Positive Energy

From rechargeable batteries to fuel cells: electrochemical energy as one of the fascinating and green alternatives to combustion engines

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Abstract

Skyrocketing gas prices, depleted stockpiles of fossil fuels and increasing concern for the environment have brought the issue of energy production and exploitation to the public agenda. Furthermore, it has led many initiatives and "*green*" companies to look for alternative energy sources. In this article, we survey recent innovations and challenges in electrochemical devices such as rechargeable batteries and fuel cells, which in the future could replace the combustion engine. We equally stress the connection between fundamental principles of thermodynamics and, in particular, entropy to any further progress in electrochemical devices and hydrogen economy.

What is energy?

For most people the concept of energy has intuitive meaning, which generally relates to the ability to perform mechanical or electric work. Few people are familiar with the precise (and rather complicated) definition of this physical concept. The word *"energy"* was borrowed in ancient times from the Greek word "*energeia*" which means a system or state in action. Only at the start of the 19th century British scientist Thomas Young and others began to use the word in a scientific context in order to describe what is today called "*kinetic energy*" – energy related to movement of particles.

In fact it is the principle of energy conservation that defines what energy is, and therefore this should be clarified first. This principle determines that in any closed system, isolated from its environment, there is a quantity called "*energy*," which preserves a constant numerical value over time. The physical explanation for the fact that energy remains constant has a profound connection to the concept of time, and in particular to the fact that the physical laws of nature which determine the way the world works in the present will remain the same in the future, just as they have been in the past. In other words, energy remains constant because the laws of nature do not care about the date, hour or moment…

Working out the total energy requires complicated calculations which include, for example, the velocity of all the particles in the system, as well as their mass, their electric charge, their position in relation to other particles and more. The total energy is made up of parts called "*forms of energy*" that have different physical significance.

For example, the energy describing particle motion is called kinetic energy; that which takes into account the attractive force between any two massive bodies (for instance the earth and sun) is called gravitational energy; the part which includes attraction or repulsion of electrically charged particles is called electrostatic energy, and so on. The law of energy conservation determines that the total energy of an isolated system will remain constant as long as there is no possibility of energy exchange with the environment. But the different parts of this expression (the different forms of energy) may be transformed one into another. Thus we can produce one form of energy from other forms. For instance in an electric power plant the chemical energy stored in fuel (fuel oil, coal or natural gas) is transformed into heat (through combustion with oxygen in the air), which in turn is used to heat water into steam. Steam under high pressure has large kinetic energy and is used to rotate large turbines, producing electricity similar to a dynamo that produces electricity from rotation of bicycle wheels.

Electrochemical Energy

Molecules are the most basic unit of matter, made up of atoms that are attached to each other by chemical bonds. These bonds determine the energy state of the molecule, that is, its chemical energy. In chemical processes it is possible to perform a reaction in which several reactants create a new molecule. When the energy state of the products is greater than that of the reactants this means that energy from an external source has been invested (Figure 1a). However, when the final state has lower chemical energy than that of the reactants, the energy difference will be transformed to another form of energy, such as heat which is released to the environment (Figure 1b). This difference is called the energy of the chemical reaction.

In electrochemical devices the chemical energy of the process is transformed to electrical energy and to heat. A well known example is the electric battery, invented by Italian physicist Alessandro Volta over 200 years ago.

Electrochemical devices which transform chemical energy to electrical energy appear usually in one of two forms: batteries and fuel cells. Everyone is familiar with batteries, due to their frequent use in daily life. In contrast fuel cells are less well known because their main application so far has been in space programs. However, in the last few decades' great effort has been invested in applying fuel cells to electricity production in the automobile and microelectronic industries, as we shall see below.

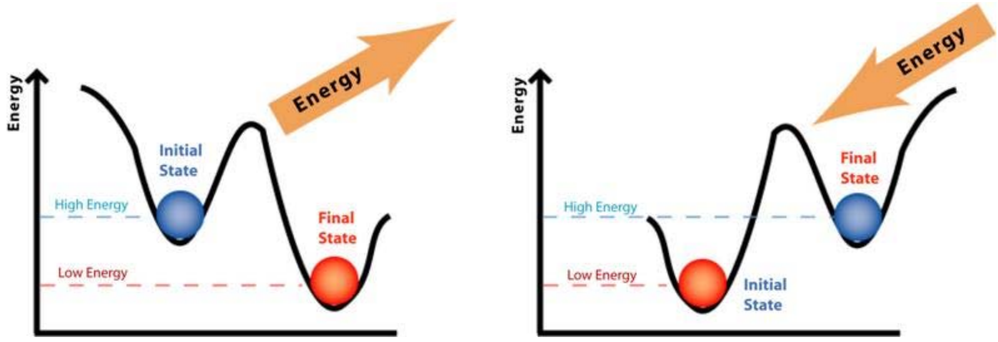


Figure 1. | Energy scheme. (Right) The system passes from an initial state with low energy to a final state with higher energy through use of external energy (for example, climbing stairs). (Left) The system passes from an initial state with high energy to a final state with lower energy, and the excess energy is released to the environment.

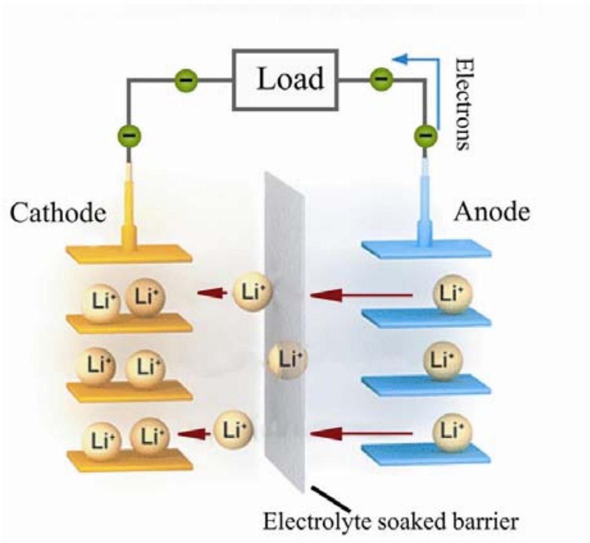
How does an electric battery work?

A battery is an independent unit (cell) in which stored chemical energy can be transformed to electrical energy on demand. One usually distinguishes between primary batteries (cells) which are disposable and rechargeable ones. Figure 2 shows a schematic of a rechargeable ion-lithium battery. The electrical energy is created by chemical reactions which occur simultaneously in both electrodes (poles of the battery). The anode is the negative pole ("*minus of the battery*") and the cathode is the positive pole ("*plus*").

Today a large number of batteries are in use. They differ in the materials used to construct the electrodes, the type of electrolyte and their capacity, shape and working voltage. Basically they all work in a similar way, as seen in Figure 2 for the ion-lithium battery. The anode contains materials characterized by large tendency for *oxidation*. That is, it is made of materials such as lithium, zinc and lead which easily donate electrons. In contrast, the cathode is made of materials, such as manganese oxide (MnO_2), lithium cobalt oxide ($LiCoO_2$) and lead oxide (PbO_2), which are able to undergo *reduction* by receiving electrons. Between the anode and the cathode there is a porous barrier saturated with an electrolyte, also called a separator.

It now becomes necessary to clarify the difference between electrical conduction in metals and ionic conduction in an electrolyte. Metal conducts electricity because an electric potential difference in the metal enables a flow of electrons through it without any flow of the atoms. An electrolyte, on the other hand, is an insulator that does not enable electron flow, but the ions themselves are able to move through it. While the external device is operated (and the electric circuit is closed) ions move through the electrolyte soaked barrier, and this is called migration current. The electrolyte can be made of an aqueous liquid solution, non-aqueous liquid or a gel. In the liquid cells acids or bases are used, while for ion-lithium cells non-aqueous solutions containing lithium salts are used. The batteries which include electrolyte solution require a hermetically sealed package in order to prevent leakage, evaporation or infiltration of water or air. Figure 3 shows two common battery types.

Discharge of an ion-lithium battery, where chemical energy is converted to electric energy (see Figure 2), takes place simultaneously in both electrodes. In the anode ions and electrons are formed spontaneously in the oxidation process. The ions move through the electrolyte towards the cathode, while the electrons cannot pass through the electrolyte and must reach the cathode through the external circuit, the "*load*". An ion that reaches the cathode undergoes there a chemical reaction with the cathode material as well as with the electron arriving through the external circuit (the device which we are activating). This is the reduction (trapping) process of the electron. This process takes place continuously in the battery as long as the circuit is closed, and as long as there is enough reactive material in the electrodes. A considerable fraction of the energy released in this process is converted to electric energy by the electron passing through the external circuit, and this is the energy which the battery supplies.



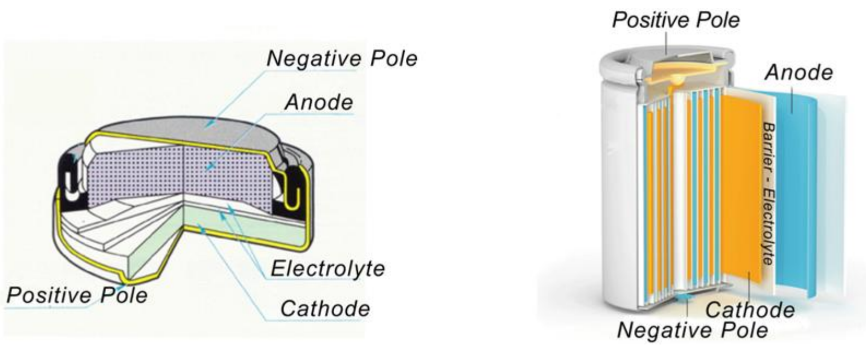


Figure 2. | Principle of operation of an electric battery.

Figure 3. | Common forms of batteries. (Right) Cylindrical battery. The most common form of battery constructed of layers of cathode – barrier (soaked with electrolyte) – anode, rolled up in order to obtain high energy capacity. (Left) Button battery used in watches, calculators, hearing aids, etc.

One of the most common forms of disposable batteries in use today is the *lithium battery*, where a film of metallic lithium serves as anode. Lithium is a chemical element from the alkaline metal family (found in the first column of the periodic table). It is light, reacts easily by giving up its electron and is an excellent candidate for conversion of chemical energy to electric energy. Other more advanced batteries in use today are the rechargeable lithium-ion batteries mentioned above. These batteries do not contain metallic lithium but rather lithium ions which are introduced into a solid carbon matrix (e.g., graphite). During the oxidation (discharge) process, lithium ions are released from the anode side and pass through the electrolyte to the cathode, where by means of the chemical reduction process they create lithium cobalt oxide. At the same time, electrons flow through the external circuit from anode to cathode and supply electric energy.

The major advantage of an ion-lithium battery is that it can be recharged (that is, the reverse process can be carried out) many times, and it has specific energy (energy per unit mass) similar to that of disposable batteries. In a disposable battery the products at the cathode and/or anode have undergone chemical reactions which do not enable recharging. In contrast, in the ion-lithium battery during the charging and discharging process, lithium ion "*visitors*" that are inserted and extracted cause only slight changes in electrode structure. Therefore, use of voltage higher than that of the battery (investment of electric energy) enables return of the lithium ions from the cathode to the anode, through the electrolyte. As the battery is recharged, electric energy is converted back to chemical energy – enabling it to be used again and again for many discharge/charging cycles.

There is yet a newer generation of rechargeable ion-lithium batteries called *lithium-ion polymer* (Li-Poly) batteries. The difference is that instead of a liquid electrolyte these batteries contain electrolyte in gel form. The use of gel decreases the danger of leakage and enables hermetic packaging in a metal foil coated with a polymer foil. These batteries are lightweight and may be shaped in various forms, such as a flat battery, about millimeter thick, which fits into a smart credit card (Figure 4).

Figure 4. | Smart credit card with a flat battery one millimeter thick. Courtesy of EMUE Co.

A number of important parameters should be considered when comparing performance of different batteries. These include: power (generated energy per unit of time), stored energy per unit of weight or volume, working temperature range, safety and efficiency of the battery. *Battery efficiency* is defined (for a primary battery) as the ratio between the amount of energy which may be converted to electricity and the total chemical energy stored in the battery. This efficiency parameter is important not only in batteries, but in all processes where stored energy is only partially converted to electricity or to work, while the remaining energy is wasted, primarily as heat.

The energy stored in the battery is usually measured in units of watt-hour (an energy unit equal to the work done by one watt operating during one hour). It is also customary to discuss energy in units of ampere per hour for a given working voltage. Choice of the most appropriate battery depends on the application. For example, in hearing aids or pacemakers, in which volume limitations are more important than weight and there is no practical possibility to recharge the batteries, it would be best to choose a disposable battery with high energy per unit volume. In other applications where weight is more important than volume, such as computers and mobile phones, we would choose rechargeable batteries with high energy per unit of weight.

Another important consideration is the amount of time needed for recharging, since the battery cannot be used during recharges. In mobile applications such as electric cars, it is a distinct disadvantage if the car may not be used for several hours while recharging. The difficulty that arises from the need to recharge the battery has found at least a partial solution in a different device which converts chemical energy to electricity: the *fuel cell*. Unlike a battery, the chemical energy of a fuel cell is not stored inside but is fed continuously from an external source of fuel (such as an external hydrogen tank) that enables mobile and continuous use.

Fuel cells in daily use: from mobile phones to illuminating cities

Rechargeable batteries and fuel cells are characterized by high efficiency, low wear and tear and relatively quiet and clean operation without discharge of greenhouse gases. These characteristics of the two technologies emphasize their potential to replace combustion engines in vehicles. Each of the two technologies has characteristic advantages and disadvantages. Fuel cells can operate in different temperature ranges and may supply power in a wide range, from single watts through megawatts (millions of watts) in the future. Apparently it will be possible to exploit these impressive characteristics in many and varied areas: from innovative batteries to mobile phones, for cars and public transport (buses and trams) and up to power plants which will be able to supply electricity to entire cities! Figure 5 shows some common fuel cells, their uses and their working temperatures.

A brief historical survey: although the term "*fuel cells*" is perceived as a novel and revolutionary invention, in fact 170 years ago, in 1839, Swiss scientist Christian Friedrich Schönbein reported electric current created as a result of combining hydrogen and oxygen. Three years later British scientist William Grove invented the first fuel cell, which he called a "*gas battery*". Technological problems deferred the development of fuel cells for over a hundred years, and only at the beginning of the 1960's did the fuel cell enter the market as a commercial product. Its first use was when NASA in cooperation with General Electric developed a fuel cell for the Gemini Spaceship project.

The oil embargo in 1973 spurred several companies to invest in development of fuel cells in the 70's. Since then the field has grown and developed, and in recent years there is a clear increase in research and development of fuel cells, while the main challenges are to find materials and processes which are more efficient and economically viable.

Fuel cell structure

Today there are several types of fuel cell on the market, differing in composition, working temperature range and power. However, their basic working principles are the same and the fuel source for the cell always includes some form of hydrogen-containing material.

The main components of the fuel cell are the anode, to which hydrogen is supplied; the cathode, to which oxygen is supplied; and an electrolyte membrane which enables the hydrogen ions but not the electrons to pass through (see box). Both anode and cathode are covered with a catalyst layer. In the presence of the catalyst the rate of oxidation-reduction rises as does the current in the cell. However, it is important to stress that the catalyst does not change the energy balance in the cell. In the anode the catalyst accelerates the rate of transformation of hydrogen molecules into hydrogen ions and electrons, whereas in the cathode the catalyst accelerates the rate of transforming oxygen, electrons and hydrogen ions into water.

How the fuel cell does produce electricity?

Basically the fuel cell exploits the release of energy in a process where water molecules are created in order to produce electric energy. The process may be compared to a waterfall: water at the top of the waterfall has higher energy than that at the bottom, and so energy is released as the water falls downward.

The falling water crashes down at the bottom of the waterfall, and the kinetic energy released in the process is wasted in creation of mist, sound, heat and swirls. However some of it can be transformed into mechanical energy if we build an appropriate device such as a water wheel, where the water does not fall to the bottom with a sudden and inefficient release of energy but rather rotates the wheel. Similarly, in the chemical reaction water molecules are created and energy is released. Without the appropriate apparatus this energy would go to waste and most of it would be transformed to heat. The unique structure of the fuel cell allows such energy to be transformed to electric energy during the process of production of water molecules. Instead of having hydrogen molecules transfer electrons directly to the oxygen molecules in a normal chemical process, the electrons are constrained to pass through the electric circuit.

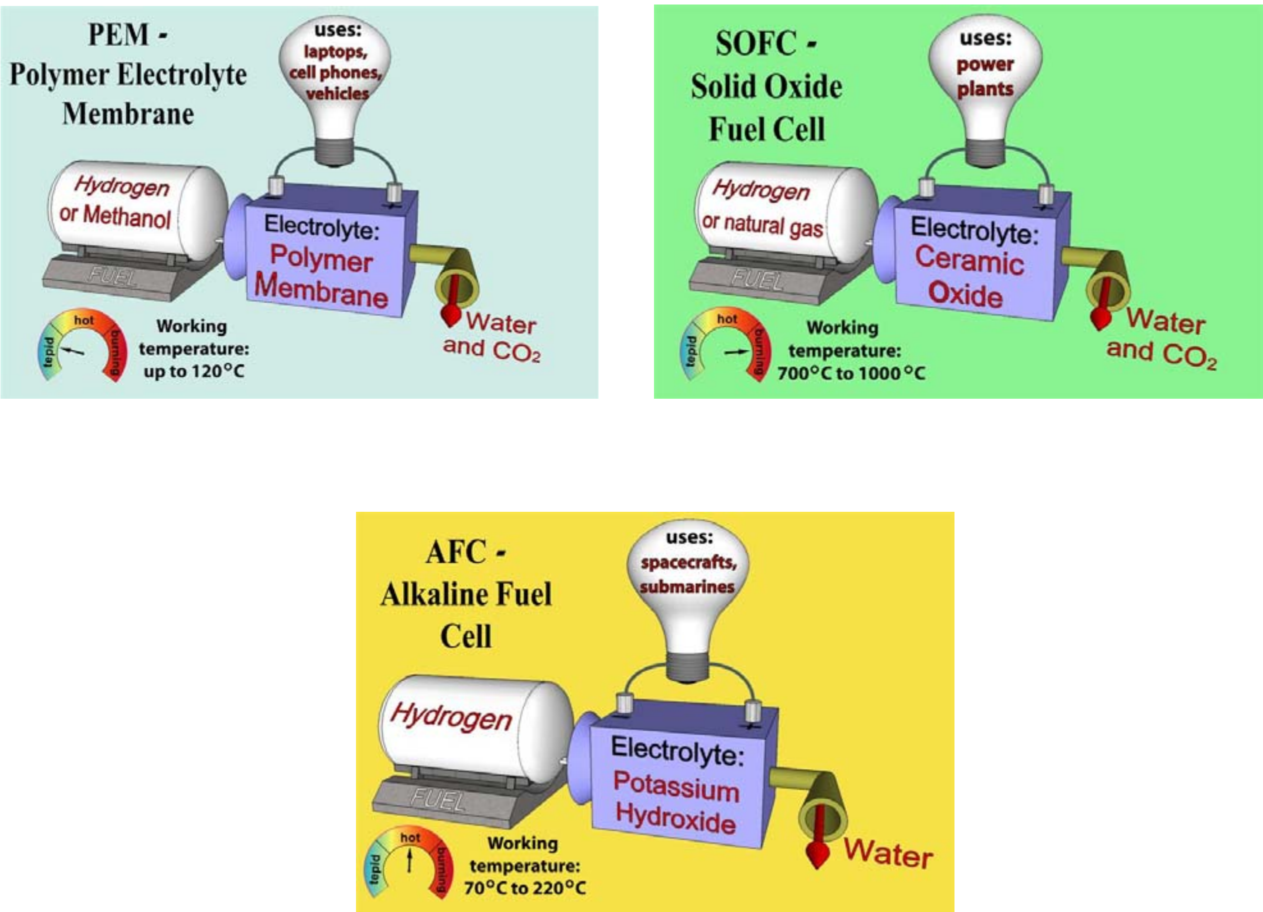


Figure 5. | Three common fuel cells and their characteristics. In each of these three cases, the fuel is hydrogen and/or hydrocarbon. Oxygen, air or another oxidant is supplied to the cathode.

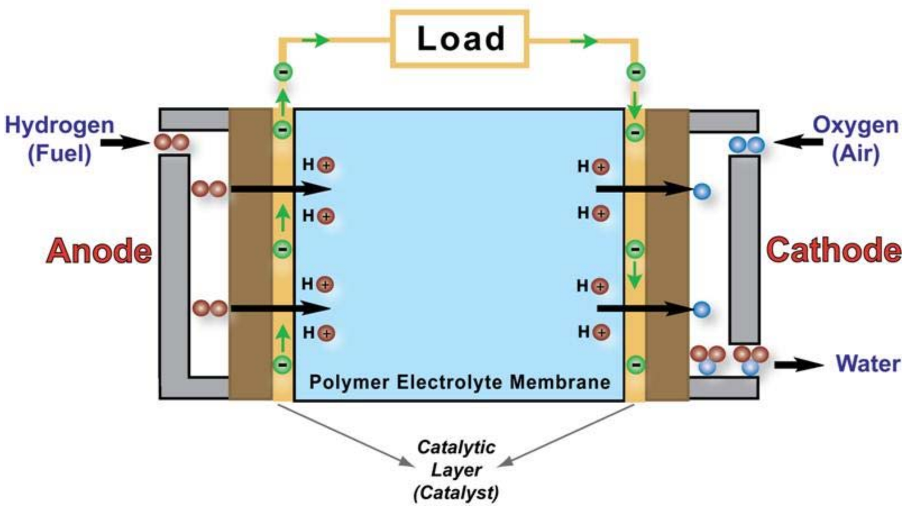


Figure 6. | Illustration of the basic operating principle of a typical PEM (Polymer Electrolyte Membrane) fuel cell.

The way chemical energy is transformed to electric energy in a fuel cell, as shown in Figure 6, has a lot in common with the principle of operation of an electric battery. First, we explain what happens in the anode, where a hydrogen molecule (H_2), made up of two hydrogen atoms, is adsorbed by the catalytic layer and breaks up into two H^+ hydrogen ions and two e^- electrons. The process is conventionally written as:

$$H_2 \rightarrow 2H^+ + 2e^- .$$

Under the influence of the electric field the hydrogen ions pass through the electrolyte membrane from the anode, where they are created and found in high concentration, to the cathode where their concentration is low. The membrane, similar to the electrolyte layer in a battery, is permeable only to ions but does not permit electrons to pass through. Therefore, electric voltage develops between the two terminals, with a maximum value of 1.23 volts. Since the electrons cannot pass through the cell, they will flow through the external circuit and reach the cathode (when such a circuit is connected to the cell). In the cathode, oxygen molecules from the air break down under the influence of the catalyst to oxygen atoms. These react both with the hydrogen ions and with the electrons arriving from the anode via the electric circuit. When the process is complete, two water molecules are created from each oxygen molecule, and the process is written as:

$$O_2 + 4H^+ + 4e^- \rightarrow 2H_2O.$$

The difference in chemical energy between the water molecules and the hydrogen and oxygen molecules is transformed into electric energy. In order to create a higher electric voltage than the voltage created by one cell, several fuel cells can be connected in series, as is customary with ordinary batteries as well.

The Electrolyte Membrane and the Catalytic Layer

The electrolyte membrane enables transport of hydrogen ions from the anode to the cathode, but does not allow passage of electrons. The membrane structure varies according to type of fuel cell, and is the central component differentiating various types of cells. One of the most common membranes, found especially in fuel cells used in the automotive and electronic industries, is a polymer membrane made of material called Nafion. This polymer has hydrophilic ("*water loving*") regions and hydrophobic (water repelling) regions. Upon contact with water this combination creates nanoscopic water channels, which enable passage of hydrogen ions through the membrane. The skeleton of the polymer structure is made of Teflon, and of negatively charge groups of sulfur trioxide (SO_3^-) that are attached to it. Therefore, the Nafion structure allows passage only of positive ions as required of the membrane.

Drying out of the water channels in the polymeric membrane is one of the principal causes of the considerable decrease in efficiency of the fuel cell with time. The ion passing through the channel due to the electric field (migration) drags along some water molecules and dries up the channels. Possible solutions to the drying problem are application of a pressure gradient between the anode and cathode causing the water to flow backwards to the membrane, or enrichment of the fuel with water vapor which will attach to the hydrogen ions entering the membrane and prevent drying out of the water channels.

The catalytic layer. The catalyst adjacent to the anode is usually constructed of nanometric particles of various platinum alloys. When a hydrogen molecule is adsorbed onto the catalytic layer, the probability for oxidation increases, and the molecule breaks down into two electrons and two protons (ionic hydrogen). Similarly, the catalytic layer adjacent to the cathode facilitates the breakdown of oxygen molecules (O_2) into two oxygen atoms. Today, great effort is invested in research on development of more efficient nanometric catalysts, particularly for oxygen reduction. The aim is to find catalysts that will reduce considerably the amount of platinum in the fuel cell, because it is an expensive raw material.

Batteries and fuel cells in the automobile industry

Among the various alternatives to combustion engines that consume fossil fuel, solutions based on electric engines stand out in particular. Rechargeable electric batteries and fuel cells are two competing technologies for supplying energy to electric engines in vehicles.

Considerable progress in development of wide variety of lithium batteries has made this technology a natural and immediate candidate in the automobile industry as well. Hybrid cars are already found on the roads, and enable about 40% saving on gas. In these cars, in addition to a small and economic combustion engine operating at constant speed (without acceleration) there is a rechargeable battery supplying part of the energy moving the vehicle. These batteries are recharged by the engine and by exploitation of the energy released while the car is braked. At present the small battery size enables only savings on gas and does not bring true ecological breakthrough such as that which could come from electric cars based 100% on rechargeable batteries. However, genuine electric cars still have some significant weaknesses: low energy content of the battery and its heavy weight enable maximum travel range of about 250 kilometers before recharging, and require extended recharging time which generally takes several hours. Additional problems include price, safety problems, a narrow range of operating temperature and cycling stability problems in ongoing battery operation. The projected aim is to reach lifetime of rechargeable lithium batteries with about 1000-2000 recharging cycles.

In this respect the *Better Place* Company of Israeli entrepreneur Shai Agassi should be mentioned. The company plans to supply infrastructure solutions for electric cars. The company vision is to provide day and night parking lots with docking stations where electric cars can be recharged, especially during the night, when average electric consumption is low. In addition, there will be a network of stations (similar to gas stations) for quick replacement of empty batteries with fully recharged ones.

Another technology which is still in early development stages is that of fuel cells whose performance approaches that of gasoline and diesel engines. Several automobile companies have successfully demonstrated use of this technology in concept cars. The principal aim in these prototypes is to increase travel range before refilling, and to manufacture more efficient fuel cells. However as of this day the main obstacle in the transition to mass production of cars based on fuel cells is not technological but economical. Production of hydrogen gas and the high cost of manufacture of fuel cells are still not competitive with the cost of fossil fuel gas and combustion engines. In order to lower manufacturing costs of fuel cells and hydrogen there is need for their mass production. Here is the source of the economic catch, a sort of "chicken and egg" paradox: the public will turn to hydrogen operated vehicles only when there will be an infrastructure of filling stations properly spread out, whereas the gas companies will spread out sufficient hydrogen filling stations only when this will be economically viable. Currently fuel cell vehicles serve only for local or regional transportation, where it is possible to reach a filling station: within cities, factories, industrial zones, testing grounds and so on. But even this limited use enables experiment and improvement of the technology and infrastructure, and constitutes an important milestone on the road towards a hydrogen economy.

For example, General Motors has recently manufactured about a hundred Chevrolet Equinox cars powered by fuel cells, in an attempt to examine the car operation and infrastructure, as well as reactions of drivers and passengers (Figure 7). The expectation is for a few thousand of these cars to go on the road in the coming decade, while the emphasis in development will be on cost reduction. Mass production of fuel cell based vehicles will become possible if these aims are realized, but it is hard to predict a timetable and whether this technology will indeed fulfill all the hopes it has aroused.

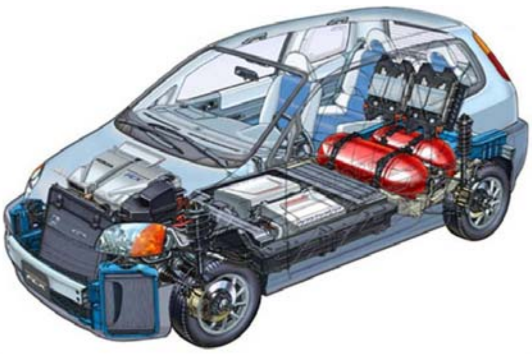


Figure 7. | (Left) A hybrid Honda FCX with hydrogen-based engine. The hydrogen in the containers (in red) feeds the fuel cell system (in white) which propels the electric engine. (Right) Chevrolet Equinox. In 2009 about a hundred of these cars were on roads in Los Angeles, New York and Washington DC area.

Micro fuel cells

The last decade has witnessed a major growth in demand for portable electronic devices, especially in the field of communication and internet. In parallel, significant development has occurred in rechargeable lithium and nickel batteries in order to meet the growing energy demands. But the next generation of portable electronic instruments requires that rechargeable batteries have large energy density. That is, production of larger energy throughput with a lower battery weight. With integration of cellular communication in the internet wireless market these requirements have become even more important, and lithium batteries are incapable of supplying in full the demand for increase of energy density and operation time between charges. This situation has brought recognition that fuel cell technology has potential in the field of portable electronic devices as well.

In contrast to the automobile industry, where it is natural to use hydrogen as fuel due to its high efficiency, in the microelectronics industry such use is problematic. Storage of pressurized hydrogen gas is complicated and expensive, particularly due to low desired weight of the portable fuel cell. Similarly, usage of compressed hydrogen for portable devices may create a safety hazard (in cars, in contrast, there is both a massive fuel cell and room to install control systems which substantially decrease the risk of hydrogen handling). For this reason liquid-hydrocarbon fuel rich in hydrogen often replaces hydrogen in portable devices, even though its efficiency is lower than that of hydrogen. For example, a methanol (CH_3OH) fuel cell containing hydrogen, carbon and oxygen may serve as an immediate source of electric energy without the need for extended battery recharging. This type of cell is known as DMFC (direct methanol fuel cell).

At the school of chemistry of Tel Aviv University an archetype of a DMFC fuel cell fed by methanol (or by a different alcohol called ethylene glycol) has been developed. It can operate a small portable computer for 6 hours (Figure 8). Similarly microelectronics companies such as Toshiba, Motorola, Samsung and NEC are developing fuel cells for use with their portable products, and perhaps the day is near when we will refill our laptops or our cell phones with alcohol instead (or in addition to) recharging them from an electric socket.

Figure 8. | Archetype of DMFC fuel cell for operation of laptop, developed at the school of chemistry of Tel Aviv University.

Figure 9. | Archetype developed by Fujistu Company: portable charger for a phone based on DMFC fuel cell. 18 cc of methanol are sufficient to charge 3 lithium batteries.

How Efficient Are Processes of Electricity Production?

Not all chemical energy released in a battery or a fuel cell can be converted to electricity. In fact, part of it will *always* be converted to heat. What is unique about electrochemical devices is that at low power operation the maximum amount of chemical energy may be converted to electric energy. In other words, at low power operation the energy conversion efficiency is close to 100%, while at higher power operation the energy loss to heat will be much greater.

It is interesting to note that although developments in batteries and fuel cells are based on contemporary technological innovations, the limitation of efficiency in processes of energy conversion is not technological but rather a deep constraint related to the science of thermodynamics, and has been known for over 150 years.

Thermodynamics is a theory developed in the 19th century, which explains conversion of energy and heat in physical, chemical and even biological systems. This theory is based on three fundamental laws. The first law of thermodynamics is the law of energy conservation, which determines that the total energy in a closed system remains constant at all times, provided that no energy or particle flow in or out is permitted. The second law is related to the concept of *entropy*, which is a measure of the disorder of the system. This law determines that the entropy of a closed system can either remain constant or increase – but it will never decrease (see box).

In processes such as those occurring in electrochemical cells (fuel cells and batteries) the second law has an important implication for efficiency limitations. If we compare the entropy of the reactants to that of the products it would seem that the entropy in the process decreases, in contradiction of the second law. This mistake results from our taking into account only the fuel cell or battery structure, while we have not considered the total entropy, which includes the external environment of the cell as well. Indeed, after a chemical reaction has occurred in the electrochemical cell the entropy of the environment has increased, so that the total entropy in the system (cell and its environment) has not decreased, exactly as the second law dictates. How has the entropy of the environment increased? By the flow of heat from the cell to its close environment! Since the total energy in the process is conserved, the more energy we waste by emission of heat to the environment, the less energy we can exploit for production of electricity. On the other hand when entropy increases during the process of battery discharge, the battery draws heat in from the environment (and from the battery) and converts it to electric energy at a theoretical efficiency of 100%.

Entropy and the second law of thermodynamics

Let us consider a system, composed of a large number of atoms and molecules. System characteristics such as pressure and temperature do not depend on the specific state of each and every microscopic particle in the system, but only on their average characteristics (just as there is no need to measure the velocity of all atoms in order to determine body temperature). These characteristics define the general macroscopic state of the system. And indeed each macroscopic state may result from a huge number of microscopic states, and this number of states is related to the entropy of the body (more precisely, the entropy is related to the logarithm of this number of states).

We proceed by an illuminating example. When a drop of ink (or food coloring) drips into a glass of water, the drop mixes with the water by itself without external intervention. This process is closely related to entropy, because the number of microscopic possibilities that the water and ink molecules have in the glass is enormous. Relative to this number, the number of possibilities that the water and ink molecules remain separate is miniscule. In the language of thermodynamics we can say that the entropy of the system in which the ink and water are separate is much smaller than in the case where the two liquids are mixed together. The second law of thermodynamics states that entropy will never decrease in physical processes, and it looks fairly intuitive from this example: if we leave the glass standing for a long time we will not expect to find it returning on its own to the initial state in which the water and ink were completely separate. On the contrary, the system will reach the state where entropy is maximal – when the water and ink molecules are completely mixed. It is important to note that the second law is valid only in physical processes taking place in a closed system that is energetically isolated from its environment. For example, during water purification process, energy is invested from outside in order to separate unwanted solutes and impurities from the water. In this process the system is not closed and its entropy actually decreases, in perfect agreement with the second law.

The concept of entropy is closely related to heat. Heat results from motion of an enormous number of particles moving in random directions at different velocities, and so heat may be seen as a form of entropic energy. In contrast, other forms of energy are usually more 'ordered', such as mechanical energy, which is related to motion of bodies in defined directions and velocities. The second law limits our ability to efficiently convert heat to other forms of energy, e.g., to mechanical propulsion. The reason for this is that energy conversion of random motion (heat) to energy of directed motion (propulsion) involves decrease of the entropy, and we will have to 'pay' for this with wasted energy.

Why is an electric engine more efficient than an internal combustion engine?

Generally speaking the efficiency of an electric engine is significantly greater than that of combustion engines. The main reason for this is related to the so called *Carnot's energy conversion bound*. Sadi Carnot was an exceptional French scientist and engineer who lived in the 19th century. He was the first to understand that there is an upper threshold to the efficiency of engines in which heat is released. The combustion (or steam) engine works by the principle of transfer of energy from a hot area (the engine's combustion chamber) to a cold area (the air outside of the car). In the combustion process hot gases under high pressure are created in the combustion chamber. As these gases are transferred outside, part of the energy is converted to mechanical work. The Carnot bound, which is Carnot's efficiency threshold, determines that all of the heat energy cannot be converted to mechanical energy. Part of the heat energy will necessarily be released to the environment. This is the upper limit to the ideal efficiency of combustion engines, but it is not applicable to electric engines. The reason for this is not fully explained here and is related to the concept of entropy and the second law of thermodynamics. A simplistic explanation is that the slower and more controlled the process, such as in an electric engine, results in a smaller change in entropy. Namely, less heat is created and wasted.

Comparing the efficiency of different engine types is not at all simple, but it is clear that the efficiency of a combustion engine is considerably smaller than the process where energy is first converted to electric energy using a fuel cell or battery, and only afterwards it is further converted to mechanical energy by means of an efficient electric engine. The slow oxidation process taking place in a battery or fuel cell releases less heat than the quick burning of fuel at a very high temperature, or the quick expansion of air in the pistons of a combustion engine.

As shown in Figure 10, cars propelled by means of hydrogen fuel have a long energy chain: starting with the process of hydrogen production, through its compression, storage and transport. It is important to remember that part of the energy invested for the purpose of propelling the car will be wasted even in the most efficient process, and greenhouse gases will still be released. However, such processes are far more efficient than combustion engines.

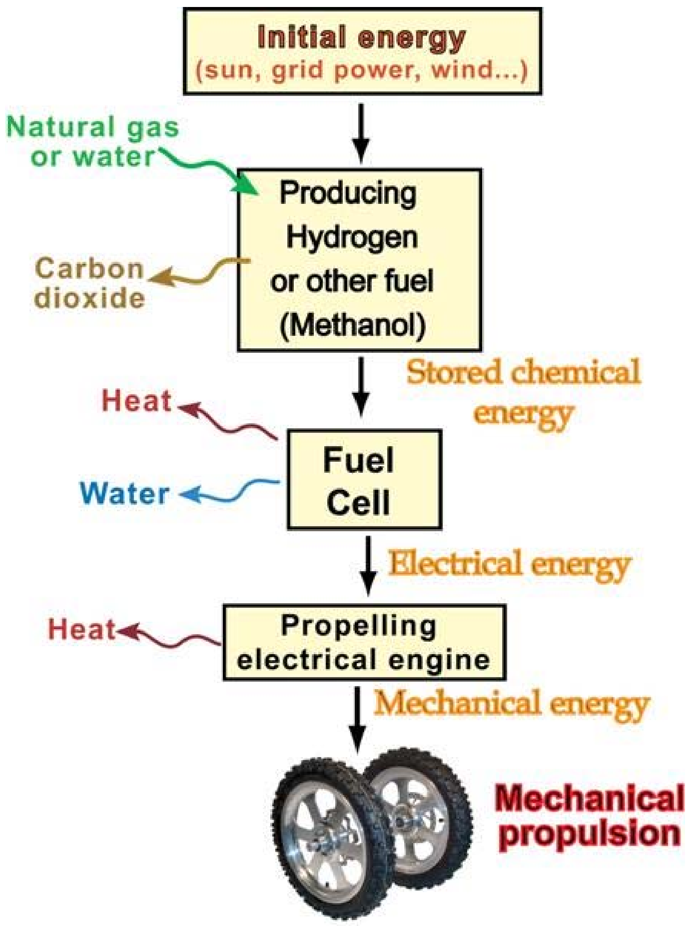


Figure 10. | The energy chain of energy productions and transformations.

Hydrogen economy and ecology

Hydrogen is the most abundant element in the universe, and it makes up about 75% of the Earth's mass. In contrast, the earth's atmosphere contains hydrogen gas (H_2) in very small concentration, because the gas easily escapes from the atmosphere to outer space due to its low density relative to other atmospheric gases. On earth hydrogen is common in the form of chemical compounds with carbon (hydrocarbons) or water (H_2O) found mainly in the oceans. For this reason, use of hydrogen as fuel requires the production of molecular hydrogen from other sources, and all calculations related to efficiency and cost must take this process into account.

Hydrogen is a flammable and volatile gas, as is borne witness by the explosion of the German airship Hindenburg which led to the death of 36 people in full view of journalists' cameras in 1937. The main concern in use of hydrogen gas is the fact that it ignites in a wide range of concentrations, and that it is nearly impossible to observe its flame. However with proper engineering design taking into account the low density of hydrogen, its quick dispersion that prevents it from achieving volume concentrations required for ignition, as well as the high temperature at which hydrogen ignites, it is possible to obtain fairly safe hydrogen usage. And, indeed, many industrial facilities routinely make use of hydrogen without accidents.

Engine efficiency

An engine is a machine that converts energy from some source to mechanical energy for doing work. In general, engines can be divided into different types depending on the kind of energy the engine uses. The two most common engines are the internal combustion engine and the electric one.

The internal combustion engine, like that found in cars, is in fact a heat engine that "absorbs" heat from its environment (combustion chamber) and converts it to mechanical work. The Carnot threshold strongly limits the efficiency of a heat engine, and for a car engine whose combustion chamber reaches a temperature of about 700^{o}C degrees Celsius, the ideal efficiency will not exceed about 70%. The significance of this bound is that between a quarter and a third of the energy stored in the fuel will be wasted as heat even in the most efficient engine. In reality, the efficiency of combustion engines is far lower even than this.

The electric engine is an engine that converts electric energy to mechanical one. In this engine too part of the electric energy is wasted as heat due to friction and electrical resistance, but the typical efficiency of an electric engine is over 90%. Electric energy is usually supplied by an electric battery or an A/C power supply, and at times by a fuel cell or solar cell. Each of these methods of electricity production has its own efficiency. The efficiency of conversion of solar energy to electric energy, in a typical solar cell is low and usually ranges from 5% to 20%. However, solar energy is readily available and need not be manufactured. The efficiency of conversion of the chemical energy stored in hydrogen to electric energy for a fuel cell is far greater and ranges as a rule from 50% to 70%, but this estimate does not take into account the energy invested in the process of hydrogen production!

Is hydrogen a green and environmentally friendly fuel?

It appears that in the process of hydrogen combustion or oxidation only water is emitted to the environment and not greenhouse gases (such as carbon dioxide). Hence, it seems that hydrogen is a completely green gas. However, since pure hydrogen is extremely rare on the earth and has no natural reserves, it becomes necessary to produce hydrogen from other materials with artificial processes, which by themselves consume energy and are often accompanied by emission of greenhouse gases.

The production of hydrogen is a fairly routine matter, and about two percent of global energy consumption is used at present in its production as an intermediate product in various industries (High Hopes for Hydrogen**,** *Scientific American* **295,** 94, 2006). The reason for this is that hydrogen is used in oil refineries to purify oil from sulfur, to break up large molecules contained in crude oil and to produce ammonium and other chemicals. In fact if we were to use all the hydrogen produced today solely as fuel for the automobile industry, we could fuel up about 20% of the global fleet of vehicles.

The vast majority of hydrogen serving the petrochemical industries is produced from natural gas and petroleum. The drawback in this method is that carbon dioxide is emitted to the atmosphere – exactly what we tried to prevent in the first place by changing over from combustion engines to fuel cells and electric engines! Nonetheless, there is a major advantage. Even though greenhouse gases are emitted when producing hydrogen from natural gas, these can be supervised and controlled far more efficiently than emission of greenhouse gases by combustion engines. Needless to say, the ultimate aim is to manufacture hydrogen with minimal greenhouse gas emission, if any.

One of the more attractive ideas is the production of hydrogen gas from biomass and from organic fertilizer by controlled heating to high temperatures in the presence of oxygen and water vapor. On balance this process will not add greenhouse gases to the atmosphere because the organic material is based on vegetation which absorbed a similar amount of greenhouse gases from the atmosphere during its growth by photosynthesis. These gases would be emitted in any event back to the atmosphere in the process of rotting and natural decomposition that characterizes the decay of organic materials. Another clean possibility for hydrogen production is the breakup of water by electrolysis using 'green' energy, such as windmills, solar energy and hydraulic energy. However these clean methods of hydrogen production require many more years of development. In particular, in order to decrease their high production costs.

It appears that in the near future the use of natural gas for hydrogen production will feed the future hydrogen economy. Although this is not the perfect solution in terms of air pollution, it is this solution which will push forward massive use of hydrogen and will enable the transition to production of "cleaner" and "greener" hydrogen in the future.

Hydrogen – cheaper than gas?

Right now hydrogen is more expensive than gasoline and diesel and it has a few drawbacks. Transport of hydrogen is a complicated and expensive process. In order to efficiently transport hydrogen it must be compressed at a pressure of 700 atmospheres or chilled to a temperature of minus 253°C, and transported in liquid form. Hence, storage of the hydrogen requires very low temperatures or use of sturdy containers able to withstand very high pressures. These facts not only make the use of hydrogen more expensive, but also predict the future of hydrogen production. Since hydrogen can be produced in a wide range of processes, it will be produced locally according to need, making use of the natural resources available in each area. For example, in sunny areas solar energy can be used to break up water into hydrogen, and hydrogen will need to be transported from afar only to isolated areas. Manufacture of hydrogen by means of clean energy is a very expensive process, and even hydrogen production using natural gas is more expensive than gasoline. Reduction of cost will become possible in the future when the demand for hydrogen will grow and its production will be more common, along with increase of carbon fuel prices as a result of depletion of natural resources. Even if the price of hydrogen would be double that of carbon fuel (per unit energy), fuel cells with double the efficiency of an internal combustion engine would cancel out the price differences. And this seems to be an achievable goal.

In conclusion

Two important reasons lie behind the search for alternative energy sources that will reduce the massive dependence on carbon fossil fuel. The first is the global energy crisis, in which depletion of resources of oil, natural gas and coal are reaching a disturbing extent. The second is related to increased emission of greenhouse gases due to wasteful burning of carbon fuel. This wasteful burning makes a major contribution to increase of the entropy in the world. The term "*entropy crisis*" is a more precise reflection of the "global energy crisis" as Guy Deutscher, a physicist from Tel Aviv University, claims in his recent book bearing the same name. Wasteful and inefficient energy consumption such as that of combustion engines increases global entropy and has destructive and possibly irreversible effects on the ecology and global climate.

In the coming decades the demand for alternative energy sources will require long term solutions, forcing us to reexamine our energy needs and their environmental implications. Proposed solutions include conversion of chemical energy (as described above), use of wind and wave energy, use of bio-fuels, controlled release of nuclear energy and exploitation of solar energy. In fact, the sun is the sole source of renewable energy on earth. Except for nuclear energy all other sources of energy derive directly or indirectly from the sun. For example, carbon fuel was created many millions of years ago as a result of photosynthesis of plants with sunlight. The sun, which is actually a huge nuclear reactor, releases enormous amounts of energy. But although this energy is available to all of us on earth, the process of its conversion to other forms of energy (for example, electrical or mechanical) has environmental implications. It is important to understand that even alternative energy solutions are not magical – they are indeed far more efficient, but they too waste energy in the form of heat emitted to the environment, and increase global entropy.

Along with the development of new technologies we will have to reduce use of energy as much as possible and to "save" on entropy during energy conversion processes. Use of electrochemical energy to replace combustion engines is one way to achieve this. However, energy supply, consumption and conservation must start to play a major role on the global arena. Increase of public awareness and regulation at the national and world-wide levels are imperative for our continued existence as an advanced society.

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References

What are Batteries, Fuel Cells, and Super capacitors, *Chemical Review* **104**, 4245-4269 (2004).

High Hopes for Hydrogen**,** *Scientific American* **295,** 94-101, September 2006.

Micro-fuel Cells—Current Development and Applications**,** *Journal of Power Sources* **170**, 67–78 (2007).

www.fuelcell.no Norwegian internet site on fuel cells.

Guy Deutscher, *The Entropy Crisis*, World Scientific, 2008.

http://www.allaboutbatteries.com Internet site on batteries.

http://www.betterplace.com/ Home page of a modern initiative to build a network for recharging electric cars.