incident light, the SPPs can be much shorter in wavelength.[1]

The properties stem from the unique structure of the metal-dielectric composites, with features smaller than the wavelength of light separated by subwavelength distances. Light hitting such a metamaterial is transformed into surface plasmon polaritons, which are shorter in wavelength than the incident light.

Materials

Silicon sandwich

Negative refraction for visible light was first produced in a sandwich-like construction with thin layers. An insulating sheet of silicon nitride was covered by a film of silver and underlain by another of gold. The critical dimension is the thickness of the layers, which summed to a fraction of the wavelength of blue and green light. By incorporating this metamaterial into integrated optics on an IC chip, negative refraction was demonstrated over blue and green frequencies. The collective result is a relatively significant response to light.[4][5]

Graphene

Graphene also accommodates surface plasmons,[15] observed via near field infrared optical microscopy techniques[16][17] and infrared spectroscopy.[18] Potential applications of graphene plasmonics involve terahertz to midinfrared frequencies, in devices such as optical modulators, photodetectors and biosensors.[19]

Superlattice

A hyperbolic metamaterial made from titanium nitride (metal) and aluminum scandium nitride (dielectric) have compatible crystal structures and can form a superlattice, a crystal that combines two (or more) materials. The material is compatible with existing CMOS technology (unlike traditional gold and silver), mechanically strong and thermally stable at higher temperatures. The material exhibits higher photonic densities of states than Au or Ag.[20] The material is an efficient light absorber.[21]

The material was created using epitaxy inside a vacuum chamber with a technique known as magnetron sputtering. The material featured ultra-thin and ultra-smooth layers with sharp interfaces.[21]

Possible applications include a “planar hyperlens” that could make optical microscopes able to see objects as small as DNA, advanced sensors, more efficient solar collectors, nano-resonators, quantum computing and diffraction free focusing and imaging

The material works across a broad spectrum from near-infrared to visible light. Near-infrared is essential for telecommunications and optical communications, and visible light is important for sensors, microscopes and efficient solid-state light sources.

Semiconductors-

Semiconductors, as we noted above, are somewhat arbitrarily defined as insulators with **band gap energy $\leq$ 3.0 eV** (~290 kJ/mol). This cutoff is chosen because, as we will see, the conductivity of undoped semiconductors drops off exponentially with the band gap energy and at 3.0 eV it is very low. Also, materials with wider band gaps (e.g. $SrTiO_3$, E_{gap} = 3.2 eV) do not absorb light in the visible part of the spectrum

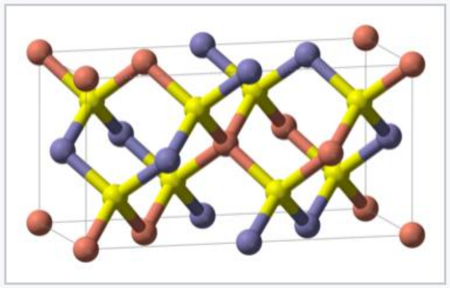
There are a number of places where we find semiconductors in the periodic table:

- Early transition metal oxides and nitrides, especially those with d^0 electron counts such as TiO_2, TaON, and WO_3
- Oxides of later 3d elements such as Fe_2O_3, NiO, and Cu_2O
- Layered transition metal chalcogenides with d^0, d^2 and d^6 electron counts including TiS_2, ZrS_2, MoS_2, WSe_2, and PtS_2
- d^{10} copper and sliver halides, e.g., CuI, AgBr, and AgI
- Zincblende- and wurtzite-structure compounds of the p-block elements, especially those that are isoelectronic with Si or Ge, such as GaAs and CdTe. While these are most common, there are other p-block semiconductors that are not isoelectronic and have different structures, including GaS, PbS, and Se.

A 2" wafer cut from a GaAs single crystal. GaAs, like many p-block semiconductors, has the zincblende structure.

The **p-block octet semiconductors** are by far the most studied and important for technological applications, and are the ones that we will discuss in detail.

Zinc blende- and wurtzite-structure semiconductors have 8 valence electrons per 2 atoms. These combinations include 4-4 (Si, Ge, SiC,…), 3-5 (GaAs, AlSb, InP,…), 2-6 (CdSe, HgTe, ZnO,…), and 1-7 (AgCl, CuBr,…) semiconductors. Other variations that add up to an octet configuration are also possible, such as $Cu^{I}In^{III}Se_2$, which has the **chalcopyrite** structure, shown at the right.



The **chalcopyrite structure** is adopted by ABX_2 octet semiconductors such as $Cu^{I}In^{III}Se_2$ and $Cd^{II}Sn^{IV}P_2$. The unit cell is doubled relative to the parent **zincblende structure** because of the ordered arrangement of cations. Each anion (yellow) is coordinated by two cations of each type (blue and red).

How does the **band gap energy** vary with **composition**? There are two important trends

(1) Going **down a group** in the periodic table, the gap **decreases**:

E_{gap} (eV): 5.4 1.1 0.7 0.0

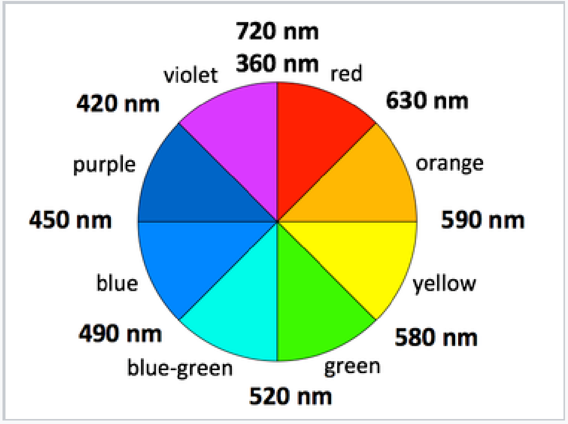
This trend can be understood by recalling that E_{gap} is related to the **energy splitting between bonding and antibonding orbitals**. This difference decreases (and bonds become weaker) as the principal quantum number increases.

(2) For isoelectronic compounds, **increasing ionicity** results in a **larger band gap**.

This trend can also be understood from a simple MO picture, as we discussed in Ch. 2. As the electronegativity difference $\Delta\chi$ increases, so does the energy difference between bonding and antibonding orbitals.

The band gap is a very important property of a semiconductor because it determines its color and conductivity. Many of the applications of semiconductors are related to band gaps:

- Narrow gap materials ($Hg_xCd_{1-x}Te$, VO_2, InSb, Bi_2Te_3) are used as infrared photodetectors and thermoelectrics (which convert heat to electricity).
- Wider gap materials (Si, GaAs, GaP, GaN, CdTe, $CuIn_xGa_{1-x}Se_2$) are used in electronics, light-emitting diodes, and solar cells.



Color wheel showing the colors and wavelengths of emitted light.

Semiconductor solid solutions such as $GaAs_{1-x}P_x$ have band gaps that are intermediate between the end member compounds, in this case GaAs and GaP (both zincblende structure). Often, there is a linear relation between composition and band gap, which is referred to as **Vegard's Law**. This "law" is often violated in real materials, but nevertheless offers useful guidance for designing materials with specific band gaps. For example, red and orange light-emitting diodes (LED's) are made from solid solutions with compositions of $GaP_{0.40}As_{0.60}$ and $GaP_{0.65}As_{0.35}$, respectively. Increasing the mole fraction of the lighter element (P) results in a larger band gap, and thus a higher energy of emitted photons.

Colors of semiconductors

The color of absorbed and emitted light both depend on the band gap of the semiconductor. Visible light covers the range of approximately 390-700 nm, or 1.8-3.1 eV. The **color of emitted light** from an LED or semiconductor laser corresponds to the band gap energy and can be read off the color wheel shown at the right.

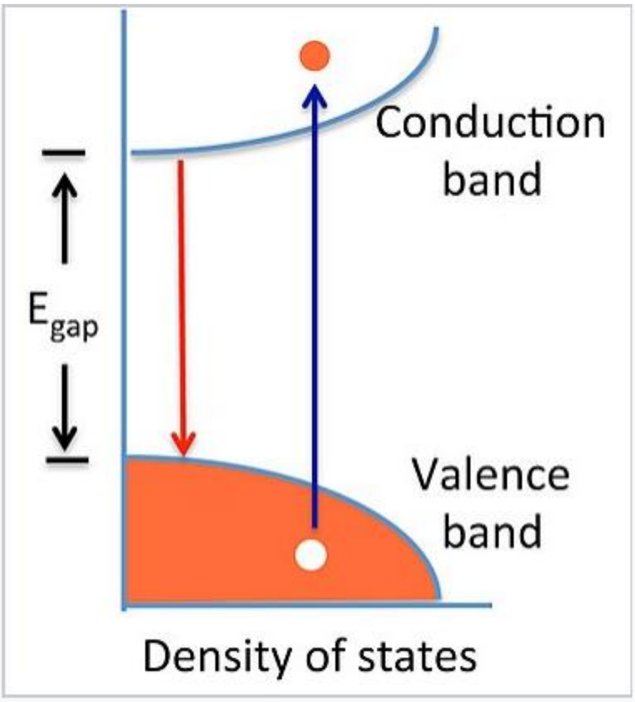
Fe_2O_3 powder is reddish orange because of its 2.2 eV band gap

The color of **absorbed light** includes the band gap energy, but also all colors of higher energy (shorter wavelength), because electrons can be excited from the valence band to a range of energies in the conduction band. Thus semiconductors with band gaps in the infrared (e.g., Si, 1.1 eV and GaAs, 1.4 eV) appear black because they absorb all colors of visible light. Wide band gap semiconductors such as TiO_2 (3.0 eV) are white because they absorb only in the UV. Fe_2O_3 has a band gap of 2.2 eV and thus absorbs light with $\lambda < 560$ nm. It thus appears reddish-orange (the colors of light reflected from Fe_2O_3) because it absorbs green, blue, and violet light. Similarly, CdS ($E_{gap} = 2.6$ eV) is yellow because it absorbs blue and violet light.

Electrons and holes in semiconductors

Pure (undoped) semiconductors can conduct electricity when electrons are promoted, either by heat or light, from the valence band to the conduction band. The promotion of an **electron** (e^-) leaves behind a **hole** (h^+) in the valence band. The hole, which is the absence of an electron in a bonding orbital, is also a mobile charge carrier, but with a positive charge. The motion of holes in the lattice can be pictured as analogous to the movement of an empty seat in a crowded theater. An empty seat in the middle of a row can move to the end of the row (to accommodate a person arriving late to the movie) if everyone moves over by one seat. Because the movement of the hole is in the opposite direction of electron movement, it acts as a positive charge carrier in an electric field.

The opposite process of excitation, which creates an electron-hole pair, is their recombination. When a conduction band electron drops down to recombine with a valence band hole, both are annihilated and energy is released. This release of energy is responsible for the emission of light in LEDs.



An electron-hole pair is created by adding heat or light energy $E \geq E_{gap}$ to a semiconductor (blue arrow). The electron-hole pair recombines to release energy equal to E_{gap} (red arrow).

At equilibrium, the creation and annihilation of electron-hole pairs proceed at equal rates. This dynamic equilibrium is analogous to the dissociation-association equilibrium of H^+ and OH^- ions in water. We can write a mass action expression:

$n \times p = K_{eq} = n_i^2$

where n and p represent the number density of electrons and holes, respectively, in units of cm^{-3}. The intrinsic carrier concentration, n_i, is equal to the number density of electrons or holes in an undoped semiconductor, where $n = p = n_i$.

Note the similarity to the equation for water autodissociation:

$[H+][OH-]=Kw$

By analogy, we will see that when we increase n (e.g., by doping), p will decrease, and vice-versa, but their product will remain constant at a given temperature.

Temperature dependence of the carrier concentration. Using the equations $K_{eq}=e^{(-\Delta GoRT)}$

and $\Delta G^o = \Delta H^o - T\Delta S^o$

, we can write:

$n\times p=n_i^2=e^{(\Delta SoR)}e^{(-\Delta HoRT)}$

The entropy change for creating electron hole pairs is given by:

$\Delta S^o=Rln(N_V)+Rln(N_V)=Rln(N_CN_V)$

where N_V and N_C are the effective density of states in the valence and conduction bands, respectively.

and thus we obtain

$n_i^2=N_CN_Ve^{(-\Delta HoRT)}$

Since the volume change is negligible, $\Delta Ho\approx\Delta Eo$

, and therefore $\Delta HoR\approx Egapk$

, from which we obtain

$n_i^2=N_CN_Ve^{(-Egap/kT)}$

and finally

$$\mathbf{n = p = n_i = (N_CN_V)^{1/2}e^{(-Egap/2kT)}}$$

For pure Si (E_{gap} = 1.1 eV) with $N \approx 10^{22}/cm^3$, we can calculate from this equation a carrier density n_i of approximately $10^{10}/cm^3$ at 300 K. This is about 12 orders of magnitude lower than the valence electron density of Al, the element just to the left of Si in the periodic table. Thus we expect the conductivity of pure semiconductors to be many orders of magnitude lower than those of metals.

Conductivity of intrinsic semiconductors

The conductivity (σ) is the product of the number density of carriers (n or p), their charge (e), and their mobility (μ). Recall from Chapter 6 that μ is the ratio of the carrier drift velocity to the electric field and has units of cm^2/Volt-second. Typically electrons and holes have somewhat different mobilities (μ_e and μ_h, respectively) so the conductivity is given by:

$\sigma = ne\mu_e + pe\mu_h$

For either type of charge carrier, we recall from Ch. 6 that the mobility μ is given by:

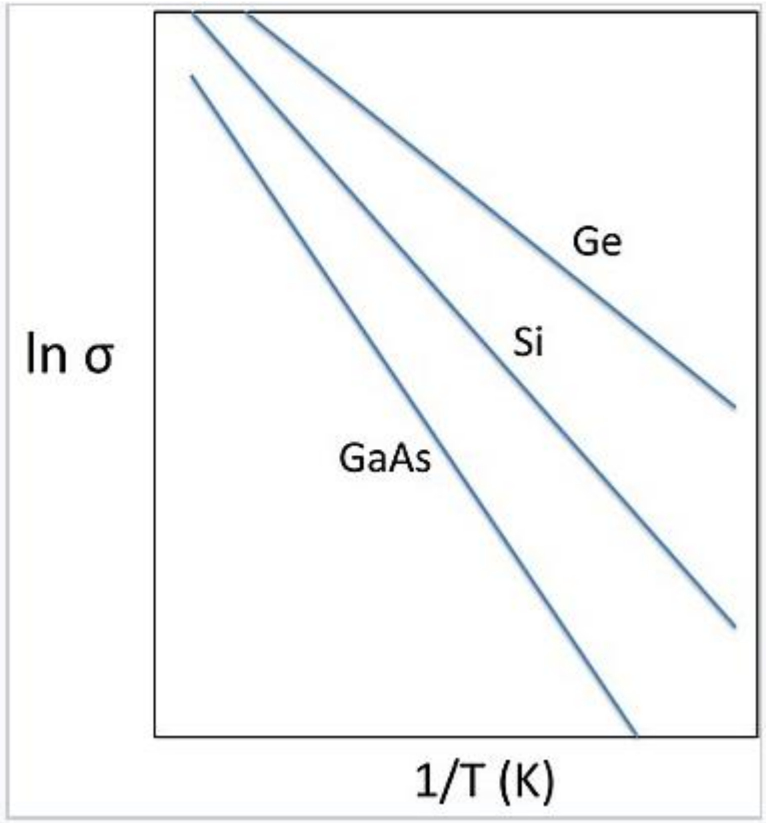
$\mu=v_{drift}/E=e\tau/m$

where e is the fundamental unit of charge, τ is the scattering time, and m is the effective mass of the charge carrier.

Taking an average of the electron and hole mobilities, and using n = p, we obtain

$\sigma = \sigma_o e^{(-E_{gap}/2kT)}$ *where* $\sigma_o = 2(N_C N_V)^{1/2} e\mu$

By measuring the conductivity as a function of temperature, it is possible to obtain the activation energy for conduction, which is $E_{gap}/2$. This kind of plot, which resembles an Arrhenius plot, is shown at the right for three different undoped semiconductors. The slope of the line in each case is $-E_{gap}/2k$.

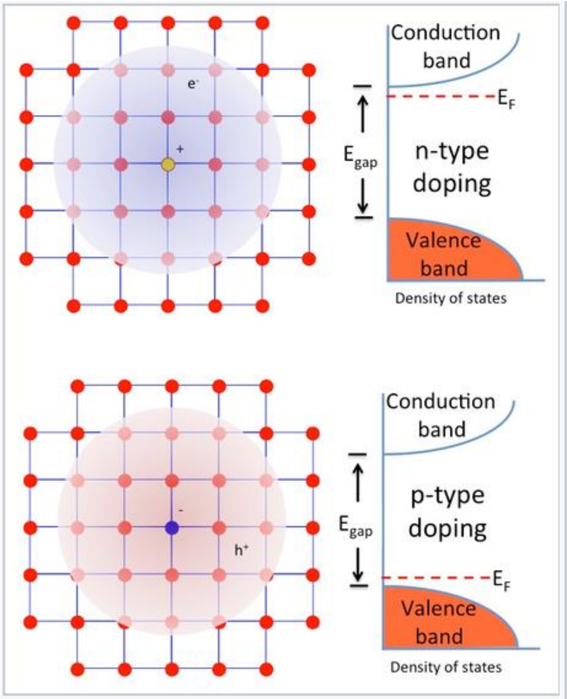


Plots of ln(σ) vs. inverse temperature for intrinsic semiconductors Ge (E_{gap} = 0.7 eV), Si (1.1 eV) and GaAs (1.4 eV). The slope of the line is $-E_{gap}/2k$.

Doping of semiconductors. Almost all applications of semiconductors involve controlled **doping**, which is the substitution of impurity atoms, into the lattice. Very small amounts of dopants (in the parts-per-million range) dramatically affect the conductivity of semiconductors. For this reason, very pure semiconductor materials that are carefully doped - both in terms of the concentration and spatial distribution of impurity atoms - are needed.

n- and p-type doping. In crystalline Si, each atom has four valence electrons and makes four bonds to its neighbors. This is exactly the right number of electrons to completely fill the valence band of the semiconductor. Introducing a phosphorus atom into the lattice (the positively charged atom in the figure at the right) adds an extra electron, because P has five valence electrons and only needs four to make bonds to its neighbors. The extra electron, at low temperature, is bound to the phosphorus atom in a hydrogen-like molecular orbital that is much larger than the 3s orbital of an isolated P atom because of the high dielectric constant of the semiconductor. In silicon, this "expanded" Bohr radius is about 42 Å, i.e., 80 times larger than in the hydrogen atom. The energy needed to ionize this electron – to allow it to move freely in the lattice - is only about 40–50 meV, which is not much larger the thermal energy (26 meV) at room temperature. Therefore the Fermi level lies just below the conduction band edge, and a large fraction of these extra electrons are promoted to the conduction band at room temperature, leaving behind fixed positive charges on the P atom sites. The crystal is **n-doped**, meaning that the majority carrier (electron) is negatively charged.

Alternatively, boron can be substituted for silicon in the lattice, resulting in **p-type** doping, in which the majority carrier (hole) is positively charged. Boron has only three valence electrons, and "borrows" one from the Si lattice, creating a positively charged hole that exists in a large hydrogen-like orbital around the B atom. This hole can become delocalized by promoting an electron from the valence band to fill the localized hole state. Again, this process requires only 40–50 meV, and so at room temperature a large fraction of the holes introduced by boron doping exist in delocalized valence band states. The Fermi level (the electron energy level that has a 50% probability of occupancy at zero temperature) lies just above the valence band edge in a p-type semiconductor.



n- and p-type doping of semiconductors involves substitution of electron donor atoms (light orange) or acceptor atoms (blue) into the lattice. These substitutions introduce extra electrons or holes, respectively, which are easily ionized by thermal energy to become free carriers. The Fermi level of a doped semiconductor is a few tens of mV below the conduction band (n-type) or above the valence band (p-type).

As noted above, the doping of semiconductors dramatically changes their conductivity. For example, the intrinsic carrier concentration in Si at 300 K is about 10^{10} cm^{-3}. The mass action equilibrium for electrons and holes also applies to doped semiconductors, so we can write:

$n\times p=n2i=1020cm-6at300K(10.5.9)$

If we substitute P for Si at the level of one part-per-million, the concentration of electrons is about 10^{16} cm^{-3}, since there are approximately 10^{22} Si atoms/cm^3 in the crystal. According to the mass action equation, if $n = 10^{16}$, then $p = 10^4$ cm^{-3}. There are three consequences of this calculation:

- The density of carriers in the doped semiconductor (10^{16} cm^{-3}) is much higher than in the undoped material ($\sim 10^{10}$ cm^{-3}), so the conductivity is also many orders of magnitude higher.
- The activation energy for conduction is only 40–50 meV, so the conductivity does not change much with temperature (unlike in the intrinsic semiconductor)
- The minority carriers (in this case holes) do not contribute to the conductivity, because their concentration is so much lower than that of the majority carrier (electrons).

Similarly, for p-type materials, the conductivity is dominated by holes, and is also much higher than that of the intrinsic semiconductor.

Chemistry of semiconductor doping. Sometimes it is not immediately obvious what kind of doping (n- or p-type) is induced by "messing up" a semiconductor crystal lattice. In addition to substitution of impurity atoms on normal lattice sites (the examples given above for Si), it is also possible to dope with vacancies - missing atoms - and with interstitials - extra atoms on sites that are not ordinarily occupied. Some simple rules are as follows:

- For substitutions, adding an **atom to the right** in the periodic table results in **n-type** doping, and an atom to the **left** in **p-type** doping.

For example, when TiO_2 is doped with Nb on some of the Ti sites, or with F on O sites, the result is n-type doping. In both cases, the impurity atom has one more valence electron than the atom for which it was substituted. Similarly, substituting a small amount of Zn for Ga in GaAs, or a small amount of Li for Ni in NiO, results in p-type doping.

- **Anion vacancies** result in **n-type** doping, and **cation vacancies** in **p-type** doping.

Examples are anion vacancies in CdS_{1-x} and WO_{3-x}, both of which give n-type semiconductors, and copper vacancies in $Cu_{1-x}O$, which gives a p-type semiconductor.

- **Interstitial cations** (e.g. Li) donate electrons to the lattice resulting in **n-type** doping. Interstitial anions are rather rare but would result in p-type doping.

Sometimes, there can be both p- and n-type dopants in the same crystal, for example B and P impurities in a Si lattice, or cation and anion vacancies in a metal oxide lattice. In this case, the two kinds of doping **compensate** each other, and the doping type is determined by the one that is in higher concentration. A dopant can also be present on more than one site. For example, Si can occupy both the Ga and As sites in GaAs, and the two substitutions compensate each other. Si has a slight preference for the Ga site, however, resulting in n-type doping.