

Transcript Lesson 4d. Chemical energy

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Welcome to Module 4d, Chemical Energy, part of the course Renewable Energy Integration in the Energy System, developed by The Hague University of Applied Sciences.

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In this module, we explore two important systems to deliver or store chemical energy. In some cases, chemical energy is the final energy form — for example, when an electrolyser produces hydrogen that is further used in chemical processes in industry. In other cases the chemical energy is used to store energy, such as in the case of a battery. This energy can be converted back again into electricity, where the chemical energy has been able to store energy for later uses.

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In the overview of energy transfer and conversions, it can be seen that two main systems exist for interchanging chemical energy and electricity: batteries and the combination of electrolysis and fuel cell. The working principles of electrolyser and fuel cell are so much similar that we will treat them as two subsystems. Therefore we will first look at the electrolyser / fuel cell and then at batteries. Both electrolysers and fuel cells are currently under study for implementation in the renewable energy system, which is why we will look at the available technologies in more detail. And although batteries are probably well known, their embedding in the renewable energy system on a large scale is new and we will also explore that more deeply.

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An electrolyser is a piece of equipment that can transform electrical energy into chemical energy. The transformation of molecules costs energy and when this transformation (or reaction) is reversible, we can harvest this energy again. For that we use the fuel cell, where molecules that we call now fuel is converted directly into electricity. That distinguishes it from combustion, where also chemical energy is released but then primarily as heat or motion.

Apart from the conventional and fossil based fuels, fuel cells can also run on a fuel like hydrogen, which in turn can be made in an electrolyser directly from water. This completely removes the carbon containing (hence carbon dioxide producing) fuels from the energy system. So let us look in more detail into the electrolyser first.

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Electrolysis, the process taking place inside an electrolyser, is the process of using an electric current to run a chemical reaction. Usually it takes place in a liquid medium, as illustrated here. Thus, two electrodes are placed into a liquid. When a potential is applied and the liquid is conducting, an electric current is starting to run. On the positive electrode, called the cathode, electrons are liberated while forming cations by a chemical reaction called a reduction. At the negative electrode, anions are reacting in an oxidation reaction and the electrons are brought back into the electrical (external) system.

This has already been discovered as early as 1785 and was further developed by well-known scientists as Alessandro Volta, Luigi Galvani and Michael Faraday. Some larger industrial processes are based on this reaction, such as the production of aluminium from bauxite ore or production of chlorine gas and sodium hydroxide as base chemicals from salt. The latter is called the chloralkali process, as it produces an alkaline material and chlorine.

The example that we will investigate a bit further is the dissociation of water. In that process both oxygen gas and hydrogen gas are formed.

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To understand water dissociation, we should first understand that in water some acid and some base is present, making water itself a conducting liquid. This is due to the autoprotolysis of water as shown in the first reaction. When we apply a potential across a bath of water, at the anode negatively charged hydroxide reacts and forms electrons, water and oxygen gas. At the cathode, the acidified water reacts by consuming electrons and forming water and hydrogen gas.

When this reaction occurs in an open vessel, hydrogen and oxygen react violently with each other (called an explosion). So don't try this at home! If we separate the reactions at anode and cathode, this is prevented and we can harvest the chemical energy and store it in the form of hydrogen gas. This separation is done by a membrane, that must be permeable to at least one of the reacting species to transport charge in the electrolyser.

As we can see from the individual reactions in water electrolysis, it requires a certain potential to let the reaction run. Hence, if the voltage is too low, no reaction happens. Do we exceed the minimum potential, we start to produce hydrogen (and oxygen). Changing reaction or reaction conditions (the amount of hydroxide and acid changes with pH) the required potential will also change, which we can exploit to increase reaction rates.

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In (water) electrolysis, there are currently four types of electrolysers that are of commercial interest. This is typically expressed on a technology readiness level, where one stands for very theoretically investigated to full commercial application at level eleven. Industrial demonstrations are typically from level 6, as can be seen in the

diagram at the right hand side. So for this module we will only consider the electrolyser techniques that are above TRL six.

Electrolysers can be classified by the species that is transported across the membrane. This membrane separates anode and cathode and prevents the produced hydrogen and oxygen from immediate and explosive reaction when produced.

On the one hand we have the acidic electrolyte, where the membrane is able to transport positively charged hydrogen ions (H^+) from anode to cathode. As the membrane that is used consists of an acid conducting polymer, this type is typically referred to as a Proton Exchange Membrane electrolyser or PEM.

At the other hand we have the alkaline transport across the membrane. When this is done with a liquid electrolyte and a diaphragm, it is called an alkaline electrolyser. This is probably the most common one, as it is mostly used in large scale industrial applications such as the chloralkali process. When a solid, polymeric membrane is used without a liquid, we call this anion exchange membrane electrolysis or AEM.

The last example is one where a solid, ceramic membrane separates the electrodes. The solid conducts oxygen anions, or negatively charged oxygen atoms, across a ceramic material. This is often called a solid oxide electrolysis cell or SOEC. Since the solid oxide only conducts oxygen anions at high temperature, this is also referred to as high temperature electrolysis or HT.

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The reactions inside an electrolyser take place in a cell. Here a typical cell for an alkaline electrolyser is shown. By combining multiple cell next to each other, we can build a stack. Thus we can increase the amount of hydrogen produced, where for example gas handling and power supply is shared across cells.

The single cell contains in the case of alkaline electrolysis a diaphragm that separates the two electrodes. Since the whole cell is filled with an alkaline solution, all materials must be able to withstand this corroding liquid. So a special diaphragm has to be applied plus electrode materials that are resistant to strong alkaline medium, typically nickel in modern water electrolysers. But also the cell walls, typically called bipolar plates, need to be treated with nickel to withstand the alkaline liquid.

An electrolyser consists then of a stack of the cells. To separate the produced hydrogen and oxygen from the liquid, we need separators. As the alkali in solution is used at the anode and produced at the cathode, we need to constantly pump the solution around to replenish it.

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For the anion exchange membrane, the system components are very similar to an alkaline electrolyser. However, here the diaphragm is a solid polymer that conducts hydroxide anions. Since the polymer itself conducts these anions, we can here suffice with pumping water into the system, which at least reduces the costs of materials for

pumps significantly. When applying an alkaline solution, the required voltage is lower, which is why more often than not an alkaline solution is still preferred.

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The system for the proton exchange membrane is pretty similar to the one for an anion exchange membrane. Here only pure water is needed, simplifying the feed pump system. The membrane is a fluorinated polymer that can withstand the acidic environment. All the other materials in the cell need to be acid resistant as well, necessitating special materials. For the anode iridium oxide is used, while the cathode consists of platinum. These are precious metals, that are both expensive and becoming scarce. As also the bipolar plates need to be treated, either with platinum or gold, the price of these metals is what mainly determines the cost of the electrolyser.

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The solid oxide electrolyser operates at high temperatures, typically between 600 and 1000 degrees Celsius. This means that water needs to be added as steam, necessitating the addition of a steam generator to the overall system. And with these high temperatures, insulation of the hot parts becomes important to prevent heat losses.

The electrolysis cell itself also needs to be able to withstand high temperatures, which is why most of the materials (electrolyte and electrodes) is made from ceramic materials. The membrane is an yttrium stabilized zirconium. The cathode is the same material, coated with nickel. The anode is another ceramic material called perovskite, usually doped with metals like lanthanum and strontium. The most common anode material is lanthanum-strontium manganate or LSM.

As the supporting plates are of high-temperature resistant steel, special care needs to be taken to make the cells leak tight. As different materials have different expansion coefficients, seals of glass or ceramic are employed to used to fuse steel and ceramics together.

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Apart from the differences between the electrolyzers, it is good to know that for all of them a major part of the cost is in the so-called balance of plant. This is the equipment that for example provides the power to the stack, but also heat exchangers as all of the electrolyzers run above room (or air) temperature. Water quality and hydrogen gas quality are important, necessitating the addition of purification units. Finally, to store a significant amount of hydrogen, we need to compress the gas. At elevated pressures we can store more hydrogen per volume of storage tank.

Overall, a large share of the cost of the equipment is thus located in the balance of plant. For operating an electrolyser, by far the largest contribution to the operating expenditure (or Opex) is the amount of electricity needed to drive the reaction. A good second opex is the power to run the compressor.

So when evaluating the various commercially available, we need to carefully choose for each situation the optimal type of electrolyser. Alkaline is a proven technology with good long-term performance. It can only run on relatively low current density, so the electrical efficiency and production are low. Since it works with an alkaline solution, all materials need to be resistant.

Anion exchange membrane electrolyzers are relatively new and have not yet proven long term stable operation. It handles high current densities (high production rates of hydrogen) and needs low cost materials. Part of the stability problem is that hydrogen can cross the membrane, necessitating careful monitoring to prevent an explosive atmosphere inside the electrolyser.

The same holds for the proton exchange membrane. As this runs on higher pressures, it can be more compact and we need less compressor power. It can easily ramp up from low production rates (about 10%) to maximal conversion (100%), making it suitable for application in intermittent circumstances. The materials used are the major drawback, both the noble metals, the need for acid resistant materials and the use of a fluorinated membrane (part of the so-called forever chemicals).

Solid oxide is sensitive to temperature fluctuations due to the various expansions of the materials used which also influences the life time. As it is relatively new, commercial production of these electrolyzers is still in its infancy, making it relatively expensive and not yet fully commercially proven on a large scale. It is however highly electrically efficient and since running at higher pressures relatively compact. Given that power is a huge contributor to the operational costs, both are beneficial.

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As hydrogen is a gas, we need to store it in gas cylinder. To store larger quantities, it needs to be pressurized. Currently storage options in salt caverns or former gas fields is being investigated, but this is not yet done on large scale. For smaller scale storage, solutions like large pressurized tanks are still the best options. Specifically with intermittency of renewable energy, the storage can become cost-prohibitive. When for example security of supply or lack of available alternatives become important, such as on a ship, this can become interesting as in the case of the energy observer vessel depicted here.

Another option is liquid hydrogen. As the condensation temperature of hydrogen is -253 degrees Celsius, making hydrogen liquid means deep cooling and keeping it at those low temperatures. That requires quite some effort, hence energy. Thus, a large part of the energy is lost as to cool the hydrogen and keep it at those low temperatures.

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Compared to other types of energy, converting electricity into chemical energy in the form of hydrogen creates a large storage capacity. This is especially so when comparing to the other chemical energy, batteries, which we will cover later. Hydrogen can be stored for a long time.

Storing hydrogen requires dedicated storage capacity, either in the form of high-pressure tanks or large (underground) salt caverns or gas fields. This is expensive to maintain, and some options are only in the research phase. Furthermore, the round-trip efficiency (electricity to hydrogen to electricity) is low, meaning that large quantities of energy are lost, mainly in the form of low-grade heat. When combined with heat recovery, the losses are reduced but still significant.

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Once we have hydrogen available, we can also run the reverse process of electrolysis. This is hydrogen oxidation and to do that in a controlled way, we can make use of a fuel cell. Some fuel cells can not only run the oxidation of hydrogen, but other fuels as well, such as carbon monoxide. Carbon monoxide in turn can be made from hydrocarbons by means of reforming and when done with water vapor (steam) present this is called steam reforming. In this reaction, not only carbon monoxide is formed but additional hydrogen as well, creating even more fuel for the fuel cell.

The fuel cells commercially available are mainly based on proton exchange membranes or solid oxides. The cells and materials are similar to the electrolyzers already discussed. In fact, for solid oxide the electrolyser and fuel cell are literally the same cell, which gives the opportunity to run both reactions (electrolysis and fuel oxidation) in the same equipment. We talk then about a reversible solid oxide cell or rSOC.

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Fuel cells are even more widely applied than electrolyzers. Solid oxide fuel cells have been applied long time in special applications, such as space rockets and lunar modules (Apollo), but also at submarines. They have been tested as power sources for electronics, residential applications such as house heating, transportation but also in large power plants. Hydrogen availability is the limiting factor, but with fuel flexibility (hydrocarbons such as fossil fuels) they can play a role in the change from fossil based power to renewable energy.

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One of the advantages of applying hydrogen is that the only product formed is water, making it a clean solution. Since the reaction of oxygen is separated from the conversion of the fuel (remember the two separate compartments in the electrolyser, to prevent reaction of oxygen and hydrogen directly), no byproducts such as NO_x are formed, which is a disadvantage of direct hydrogen combustion. So in place where stringent air pollution control is required or desired, hydrogen fuel cells can help out. So modular fuels cells for construction sites or (environmentally conscious) festivals are ways forward. Also heavy transportation related to construction sites is becoming more common place. However, for regular transportation, we suffer from the common chicken-and-egg problem: low availability of hydrogen fuelling stations means low interest for hydrogen cars. And limited number of hydrogen cars means slow business for hydrogen fuelling stations.

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A similar issue has been observed previously with electric cars. There, infrastructure and market penetration are going hand in hand, but it has been hampering large scale application for a long time.

Electric cars are driven by an electro motor, which is powered by batteries. Batteries are the second version of chemical energy storage we will be considering in this module. The working is somewhat similar to what we have seen for electrolyser and fuel cell. It consists of two electrodes, separated by an electrolyte. By closing the electric loop, we can harvest the stored chemical energy inside the battery in the form of electricity. When the battery is rechargeable, we can also convert electricity to chemical energy.

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The reactions inside a battery are fundamentally different from those in an electrolyser or fuel cell. As electrolyser and fuel cell work with gases, inside a battery this is completely out of the question. So we need to have a solid-solid reaction taking place. In conventional batteries, the ones most people know such as the AA or the AAA type batteries, this is a reaction of manganate on the cathode and either zinc (alkaline batteries) or lithium (lithium batteries) on the anode. For most batteries the electrolyte is a paste of potassium hydroxide. Again, we don't want materials to leak out of the battery.

The most well-known rechargeable battery is the typical car battery, sometimes referred to as accu. The lead plates react with the sulfuric acid in the battery. The two types of nickel-based rechargeable batteries are probably well-known from household applications. Lithium-ion batteries are present in laptops, telephones and also in the electric car (apart from a secondary battery, similar in use to the one in conventional cars).

The solid-state battery promises large storage capacities with extremely low degradation. Unfortunately, this option is currently only available in lab environments, but it could certainly change the story.

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On the rechargeable batteries, the lead acid (car) battery is the oldest. The search for more robust and hassle-free options, first the nickel metal hydride battery has emerged from the mid 1980s. Nowadays lithium ion technology delivers the largest energy per battery mass, making mobile phones and electric vehicles economically feasible and practical. As already mentioned, the currently heavily researched solid-state batteries will bring us another leap forward in the storage capacity but are not yet applied in real customer applications.

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The advanced storage capacities of batteries, combined with the rise in solar photovoltaic panels, has led to the growth in popularity of home battery options. So instead of sending the excess energy that is generated by PV panels into the grid, which

is not storage but redistribution, home batteries are now used to store excess energy. Apart from storage of produced electricity and thus contributing to peak shaving and increasing grid stability, you could also use your home battery to trade on the energy market, based on spot pricing.

Although prices are quickly coming down, a home battery is still an expensive system. With uncertainties in (solar or wind) energy production, home battery penetration in the market and generally fluctuating prices of electricity, the payback time is difficult to predict. This makes people often hesitant to invest in a home battery, coupled to solar PV panels.

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Investment and payback time are not only uncertain due to the pricing and availability of electricity, also the capacity losses of your home battery and an important factor when doing a long-term economic analysis. From the older price comparison shown here, it is clear that in doing this analysis, it is important to take into account whether the peripheral equipment (inverters, chargers) are included in your system or not. Also the amount of cycles (one per day, most likely for home consumption, or multiple when trading energy) and expected life times of batteries are major factors.

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Alternative forms for peak shaving includes load sharing. Regulations are slowly being adapted to make this possible. The principle is based on the fact that although most people use energy at roughly the same time, 100 percent co-incidence of energy uses is quite rare. Individual peaks per household are levelled off when combining for example multiple households. Even more ideal would be to include other users, such as schools or offices that use most energy when homes don't. Including communal batteries will increase the potential for sharing even more, thereby preventing expensive expansions of the existing grids. Fact remains that these systems are not cheap and ownership and responsibilities need to be carefully organised.

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These are the references used in this lesson. Additional references are included on the individual slides.

Thank you for your attention, and see you in the next and last module.