Materials in Hydrogen Production

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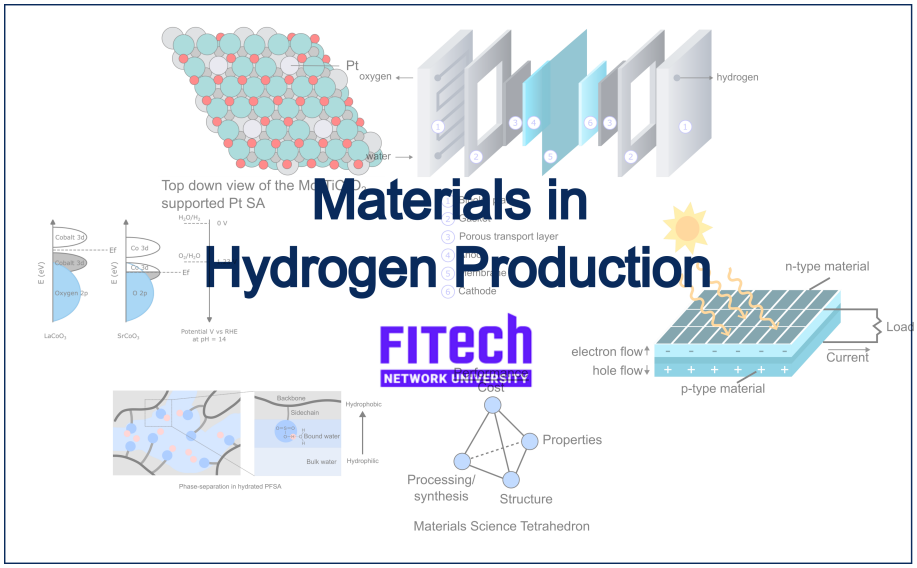


Introduction

Welcome to the "Materials in Hydrogen Production" course document! This document belongs to the two-part "Catalytic processes and materials in sustainable hydrogen production" course, and has been adapted from the material of the course Moodle to be shared publicly through JOTPA. Students from all over Finland from varying academic and professional backgrounds successfully completed the 2 ECT part of the course which was available through FITech studies in 2023-2025. The course was graded as pass-fail. Viewing all course content and a passing grade (85% of total points) from two online quizzes was required for course completion. The quizzes had an unlimited number of retries, and quiz grades had no effect on how many ECTS were awarded.

The second part of the course focuses on the material properties and novel catalyst discovery for electro- and photocatalytic hydrogen production and storage.

Learning Goals:

- student is introduced to fundamental physical and chemical phenomena in materials science
- student is familiar with materials used in photochemical and electrocatalytic processes
- student understands the required physical and chemical properties of materials used in hydrogen production and how they relate to the atomic and electronic properties of materials.
- student is familiar with the challenges related to materials used in hydrogen production and how new materials can be developed.

The contents are divided into chapters which contain text, images, and multiple choice questions (answers are given at the end). At the end of each chapter, there is a set of problems to test your understanding (these sets correspond to the Moodle quizzes).

Materials Science Concepts

Searching for new materials

Replacing fossil fuels with renewable energy is an important goal in the fight against climate change. One challenge is how to deal with the intermittent nature of solar and wind energy. The "hydrogen economy" refers to the usage of hydrogen as the main energy carrier and fuel, and involves the production, storage, and utilization of hydrogen. Hydrogen economy could act as a complementary system alongside renewable energy that could help regulate the availability of energy when solar and wind aren't producing enough.

In order to integrate hydrogen to renewable energy systems, the production of hydrogen itself should utilize renewable energy and feedstocks. In fact, hydrogen can be produced from water with electricity, by a process called electrolysis. Hydrogen produced by electrolysis using electricity from renewable energy sources is referred to as "green hydrogen".

However, almost all hydrogen is currently produced via fossil based methods such as steam methane reforming or coal gasification, which leads to massive CO_2 emissions. Today, this "black" or "grey" hydrogen is much cheaper than green hydrogen.

The price of green hydrogen decreases as electricity from renewables becomes cheaper. Even so, electrolysis relies on expensive and scarce materials such as noble metals, which limit the wide scale adoption of electrolysis as the main hydrogen production method.

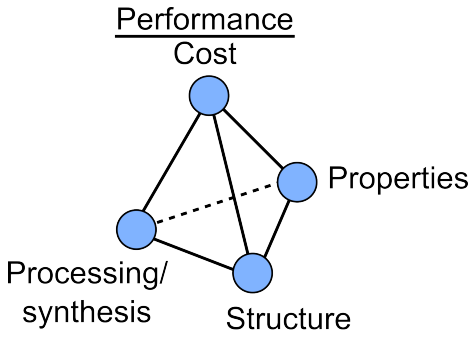
Much effort must be put into searching for new materials that are suitable for industrial scale hydrogen production by water electrolysis. The materials must be efficient, stable, cheap, and environmentally benign, which is no small task.

Historically, new materials have been either found naturally occurring, or by trial-and-error i.e. combining known materials together and seeing what happens. The worst way to do this trial-and-error would be completely at random:

the number of possible combinations is too high. Instead, the method relies on some previously known information of the material properties and how they might combine together.

Using trial-and-error aided by some intuition may be efficient enough to find a new material if the target property is very simple, such as "hard shiny metal". However, the properties required of new electro- and photocatalysts, electrolytes, and membranes are highly sophisticated, and require a more modern approach.

Materials discovery by "rational design" involves knowing how fundamental properties of materials relates to their performance, and further how properties of materials arise from their atomic structure. These relations between material structure, properties, and performance allows for rational design of novel materials.



Materials Science Tetrahedron

The first chapter will introduce the fundamental physical concepts that are central to understanding the atomic structure and physical/chemical properties of condensed matter. The material is based on the following textbooks:

- The Oxford Solid State Basics by Simon, S. H. Atkins' physical chemistry (11th edition) by Peter Atkins, Julio de Paula, and James Keeler. ISBN: 978-0-19-876986-6
- Physical chemistry: a molecular approach by Donald A. McQuarrie and John D. Simon. ISBN: 978-0-935702-99
- Concepts of modern catalysis and kinetics by Ib Chorkendorff. ISBN: 9783527332687
- Solar to chemical energy conversion, theory and application by Masakazu Sugiyama, Katsushi Fujii and Shinichiro Nakamura . ISBN: 978-3-319-79783-0

Atomic scale structure

Different scales of material structure

Properties of different materials and objects are a result of their composition and structure. The structure of a material can be described at different length scales, from the atomic scale, i.e. the local bonding between platinum atoms, to the macroscopic scale, i.e. the shape and thickness of an electrode.

Modifications at all length scales could result in a better performance of a material for a given application. The atomic scale structure still sets the boundaries for the type of behavior a material can exhibit. For example, the resistance in a wire is inversely proportional to the cross-sectional area of the wire, but it is still also determined by the resistivity, or intrinsic resistance of the material the wire is made of. In addition, certain properties such as brittleness and toughness only manifest at the macroscopic scale of the bulk material, however these are properties that result from the material having a certain atomic composition, bonding, and crystal structure at the atomic scale.

Condensed matter

All everyday objects are made of ordinary matter, which is made of atoms, which are in turn made of protons, neutrons, and electrons. In addition, materials that are technologically relevant to hydrogen production are in solid or liquid phase. Liquids and solids are condensed matter, and they are composed of large numbers of constituents (atoms/molecules) that interact strongly with each other.

Condensed matter has different physical and chemical properties which ultimately derive from their atomic scale structures. The spatial ordering, elemental identity, and bonding between constituent atoms determine whether the material is solid or liquid at a given temperature, whether a solid is a metal or an insulator, and whether it can be easily oxidized or reduced under reaction conditions, to name a few.

Periodic table of elements

Atoms consist of a nucleus that contain protons and neutrons, and electrons that surround the nucleus. An element is a substance whose atoms all have the same number of protons. In the periodic table of elements, all known elements are arranged into rows (periods) and columns (groups) by their atomic number (number of protons in the nucleus) and electronic configurations. Elements in the same group exhibit similar chemical behavior. Besides groups and periods, the periodic table is divided into "blocks", which indicates what type of orbital is being filled as you move to the right in the table. An atomic orbital is a quantum mechanical description of the possible location and energy of an electron in the atom. The electronic configuration of an element describes how the electrons are distributed in the atomic orbitals. Each orbital is described by a number and a

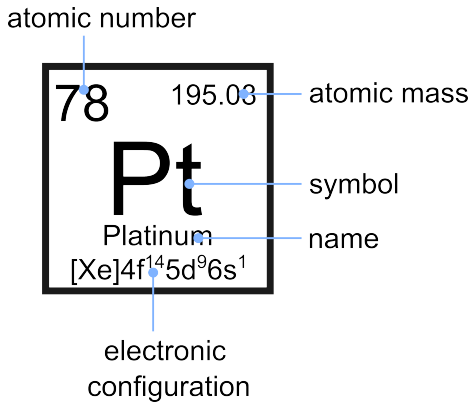
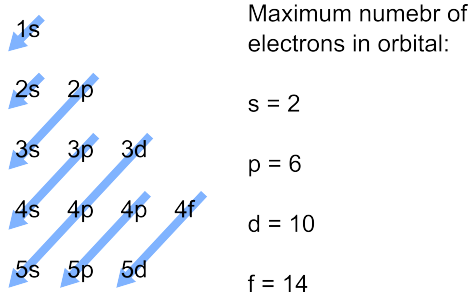


Figure 1: Example of an entry in a periodic table.

letter, which indicate the energy level and "shape" of the orbital. Commonly, the electron configuration begins with a shorthand notation [X] , where X is the symbol for a noble gas that precedes the element in the periodic table. In this noble gas notation, only outer electrons are explicitly written out.

Only two electrons are allowed in each orbital (Pauli exclusion principle), so when the number of electrons that an atom has increases, orbitals of higher energy and different shape are filled (Aufbau rule). With these two principles, knowing the number of electrons an element has enables one to write its electronic configuration, although there are some exceptions to the filling order of orbitals. The number, labels, and filling order of orbitals are presented below.



Elemental composition

The elemental composition of a material is an essential characteristic that defines a material. Pure substances have the same composition throughout the entire material. Pure substances are either:

- Elements, which only consist of atoms of one type. E.g. platinum, mercury, oxygen, hydrogen

- Compounds, which consist of two or more elements that are bonded together in fixed proportions. E.g. water, sodium chloride, carbon dioxide

Changing the elemental composition of a substance can be done by adding an element or changing the atomic ratio of the existing constituent elements. These modifications will lead to measurable changes in the physical and chemical properties of the material, if the change is significant enough. For example, small amounts of yttrium are added to zirconia to increase its resistance to phase transitions. How to actually change the composition in a controlled way experimentally is often not trivial.

Both elements and compounds are utilized extensively by humans. However in reality, most materials used in industry are not really pure substances, but composites. A composite may be a simple physical mixture of two different substances, a substance deposited on a support of different substance, or a material with different substances layered together, to name a few. For example, industrial catalysts are often composites where metals, such as Pt, Pd, and Ru, are supported on oxides, such as TiO_2, CeO_2, and Al_2O_3.

Chemical bonds

To form a molecule or compound, atoms must be bonded together. Two atoms that are chemically bonded are held together by an attraction to each other, the attraction being a result of the behavior of the valence electrons. Valence electrons are the outermost electrons of the atom, and the number and type of valence electrons an atom (or molecule) has determines its chemical/bonding behavior. The "type" of electron here means which atomic orbital the electron is associated with.

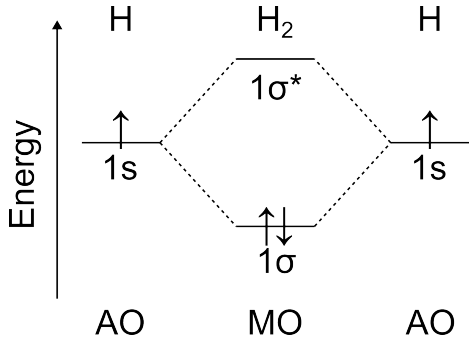
Ionic bonding occurs when two atoms have very different electronegativities, and the electrons involved in bonding are much more attracted by the more electronegative atom. The electron density is located almost entirely on the more electronegative atom, giving it a partial negative charge, while the other atom has a partial positive charge. The atoms are held together by the attractive electrostatic, or Coulomb, interaction.

In covalent bonding, the electronegativities of the atoms are very similar (only strictly true for atoms of the same element), which means that the bonding electrons are shared equally between the atoms. In this case, the chemical bonding cannot be fully understood only in terms of the classical Coulomb attraction between opposite charges. To explain the covalent bond properly, a quantum mechanical treatment is needed.

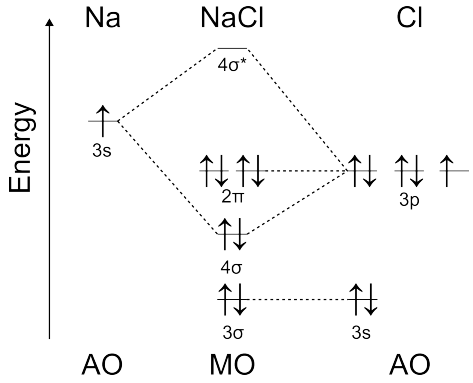
The distinction between ionic and covalent bonding is a sliding scale, but both can be described using molecular orbital theory, which is based on quantum mechanics. Within molecular orbital theory, atomic orbitals of participating atoms with compatible energy and symmetry combine together to form new molecular orbitals. For each pair of atomic orbitals two new molecular orbitals,

a bonding and an anti bonding orbital are formed. Atomic orbitals that do not interact with each other are non-bonding, and remain largely unchanged. The molecular orbitals are filled with electrons from both atoms starting from the lowest energy orbital. This electronic configuration characterizes the bonding, and determines the chemical behavior of the molecule. Bonding between atoms can be illustrated by constructing a molecular orbital (MO) diagram. Usually only valence electrons are included in the diagram.

The MO diagram for a hydrogen molecule is presented below, showing the atomic 1s orbitals of each hydrogen atom, and the bonding 1σ and antibonding $1\sigma^*$ molecular orbitals that form when they are bonded together. Each hydrogen atom contributes one electron from their 1s orbital, which occupy the bonding MO. As the MO is lower in energy than the AOs, this leads to a stabilization, i.e. a bond between the atoms is favorable.



The MO diagram for NaCl is presented below. The electronic configuration of sodium is [Ne]3s1, it has only one valence electron. Chloride has 7 valence electrons, its electronic configuration is [Ne]3s23p5. The MO diagram shows the 3s and 3p AOs of Na and Cl, the MOs that are formed from them, and their electronic occupations. The energetic spacing between the orbitals is not to scale. Most of the AOs are unchanged, non-bonding, but the Na 3s and one Cl 3p orbital combine to form the bonding 4σ and antibonding $4\sigma^*$.



Bonding in solids

In a solid, the individual atomic or molecular components are bonded together by a network of chemical bonds. The bonding network of a solid can be typically described as belonging to one of the three categories below:

- Ionic
- Covalent
- Metallic

Ionic solids have a network of ionic bonds between positively and negatively charged ions. As the electrostatic attraction is strong, ionic solids are often hard, have high melting temperatures, and are very brittle. Examples of ionic solids are NaCl and other alkali metal halides, and some oxides such as MgO.

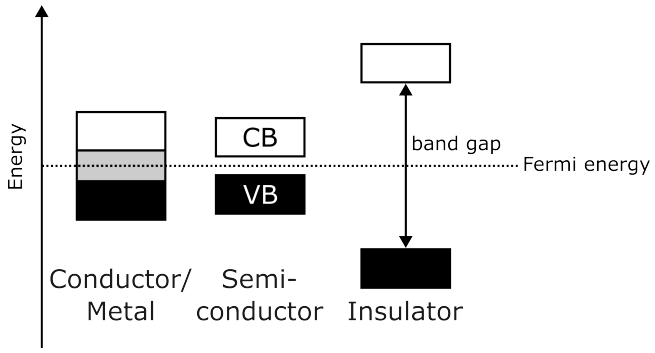
Covalent solids are bonded by a network of covalent bonds, i.e. the atoms share electrons. Covalent bonds are directional, which means that it takes energy to distort the structure. Covalent solids are therefore quite hard and brittle. Examples of covalent solids are diamond (allotrope of carbon), quartz (polymorph of SiO_2), silicon, and ice (solid H_2O).

Metallic bonding in solids is very similar to covalent bonding, however the special feature is that there are mobile (often referred to as 'free', although they are still bound to the metal) electrons that are delocalized over the entire bonding network. This gives the metal its good electronic and thermal conductivity. Metals in their elemental forms, e.g. gold, platinum, nickel, and iron, are metallic solids, but also mixtures of metal elements such as brass (alloy of copper and zinc) are most often metallic.

For any macroscopic amount of substance, i.e. bulk material, the number of atoms is very large. In a similar way that molecular orbitals result from the overlap of atomic orbitals, the orbitals of adjacent atoms in the solid overlap forming bonding and anti-bonding energy levels, and because the number of atoms is very large, the discrete electron energy levels combine into (nearly) continuous bands of allowed energies. In between the bands are 'gaps', or ranges of energies which electrons cannot have, as there is no combination of orbitals that correspond to those energies.

An energy band may be filled or partially filled by electrons, or empty. Electrons fill the bands starting from lowest to highest. In many materials there is an energy gap (band gap), between the highest energy filled band (valence band, VB) and the lowest energy unfilled band (conduction band, CB). Empty and filled bands do not contribute to electrical current, so these materials are either electrical insulators or semiconductors. In metals, there is overlap between the VB and CB, which means that there is no band gap, and the empty states of the CB are freely available to electrons.

Semiconductors differ from insulators in that the band gap is small enough (¡4



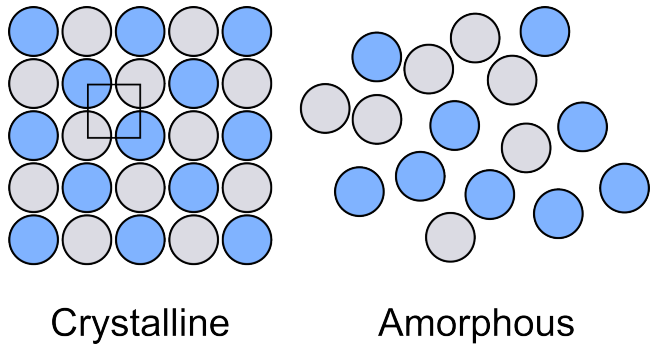
eV), that thermal excitation of electrons from the VB to the CB is possible at moderate temperatures. Thermal excitation leaves a hole in the VB and an electron in the CB, which enables current to flow.

The chemical potential of electrons in metals is determined by the Fermi level, the highest occupied energy level of the system at absolute zero. For semiconductors the situation is a bit more complicated, as the level is located in the band gap, and so does not correspond to an allowed energy state that an electron can have.

Crystal structure

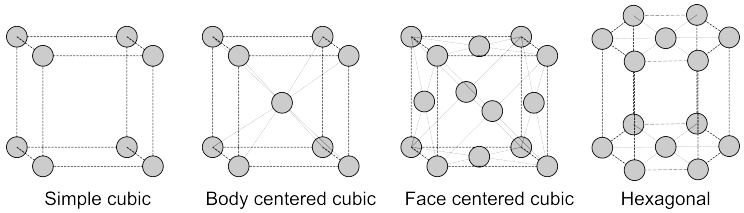
The spatial arrangement of particles in a solid is its structure, and it determines the physical properties of the material, such as what kind of surfaces it forms, the electronic band structure, hardness, density, thermal stability, optical properties and so on.

The arrangement of the constituent particles can be ordered or disordered. Crystalline materials are those whose constituents are highly ordered and are formed by structures which repeat in three dimensions, called unit cells. Amorphous materials, such as glasses, do not have repeating structural patterns (in long range).



All pure elements and many pure compounds (that are solid at room temperature) have crystalline structures. Compounds and elements can have multiple stable crystal structures, which are referred to as polymorphs in the case of compounds and allotropes in the case of elements. Some compounds, such as plastics, preferentially exist in amorphous form, and most compounds can be made into amorphous solids by melting and cooling very rapidly. Even some pure elements can exist in amorphous forms.

Below are schematic representations of the four simplest crystal structures:



Interstitial sites are the empty space within the lattice, e.g. the middle of the cube in simple cubic structure is 'interstitial', and when it is filled, the body centered cubic structure is formed. The structure of crystalline compounds can be defined in terms of the arrangement of the cations, with anions filling the interstitial sites in the 'host' structure. For example in cubic zirconia, the Zr cations form a face centered cubic lattice, with oxygens occupying the tetrahedral interstitial positions formed by three Zr on the faces, and one in the corner of the lattice.

The main takeaway should be that solids can have the same atomic composition, but still behave in a very different manner depending on the crystal structure, essentially making different polymorphs/allotropes of the same compound/element completely different materials.

Surface, size, and shape effects

Surfaces

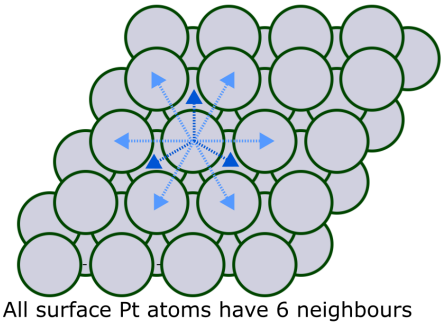
In heterogeneous catalysis (which electrocatalysis falls under) chemical reactions take place on the catalyst surface. Electrocatalytic activity of a material is dictated by its surface. Moreover, when two components of an electrochemical cell are in contact, their surfaces form an interface between the materials. The properties of these interfaces are dependent on the properties and interactions between the two surfaces, and they are very important for phenomena such as charge or mass transport across the system.

Well defined surfaces are formed when a bulk material is "cut" along a certain direction. To achieve this, bonds between atoms must be broken, which requires energy or work. The term surface energy is used to denote the amount of energy. In general, the more "dangling bonds" the atoms on the surface have,

the greater the surface energy. The higher the surface energy, the more unstable and generally more reactive the surface is.

Surfaces cut from a material in different directions are identified using Miller indices which label the directions that the crystal is cut. For three dimensional crystals three numbers are needed to specify a surface plane, e.g. (100), (110), and (111).

A crystalline solid will have a 2d periodic surface structure. The arrangement of atoms on the surface depend on the bulk crystal structure and facet. Many metals encountered in this course have face-centered cubic (fcc) crystal structures, e.g. Ni, Ir, and Pt. For them, the most stable surface is the (111) surface. For such fcc-metals, the (111) facet is very simple, as the top layer contains only one type of atom: metal atoms that are each connected to 9 neighboring atoms (pictured below).



All surface Pt atoms have 6 neighbours
in the same layer (light blue arrows),
and 3 in the layer below (dark blue arrows)

For other materials the (111) surface can be much more complex, such as the (111) facet of indium oxide (In_2O_3) which contains indium and oxygen atoms with multiple different coordination numbers.

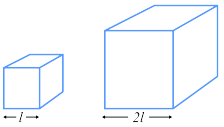
More stable surface facets are thermodynamically favored, and therefore the majority of a particle surface can be expected to be formed by those surfaces. However, this can pose a problem for electrocatalytic applications, as the most stable surfaces could be inert. In these cases, surface engineering is required to somehow stabilize the more reactive surface facets. The strategies presented in the next two section take advantage of the effect size and shape have on the surface properties.

Further reading:

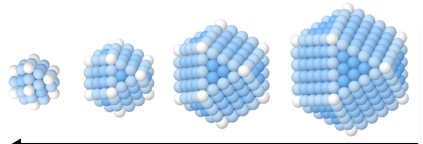
Bentley, C. L., Kang, M., & Unwin, P. R. (2018). Nanoscale surface structure–activity in electrochemistry and electrocatalysis. Journal of the American Chemical Society, 141(6), 2179–2193.
https://doi.org/10.1021/jacs.8b09828

Size effects

The simplest kind of size effect is how the surface area and volume of an item, such as a metal particle, scale as the particle grows. Smaller particles have a higher surface area to volume ratio, which means that more surface sites are available compared to the amount of material required. This leads to an increase in catalytic activity per mass of catalyst with decreasing particle size. Another effect of similar nature is that smaller particles will have more low coordinated atoms (corners and edges, and atoms directly next to such sites) compared to the total number of surface atoms. Low coordinated sites are often more active than more coordinately saturated atoms, which leads to an increase in activity with respect to the total surface area.



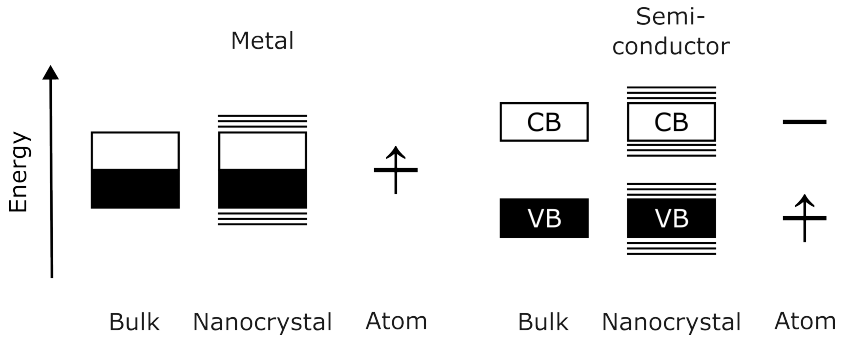
For a cube, area scales as l^2, but volume scales as l^3. Therefore surface:volume ratio scales as $1/l$.Similar scaling exists for other 3d shapes.



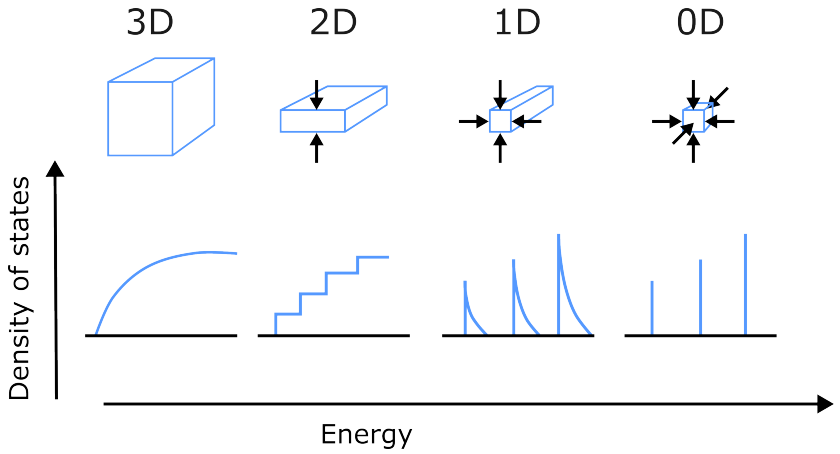
Number of surface atoms decreases faster than number of edge and corner atoms, therefore ratio of corner/ edge to surface atoms increases with decreasing particle size

Catalyst 'miniaturization' is a concept where the aim is to use smaller and smaller particles as catalysts, which would maximize the material utilization. Single atom catalysts (SAC) are the ultimate miniaturized catalyst, where the active site is just one atom, typically a metal, supported on a less expensive material such as an oxide or graphene. Using platinum SAC have been suggested as one strategy to reduce the amount of platinum needed for efficient catalysis of acidic HER.

However, the effect of decreasing the particle size is not quite as straight forward. Bulk materials have a band structure, but as the size is decreased, eventually the energy levels will start to become more discrete. This will alter the bonding behavior, charge transfer and catalytic activity, and in the case of semiconductors also light absorption properties.



As knowledge of nanoscale systems has increased, it is now recognized that for nano sized particles there are also quantum electronic effects. When the material is restricted to the nanometer scale (smaller than Bohr radius of electron, hole, or exciton) in some direction, the electrons are subject to quantum confinement along that direction. A material may be nanoscaled in one, two, or three dimensions, the resulting structures are 2D, 1D, and '0D' nanostructures.



2D structures are commonly referred to as nano sheets, whereas examples of 1D structures include (nano) wires, rods, and tubes. Quantum dots and nanoparticles are 0D nanostructures. The empty space within a material, i.e. pores, can also be nano sized. Such nanopores are present in zeolites and metal-organic frameworks (MOFs).

Further reading:

Wang, H., & Lu, J. (2020). A review on particle size effect in metal-catalyzed heterogeneous reactions.Chinese Journal of Chemistry, 38(11), 1422–1444. https://doi.org/10.1002/cjoc.202000205

Nanoshaping

As nano fabrication methods have advanced, it has become possible to synthesize catalyst particles with definite 3d shapes, such as cubes and rods. Another form of nano shaping is the design of pore shapes and sizes.

Especially nanoshapes MoS_2 has been demonstrated to be more active for HER when synthesized with structural control. The nanostructuring maximizes the number of edge sites in relation to bulk sites, which boosts activity. In many cases, the nano shaping is employed to increase the surface area or stabilize less thermodynamically favorable phases that are more active.

Effect of reaction conditions

Gaps in materials research

In many scientific fields mismatches between areas of knowledge have been identified, and are referred to as 'gaps'. In materials science a gap may be caused by the different methods and conventions used in fundamental research and between industrial application.

Pressure gap

The operational pressure in electrolysis stacks can vary between 1-70 bars. These are high pressures, and are out of the reach of traditional surface science techniques. This means that the structure of the surface cannot be directly observed under the typical pressures it is exposed to in the industrial application it is meant for. It is extremely difficult to characterize the surface under high pressures, and therefore difficult to know what the nature of the active sites is under reaction conditions. This makes it more challenging to design materials with a rational approach.

Materials gap

Materials gap refers to the disparity between well defined catalytic model systems used in fundamental studies and more complex real technical materials used in the industry. It is also sometimes used to refer to the disparity between what is thought to be the active material, and what the material actually becomes under reaction conditions.

When choosing materials for a certain application based on its properties, it is essential to consider what operating conditions it will be exposed to. It is very easy to make a spoon out of gallium metal, however it is not very useful for stirring tea due to the low melting point. This naive example illustrates a concept that is also true for more complex materials. Although sometimes we are lucky and the material performs the same or even better after transforming to something else in situ, a lot of the time the material becomes unsuitable for its original purpose (like the gallium tea spoon). It is important to know what the form of the material is under operating conditions, because only then it is possible to understand material properties and performance relationships.

pH and potential

As discussed previously, the state of a material is a function of the reaction conditions, such as pressure and temperature. In aqueous electrochemical systems there is the added effect of pH and cell potential. Pourbaix diagrams are essential for predicting the equilibrium state of electrocatalysts under reaction conditions, they can be thought of as a type of phase diagram for electrochemical systems.

Below is an example of a pourbaix diagram of ruthenium:

Figure removed due to copyright

On the y-axis the cell potential is plotted, and on the x-axis is pH. As can be seen from the diagram, the most stable state of the catalyst ranges from metallic Ru at low pH and less positive cell potential to ruthenium oxides at higher pH and more positive cell potential. It should be obvious that this makes a huge difference for the properties and performance of the catalyst when going from alkaline to acidic conditions.

Temperature

The operational temperature in AEL, PEM, and AEM electrolysis stacks varies from 50 to 90 °C, and even above 700 °C in solid oxide electrolysers. Higher operating temperatures, in SOEC especially, make water electrolysis more efficient in terms of electricity usage and accelerates reaction rates, but it also leads to faster degradation of the stack components.

In general, degradation mechanisms that are exasperated by an increase in temperature can be divided into:

- mechanical
- chemical
- physical

Materials typically increase in volume when heated, and this thermal expansion occurs at different rates depending on their thermal expansion coefficient. Stack components are made of different materials, and are not free to expand according to their linear expansion coefficients. This causes mechanical stress in the stack that can cause physical breakage of stack components.

One of the main degradation mechanisms that limit the lifetime of SOEC especially is delamination of the anode. Delamination is the detachment of the electrode material from the electrolyte, which is thought to be mostly due to the high local pressure of oxygen at the interface between the electrode and electrolyte material.

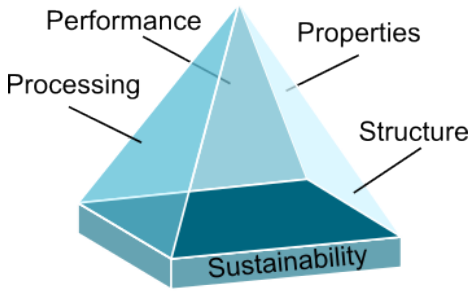
Chemical degradation mechanisms are accelerated by temperature incerease, because increasing the temperature makes activated chemical reactions faster. Some examples of chemical degradation include

- corrosion
- catalyst agglomeration
- catalyst dissolution
- catalyst detachment

Electrolysis Cell Materials

Materials challenge

Production of green hydrogen using renewable energy currently relies on the use of expensive and scarce materials. Commercial electrolyzers heavily depend on platinum group metals such as platinum and iridium, as well as titanium and nickel. In the modern paradigm of material science, it is essential to also take into account the overall sustainability of the materials instead of their performance and cost alone. Some worry that moving from fossil fuels to renewable energy that relies on such scarce materials only replaces one problem with another. However, whereas fossil fuels are used to release the energy that is stored in them, destroying the fuel in the process, the elements used in materials for electrolysers are not destroyed, and can in principle be recycled and reused.



Nevertheless, in order to lower the cost of hydrogen produced by electrolysis, novel materials based solutions are required to reduce or replace the use of these

elements, especially platinum and iridium. Besides the high cost, platinum, iridium, and titanium are on the EU list of critical raw materials (2023), meaning that they are economically highly important and have high risks associated with their supply.

For emerging technologies the materials challenge is to improve the stability and performance of the electrolyser components such as the membranes in anion membrane electrolysers, and light absorbers for photocatalytic hydrogen production technologies.

Water splitting and electrolysis cells

Water splitting

Electrolyzers are devices that generate hydrogen via the water splitting reaction:

$$2H_2O \rightleftharpoons 2H_2 + O_2$$

The reaction is endothermic at room temperature, and the standard Gibbs energy change is +237 kJ /mol, which means that at least as much energy must be provided to the system as non-expansion work, such as electric work. In electrolysis, the work is supplied by applying a cell potential.

The theoretical minimum cell potential required can be obtained from the standard Gibbs energy:

$$\phi^{\circ}_{cell} = \frac{\Delta_r G^{\circ}}{-nF} = \frac{237\text{kJ/mol}}{-2\text{mol} \cdot 96485\text{C}} = -1.23\text{V}$$

The Gibbs energy change is less positive at higher temperatures due to the positive entropy change of the reaction, which means the portion of energy that must be supplied to the reaction as work is smaller at high temperatures. Temperature of over a few thousand Celsius is required for pure thermochemical splitting (thermolysis) of water.

It can be more economical to operate at higher temperatures to lower the electricity demand. However, the higher operational temperature imposes restrictions for what kind of materials can be used when constructing the cell. Solid oxide electrolysis cells are designed to operate at temperatures of 700-850 °C.

To convert the chemical energy stored in hydrogen back into electrical energy, hydrogen and oxygen can be reacted to produce water and electricity. This is simply the reverse reaction of water electrolysis, and takes place in fuel cells. Although this course focuses on materials used in hydrogen production, similar material requirements and principles apply to both electrolyzers and fuel cells.

	PEM	Alkaline	AEM	SOEC
operating temperature	50-80 °C	70-90 °C	40-60 °C	700-850 °C
operating pressure	<70 bar	1-30 bar	<35 bar	1 bar
electrolyte	PFSA-membrane	KOH, NaOH (5-7 M)	polymeric membrane, KOH, $NaHCO_3$	YSZ
separator	solid electrolyte	diaphragm (Zirfon)	solid electrolyte	solid electrolyte
anode material	IrO_2	Ni plated steel	Ni or NiFeCo	Perovskite
cathode material	Carbon supported Pt	Ni plated steel	Ni	YSZ supported Ni

Existing technologies

The complete electrolysis system consists of the electrolysis stack and balance of plant (BoP). The main water splitting process occurs in the electrolysis cells of the stack, while BoP provides the power and water supply, water purification, hydrogen processing etc. The electrolysis stack accounts for around half of the total cost of commercial proton exchange membrane and liquid alkaline electrolyser systems.

Four main types of electrolysis cells exist today:

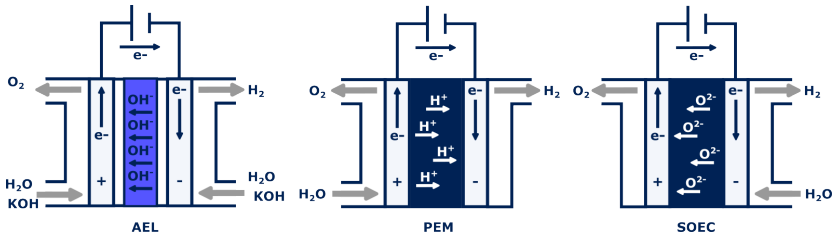
- alkaline (AEL)
- proton exchange membrane (PEM)
- anion exchange membrane (AEM)
- solid oxide (SOEC)

The cell technologies differ greatly in maturity and cost, as well as operating conditions and materials used. Alkaline electrolysis and PEM cells are considered mature and are commercially available, while AEM and SOEC are in early research and development stages. Typical reaction conditions and materials used in the four technologies are summarized in the table below.

Cell stacks

The part of the electrolyzer where the water splitting reaction takes place is the cell stack. The stack is composed of many (even hundreds) individual electrolysis cells connected to each other in series, stacked on top of one another. The stack architecture depends on the specific cell technology.

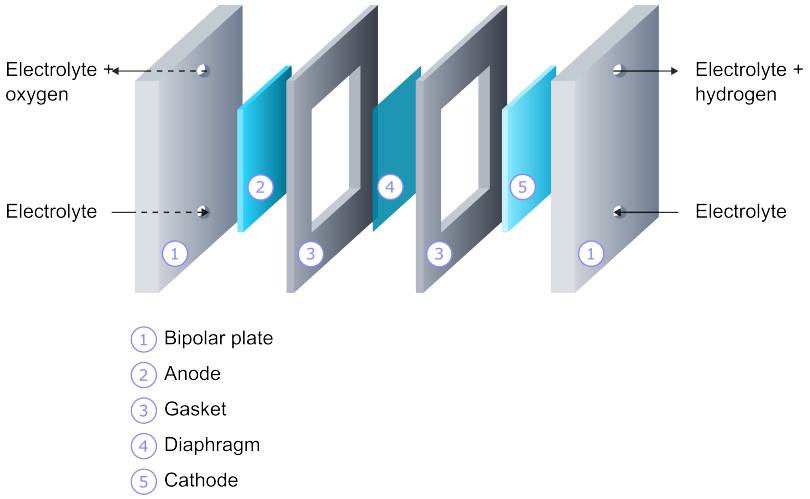
The simplified diagrams below show how electrons, protons and ions move between the cathode, anode, electrolyte and the external circuit. They give an idea of how the operating principles of the cell types differ from each other, but no physical dimensions of any of the components, nor how they are arranged in space. Diagrams of generic stack constructions showing typical com-



ponents of AEL, PEM/AEM and SOEC cell stacks are presented in the next few pages.

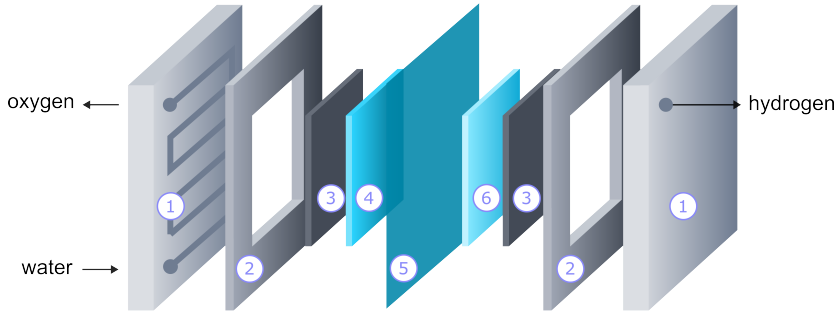
AEL stack

The video behind the link shows how a simple AEL stack is built: https://youtu.be/NYlgRUMdZ4o. Note that the cell in the video is not intended for industrial applications.



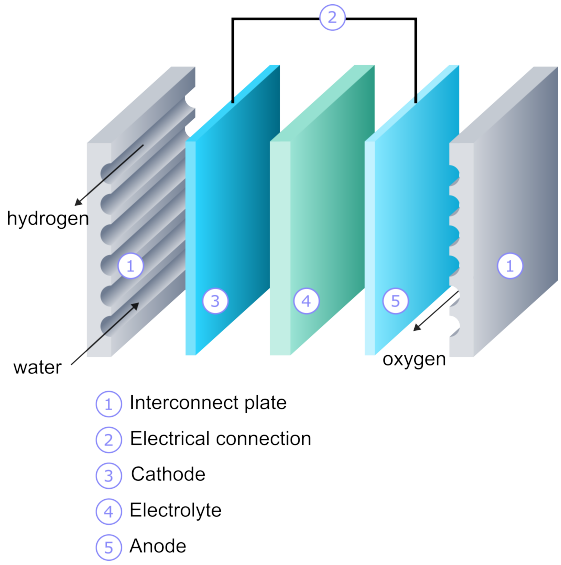
PEM/AEM stack

The video behind the link shows a PEM electrolysis cell being dismantled: https://youtu.be/N-uOW0DNDO0.



1. Bipolar plate
2. Gasket
3. Porous transport layer
4. Anode
5. Membrane
6. Cathode

SOEC stack



The next few sections introduce the materials used in two key (from the point of view of this course) components of the stacks, i.e. electrolytes and bipolar plate. Electrocatalysts (and electrodes) are covered in their own separate chapters.

Electrolytes

Liquid electrolyte

Commercial liquid alkaline (AEL) and anion exchange membrane (AEM) electrolyzers employ liquid electrolytes which circulate in the cell stack. The liquid is responsible for ion transport in the cell. In AEL cells, the presence of the electrolyte is a fundamental part of the cell design, but in AEM the goal is to eventually eliminate the need for it.

The main role of the electrolyte is to conduct ions between the electrodes, but it also physically separates the electrodes, which prevents short circuiting. Pure water has a pH of 7, i.e. it contains 10-7 mol/L of H+ ions and 10-7 mol/L of OH- ions, which is an extremely low amount. This leads to a very low ionic conductivity, movement of charge from electrode to electrode, therefore pure water cannot be used as an electrolyte (although it would be extremely convenient). In contrast, aqueous solutions of salts, bases, and acids, all contain ions and can act as electrolytes.

In both AEL and AEM the electrolyte is an aqueous solution of potassium hydroxide, KOH. In AEL the solution is more concentrated, around 5-7 M or mols per liter, which makes it strongly basic/alkaline and corrosive. The reason for

the high concentration is that it improves ionic conductivity.[1] In the AEM cells the KOH electrolyte is added so that the reaction conditions are basic, which enables the use of cheap earth abundant catalysts, rather than improving the conductivity, therefore the concentration can be much lower (around 1 M).

So why is KOH in particular a suitable electrolyte for water splitting? It should be recognized that any additional ions present in the reaction mixture have the potential to take part in electrochemical reactions at the electrodes if they come in contact with them. This could lead to some problems if the generated species are harmful. The reducing potential of the cathode is enough to generate hydrogen, but not to reduce potassium ions into the metallic form, which means the K+ ions pose no problem. At the anode, the OH- ions are oxidized but there is no problem with this either, as it is exactly the same as the OER half-reaction. It does not make a difference. If the negative ion were Cl- instead, this could pose a problem as the potential to oxidize Cl- is close to the OER potential. The reaction would produce chlorine gas, which is very toxic.

1. GILLIAM, R., GRAYDON, J., KIRK, D., & THORPE, S. (2007). A review of specific conductivities of potassium hydroxide solutions for various concentrations and temperatures.International Journal of Hydrogen Energy, 32(3), 359–364. https://doi.org/10.1016/j.ijhydene.2006.10.062

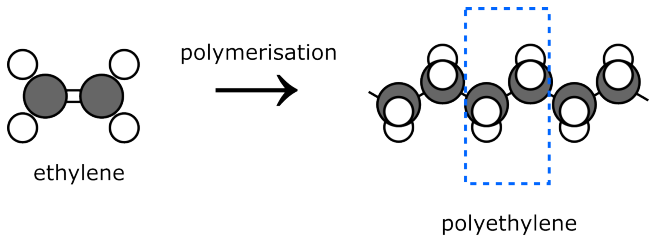
Membrane electrolyte

In PEM electrolysers the electrodes are separated by a flexible membrane which acts as the electrolyte and separator simultaneously. The membrane must conduct protons but not let gases through. It should also absorb water well, but have low swelling i.e. change of volume upon water absorption. Volume change would lead to distortions that could physically break the membrane. Other requirements are good chemical and mechanical stability. The most commonly used commercial membrane is the perfluorosulphonic acid (PFSA) polymer (trade name Nafion).

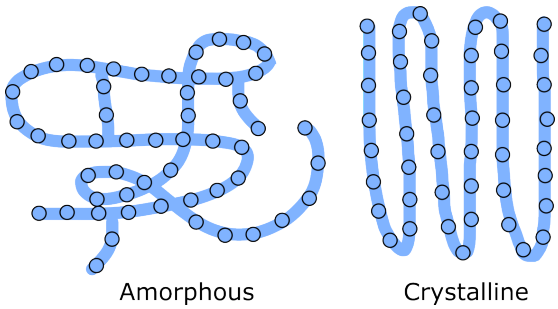
What is a polymer?

Polymers are large molecules that are composed of repeating units called monomers that are chemically bonded together. Polymers are usually named after the monomer unit, e.g. polyethylene is a polymer whose smallest repeating unit is ethylene (note that the double bond is lost upon polymerization between the ethylene molecules).

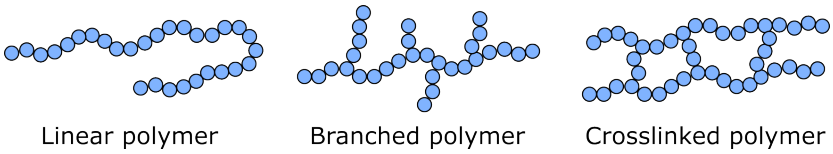
Polymers are very long and generally flexible along the chain, which means they can easily fold in on themselves. Different parts of the chain interact with each other through van Der Waals forces and can form hydrogen bonds. Depending on the chain structure of the polymer, it can exist in an amorphous (randomly folded/tangled) or crystalline (ordered 'folding' of the chain) form. A semi-crystalline polymer has both amorphous and crystalline regions in its



structure.



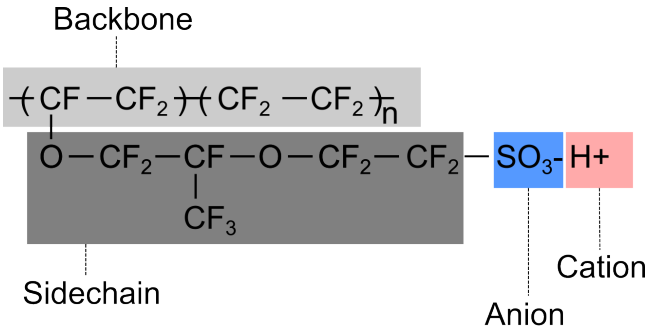
During synthesis it is also possible to introduce branches or crosslinks in the structure, which affects the crystallinity and other physical properties such as density of the polymer.



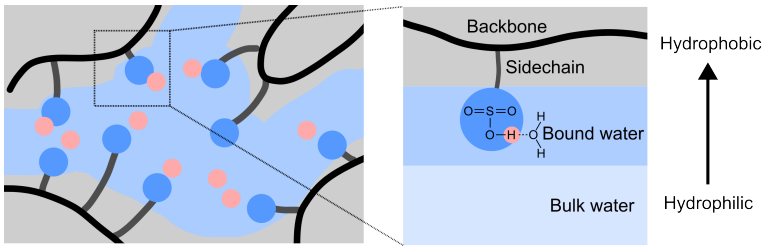
PFSA structure

Perfluorosulfonic acid is a branched semicrystalline polymer that consists of a polytetrafluoroethylene (PTFE) backbone and perfluorinated vinyl ether side-chains. The side-chains have negatively charged sulfonate (SO3-) groups at the end, which are balanced by protons (H+). Polymers that contain a neutral backbone with ionic side-chains are commonly referred to as ionomers.

In PFSA type membranes the backbone provides the mechanical strength and structure, while the terminal anionic groups determine the proton transport properties.

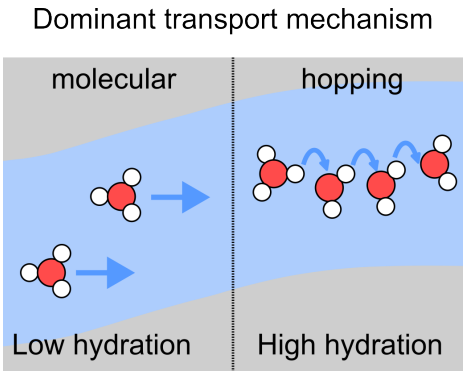


Proton transport The PTFE backbone is hydrophobic, while the sulfonate groups are hydrophilic. When the membrane is hydrated, i.e. water is introduced in to the structure, the presence of hydrophobic and hydrophilic regions leads to a phase separation (see figure).



Phase-separation in hydrated PFSA

The water network mediates proton transport via a hopping mechanism at high hydration levels, while diffusion of hydronium ions dominates at low hydration.



Membrane degradation

The thickness of the membranes also affects the ionic conductivity. The thinner the membrane, the smaller the ohmic losses and resistance are. However, gas permeability increases when the membrane thickness is decreased, which leads to reduced hydrogen purity, potential safety hazards, and decreased stability of the membrane. H_2 crossover to the anode side is a particular problem, and is one of the main mechanisms of membrane degradation. Only 4% hydrogen in oxygen is an explosive mixture, which is a safety hazard. In addition, uncontrolled recombination of hydrogen and oxygen at the anode releases a large amount of heat which can destroy the membrane and entire stack. Another chemical degradation mechanism is the formation of H_2O_2 and its decomposition into radical species that can degrade the membrane. A thinner membrane also has decreased mechanical strength and durability.

Developing new membranes

In addition to the gas crossover problem, Nafion PFSA membranes suffer from high cost and decreased proton conductivity under high temperature conditions (above 100 °C). Operating PEM at higher temperature would consume less electricity and benefit reaction kinetics, however the membranes quickly degrade at elevated temperatures. Alternative membrane architectures have been proposed to combat the problems of traditional PFSA membranes.

To reduce the permeation of hydrogen to the anode, a Pt nanoparticle containing intermediate layer can be added between two membranes. The Pt nanoparticles act as recombination catalysts and remove the gases before they reach the electrodes. However, the addition of a Pt interlayer was found to increase ohmic losses. Another strategy is to use a nafion/graphen/nafion sandwitch structure. The graphene layer allows protons through, but is impermeable to hydrogen, retaining the proton conductivity properties while simultaneously hindering gas crossover.

Recently, composite and hydrocarbon membranes have been investigated for operation at elevated temperatures. Composite membranes using a hygroscopic TiO2 or SiO_2 filler have been demonstrated to operate above 100 °C. The performance is increased due to improved water retention.

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Klose, C., Trinke, P., Böhm, T., Bensmann, B., Vierrath, S., Hanke-Rauschenbach, R., & Thiele, S. (2018). Membrane interlayer with PT recombination particles for reduction of the anodic hydrogen content in PEM water electrolysis.Journal of The Electrochemical Society, 165(16).
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Solid oxide electrolytes

In SOEC stacks there is a layer of solid oxide between the anode and cathode, that works as the electrolyte by conducting O_2- anions. Water is fed to the cathode as steam, which reacts to form hydrogen gas and the O_2- anions. The O_2- anions are transported to the anode to form oxygen gas. The electrodes are porous so that the gases formed at the electrode-electrolyte interface can be transported to the electrode surface.

The electrolyte material must

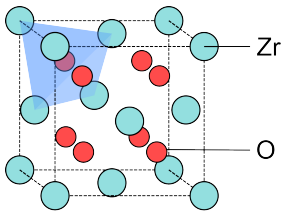
- be stable chemically at oxidizing and reducing conditions
- be thermally stable at elevated operation temperatures of SOEC
- have high ionic conductivity but low electronic conductivity
- must be non-permeable to gaseous H_2 and O_2 even in thin layers, in order to minimize the recombination reaction, ohmic losses, and physical size of stack
- be relatively low cost and easy to manufacture

The state of the art electrolyte in SEOC is yttria-stabilized zirconia (YSZ). Although other materials such as bismuth oxide have better ion conductivities at elevated temperatures, YSZ has the advantage that it has a very low electron/hole conductivity.[1] Zirconia is also quite cheap, and is not considered a critical or scarce material.

Zirconia

Zirconia is an oxide of zirconium metal with the chemical formula ZrO_2. It occurs naturally in mineral form as baddeleyite, or can be manufactured by thermal dissociation from the silicon containing mineral zircon.[2] Zirconia mainly

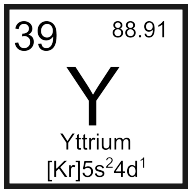
exists as one of three polymorphs: monoclinic, tetragonal, and cubic. The tetragonal and cubic zirconia are better candidates for solid electrolytes, however they undergo phase transition into the more stable monoclinic form. This can be prevented by combining zirconia with alkaline or rare earth metal oxides such as yttria (Y_2O_3), magnesia (MgO), or ceria (CeO_2). Cubic zirconia has



Fluorite structure
of cubic ZrO_2

a fluorite structure (see figure). The fluorite structure has a general formula MO_2 and is a face-centred cubic arrangement of cations with the oxygen anions occupying all tetrahedral sites (highlighted with blue in figure). As octahedral sites (center of the cell in the figure) are left unoccupied, the structure has a lot of 'open space'. This allows for fast ion diffusion within the lattice.

Doping with Yttria

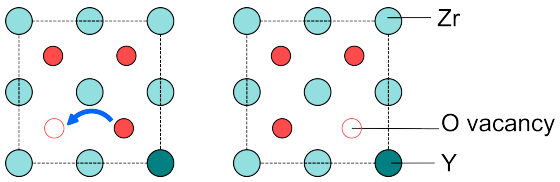


Doping cubic zirconia with yttria essentially means replacing some of the Zr4+ cations with Y3+ cations in the cubic structure. As the yttrium cation is slightly larger than zirconium, the cubic structure is stabilized against the undesirable phase transition. Since the valence of yttrium is lower than zirconium, there will also be oxygen vacancies, i.e. empty lattice positions in the cubic structure that would normally be occupied by an oxygen anion.

How the oxygen anions move

Oxygen ions diffuse through the lattice by moving from between point defects in the oxygen sub lattice, i.e. oxygen vacancies. The anion conductivity of the material therefore depends strongly on the defect concentration. Even a pure ZrO_2 crystal will contain point defects, however the concentration of intrinsic oxygen defects is very low. Doping with yttria introduces more oxygen vacancies leading to an increased ion conductivity.

Although the YSZ electrolyte already exhibits acceptable performance, some



Top-down view of YSZ with
oxygen hopping to a defect site

novel alternative materials such as perovskites have been explored. Perovskites will be introduced later in the course.

Sources and further reading:

1 Kilner, J. A., Druce, J., & Ishihara, T. (2016). Electrolytes. High-Temperature Solid Oxide Fuel Cells for the 21st Century, 85–132.
https://doi.org/10.1016/b978-0-12-410453-2.00004-x

2 Nielsen, R. H., & Wilfing, G. (2010). Zirconium and zirconium compounds. Ullmann's Encyclopedia of Industrial Chemistry.
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3 Favot, M., & Massarutto, A. (2019). Rare-earth elements in the circular economy: The case of yttrium. Journal of Environmental Management, 240, 504–510.
https://doi.org/10.1016/j.jenvman.2019.04.002

4 Kamlungsua, K., Su, P. -C., & Chan, S. H. (2020). Hydrogen generation using solid oxide electrolysis cells. Fuel Cells, 20(6), 644–649.
https://doi.org/10.1002/fuce.202070602

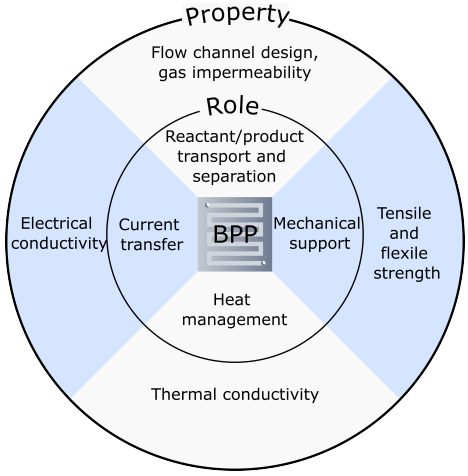
Bipolar plates

What do they do?

In the cell stack, bipolar plates are placed between the cathode and anode of adjacent cells. The plates have two sides, the anodic and cathodic side. The purpose of the bipolar plates to facilitate current flow from one cell to another, so they must be efficient electrical conductors to reduce ohmic losses. The plates have channels, inlets, and outlets where water, hydrogen, and oxygen are transported through the stack. The plates are also referred to as flow field plates in the literature.

To prevent leakages in the stack, the bipolar plates must be impermeable to gasses. The plates should have high mechanical strength so that they do not bend or break under pressure. Good thermal conductivity is also required to keep an even temperature throughout the stack.

In AEL and AEM the conditions are alkaline, which means that the materials do



not have to withstand a harsh acidic environment as in a PEM, and nickel coated stainless steel can be used on both the anode and cathode side. Steel is strong, conducts electricity and heat, and is relatively cheap and easy manufacturing process. In solid oxide electrolysers the anodic do not contain BPP, and the cathodic side can utilize nickel coated steel plates like AEL and AEM.

While in AEL, AEM, and SOEC devices the BPP can be composed of cheaper and easier to manufacture materials and do not form such a large percentage of stack cost, in PEM electrolysers today, the BPP components contribute significantly to the price of the stack, about 50%. Therefore the BPP is a main target for materials based development for PEM devices.

Further reading:

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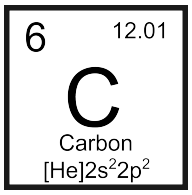
Zhou, Y., & Chen, B. (2023). Investigation of optimization and evaluation criteria for flow field in Proton Exchange Membrane Fuel Cell: A critical review. Renewable and Sustainable Energy Reviews, 185, 113584. https://doi.org/10.1016/j.rser.2023.113584

Graphite

Graphite as raw material

Graphite has been previously used as bipolar plate material in PEM cells due to its great electrical conductivity and corrosion resistance. The main use of graphite in Europe is as a refractory material in the steel industry. Graphite is also used in the renewable energy sector as an anode material in EV batteries, and its demand is predicted to rise due to this sector. Graphite is a naturally



occurring allotrope of carbon, and was added to the list of critical raw materials for EU by the European Commission in 2020. Majority of natural graphite is mined and processed in China, which is also a major source for graphite in the EU1. There are graphite mines in Austria, Germany and Norway, however around only 3% of graphite consumed in EU is sourced domestically (Note: Norway is not EU, therefore not counted as domestic, although 8% of graphite in EU is sourced there).The largest graphite deposits in the EU are located in Sweden, Czech Republic and Finland, but none are currently mined.

Structure and properties

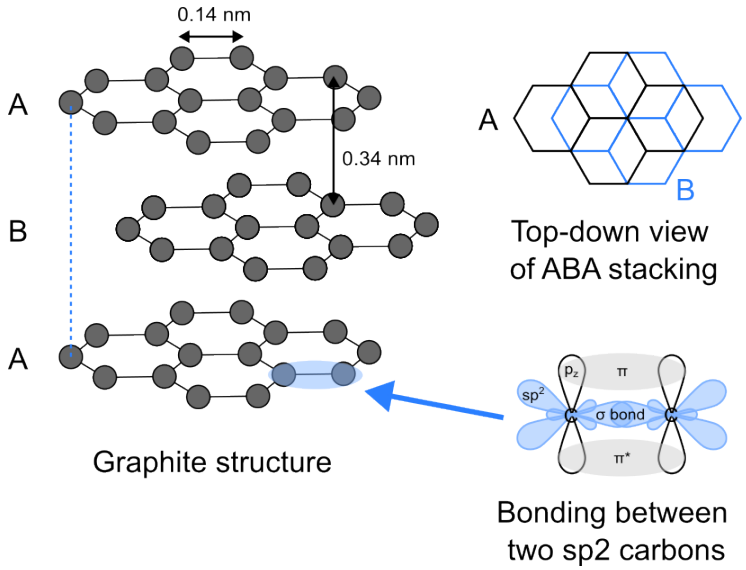
Graphite consists of stacked layers (see figure), each individual layer has a graphene structure. The graphene sheet is one atom thick and has a repeating pattern of six membered carbon rings. The carbon atoms are sp2-hybridized, and from a strongly covalently bonded network. Each carbon atom is bonded to three neighboring atoms in the same layer, with three of the valence electrons occupying the σ-band which is formed by the sp2-orbitals. The fourth valence electron is in the π-band formed by the unhybridized p-orbitals. Graphite has no band gap between the conduction and valence bands, and is a good conductor of electricity (and heat), with the π-electrons acting as charge carriers. The most stable stacking for graphite is the ABA "Bernal" stacking (see figure above). The layers are held together through π-π interactions, a sub-type of van Der Waals interaction. The interaction is relatively weak, and the layers can easily slide or 'slip' relative to each other, which makes graphite soft. Combined with the strong covalently bonded network this leads to the brittleness of pure graphite.

Beyond graphite

The corrosion resistance and light weight if graphite make it an excellent material for bipolar plates. However, it is also brittle which makes it difficult to manufacture and has a rather low mechanical strength. Research efforts have been put to developing graphite-polymer composite materials for BPP which would circumvent these issues.

Further reading

1 European Commission, Directorate-General for Internal Market, Industry, Entrepreneurship and SMEs, Grohol, M., Veeh, C., Study on the critical raw materials for the EU 2023 : final report, Publications Office of the European Union, 2023,



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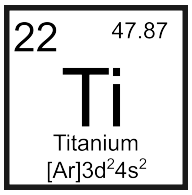
2 Kotakoski, J. (2021). Atomic and electronic structure of graphene. Graphene, 15–26.
https://doi.org/10.1016/b978-0-08-102848-3.00003-7

3 Link to graphite structure (log in required for interactive view):
https://next-gen.materialsproject.org/materials/mp-48

Titanium

Metal sheets are in general good candidates for BPP as they are mechanically stable, conduct electricity and heat well, and can be stamped to a shape to make flow channels for gas and liquid transport. In particular they are easier to manufacture and stronger than the brittle graphite sheets.

However, in PEM cells operate at very low pH. At such acidic conditions metals plates are vulnerable to corrosion and dissolution. Dissolved metal ions in the PEM membrane are problematic, as they can lower the ionic conductivity. Corrosion of the metal surface creates a corrosion layer of metal oxide/hydroxide, which decreases the electrical conductivity of the plate. Metals can be protected from corrosion/dissolution by adding a protective coating of another metal or a thin passivation layer of oxide. The state-of-the-art material for metallic BPP is titanium. Titanium is a transition metal that was added to the EU list of critical raw materials in 2020. Titanium supply to the EU relies entirely on imports. More than 95% of all extracted titanium ore is used to produce titanium oxide. The major global producers and EU suppliers are tabulated below (2016-2020 average).



Global producers	% share	EU suppliers	% share
China	25	Norway	23
South Africa	13	South Africa	16
Australia	12	Canada	14
Mozambique	10	Mozambique	10
Canada	8	Ukraine	9
Ukraine	6	UK	9
Kenia	4	Australia	6
Senegal	4	Sierra Leone	6

Coated titanium

Titanium tends to form an oxide layer on the surface at PEM operating conditions (consult a pourbaix diagram e.g. on Wikipedia, original figure has been removed due to copyright), which increases contact resistance. To prevent the passivation layer from forming, the BPP is coated with another more noble metal. The protective layer is platinum on the anode side, and gold on the cathode side. The use of gold and platinum further increases the cost of titanium BPP.

Titanium components (BPP and porous transport layers) contribute significantly to the high cost of PEM, but the price is related to the expense of manufacturing the titanium BPP, rather than the raw material cost. The long term goal is for PEM to be completely titanium-free, some promising replacements are tantalum, niobium, and even stainless steel -based materials.

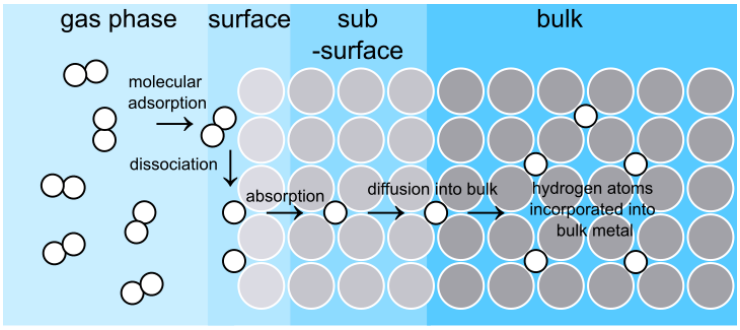
1 European Commission, Directorate-General for Internal Market, Industry, Entrepreneurship and SMEs, Grohol, M., Veeh, C., Study on the critical raw materials for the EU 2023 : final report, Publications Office of the European Union, 2023,
https://data.europa.eu/doi/10.2873/725585

Dealing with Hydrogen

Hydrogen embrittlement

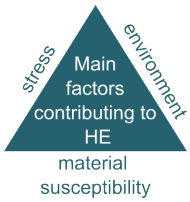
Hydrogen is the smallest atom, so small that it can go through solid materials. Incorporation of hydrogen into the microstructure of a material makes it more susceptible to fracture under stress, i.e. more brittle, giving the phenomenon

its name, hydrogen embrittlement. Metals, especially steel, are susceptible to hydrogen embrittlement (HE). The first experimental evidence of HE in iron and steel was reported ca 150 years ago.



schematic representation of incorporation of hydrogen into the bulk structure of a metal

HE is a key factor in the reduction of structural integrity of metallic materials in green hydrogen applications. The effect is especially problematic for hydrogen storage (and transport), where HE could lead to catastrophic material failures, posing a significant safety risk.



Further reading:

Del-Pozo, A., Villalobos, J. C., & Serna, S. (2020a). A general overview of hydrogen embrittlement. Current Trends and Future Developments on (Bio-) Membranes, 139–168.
https://doi.org/10.1016/b978-0-12-818332-8.00006-5

Yu, H., Díaz, A., Lu, X., Sun, B., Ding, Y., Koyama, M., He, J., Zhou, X., Oudriss, A., Feaugas, X., & Zhang, Z. (2024). Hydrogen embrittlement as a conspicuous material challenge-comprehensive review and Future Directions. Chemical Reviews, 124(10), 6271–6392.
https://doi.org/10.1021/acs.chemrev.3c00624

HE mechanisms

HE is a complicated phenomenon, with many different possible mechanisms that depend on the material and conditions such as temperature. The main

mechanisms of HE are:

- Hydrogen-enhanced decohesion embrittlement (HEDE)
- Hydrogen-enhanced local plasticity (HELP)
- Absorption-induced dislocation emission (AIDE)
- High-temperature hydrogen attack (HTHA)
- Hydride formation and fracture

HEDE

The attraction of like atoms is also called cohesion, and the weakening of interatomic bonds between like atoms is sometimes referred to as decohesion, hence the name of this mechanism. In HEDE, the presence of hydrogen atoms in the metal bulk cause the metal-metal bonds to become weaker. It has been suggested that in steel, hydrogen donates 1s electrons to unfilled 3d shells of iron atoms, which causes the weakening of the iron-iron bonds. This ultimately leads to lower stress tolerance and cracking.

HTHA

This type of hydrogen damage occurs at high temperatures, typically ranging between 200-540 °C. The damage is cause by a reaction between absorbed hydrogen and internal carbides within the steel, which produces methane bubbles. The bubbles cause an internal pressure of about 21 MPa along the grain boundaries. Unlike hydrogen, methane cannot diffuse out of the metal, which cause internal stress and eventually cracking.

Further reading:

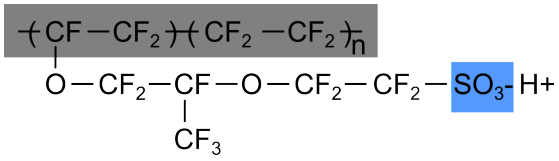
Del-Pozo, A., Villalobos, J. C., & Serna, S. (2020a). A general overview of hydrogen embrittlement. Current Trends and Future Developments on (Bio-) Membranes, 139–168.
https://doi.org/10.1016/b978-0-12-818332-8.00006-5

Yu, H., Díaz, A., Lu, X., Sun, B., Ding, Y., Koyama, M., He, J., Zhou, X., Oudriss, A., Feaugas, X., & Zhang, Z. (2024). Hydrogen embrittlement as a conspicuous material challenge-comprehensive review and Future Directions. Chemical Reviews, 124(10), 6271–6392.
https://doi.org/10.1021/acs.chemrev.3c00624

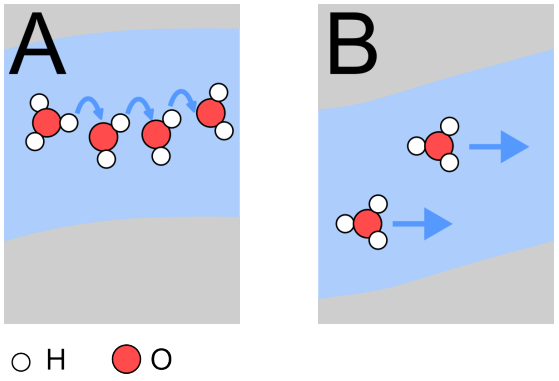
Electrolysis cell materials Quiz

1. Fill in the blanks In _____ electrolysers, the _____ is a solid but flexible membrane. The membrane must conduct _____ but not _____. The cell performance typically _____ when the membrane is made thinner, but this increases _____.

   The image below depicts the chemical structure of a PFSA monomer. The part highlighted in grey is the _____, which is _____. The part highlighted in blue is the _____, which is _____.



   _____ can be transported through the membrane by the vehicular/molecular mechanism (figure_____) , or the structural/hopping mechanism (_____). The mechanism in figure _____ dominates at high hydration levels.



2. Match the materials development targets with appropriate cell stack technologies. These are targets that have a high potential for improving the performance, lifetime, or efficiency of the stack, but have also been identified as difficult or moderately challenging to achieve.

   (a) Noble metal free protective layers and titanium free porous transport layers and bipolar plates

   (b) Increase stability of ionomer (OH- transport)

   (c) Eliminate electrode delamination from electrolyte

   (d) Improved kinetics for both HER and OER with novel nickel-based materials

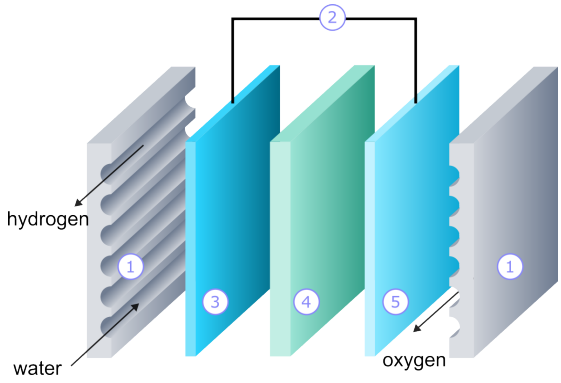
A PEM

B AEL

C AEM

D SOEC

3. Name the cell stack components numbered in the diagram below:



4. For the stack type presented in Question 3, choose an appropriate material for the stack components.

(a) Cathode

(b) Anode

(c) Electrolite

A Perovskite

B Yttria-stabilized zirconia

C Nickle doped yttria-stabilized zirconia

5. What type of stack is the one presented in Question 3?

(a) PEM

(b) AEL

(c) AEM

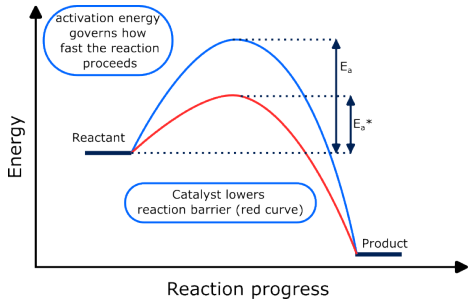
(d) SOEC

Electrocatalysts

Role of the electrocatalyst

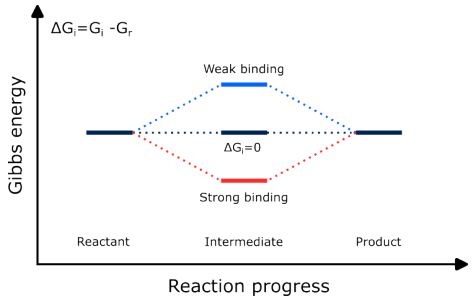
Although the room temperature equilibrium potential for the water splitting reaction is 1.23 V, much higher applied potentials are required to drive the water splitting reaction experimentally. The overpotential is the difference between the applied potential required to achieve a given current density, and the minimum theoretical cell potential. The bigger the overpotential, the more extra electric work must be supplied to the system.

There are many factors that contribute to the overpotential of an electrochemical reaction. A significant portion is due to the kinetic barriers associated with the (electro)chemical reactions taking place on the electrodes. The kinetic overpotential of the water splitting reaction can be reduced by lowering the activation barriers of the anode and cathode half-reactions.



It is also possible for there to be a thermodynamic overpotential. When the equilibrium potential is applied, the reactant and product have the same Gibbs energy (at equilibrium $\Delta G = 0$). However, the reaction intermediates bound to the catalyst surface may be lower or higher in energy (see figure below). For the reaction to be thermodynamically favorable, the catalyst must bind all intermediates in such a way that all elementary steps are either thermoneutral or exergonic. In the simple scheme below, if the intermediate is higher in energy (weak binding), the first step is 'uphill', and if the intermediate is lower in energy (strong binding), the second step is uphill. Thermodynamic overpoten-

tial, η_{TD}, is the minimum overpotential needed to make all elementary reaction steps either thermoneutral or exergonic. The thermoneutral landscape (dark lines) below is ideal, i.e. η_{TD}=0 . Any deviation from this leads to a non-zero η_{TD}.



Electrocatalysts are materials that lower the activation barriers of the half-reactions and are thermodynamically ideal (thermodynamically ideal catalyst is often the one with lowest barriers), which means that a smaller applied potential can be used to achieve a given current density and hydrogen production rate.

Novel OER/HER electrocatalysts are a heated research topic, with new materials being predicted, synthesized and tested constantly. Therefore it is not feasible to introduce all currently studied materials in this introductory course. In this module, the currently used water splitting electrocatalysts (namely Pt, IrO_2, and Ni based materials) are introduced first. General strategies for improving catalysts are presented, and finally we provide some well studied examples of novel HER and OER catalysts. For more examples and expanded background, the students are encouraged to familiarize themselves with the cited literature listed at the bottom of each page.

Further reading

Ooka, H., Huang, J., & Exner, K. S. (2021). The Sabatier principle in electrocatalysis: Basics, limitations, and extensions. Frontiers in Energy Research, 9. https://doi.org/10.3389/fenrg.2021.654460

HER and OER and the conventional catalysts

HER

Hydrogen evolution reaction (HER) is the cathodic half-reaction of water electrolysis. In both basic and acidic media, the generally accepted HER mechanism involves 2-3 steps:

HER under acidic conditions

$$H^+(aq) + * + e^- \rightleftharpoons H_{ads} \quad \text{adsorption (Volmer)}$$
$$H_{ads} + H_{ads} \rightleftharpoons 2* + H_2(g) \quad \text{chemical desorption (Tafel)}$$
$$H_{ads} + H^+(aq) + e^- \rightleftharpoons * + H_2(g) \quad \text{electrochemical desorption (Heyrovsky)}$$

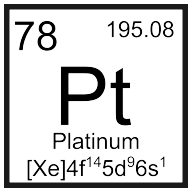
HER under basic conditions

$$H_2O(l) + * + e^- \rightleftharpoons H_{ads} + OH^-(aq) \quad \text{adsorption (Volmer)}$$
$$H_{ads} + H_{ads} \rightleftharpoons 2* + H_2(g) \quad \text{chemical desorption (Tafel)}$$
$$H_{ads} + H_2O(l) + e^- \rightleftharpoons * + H_2(g) + OH^-(aq) \quad \text{electrochemical desorption (Heyrovsky)}$$

The reaction takes place on the electrode surface with the help of a catalyst, and the reaction is a few orders of magnitude faster under acidic conditions. The hydronium ion (H_3O^+) is a much better proton donor than water, which affects the reaction rates of the Volmer and Heyrovsky steps. The trade-off for the faster kinetics is that all materials used must be able to withstand the acidic environment. This limits the selection of suitable materials.

Platinum

The current state-of-the-art electrocatalyst for the HER reaction in acidic media is platinum. The commercial Pt catalyst consists of platinum nanoparticles supported on carbon black, and is used in PEM electrolysers.



Platinum is extremely rare: Earth's upper crust has a platinum concentration of only about 0.0005 ppm. Platinum mining is currently highly concentrated in South Africa, with the majority of processing taking place there as well.[1] The major global and EU platinum suppliers are tabulated below:

Global producers	% share	EU suppliers	% share
South Africa	71	UK	52
Russia	12	South Africa	18
Zimbabwe	8	Switzerland	8
-	-	Russia	7

Note: These numbers are averages of the years 2016-2020, prior to the Russian invasion of Ukraine

Over 90% of platinum reserves are located on or near indigenous or rural land that are facing water risk, conflict and food insecurity.[2] Mining projects in such vulnerable areas have the potential to exasperate these risks, if the materials are not extracted and processed responsibly. Minimizing the negative impacts on the local communities and nature is essential. Another issue is the so-called "resource curse", i.e. countries that are rich in natural resources often end up not benefiting from their value due to exploitation.

Platinum structure

Platinum has a face centered cubic (fcc) crystal structure, which has three low Miller indexes facets, (111),(100), and (110), depicted below (image removed due to copyright, refer to Figure 1. in https://doi.org/10.1016/j.rsurfi.2021.100006). In the figure, the plane along which each surface is cut from the bulk is shown with a grey surface inside the cubic unit cell. In the hard sphere models of the surfaces, the atoms that lie on the plane (darker grey spheres) are highlighted with black dots.

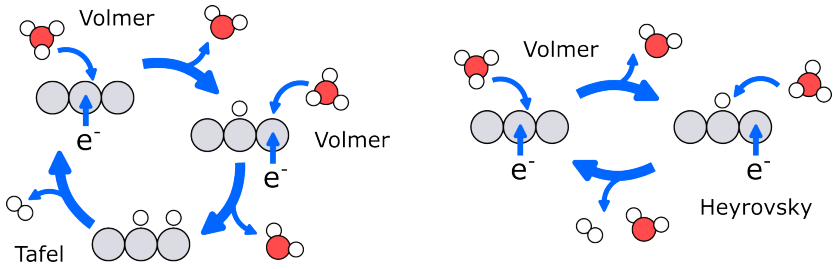
Each surface exposes different kind of sites and different surface energy. The adsorption behavior of reactants, intermediates, and products can differ greatly from surface to surface. For example, hydrogen has been found to bind weaker on the Pt(111) surface than on the (100) or (110) surfaces.[3] The adsorption site is a three fold hollow site, which is not present on the (110) or (100). Adsorption strength of hydrogen in particular is expected to have a strong influence on HER activity. The HER exchange current density (j_0) has been found to increase in the order (111) $<<$ (100) $<$ (110), with j_0 on the (110) surface being 3 times that on the (111) surface.[4]

The presence of low-coordinated Pt atoms (e.g. step, edge, or corner atoms) have been found to promote HER activity, especially in alkaline solutions, possibly due to the more facile dissociation of the water molecule on such sites.[5] This indicates that in addition to the optimal hydrogen binding energy, increasing the number of low coordinated metal sites would benefit the HER performance of metal catalysts.

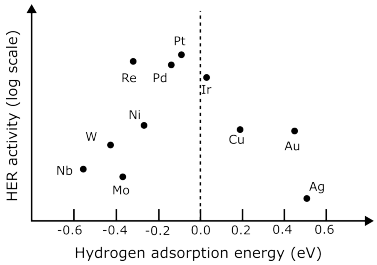
In real electrodes platinum is not a single crystal, but polycrystalline, i.e. there are many different atomic arrangements present and the orientation of the crystal facets are random. This means that the electrocatalytic activity is averaged over the contributions from all surfaces. This is further complicated by the dynamic nature of the surface under reaction conditions, i.e. even if a (nearly) defect free single crystal electrode could be used it is likely to restructure due to interaction with chemical species present and the applied potential.[6]

HER mechanism

Below is a schematic of two alternative HER mechanisms over a clean Pt surface



Hydrogen is the most important (or even only) surface intermediate, hence the hydrogen adsorption energy is commonly used as an activity descriptor for HER catalysts. This means that it would be possible to predict the activity of a new material towards HER by only calculating the hydrogen adsorption energy for that material. When measured HER activities of known materials are plotted against hydrogen adsorption energy calculated using computational methods, one obtains a volcano-like relationship (below).



The top of the volcano represents the highest activity. The optimal adsorption energy corresponding to the top of the volcano is predicted to be nearly thermoneutral for HER. Platinum is the most active (acid) HER catalyst, as it appears at the top of the volcano i.e. has a nearly optimal hydrogen adsorption energy.

As a transition metal, the bonding behavior of platinum is determined in large part by its d-band structure, which also determines the hydrogen adsorption energy. One strategy to reduce the need for platinum is to mimic its electronic structure by e.g. alloying some other metals together.

Sources and further reading:

1. European Commission, Directorate-General for Internal Market, Industry, Entrepreneurship and SMEs, Grohol, M., Veeh, C., Study on the critical raw materials for the EU 2023 : final report, Publications Office of the European Union, 2023,
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sults in Surfaces and Interfaces, 3, 100006.
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3. Vurdu, C. D. (2018). The adsorption and diffusion manners of hydrogen atoms on pt (100), Pt (110), and Pt (111) surfaces. Advances in Condensed Matter Physics, 2018, 1–10.
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5. Strmcnik, D., Lopes, P. P., Genorio, B., Stamenkovic, V. R., & Markovic, N. M. (2016). Design principles for hydrogen evolution reaction catalyst materials. Nano Energy, 29, 29–36.
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https://doi.org/10.1021/acs.jpclett.9b02544

OER

Oxygen evolution reaction (OER) is the anodic half-reaction of water electrolysis. The reaction mechanism of OER is much more debated than that of HER, but mechanisms often proposed under acidic and basic conditions are presented below.

OER under acidic conditions

$$
\begin{aligned}
&H_2O(l) + * \rightleftharpoons OH_{ads} + e^- + H^+(aq)\\
&OH_{ads} \rightleftharpoons O_{ads} + e^- + H^+(aq)\\
&O_{ads} + O_{ads} \rightleftharpoons 2* + O_2(g)\\
&O_{ads} + H_2O(l) \rightleftharpoons OOH_{ads} + H^+(aq) + e^-\\
&OOH_{ads} + H_2O(l) \rightleftharpoons * + O_2(g) + H^+(aq) + e^-
\end{aligned}
$$

OER under basic conditions

$$
\begin{aligned}
&OH^-(aq) + * \rightleftharpoons OH_{ads} + e^-\\
&OH_{ads} + OH^-(aq) \rightleftharpoons O_{ads} + H_2O(l) + e^-\\
&O_{ads} + O_{ads} \rightleftharpoons 2* + O_2(g)\\
&O_{ads} + OH^-(aq) \rightleftharpoons OOH_{ads} + e^-\\
&OOH_{ads} + OH^-(aq) \rightleftharpoons * + O_2(g) + H_2O(l) + e^-
\end{aligned}
$$

The reaction mechanism generally involves multiple proton-coupled electron transfers (PCET) to the electrode, the generation of OH_{ads} and O_{ads} intermediates, and $O_2(g)$ production via chemical desorption or alternatively electrochemical desorption through OOH_{ads} intermediate.

Nickel

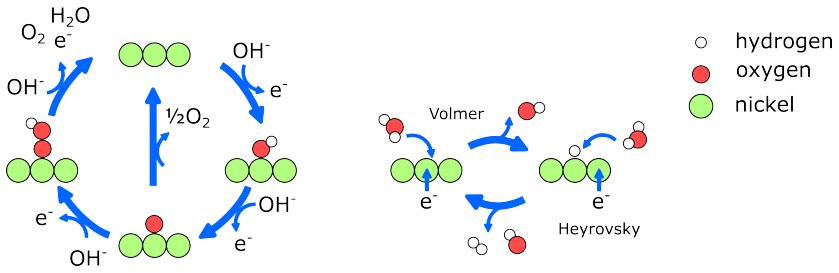
Under acidic conditions, noble metals and metal oxides must be used due to the aggressively corrosive environment. Non-noblemetals can react with acids to form oxides and hydroxides, which changes the catalyst structure and properties. These changes are accompanied by a loss of catalytic activity. In contrast, under alkaline conditions corrosion and dissolution is not as significant, which permits the use of much cheaper materials and leads to the lower cost of AEL cells compared to PEM. The lower price comes at a cost, as the HER reaction especially is more sluggish under neutral or alkaline conditions.

Nickel-based electrocatalysts are currently the popular choice for commercial AEL devices. Nickel is electrically conductive and has a high thermal stability, and has been demonstrated to be active for both HER and OER under alkaline conditions. The typical support for nickel is perforated stainless steel. Nickel is also used as the HER catalyst in SOEC devices, where it is supported on yttria-stabilized zirconia.

Nickel is about 1000 times cheaper than platinum at the time this Moodle course was created. In the EU, over half of refined nickel is sourced from Russia (29%), Finland (18%), and Norway (11%). Although the EU relies heavily on import (70%), Finland is the leading supplier of nickel within the EU.[1]

Mechanism and active site On nickel, the OER reaction mechanism may be classified as an adsorbate evolution mechanism (AEM) with the reaction taking place on surface nickel atom sites. This is analogous to the Langmuir-Hinshelwood or Eley-Rideal type mechanisms found in thermocatalysis. Proposed AEM mechanism for OER and the Volmer-Heyrovsky mechanism for HER under alkaline conditions are presented below:

Nickel shows the most optimal hydrogen binding energy among non-noble metals, and is therefore a good compromise between price and performance for HER. The performance of nickel can be improved by e.g. forming binary or multicomponent alloys with other metals such as molybdenum, cobalt, aluminum, and iron, or forming compounds with non-metals.



Improved Nickel- based materials

Many nickel-based materials have been investigated to improve the catalytic activity towards HER/OER. Nickel phosphides (NixPy) have shown relatively high HER and OER activity and stability, and further benefit from only including cheap and abundant Ni and P. Nickel nitrides and sulfides have also been studied (further reading in ref 4 and 5).

Ni12P5 in particular exhibits high OER activity. A combined ab initio molecular dynamics simulation (AIMD) and computational density functional theory (DFT) study demonstrated that the overpotential is lower on $Ni_{12}P_5$ than other nickel phosphides, which explains its better OER performance.[2] Furthemore, they show that the surface P atom is the active site.

For HER in acid, the activity trend is $Ni_3P \approx Ni_5P_4 > Ni_2P > Ni_{12}P_5$, while in base Ni_5P_4 is found to be most active. A recent DFT study has proposed that enhanced HER performance of nickel phosphides is due to the metallic character of the materials combined with the presence of non-metal (P) surface sites.[3] In particular, a three fold P hollow site on the surface was found to bind hydrogen near thermoneutrally, which is the optimal hydrogen binding strength for HER. However, on transition metal phosphide surfaces the existence of many different sites that bind hydrogen with different strengths complicates the use of the single activity descriptor.[4]

Nickel phosphates can be categorized as metal- or phosphorus-rich. Metal-rich phosphates always show better electrical conductivity and corrosion resistance due to more metal-metal bonds present in the structure. However, phosphorus-rich materials have more P-P bonds, and therefore may contain more non-metal sites, which should lead to better catalytic activity.5

Sources and further reading:

1. European Commission, Directorate-General for Internal Market, Industry, Entrepreneurship and SMEs, Grohol, M., Veeh, C., Study on the critical raw materials for the EU 2023 : final report, Publications Office of the European Union, 2023,
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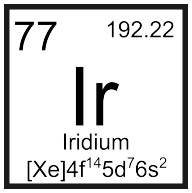
Huo, L., Jin, C., Jiang, K., Bao, Q., Hu, Z., & Chu, J. (2022). Applications of nickel-based electrocatalysts for hydrogen evolution reaction. Advanced Energy and Sustainability Research, 3(4).
https://doi.org/10.1002/aesr.202100189

Iridium

Iridium dioxide (IrO_2)is the current state-of-the-art catalyst material for the acidic OER half-reaction utilized in commercial PEM electrolysers. In fact, IrO_2 is the only material that is active and stable enough so far.



There have been reports of highly active novel OER catalysts, however the high activity is usually accompanied by poor stability. In fact, metallic iridium and ruthenium, as well as ruthenium oxide all show higher activity than IrO_2, but the dissolution/deactivation increases in the opposite order. The rate of dissolution for the more active catalysts makes them unsuitable for acid OER, therefore IrO_2 is the best catalyst material.[1]

Structure of IrO_2

Iridium dioxide has a rutile structure, where each iridium cation is surrounded by six oxygen anion, and each oxygen anion is coordinated to three iridium

cations (see figure). The formal oxidation state of iridium is 4+, however the Ir and O bonding has covalent character. IrO_2 is a peculiar transition metal oxide in that it shows metallic-type conductivity. The conducting behavior is a result of there being no band gap (see density of states plot on Materials Project).

OER mechanism on IrO_2

Rational design of active and Earth-abundant OER requires a thorough understanding of the reaction mechanism and nature of active sites of state-of-the-art iridium catalysts. On the iridium oxide, alkaline OER could occur through a lattice oxygen mediated (LOM) mechanism, which is Mars-van-Krevelen-like, or the adsorbate evolution mechanism (AEM). Proposed mechanisms for the reaction on iridium oxide are presented below:

The rate determining step has been suggested to be either the OOH formation step on the Ir5+ site (bottom right arrow in AEM mechanism), or the step after that, i.e. deprotonation of the OOH species.6 Conventionally, the active site is thought to be coordinatively unsaturated Ir metal sites on rutile IrO_2 surface.

Isotope labeling studies have found that the lattice oxygen can take part in the reaction, and also suggested that the mechanism could lead to Ir dissolution of the Ir6+ state. The mechanistic findings suggests that stabilizing the iridium 3+ and 6+ states would prevent dissolution, increasing the lifetime of the catalysts. The stabilization could be achieved by, e.g. introducing another oxide component. Such stability improvements have indeed been reported e.g. for IrOx-TiO_2 and IrOx/$SrIrO_3$ materials.

Recently, it was found that calcining IrO_2 resulted in a more dissolution resistant catalyst. It was suggested that oxygen vacancy formation and subsequent stronger Ir–Ir interaction are crucial for the observed stability increase. However, further computational and experimental studies are needed to fully understand the OER and dissolution mechanisms over IrO_2.

Replacing iridium

A major drawback of iridium is that the metal is about 10 times more rare and approximately 5 times more expensive than platinum at the time of writing. Like platinum, most of the world's iridium is mined and processed in South Africa.[2] Due to its rarity and price, finding an alternative iridium free acidic OER catalyst is one major goal in PEM electrolyzer development. In its current state, iridium demand is a bottle neck in the scale up of PEM electrolyzers to the GW per year production scale.[4]

One strategy would be to improve the performance of the catalysts while reducing the amount of iridium (loading). There is room to improve, as OER is a significant source of kinetic overpotential (0.35 V) even when the state-of-the-art iridium anode is used. Furthermore, it has been estimated that the recycling rates of end-of-life iridium catalysts must reach at least 90 %.

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Novel HER catalysts

Will anything beat Platinum?

It is undeniable that platinum is an exceptionally active HER catalyst. The HER reaction over platinum is so fast that it is limited by mass transport rather than surface kinetics, which means that the intrinsic activity is still underestimated. No other catalyst can beat Pt in terms of intrinsic activity (yet).

The measure of intrinsic activity of an electrocatalyst is the turnover frequency, TOF(η).3 TOF(η) is the number of chemical conversions of the reactant molecule per unit time per a single active site at overpotential η. Although TOF(η) is the only rigorous way to compare the intrinsic activities of catalyst, it is typically very difficult to quantify the number of active sites present, and so the

activity of novel catalysts is often reported in terms of total electrode activity, i.e. the potential required to achieve a given current density (current per geometric electrode area). A better way to compare activities is to normalize the activity by mass or the electrochemically active surface area (ECSA). These activity metrics are useful but still approximate measures of the true intrinsic activity.

The Gibbs energy of hydrogen adsorption on platinum is nearly thermoneutral, which corresponds to the top of the activity volcano. This seems to imply that nothing can ever perform better than platinum for HER. However, the simple volcano-like relationships do not represent the whole picture. There are issues with the accuracy of activity measurements, influence of hydrogen coverage on the adsorption energies, and the nature of the catalyst under reaction conditions (some may not be metallic, but hydrides) which the plots do not account for. The validity of peak position of the original volcano plot has also been questioned in recent years [1,2] This means that predicting the activity of new catalysts is not as straightforward. There is also hope that some other material may perform even better than platinum despite it being at the top of the volcano.

Another way of improving catalyst activity, besides increased intrinsic activity, is to increase the number of active sites by increased catalyst loading or mesh/nano structuring. This can be economically viable especially if the catalyst material is significantly cheaper than precious metals. However, increased loading can improve the activity only unto a certain limit, and thicker electrodes can also suffer from increased mass transport limitations. The combination of these effects could lead to higher operational costs compared to Pt based systems, which defeats the point of replacing Pt as the active material.

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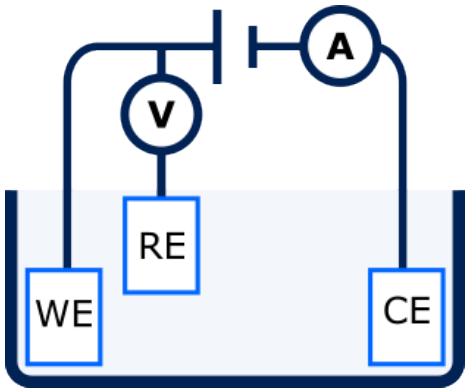
Choice of counter electrode

A matter that complicates the evaluation of novel catalysts is that the choice of the counter electrode (CE) could have an influence on the reported activity.[1] In the picture below, a typical three electrode setup is shown. The catalyst

candidate is fixed to a substrate on the working electrode (WE), and there is a current flowing between it and a counter electrode (CE).



As voltage is applied to the cell, a current is produced as a result of HER on the WE. The current that passes through the CE must perfectly match the current through the WE. For this, an oxidation reaction must take place at the CE, and this will be the reaction that occurs at the least positive potential. For water splitting, the only possible reaction at the anode is OER. This causes issues, however, as one of the most popular CE materials is platinum, which can be dissolved during OER. Dissolved Pt can contaminate the WE, and lead to an increase in the observed current, with Pt acting as the active electrocatalyst instead of the novel material.

One way to solve this issue is to saturate the electrolyte with hydrogen by continuously bubbling the electrolyte with 1 atm H_2 gas. This enables the hydrogen oxidation reaction (HOR) to occur on the CE instead of OER (HOR has a lower potential than OER). As platinum is a good HOR catalyst, the cathodic current can be balanced by HOR, avoiding Pt dissolution. The other alternative is to use a separator between the WE and CE compartments to prevent the deposition of the dissolved Pt species on the WE surface.

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Replacing or reducing Pt

Despite the challenges in predicting and comparing activities, many seemingly active novel HER catalysts have been proposed. In general, two broad categories for novel HER catalyst designs exist

- reducing platinum content
- replacing platinum completely

Because platinum's intrinsic HER activity is so exceptionally high, it could be possible to scale up hydrogen production by PEM electrolysers even using Pt-based electrocatalysts by using a lower loading of Pt.1 The reduction of platinum content faces the challenge of maintaining the high activity of platinum while simultaneously using less of it.

Replacing platinum on the other hand requires finding completely new catalysts that have superior HER performance compared to Pt while only using abundant and cheap elements. Transition metal compounds, such as sulfides, carbides, nitrides, and phosphides, and N-4 macrocycle based materials have shown promise in HER.

Nickel phosphides were briefly discussed in the conventional HER catalyst section. The next sections will introduce some examples of the most extensively studied promising novel HER catalysts that reduce or replace Pt.

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How to use less Pt?

Rather than completely replace platinum as the HER catalyst completely, two strategies are available for reducing the amount of platinum needed

- improving efficiency of Pt utilization
- combining with less expensive metals

Current commercial Pt based HER catalysts employ supported PT nanoparticles (NPs). As only the atoms on the surface of the nanoparticle can act as catalytic active sites for the HER reaction, the atoms in the core of the NP are 'wasted'. Reducing the size of the particles to clusters or even to single atoms is a potential way to increase the utilization of Pt, as the surface to volume ratio is increased with decreasing particle size. This means more active sites are exposed per unit mass of Pt. However, smaller Pt species are more vulnerable to aggregation, oxidation, dissolution and Ostwald ripening.

Pt single atom catalysts

Single-atom catalysts (SAC) or single-site catalysts (SSCs) have gathered more and more interest in the recent years as promising materials for heterogeneous catalysis. In SAC, each metal atom/site is isolated from one another, at least by a distance greater than the metal-metal bond. Despite the name, the active site

of the SAC/SSC always includes a contribution of the substrate/support, which acts in an analogous way to the ligands of a metal complex in homogeneous catalysis. The motivation for using the term "single-site catalyst" instead of "single-atom catalyst" is to draw attention to the fact that the function of the active site is not only determined by the active metal atom, but the surrounding atoms it is bonded to as well. In the literature, you will encounter both terms used interchangeably.

One major challenge of using SAC for HER (or any reaction for that matter) is the relatively poor stability of single atoms.Single atoms tend to agglomerate and form clusters, which is can lead to deactivation of the catalyst. SA are commonly stabilized by introducing anchoring sites, such as atomic vacancies on the support. The SA is bound stronger to the vacancy than the pristine surface, and is stabilized against migration on the surface.

Platinum SA supported on cerium oxide are some of the most well studied SAC, but not for electrocatalysis. The Pt_1/CeO_2 is a catalyst candidate for low temperature CO oxidation, the major reaction occurring in a catalytic converter. Eventhough the system has been studied for many years now, there is still debate on what the nature and bonding environment of the single-atom is during operating conditions. It has been suggested, with rather strong evidence, that under reaction conditions the Pt SA agglomerate to form small few atom clusters, which are more active for the reaction than the as synthesized SA.

The real target for materials design of Pt SAC/SSC electrocatalysts is the support. The support matrix should be electrically conductive and the interaction of the SA with the support should be strong. Strong covalent bonds between the SA and support would anchor the SA to the specific site on the surface and hinder deactivation by agglomeration. Atomically dispersed Pt supported on mesoporous carbon, nitrogen-containing porous carbon particles, nanoporous $Co_{0.85}Se$, and $Mo_2TiC_2O_2$ nanosheets have been synthesized and tested for HER activity. All studies claim the atomically dispersed Pt sites to have higher activities than the commercial nanoparticulate Pt/C catalyst.

Despite the promising HER performance of platinum SAC, the nature of the catalysts under operating conditions is not well understood. More in depth operando structural characterization and computational studies addressing the catalyst properties and mechanism are needed to rationalize the high performance of these materials. Operando spectroscopical methods and computational studies are also needed for better understanding for the degradation mechanisms of Pt SAC in order to combat it.

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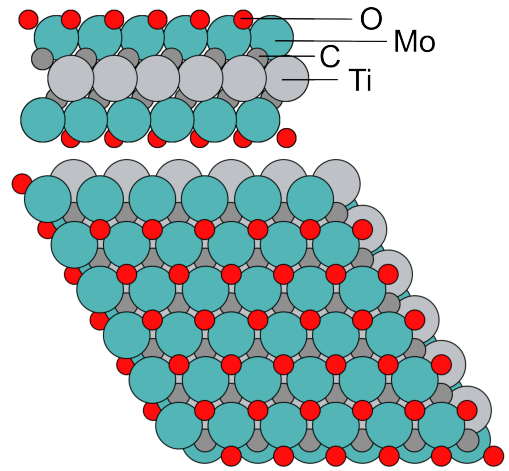
MXenes - The $Mo_2TiC_2T_x$-Pt case

MXenes are a group of 2D transition metal carbides or nitrides, with the general formula $M_{n+1}X_nT_x$ where M is a transition metal (Ti, V, Mo, ...), X is nitrogen or carbon, and T is a surface functional group (OH, O, ...), and n stands for number of layers. Oxygen terminated MXenes in particular are a family of promising HER catalysts. [1,2] DFT calculations have shown that the adsorption of hydrogen is nearly thermonetural on the terminating oxygen atoms, which is the first indicator for high HER activity.

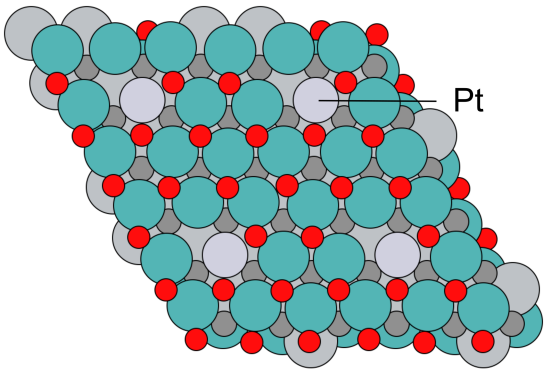
The $MO_2TiC2Tx$ (figure below) MXene has also been studied as a support matrix for Pt atoms for acidic HER.[3] The $MO_2TiC2Tx$ structure consists of a C-Ti-C trilayer sandwiched between Mo layers, and the active form is oxygen terminated (MO_2TiC2O_2).



Side (above) and top down (below) view of the oxygen terminated $Mo_2TiC_2T_x$

In the reported synthesis, the support is electrochemically exfoliated in situ to form thin nanosheets with Mo vacancies. Pt atoms are then deposited on to the support by dissolution of the Pt counter electrode. The Pt atoms are anchored by the Mo vacancies (figure below) and stabilized against agglomeration. The Pt atom is strongly covalently bonded to the carbon atoms in the support.

The Pt SA modified MXene was found to be more active than the unmodified MXene, and exhibited a much higher mass normalized activity than the com-



Top down view of the $Mo_2TiC_2O_2$ supported Pt SA

mercial Pt/C catalyst. The overpotential was found to be slightly lower for the SA modified MXene than the commercial catalyst. For polarization curves, tafel slopes, exchange current densities and mass activity for unmodified MXene, Mo vacancy containing MXene, SA modified MXene and Pt/C catalyst see ref 3 (Figure removed due to copyright).

DFT studies found that hydrogen adsorption on the Pt SA site is more thermoneutral than on the terminating oxygens of the unmodified MXene support, which could explain why the addition of Pt SA to the support boosts HER activity, and can even compete with the commercial catalyst.

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Chalcogenides - Case of MoS2

Chalcogenides

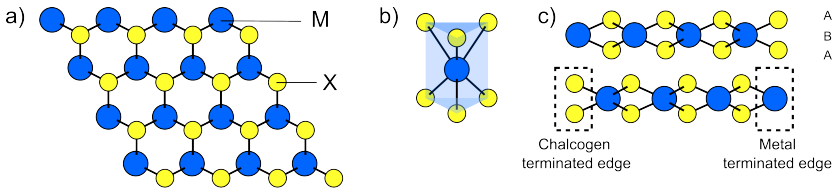
Chalcogenides are compounds that have the chemical composition MX, MX_2,MX_3,

or MX_4 where M is a metal and X is a chalcogen. Chalcogen is the name used to refer to group 16 elements in the periodic table, which include oxygen(O), sulfur (S), selenium (Se), tellurium (Te), polonium (Po) and livermorium (Lv), however compounds of oxygen are not usually included in chalcogenides.

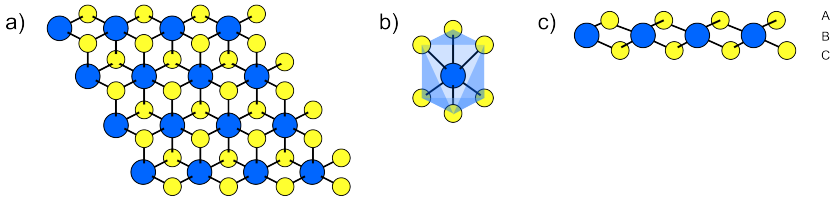
In particular, transition metal dichalcogenides (TMDs) have been of interest recently because they are low cost, and relatively active for acid /alkaline HER and alkaline OER. They also exhibit highly tunable morphologies and electronic structures, the general chemical formula is MX2 where M is a transition metal (such as Mo, W, Ti, V) and X is sulfur, selenium or tellurium. Despite their promising performance as electrocatalysts for water splitting, using TMDs in electrolyzer devices is not yet at a practical level.

TMD structure

The bulk TMD structure is formed by stacked X-M-X layers. The X-M-X layer is a sandwich structure of a transition metal atomic layer between two chalcogen atomic layers. The coordination geometry of the metal to the six surrounding chalcogens (three in the top and three in the bottom layer) gives rise to different polymorphs. The two most common ones exhibited by TMDs are the 1T and 2H phases, with the 2H phase being more thermodynamically stable than 1T.



a) Top-down view of monolayer TMD 2H phase,
b) Trigonal prism metal coordination geometry
c) Stacking in 2H



a) Top-down view of monolayer TMD 1T phase,
b) Octahedral metal coordination geometry
c) Stacking in 1T

The in-plane metal-chalcogen bonds are strong and covalent by nature, but between layers are weak van der Waals interactions, similar to graphene. This makes it possible to construct (few) monolayer thin sheets with relative ease. Intercalation of atoms, ions, or molecules into the van der Waals gap is also

possible, which adds another degree of freedom for tuning the properties of TMDs.

MoS_2

In nature, the many nitrogenase enzymes contain an active center of iron sulfur (Fe–S) clusters with a Mo atom bound to it. The active centers evolve hydrogen during ammonia fixation, which was the inspiration to originally study hydrogen binding on MoS_2 using density functional theory (DFT) calculations. It had also been found decades earlier that MoS_2 coating promotes the alkaline HER activity of NiS electrodes. The DFT calculations showed that hydrogen binding energy on the sulfur terminated edges of MoS_2 is near the top of the HER volcano plot, and the experimental polarization curves showed that MoS_2 supported on graphite exhibited reasonable activity towards HER. MoS_2 was also recently found to have a comparable stability to the Pt catalyst under acidic HER.

MoS_2 structure

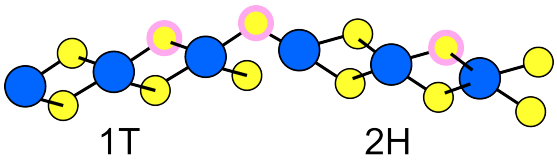
Molybdenite or molybdenum sulfide (MoS_2) is a naturally occurring, not particularly rare mineral. Molybdenum sulfide preferentially crystallizes in the semiconducting 2H phase, although many other polymorph structures, such as 1H-MoS_2, 1 T-MoS_2, 1 T'-MoS_2 and 3R-MoS_2 are possible.

The thermodynamically stable 2H phase with trigonal prism Mo coordination exhibits relatively low carrier concentration and poor electrical conductivity. Furthermore it is known that only the 2H-MoS_2 nanosheet edge atoms are active for HER, which means that the majority of the surface is inert towards HER. Therefore, a possible strategy for increasing the activity of 2H-MoS_2 catalysts is to nanofabricate the catalyst so that it exposes more edge sites as compared to the inert bulk basal plane sites. Another strategy is to improve the intrinsic activity of the basal sites by intercalation, introducing defects (vacancies), doping, or integrating the MoS_2 with another material in order to tune the hydrogen adsorption energy.

The 1T-phase of TMDs typically out performs the 2H phase for HER, because the 1T phase is metallic in character which reduces charge transfer resistance. S atom sites at the 1T-2H phase boundary (see figure below) in particular have been identified as potential active sites for the HER due to favourable hydrogen binding.

As the 1T phase is only metastable and readily transforms into the less active 2H phase, stabilizing the 1T structure is essential for improved HER activity. Intercalation with e.g. potassium, lithium, or organic molecules has been found to be able to induce phase transition from 2H to 1T, and to stabilize mixed phase 2H-1T structures. In particular, Li intercalation induced 2H to 1T transition was demonstrated to boost HER activity of MoS_2.

Recently, it was demonstrated that the metastable 1T'-MoS_2 phase (Mo coordination is distorted octahedral) was found to be more active for HER than



1T-2H boundary with favorable H adsorption sites (S atoms) highlighted in pink

the 2H phase. More remarkably, it was found that it is the basal sites that are more active, which was attributed to the distorted octahedral crystal structure. However, the 1T' phase is readily transformed into 2H at mild conditions, which results in an activity drop.

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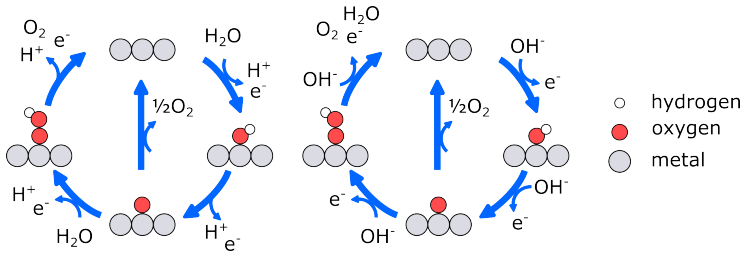
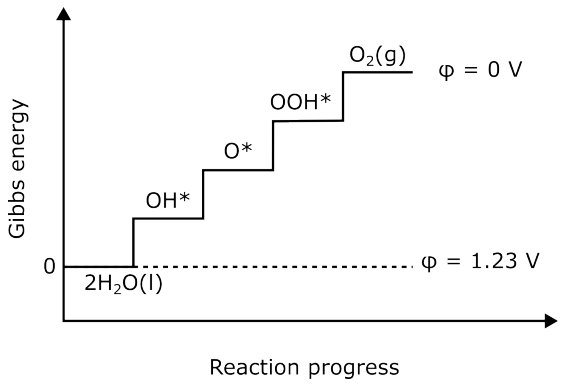
Novel OER catalysts

The OER problem

Out of the two water splitting half reactions, OER is slower and therefore more rate limiting. It is also less well understood than HER. Traditionally, the reaction mechanism has been described as taking place on the electrocatalysts with the surface atoms acting as the active sites:



The energetics of the mechanism can be described with the help of a Gibbs energy diagram:



The thermodynamic criterion is that all elementary steps in the reaction mechanism should have a reaction free energy of zero at the equilibrium potential (dashed line in the Gibbs energy diagram). An ideal catalyst would stabilise all surface species in such a way that the reaction free energies of all steps are of equal magnitude at zero potential (solid line in the Gibbs energy diagram above). The ideal energy difference between each step in the diagram above is 1.23 eV (do not confuse units with V!).

However, the adsorption energies of surface species are related to each other by scaling relations. For example, the universal scaling relation between the adsorption free energies of OH and OOH intermediates is $\Delta G(*OOH) = \Delta G(*OH) + 3.2 \pm 0.2$ eV.[1] The adsorbate binding strength of these species cannot be optimized independent of each other, which implies that the optimal reaction energy landscape is extremely difficult to achieve.

The optimal separation of OH and OOH adsorption Gibbs energies is 2.46 eV (they are separated by two steps), as this would imply no added thermodynamical overpotential. However, according to the scaling relation $\Delta G(*OOH) = \Delta G(*OH) + 3.2 \pm 0.2$ eV the separation is 3.2 eV, which holds for many materials. This results in a minimum theoretical overpotential for OER of approximately 0.37 V, which imposes a limitation on the maximal catalytic activity of a material.

Going beyond this theoretical overpotential limitation requires that the adsorption Gibbs energies of OH and OOH on a given material do not obey the equation presented above, and is referred to as "breaking the scaling relation". There are a few strategies for breaking the scaling that have been proposed:

- perturb metal d states by doping, e.g. with Ni or CO
- introducing a second adsorption site so that OOH and OH adsorb on different sites
- stabilization of *OOH relative to *OH by introducing a nearby proton acceptor group

- nanoscopic confinement
- lattice oxygen mechanism

The OOH and OH Gibbs adsorption energies are reliable activity descriptors for OER over metals . However, at the high oxidizing potential of the anode, the catalyst materials are frequently oxides. For oxides, it is possible for the lattice oxygen to directly participate in the reaction in the lattice oxygen mediated (LOM) mechanism. The theoretical overpotential predicted from OH and OOH scaling relations is strictly not valid for materials where LOM is the dominant mechanism, as OOH is not a reaction intermediate.

The lattice oxygen mediated mechanism might complicate the picture, the binding energy of oxygenated intermediates could still be valid for predicting OER overpotentials of metal oxides. The established volcano plots predict binary oxides such as IrO_2, RuO_2 (at the very top of the volcano), and perovskites (e.g. $LaNiO_3$ and $SrCoO_3$) as some of the most promising materials for OER, and the theoretical activities agree rather well with experimental observations (IrO_2 and RuO_2 are currently the state-of-the-art for acidic OER).

While the possibility of breaking scaling relations gives hope that the OER overpotential might be lowered beyond 0.37 V, it is not a guarantee that the scaling breaking material will have a high OER activity.1 There are materials that break the OH/OOH scaling, but still exhibit high overpotentials. This could be because the scaling relation only considers the thermodynamic feasibility of the reaction, whereas in reality, considerable kinetic barriers could also be present leading to a higher than expected measured overpotential.

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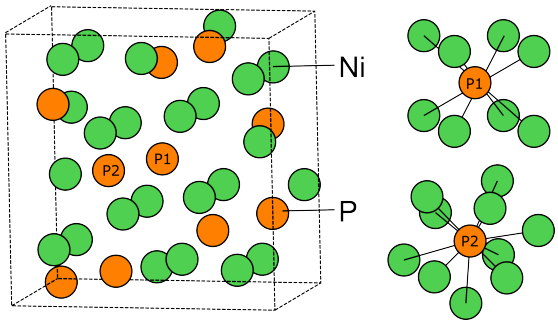
Nickel phosphide - N12P5

Nickel rich $Ni_{12}P_5$ is one of the most promising and well studied metal phosphide electrocatalyst for OER. $Ni_{12}P_5$ can be synthesized from red phosphorus and nickel chloride, nitrate, or nickel acetate by a mild hydrothermal preparation

method. Although nickel and phosphorus are much cheaper than noble metals, phosphorus and phosphate rock (source of elemental phosphorus) are both on the EU Critical Raw Materials list due to the importance of phosphorus for the agricultural sector. Finland has sizable phosphate rock reserves in Savukoski, which are currently not mined.

$Ni_{12}P_5$ structure

$Ni_{12}P_5$ crystallizes with a body-centered tetragonal structure (see figure below), with the unit cell containing 24 Ni and 10 P atoms. In the unit cell, there are two inequivalent phosphorus sites. The first phosphorus site (P1 in figure) is coordinated in a body-centered cubic geometry to eight nickel atoms. The other site (P2 in figure) is coordinated to ten nickel atoms. $Ni_{12}P_5$ has zero band gap, and exhibits metallic behavior.



Note: These kind of more complex structures are difficult to represent in 2D. For an interactive model, sign in to https://next-gen.materialsproject.org/materials/mp-2790)

OER on $Ni_{12}P_5$

$Ni_{12}P_5$ has been reported to be highly active towards alkaline OER, outperforming the commercial IrO_2 and RuO_2 catalysts, and Ni_2P. The high activity was attributed to the formation of NiIIIOOH and NiII(OH)2 species in the form of an amorphous layer on the catalyst surface. The increased amount of nickel sites on the $Ni_{12}P_5$ was considered to be responsible for the higher observed OER performance in comparison to Ni_2P.

A recent combined ab initio molecular dynamics simulation (AIMD) and computational density functional theory (DFT) study showed that the surface P atom is the active site for OER. This was attributed to the more favorable water dissociation on the P site. The calculations demonstrated that the overpotential is lower on $Ni_{12}P_5$ than other nickel phosphides, which could explain its better OER performance.2 The study also found a linear relationship between the charge of Ni and P sites and the adsorption energy of OER intermediates OH and O. As the negative charge on the P site increases, the adsorption becomes weaker, whereas on the Ni site, the more positive the charge, the stronger the

adsorption.

It should be noted that the computational model for $Ni_{12}P_5$ considered OER under acidic conditions (H_2O as reagent), and therefore did not take into account the formation of the amorphous NiOOH/Ni(OH)2 shell that is observed experimentally for the alkaline OER. Such a model would require very expensive calculations, but could shed some light on the alkaline OER mechanism.

$Ni_{12}P_5$ has also exhibited activity towards acidic HER, although it is less active than other nickel phosphides. The Volmer-Heyrovsky mechanism was assigned based on the experimental Tafel slope of 63.0 mV/dec. The catalyst showed to be stable, and the activity was suggested to be correlated with the presence of positively charged Ni and negatively charged P atoms.

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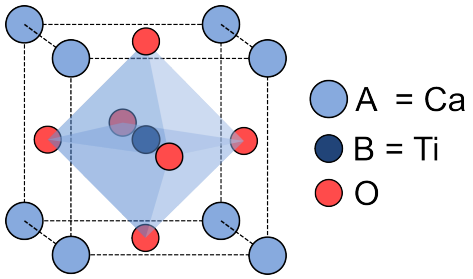
Perovskites

Perovskites have gathered a lot of interest as promising electrocatalysts of OER. Articles matching 'Perovskites' and 'OER' on WebofScience have increased 100 fold in the last 10 years. Many perovskite oxides have demonstrated great OER performance, and in addition have high ionic and electronic conductivities and structural stability, making them an attractive class of materials for electrocatalysis. Furthermore, the structure, physical and electronic properties of perovskite catalysts are highly tunable by varying the elemental composition and arrangement.



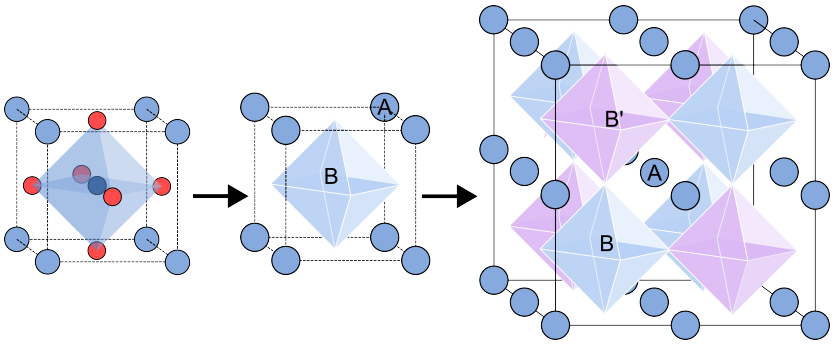
Oxide perovskites are a family of compounds whose crystal structures are based on that of calcium titanate1 ($CaTiO_3$ see figure for crystal structure), and have the general formula ABO_3 , where A and B are metals. Non-oxide perovskites also exist, in which the oxygen in the structure is replaced by another element such as carbon. Metal A is usually an alkaline earth or rare-earth element, while metal B is usually a transition metal. The metal A cations sit in the corner position of the cubic cell and are coordinated to 12 oxygens each, while the metal B cations (center of the cube) are coordinated to 6 oxygens. The oxygens occupy the face centered positions of the cubic cell. In the ideal undistorted cubic structure the B cation has an octahedral symmetry (highlighted with light blue in the structure figure).

The first perovskite to achieve an alkaline OER performance higher than the state-of-the-art IrO_2 catalyst was the $Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-\delta}$ (BSCF) catalyst.[2]

Double Perovskites

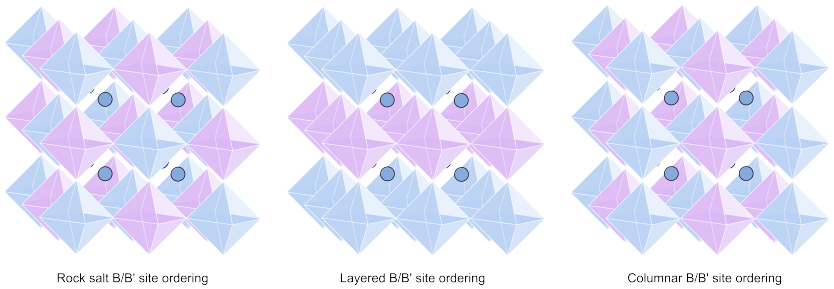
Double perovskites in the $LnBaCo_2O_{5+\delta}$' (Ln=Pr, Sm, Gd and Ho and Ln) family have been identified as highly active catalysts for alkaline OER, the $(Pr_{0.5}Ba_{0.5})CoO_{3-\delta}$ catalyst capable of even outperforming the BSCF catalyst.[3] The authors established the position of the O 2p band with respect to the Fermi level as the activity descriptor for these double perovskites, which is influenced by the identity of the substituting lanthanide.

Double perovskite structures can be formed from the simple ABO_3 structure by doubling the size of the unit cell and replacing half of the B metal sites with a different metal (B').



The resulting double perovskite formula is $A_2BB'O_6$. As the substituting B' cations have different ionic radii, expansion, contraction or tilting of the octahedral B/B' sites can occur in order to compensate. This leads to distortions from the ideal cubic structure which can further alter the electronic and physical properties.

The ordering of the B and B' sites can be modified, the structure figure above showed the simple 'rock salt' ordering. The other typical B/B' site ordering structures are layered and columnar arrangements (see figure below)



It is possible to tune the structure even further by substituting two different rare-earth or alkaline earth elements ($AA'BB'O_6$). This dramatically increases the degrees of freedom for structural diversity compared to single perovskites.

OER mechanism on Perovskites

Like for simple metal oxides, such as IrO_2 and RuO_2, the mechanism of OER on perovskites have been hypothesized to follow either the adsorbate evolution mechanism (AEM) or the lattice oxygen mechanism (LOM). However, unlike for simpler oxides the possible coexistence of the two mechanisms was accepted early on for perovskites.

Direct experimental evidence for the LOM over perovskites was obtained by isotope labeling studies in 2017.4 The group investigated the OER activity of $LaCoO_3$, $La_{0.5}Sr_{0.5}CoO_{3-\delta}$, $Pr_{0.5}Ba_{0.5}CoO_{3-\delta}$ and $SrCoO_{3-\delta}$ perovskites. The perovskites were labelled with isotope ^{18}O, and oxygen gas of different molecu-

lar weights generated during OER were identified with mass spectroscopy. They were able to show that the isotope labeled oxygen is released from $La_{0.5}Sr_{0.5}CoO_{3-\delta}$, $Pr_{0.5}Ba_{0.5}CoO_{3-\delta}$ and $SrCoO_{3-\delta}$ during OER, indicating that the lattice oxygen mechanism was at least partially responsible for the OER activity. In contrast, no mass signal consistent with the release of ^{18}O was observed for $LaCoO_3$. The reason for the different behaviour of the least active $LaCoO_3$ and most active $SrCoO_3$ in particular was related to the covalency of the metal-oxygen bond. Since strontium is divalent (Sr2+) and lanthanum is trivalent (La3+), the fermi level in $SrCoO_3$ is moved closer to the oxygen 2p states, and the metal 3d and oxygen 2p band centers are moved closer to one another (see figure below). As the O 2p states lie above the redox energy of O_2/H_2O, the oxidation of the lattice oxygen (i.e. creation of oxygen vacancy) in the perovskite becomes thermodynamically favourable at OER conditions. This facilitates the lattice oxygen mediated mechanism.

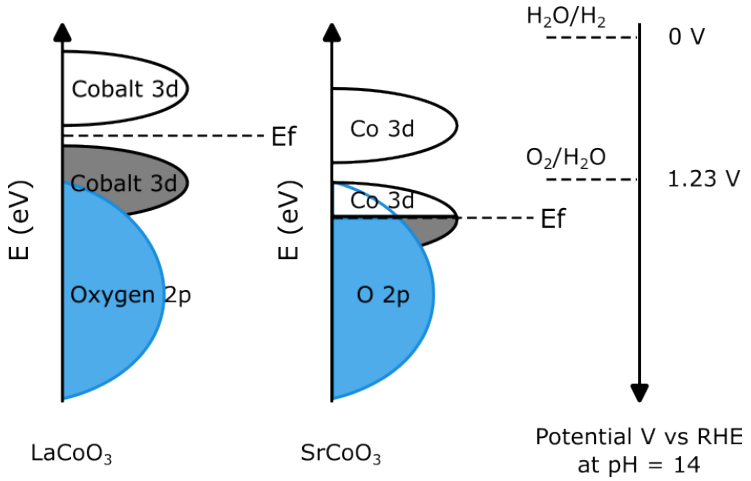


Figure 2: Schematic band structures of $LaCoO_3$ and $SrCoO_3$ showing positions of Cobalt 3d and oxygen 3d states and Fermi level (Ef) with respect to the potential. Adapted from ref 4

The previous year, another group had suggested that the ease of forming oxygen vacancies could explain the reactivity trends for cobalt based $La_{1-x}Sr_xCoO_{3-\delta}$ perovskites towards alkaline OER.[5] They found that the activity increases with increased Sr substitution of La, as the covalency of the metal-oxygen bond increased. They reported the fully substituted $SrCoO_{2.7}$ to have the highest activity in the series. Using density function theory (DFT) calculations they were able to show that the lattice oxygen mediated mechanism is more favorable on the active catalyst, however they lacked the direct experimental evidence of the release of lattice oxygen later provided by the isotope labeling study.

OER descriptors for Perovskites

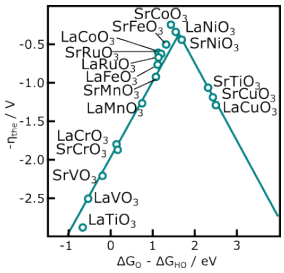
Varying the atomic composition by substituting different metals in A and B sites of the perovskite structure leads to a vast amount of potential materials. However, the structural diversity of the perovskite family also makes it quite hard to identify a single OER activity descriptor, although it would be highly desirable. Nevertheless, many descriptors have been proposed:

- number of d-electrons
- e_g band filling of the transition-metal cations
- difference between the surface binding energies of O*and HO* reaction intermediates
- oxide formation energy
- accumulation of the magnetic moment on the conduction plane atom

The lack of consensus for a single descriptor has lead to the suggestion that a descriptor network would be more suitable for predicting OER activity trends for the perovskite family.

Another complication is leaching of the cations and participation of the lattice oxygen through the LOM mechanism. Both processes can lead to surface restructuring, especially under the oxidation OER conditions.Specifically for the $Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-\delta}$ researchers have been able to show using operando spectroscopical techniques that the surface reconstructs during OER.[6] They were able to observe the growth of a self-assembled metal oxy(hydroxide) layer that was active for OER. The authors proposed that the lattice oxygen OER mechanism itself was the mechanism of the layer formation, based on the fact that the start of the growth coincides with the onset of OER activity. This kind of formation of an active phase in situ can mean that the properties of as synthesized catalysts can be unreliable descriptors.

Despite these complications, the difference between the surface binding energies of O and HO reaction intermediates has been successfully used to predict overpotentials for single perovskites.[7] The volcano plot (adapted from ref 7) below depicts the theoretical overpotential for alkaline OER as a function of the difference in binding energy of O and HO.



The OER reactivity order:

$SrCoO_3$ >$LaNiO_3$ >$SrNiO_3$ >$SrFeO_3$ >$LaCoO_3$ >$LaFeO_3$ >$LaMnO_3$

predicted from the volcano plot agrees very well with experimentally measured OER activity of these perovskites.

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https://doi.org/10.1002/cctc.201000397

Electrocatalysts Quiz

1. Match the descriptions to the appropriate electrocatalyst materials.

   (a) Catalyst whose active site is formed by a metal atom bound to a support such as graphene, MXene or oxide.

   (b) Noble metal catalyst used in PEM electrolysers for the cathodic reaction

   (c) Catalyst used in PEM electrolysers for oxygen evolution reaction

   (d) 2D transition metal carbides or nitrides that can catalyze the hydrogen evolution reaction

   (e) Non-noble metal catalyst used for alkaline HER and OER

   (f) Novel class of oxides that can catalyze alkaline OER

   A MXenes

   B Nickel

   C Platinum

   D IrO_2

   E Perovskites

   F Single atom catalyst

2. A good electrocatalyst raises the overpotential of the water splitting reaction.

   (a) True

   (b) False

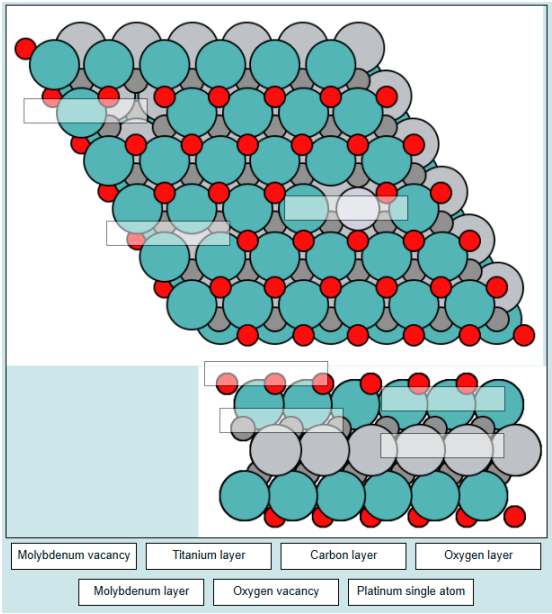
3. On which of the following materials would you NOT expect the oxygen evolution reaction to occur through the lattice oxygen mediated mechanism?

   (a) Perovskites

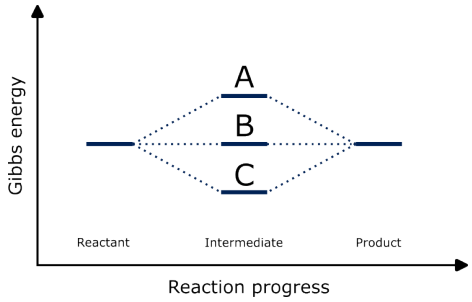
   (b) Nickel phosphides

   (c) Iridium oxide

4. Write the appropriate labels onto the structure schematic of the $Mo_2TiC_2O_2$ MXene.



5. Which of the following diagrams shows the thermodynamical ideal Gibbs energy profile for a reaction proceeding through one intermediate at the equilibrium potential?

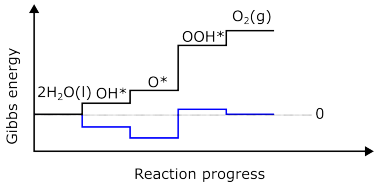


A

B

C

6. Which of the Gibbs energy profiles below depicts room temperature OER over a candidate perovskite catalyst at the equilibrium potential?



   (a) neither

   (b) black

   (c) blue

7. Is the perovskite catalyst that the diagram in question 6 belongs to thermochemically ideal?

   (a) Yes

   (b) No

8. Based on the Gibbs energy diagram depicted in question 6, which of these reaction steps determines the thermodynamic overpotential for the OER over the candidate perovskite catalyst?

   (1) $\mathrm{H_2O}(l) + * \rightleftharpoons \mathrm{OH}* + \mathrm{e}^- + \mathrm{H}^+(aq)$

   (2) $\mathrm{OH}* \rightleftharpoons \mathrm{O}* + \mathrm{e}^- + \mathrm{H}^+(aq)$

   (3) $\mathrm{O}* + \mathrm{H_2O}(l) \rightleftharpoons \mathrm{OOH}* + \mathrm{H}^+(aq) + \mathrm{e}^-$

   (4) $\mathrm{OOH}* + \mathrm{H_2O}(l) \rightleftharpoons * + \mathrm{O_2}(g) + \mathrm{H}^+(aq) + \mathrm{e}^-$

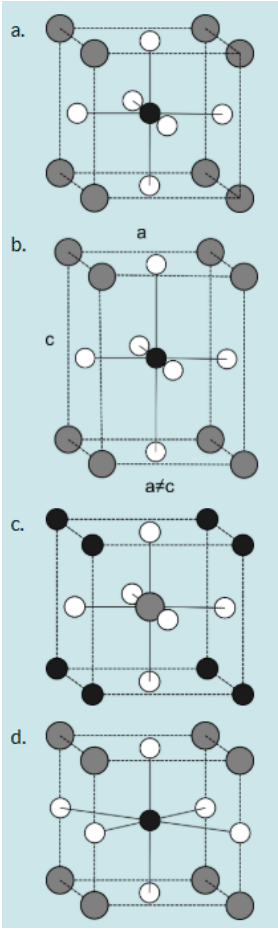
   (a) step 1

   (b) step 2

   (c) step 3

   (d) step 4

9. Which of the structures below represents the $\mathrm{CaTiO_3}$ prototype perovskite structure? White spheres are oxygen, black spheres are titanium, and grey spheres are calcium.


a.
b.
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c
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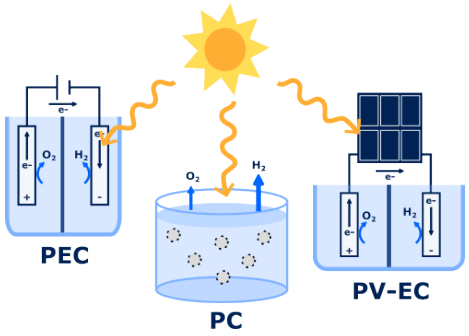
c.
d.

Materials for Solar Hydrogen

Role of the light absorber

Whereas electrolysis utilizes electricity in the production of hydrogen, with the help of catalysts, solar hydrogen production methods take further advantage of activation by sunlight.

Different solar-to-hydrogen technologies all utilise sunlight, but there are multiple approaches to introducing the photon energy with the chemical system. The three types of technologies that will be discussed in this module are:



- Photocatalytic (PC) water splitting systems. No external potential difference is needed to drive the reaction, only light.
- Photo electrochemical (PEC) systems. Combine the use of irradiation and electricity as driving forces.
- Photovoltaic-electrochemical (PV-EC) systems. Light is converted into electricity by the photovoltaic component which is used to operate an electrolyser. The components are closely integrated together.

All systems mentioned above need some sort of light absorber, and the technical material requirements depend on the application. The crucial property that

they share is that they are able to create charge carriers by exposure to natural sunlight. This can be achieved by semiconductors.

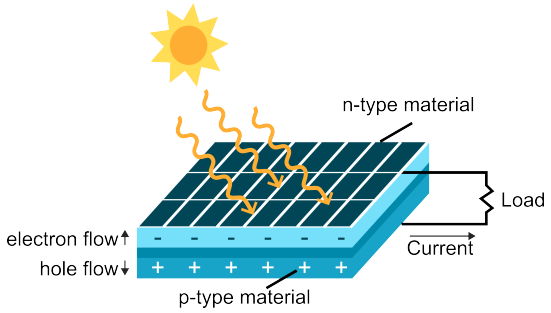
The roles of the semiconductor light absorber in PEC and PC systems is to absorb sunlight and generate charge carriers which take part in the HER and OER reactions. In addition, co-catalysts are added to lower HER and OER overpotentials and promote charge separation. In PV-EC systems, the light absorber resides in the PV part handling the solar-to-electricity conversion, but does not directly take part in the HER/OER.

The first lesson of the module introduces the photovoltaic effect that is essential for PV systems, and some related concepts that are also important for photocatalysis. The second lesson introduces the function of semiconductors as light absorber photocatalysts. Titanium oxide is the exemplary material used to illustrate the topic, but the principles can be extended to apply to other semiconductor materials as well. The third lesson introduces some multicomponent photoabsorption schemes, and the final lesson showcases some novel materials chosen from recent literature.

Photovoltaics

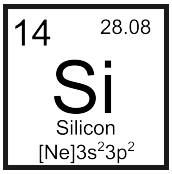
Photovoltaic effect

The photovoltaic effect is the physical process that enables a photovoltaic cell to convert sunlight into electricity. Incident sunlight on a PV cell can get absorbed and subsequently generate electricity, or it can be reflected or go through the material. For the absorption to occur, the band gap of the light absorber material in the PV must be smaller than the energy of the incoming photons, as we have seen many times during this course.



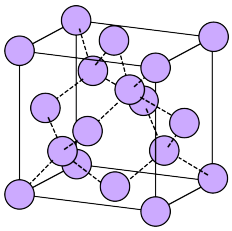
The current in a PV is generated by the potential difference caused by the built in electric field within the material. In the simplest scheme, the built in electric field is induced by bringing two different semiconductor materials in contact. A so-called 'p-n junction' consists of a contact between an n-type semiconductor and a p-type semiconductor, and we will consider n- and p-type silicon as a classic example.

Pure silicon



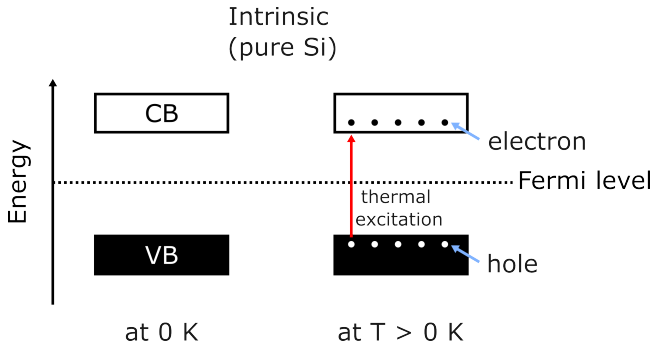
Silicon occurs naturally in the form of silicate minerals, and is the second most abundant element in the Earth's crust. The elemental form has to be extracted from minerals such as quartz. Despite its high abundance, silicon is on the EU list of critical raw materials. Although silicon is not metallic, it is listed as 'silicon metal' due to its appearance. China is the main supplier of silicon metal, with a 76 % global share. One advantage of silicon is that silicate mineral is so abundant and appears all over the globe, that in principle the production is not tied to specific locations. Norway is also a major supplier of metallic silicon to the EU (30%)

Pure silicon crystallizes in the cubic diamond structure, where all Si atoms are connected to four other equivalent Si atoms in a covalently bonded network. The Si atoms are sp3 hybridized and have a tetrahedral geometry. The crystalline solid is hard and brittle.



Silicon with cubic diamond structure

The band gap of pure silicon is about 1.1 eV. At temperatures above 0 K some electrons can be excited from the valence band to the conduction band, which enable the silicon to conduct electricity. These types of semiconductors are referred to as 'intrinsic' or i-type semiconductors.



However, at moderate temperatures the band gap of silicon is quite large compared to available thermal energy (k_bT, where k_b the Boltzmann constant and T the temperature). For semiconductors with fairly large band gaps, the average number of electrons (N) per state in the conduction band can be approximated with Maxwell-Boltzmann statistics:

$$N = e^{(\mu - E_{CB})/k_bT}$$

where E_{CB} is the energy of the state, μ is the chemical potential of the electrons (i.e. Fermi level). For an intrinsic semiconductor such as pure silicon, the Fermi level is approximately in the center of the band gap (see dashed line in the figure above), so to calculate the number of electrons at the bottom edge of the conduction band, the expression becomes:

$$N = e^{-E_{bg}/2k_bT}$$

where E_{bg} is the band gap energy (distance from the top of VB to the bottom of CB). Plugging in 1.1 eV for silicon and 300 K for room temperature one gets ca 6e-10 electrons per state, i.e. the number of electrons is extremely low. Therefore pure i-type silicon is not a very good electrical conductor.

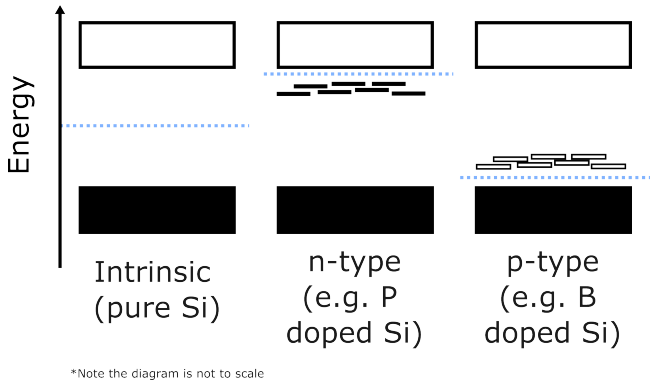
Doped silicon

To enhance the electrical conductivity of silicon, pure silicon can be doped with atoms of other elements. These dopants are essentially impurities which disrupt the normal electronic structure of the silicon crystal, which in turn affects its conductivity. Common dopants for silicon are boron, phosphorus, arsenic or gallium. Dopants can be divided into 'donors' and 'acceptors' based on their valence.

If one of the silicon atoms is replaced by a dopant that has one extra valence electron compared to silicon, four of the outer electrons will be used for bonding to the four surrounding Si atoms, while the extra 'donated' electron from the dopant atom is essentially free and acts as a charge carrier in the conduction band.

When silicon is doped with an element containing one fewer valence electrons, the 'acceptor' dopant must accept/take one more electron from Si in order to from four bonds to the surrounding Si atoms. This leaves behind a hole that acts as a charge carrier in the valence band.

More specifically, each donor dopant atom introduces a localized state (dark lines in middle image in figure on the right) just below the conduction band, while acceptor dopants introduce states above the valence band (light lines in right image in figure on the right). The states have slightly different energies due to the irregular environment of the impure crystal, and when many dopant

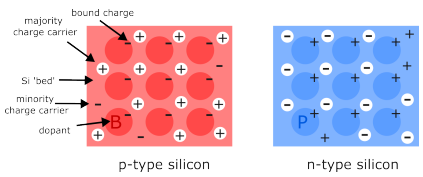


atoms are present a new "dopant band" is formed. The presence of the new filled (donor) or empty (acceptor) states causes the Fermi level to shift to the top (donor doped) or the bottom (acceptor doped) of the band gap, as indicated by the dashed blue line.

At 0 K, the donor dopant band is occupied, but as it is very close to the conduction band, even at low temperatures there is enough energy to excite them into the conduction band. As the majority charge carriers in this case are the electrons, the material is an extrinsic n-type semiconductor, where n stands for negative. The amount of promoted electrons is much larger than for undoped silicon, as the energy to excite them is much lower.

Conversely, at 0 K the acceptor dopant band is empty, but being close to the valence band means that a small amount of thermal energy is enough to excite an electron from the valence band to the donor band, leaving behind a hole in the valence band (sometimes this is described as a hole being excited from the donor band to the valence band). The holes are the majority charge carriers, therefore the material is an extrinsic p-type semiconductor, where p stands for positive.

The p-n junction



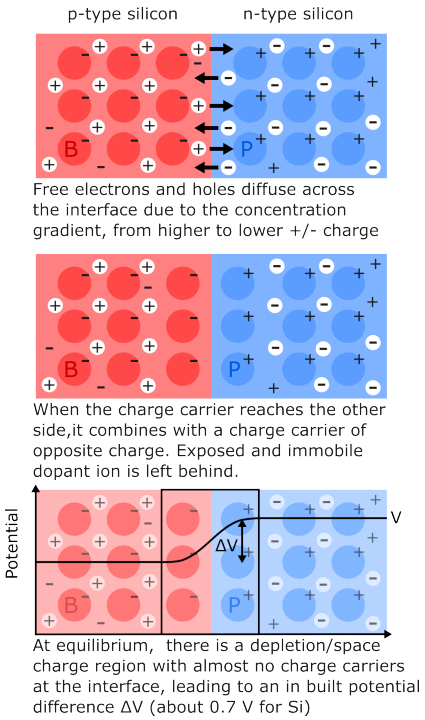
In p-type silicon, such silicon doped with boron, the majority charge carriers are holes (white circles with '+') in the valence band. In n-type silicon, e.g. phosphorus doped silicon electrons in the conduction band are the majority charge carrier. On the right, the two types os doped silicon are depicted as an arrangement of dopants in a 'bed' of Si atoms (represented by the background rectangles). The number of dopants per area is greatly exaggerated, normally the actual structure would be much more dilute. If you

look at the figure carefully you will see that the charges balance out, and both structures are neutral.

When a p-type and n-type semiconductors are brought to contact (not just by sticking them together, but by fabricating a single crystal with two phases in it), they form a structure called a 'p-n junction' at the interface between them.

Although both regions are neutral overall and across each type there is always on average the same number of free charges, there is still a concentration gradient across the interface. In other words, a free electron in the n-type sample will diffuse to the p-side because there are fewer free electrons over there.

The diffusing free electrons and holes recombine at the junction, which results in the formation of a depletion region, where almost all charge carriers are gone, and only dopant ions are present. There is now a net charge in the region, which causes an in built potential difference across the junction.



Other junctions

Besides PVs, junctions are also utilized in photocatalysis. For the photocatalytic water splitting to occur, the holes and electrons must migrate to the material surface without recombination. Charge separation and migration to separate locations is required for the OER and HER reactions to take place. The charge separation can be promoted by construction of junctions which facilitate internal electric fields. The electrons and holes have opposite charges, so they will drift in opposite directions due to the electric field, similar to the p-n junction in silicon based photovoltaics.

There are several structures that form built-in electric fields:

- p–n homojunction: one semiconductor material has two regions with different type character (e.g. p-type and n-type silicon seen before)
- p–n heterojunction: contact between two different semiconductors of different type character (e.g. n-type TiO_2 and p-type silicon)

- Schottky junction: a semiconductor equilibrates with the free electrons energy level of a metallic film (e.g. Ni metal and n-type silicon)
- Semiconductor-liquid junction (SCLJ): Semiconductor equilibrates with the ions adsorbed in the surface, forming a Helmholtz double layer (e.g. n-type TiO_2 in an alkaline electrolyte)

Multicomponent photovoltaics

Photovoltaic cells are used in PV-EC technologies, and are at a more mature stage compared to the light absorber materials used in PC and PEC. This is due to the lower technical requirements of the material. The PV part does not have to be in direct contact with the electrolyte, water, and the products, which means it does not have to be corrosion resistant. The requirement is that the PV can utilize sunlight efficiently, i.e. the band gap should be around 1 eV, and the voltage generated by the PV should be enough to overcome the thermodynamic equilibrium potential and the kinetic overpotential of the water splitting reaction, and any other losses in the system.

Crystalline silicon based photovoltaic cells dominate the PV market due to silicon being a relatively abundant, cheap, and environmentally benign material. Silicon by itself does not generate a voltage sufficient for water splitting in pure PC applications, but in PVs it can be connected in series to increase the voltage. However, single-junction solar cell efficiencies are capped by the Shockley-Queisser (SQ) limit, which is around 34% for a band gaps appropriate for solar irradiation. There is still some room for improvement, as the best real silicon PV cells do not reach the SQ limit, however it may not make economic sense to construct highly efficient systems if they are much more difficult to manufacture.

Multi-junction cells can go beyond the SQ limit, theoretically even ¿90%.[1] For maximally efficient utilization of sunlight, coupling PV to electrolyzers seems to be the most direct way forward, as opposed to more intricate photoelectrochemical systems.[2] This is also the opinion of Akira Fujishima, one of the authors of the original TiO_2 photo assisted water electrolysis paper.[3]

The confirmed conversion efficiencies of the best performing research cells are collected in a chart by the US based National Renewable Energy Laboratory (NREL). The chart can be accessed here:
https://www.nrel.gov/pv/cell-efficiency.html

1. Vos, A. D. (1980). Detailed balance limit of the efficiency of tandem solar cells. Journal of Physics D: Applied Physics, 13(5), 839–846.
https://doi.org/10.1088/0022-3727/13/5/018

2. Jacobsson, T. J. (2018). Photoelectrochemical water splitting: An idea heading towards obsolescence? Energy & Environmental Science, 11(8), 1977–1979.
https://doi.org/10.1039/c8ee00772a

3. Kamat, P. V. (2017). A conversation with Akira Fujishima. ACS Energy Letters, 2(7), 1586–1587.
https://doi.org/10.1021/acsenergylett.7b00483

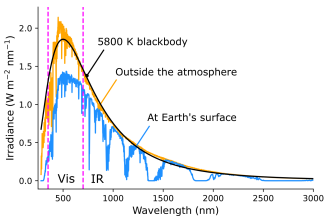
Light absorbers as photocatalysts

Light absorption

The first and most crucial step of any photocatalytic process is the absorption of light and formation of charge carriers by the light absorber material:

light absorber + hv → e + h+

The absorption of an incoming photon causes an electron to be promoted from the valence band (VB) to the conduction band (CB). An electron vacancy, or "hole", is left behind in the valence band, where it acts as a charge carrier. Light absorbers are semiconductors with appropriate band gaps for absorbing natural sun light. In PC systems, the photoabsorber also carries out the HER and OER at the surface, whereas in a PEC system, it carries out either the HER or OER, depending if it acts as an anode or cathode.



The energy of sunlight comes mostly from the IR and visible part of the spectrum. A semiconductor will be able to absorb the photon if the band gap is smaller than the energy of the photon. In addition, to drive the water splitting reaction, the energy must also be greater than the standard potential of the reaction, meaning that the theoretical minimum band gap is 1.23 eV. The overpotentials of HER and OER raise the required energy to ca 2 eV. This means that IR radiation does not possess enough energy for water splitting. The wavelength of visible light (380 to 700 nm) means that those photons have energies from 1.77 to 3.26 eV. In addition to the size of the band gap, the CB (VB) edge potential must be positioned above (below) the standard potential of the HER (OER) half-reaction.

These optical requirements make it quite hard, if not impossible, to find a single material that is suitable to act as a light absorber in a commercial system. The best performing materials currently are indeed complex composite materials, however, we will first introduce a simpler single component system for educational purposes.

Titanium oxide - the first photocatalyst for water splitting

The report of the first photocatalytic water splitting process over a semiconductor material was published by Fujishima and Honda in 1972. They had rationalised that since the potential needed for water splitting was known to

be at least 1.23 V (usually 1.5 to 2.0 V due to kinetic overpotentials and other losses), visible light of 1000 nm wavelength would possess enough energy to drive the reaction and circumvent the need to apply such a high voltage.

The photoelectrode material used in their device was n-doped (more on that later) titanium oxide, with a platinum black counter electrode. When the TiO_2 photoelectrode was irradiated with UV-vis light of ¡415 nm, they were able to produce a measurable current with no external potential applied to the cell. The wavelength corresponds to about 3.0 eV, which is consistent with the band gap of TiO_2. By measuring the direction of the electric current, they discovered the oxygen evolution reaction to take place on the TiO_2, and hydrogen evolution to take place on the Pt. This makes the TiO_2 the photoanode, simultaneously working as the light absorber, and the electrode on the anodic side.

TiO_2 is relatively cheap and abundant, very chemically stable, and the oxidizing potential of the holes is high. Fujishima was originally interested to test TiO_2, because of its sufficiently positive valence band edge for water oxidation, and because it was stable against dissolution in aqueous electrolyte solutions, unlike other conventional semiconductor electrodes of the time such as Ge, ZnO, and CdS. However, due to its large band gap, it is not capable of utilizing most of the energy from natural sunlight. Although TiO_2 is still investigated as a promising photocatalyst material, it is no longer in the form of single rutile crystals they were 50 years ago.

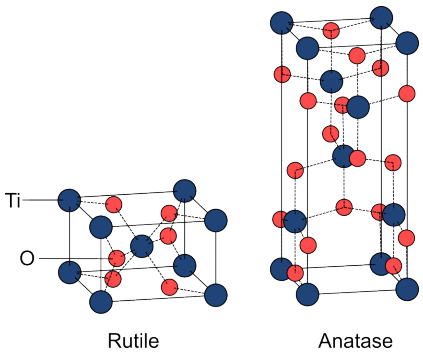
FUJISHIMA, A., & HONDA, K. (1972). Electrochemical photolysis of water at a semiconductor electrode. Nature, 238(5358), 37–38. https://doi.org/10.1038/238037a0

Q Honda and Fujishima concluded that OER occurs on the TiO_2 electrode and HER occured at the Pt electrode in their photocatalytic device based on the direction of the measured current. Which way did the current flow to reach this conclusion?

1. From TiO_2 to Pt
2. From Pt to TiO_2

Titanium oxide structure

Titanium oxide is a compound of titanium metal and oxygen. Although other oxides of titanium exist, the name 'titanium oxide' or 'titania' usually refers to titanium dioxide, or TiO_2. TiO_2 mainly exists as two polymorphs: rutile and anatase. Rutile is the most stable polymorph (and the first form used as a photocatalyst), while anatase is metastable.



In both polymorphs, the titanium atoms are octahedrally coordinated, i.e. each Ti cation is surrounded by six oxygen anions. Each oxygen is coordinated to three titanium.

Anatase and rutile have slightly different band gaps of 3.2 and 3.0 eV, respectively. The conduction band has Ti 3d character while the valence band has O 2p character (see schematic depiction of anatase band structure on the right). Although rutile has the lower band gap and therefore can absorb lower wavelength light, anatase is the most investigated polymorph for photocatalysis. This is because anatase has been found to have the highest photocatalytic activity, possibly due to higher concentrations of surface hydroxyl groups.

Despite the quite wide band gap, titania exhibits semiconducting behaviour due to the presence of oxygen vacancies, i.e. lattice positions where an oxygen atom is missing. When such a vacancy is formed, there are two "additional" electrons left in the lattice compared to the stoichiometric case (oxygen ion has a formal charge of 2-), that must go somewhere. In titania, all titanium cations normally have a formal 4+ charge state, but they are also able to be reduced to 3+ by accepting an electron from the vacancy. The extra 'defect states' are located close to the bottom of the conduction band, and the electrons there can be easily promoted from the defect states to the conduction band by thermal activation. The electrons can then act as charge carriers in the conduction band. Titania is a 'self-doped' n-type semiconductor for this reason.

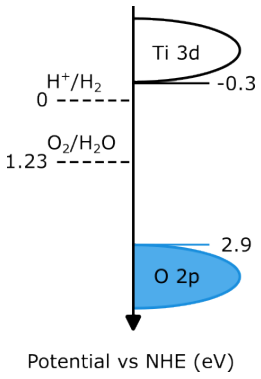


Photo OER

Photocatalytic oxygen reduction reduction takes place on the surface of titanium particles, where water molecules are oxidized by the electron hole (positive charge carrier). After being created by an incident photon, the hole must first separate from the electron that was created at the same time, and migrate to the surface of the photocatalyst. The holes and electrons are separated by the electric field inside the light absorber. Once the hole reaches the surface, it takes part in the OER as an oxidizing agent. The reaction equation for photo OER is:

$$2H_2O + 4h^+ \rightarrow O_2 + 4H^+$$

Note that the hole is a quasiparticle, which is a handy way to indicate that an electron is missing, and often conceptually easier to deal with. In the reaction, actual electrons are transferred from the reactant to the photocatalyst, where

the hole is. Photocatalytic OER is a four electron process just like electrocatalytic OER, and is also a bottleneck for the overall water splitting.

For the hole to have a sufficient oxidizing potential, the valence band (VB) level must be located above the standard redox potential of O_2/H_2O (+1.23 V) vs. NHE. As shown in the previous page, the VB of TiO_2 lies at +2.9 eV, which fulfills this criterion. However, as the conduction band of TiO_2 , where the electron goes after photo excitation, is located at -0.3 eV. This leads to a much higher band gap energy (3.2 eV) than is suitable for visible light absorption, and the light that can be utilized by unmodified anataseis only a small fraction (∼5%) of available solar energy.

Titania band gap engineering

The main shortcomings of regular titania as a photocatalyst are the large band gap that is unsuitable for sunlight utilization and fast electron-hole recombination which leads to lower efficiency. Ever since titania was discovered to be photocatalytically active, much effort has been directed towards modifying its structure and properties to combat these shortcomings.

For more efficient utilization of solar energy, band-gap engineering is essential. Band-gap engineering means controlling or altering the band gap of a material. In the case of titania, the goal would be to make the band gap smaller so that light of longer wavelengths can be absorbed. The band gap of a semiconductor can be modified by introducing dopants, nanosizing, dye sensitizing, and forming junctions.

However, the additional states that are introduced by doping can 'trap' charge carriers in them. When a charge carrier is immobilized like this, it becomes more probable that another carrier of opposite charge combines with it. Increasing trapped states concentration enhances charge carrier pair recombination, which in turn is detrimental to photocatalytic activity. In addition, excessive doping can destabilize the structure of the host photocatalyst.

Further reading Sakar, M., Prakash, R., & Do, T.-O. (2019). Insights into the TiO_2-based photocatalytic systems and their mechanisms. Catalysts, 9(8), 680. https://doi.org/10.3390/catal9080680

Beyond single material photoabsorbers

Inspiration from nature

A single-step photocatalyst light absorber material that drives the HER/OER would have to simultaneously have the following three properties

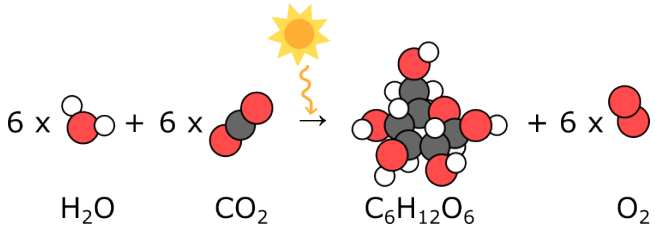
- band gap ¡3 eV
- band-edge potentials straddling HER and OER, including overpotentials
- stable at reaction conditions (aqueous, irradiation)

Many metal oxides, including the prototype TiO_2, have been shown to be photocatalytically active for water splitting, however their band structures usually inevitably lead to a gap too large for visible light absorption. This is because their valance bands are dominated by the 2p orbitals of oxygen, which have a potential of +3V wrt NHE at pH 0. To be able to also drive the cathodic reaction, the conduction band must be more negative than the water reduction potential (0 V wrt NHE at pH 0), therefore the required gap to drive both reactions becomes at least 3 eV.

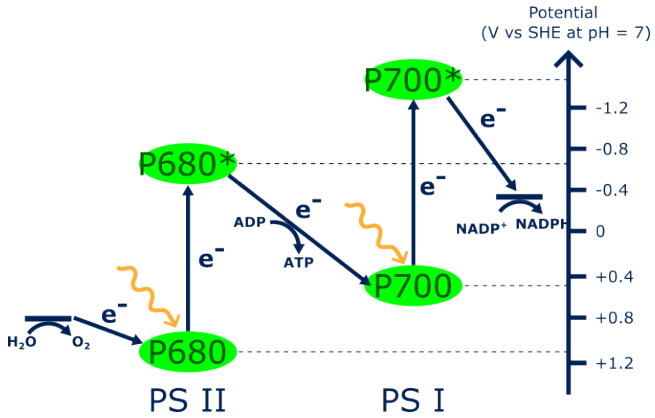
As it is extremely difficult for a single semiconductor material to achieve all three criteria simultaneously, materials research has taken inspiration from how nature drives the photosynthesis process with the so-called Z-scheme.

Photosynthesis and the Z-scheme

Photosynthesis is the process that converts energy from the sun into chemical energy. Water and carbon dioxide are used to form glucose and oxygen:



Photosynthesis is divided into two stages, the light dependent stage and light independent stage. Water is split in the light dependent stage, releasing oxygen gas and using the hydrogen to generate NADPH and ATP. The light dependent reactions take place in the thylakoid membrane, where chlorophylls act as the light absorbers. The water splitting reaction occurs in a two-stage double-excitation process, and uses two photocatalysts instead of one in the so-called 'Z-scheme'.

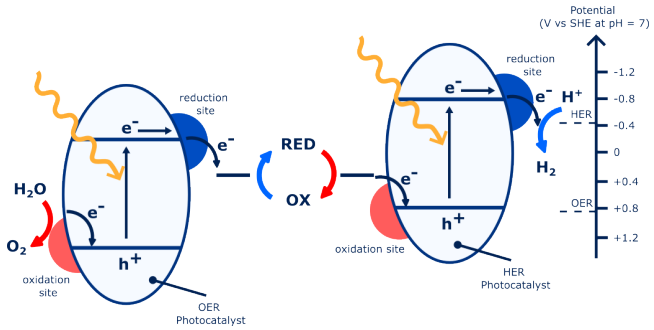


The figure above summarizes the natural Z-scheme. The system consists of two light absorbers, photosystem I (PS I) and photosystem II (PSII) and the electron transport chain. The P680 chlorophyll absorbs photons with wavelength smaller than 680 nm, generating electron-hole pairs and becoming excited (P680*). The generated holes oxidize water and produce oxygen. The excited electrons are transferred from PI to PSII through the complex multistep electron transport chain. The protons created during water oxidation convert ADP to ATP. In PS I, the P700 chlorophyll absorbs ¡700 nm wavelength light. The excited electrons reduce NADP+ to NADPH, while the holes recombine with electrons coming from PS II. This recombination increases electron lifetime in PS I. The photosynthesis system is very efficient, and can operate at quantum yields of over 95% depending on the wavelength of the light.

Semiconductor Z-scheme

Inorganic systems which mimic the natural Z-scheme use two different photocatalysts in place of PS I and PS II and a shuttle redox mediator in the place of the electron transport chain. The water splitting reaction is divided into two separate reactions.

A schematic illustration of Z-scheme water splitting is shown below. The OER photocatalyst absorbs light, generating holes with enough oxidizing potential to oxidize water to oxygen at the photocatalyst surface, possibly on a co-catalyst site. Absorption of light by the HER photocatalyst generates electrons that have a suitable reduction potential for reducing protons into hydrogen. To complete the scheme, electron transfer must take place between the two semiconductors. This is achieved by using a mediator molecule that is present in the reaction solution, and can be oxidized and reduced forming a redox pair (RED and OX in the figure below). The oxidized form (OX) is an electron acceptor, which can be reduced by the photo excited electrons produced by the OER photocatalyst. Once reduced, the species (RED) can be oxidized by the holes from HER photocatalyst, completing the redox cycle.



Because the water splitting process is divided into separate OER and HER steps, neither photocatalyst has to be able to drive both reactions simultaneously. This relaxes the requirement on the placement of the valence and conduction band

edges, i.e. there are many more potentially suitable semiconductors available than in the single absorber case. Additionally, there is a more straightforward way to separate the product gases as they are generated at different locations in the system. Systems based on the Z-scheme further benefit from a maximum solar to fuel conversion efficiency of ∼40%, whereas a single photocatalyst system has a maximum efficiency of ∼30%.

One challenge of Z-schemes is that the reduction/oxidation of the shuttle redox mediators compete with HER and OER. The low selectivity towards the water splitting reaction is the main limitation that prevents the practical application of current Z-scheme systems. To increase efficiency of the systems, those back reactions must be selectively prevented from occurring. The electron transfer mechanisms involved in the Z-scheme are not so well understood (despite the simplicity of the diagrams), and more research is needed to be able to develop more efficient systems.

Materials case studies

Selected novel materials

In this final section of the course, some selected novel materials from recently published studies are introduced. These materials have been employed in solar-to-hydrogen conversion as photocatalysts or photovoltaics. As the studies are recent, many details of how the materials operate are not known.

Three classes of materials are introduced:

- perovskites
- zeolites
- metal-organic frameworks

Perovskites have been introduced already during this course as potential OER electrocatalysts, but they have also shown great promise as light absorbers in photovoltaic cell applications.

Zeolites are porous hydrated aluminosilicate minerals that have diverse 3D crystal structures. In solar hydrogen production, zeolites could function as support/host materials for semiconductor photocatalysts as they exhibit high surface area, nanoscale porous structures, and charge/electron transfer properties that can improve the efficiency of the photocatalytic system.

Finally, metal-organic frameworks (MOFs) are crystalline porous polymers, with a network structure formed from metal cations/clusters ('secondary-building unit') connected to each other by organic ligand molecules ('linkers'). MOFs can be utilized as synthesis precursors for transition metal dichalcogenide,metal phosphides and metal nitrides on carbon frameworks in order to achieve specified particle architectures. MOFs also contain active centers and functional

groups, and some have shown activity towards the photocatalytic HER in particular.

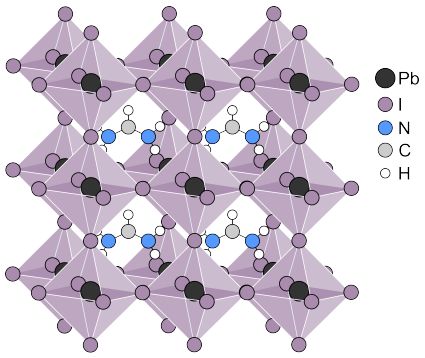
Halide perovskites - $FAPbI_3$

In the Electrocatalysis module perovskites were introduced as promising OER catalyst materials. In that context, 'perovskite' was used to refer to metal oxides with the ABO_3 perovskite structure. However, metal oxide perovskites are not suitable for photovoltaic applications. For photovoltaics, another class of perovskites has emerged: halide perovskites were discovered in the 1890s, and the first reports of halide perovskites as photovoltaic materials date to 2009.[1]

Perovskite solar cells have a layered architecture with the perovskite layer sandwiched between electron transporting layer (ETL) and hole-transporting layer (HTL).[2] In addition the structure includes electrode layers and a glass on top. The power conversion efficiencies (PCE) of single-junction perovskite solar cells have increased massively between 2009 and today, from ∼3% to ∼25%. A 25.2% PCE achieved by a certified perovskite cell corresponds to 80.5% of the theoretical limit.[3] Best single junction Si cells are at 80.9% of the theoretical limit. As such, perovskite cells a promising alternative to silicon based cells, however, not yet commercialized.

Halide perovskites are compounds with the perovskite structure, but with oxygen anions replaced by halogen anions (ABX_3 structure, where X is a halogen). Halogens are a group of elements that include fluorine (F), chlorine (Cl), bromine (Br), iodine (I), astatine (At), and tennessine (Ts). The monovalent A cation can be an organic molecule (in so-called organic-inorganic halide perovskites) such as methylammonium, dimethylammonium or formamidinium, or an inorganic such as a cesium (Cs) cation. The divalent B cation is usually a metal such as lead (Pb) , tin (Sn), or germanium (Ge).

The current PCE record holder halide perovskite is formamidinium lead triiodide ($FAPbI_3$). The material has excellent charge transport properties due to moderate defect densities, strong light absorption and long charge carrier diffusion lengths. $FAPbI_3$ has an optical bandgap of 1.45 eV, which is suitable for absorbing a broad range of the solar spectrum. $FAPbI_3$ has two polymorphs:



α-phase

- α-phase: cubic perovskite
- δ-phase: non-perovskite hexag-

onal

Only the 'black' perovskite phase is photoactive, whereas the 'yellow' hexagonal phase is the thermodynamically stable form at room temperature. The black form can be recovered by heating, but the phase transformation is reversible. This is an issue for material performance as the yellow form has a large optical bandgap and exhibits a chain-like PbI6 octahedron structure which leads to worse charge transport properties.

The photoactive α-phase can be stabilized against the phase transformation by partially replacing the formamidium cation with a methylammonium or cesium cation.4 Such structures are called mixed cation perovskites, and are generally efficient and stable. The PCE record breaking perovskite cell has a perovskite layer with a $FAPbI_3$ and 5 mol% $MAPbBr_3$ composition. The addition of very low (0.8 mol%) amounts of MAPbBr3 to the structure was found to prevent the formation of the inactive δ-phase.

Most well performing halide perovskites are lead based.5 Lead is incredibly toxic to humans and other organisms, and a serious environmental pollutant. It tends to accumulate and is very difficult to remove. This poses a severe obstacle for large-scale commercial adoption of perovskite based solar cells. Increased research effort has been put towards developing efficient and stable lead-free perovskites. To achieve this, the Pb cation could be replaced by cations of elements such as tin (Sn), bismuth (Bi), germanium (Ge), copper (Cu) etc. So far the performance of less toxic halide perovskites comes short of the lead based ones, however careful tuning of the material properties should eventually yield well performing and environmentally benign alternatives.

Sources and further reading

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The NREL chart of confirmed conversion efficiencies of the best performing research cells can be accessed here:
https://www.nrel.gov/pv/cell-efficiency.html

Zeolites

Zeolites are hydrated aluminosilicates, that can occur naturally (around 40 have been identified) or synthesized (more than 150 so far). The general chemical formula of a zeolite is $M(AlO_2)(SiO_2)_x(H_2O)_y$ where M+ is a positive ion, such as H+ or Na+. The letters x and y indicate how many SiO_2 units and water molecules are present in the structure.

The structure of zeolites can be described as crystalline network of tetrahedra, XO_4 units where X is e.g. Si or Al, which form microporous frameworks. Zeolites can exhibit ring, cage, channel and 3D tetrahedral framework structures. The shape and size of the micropores can be tailored to selectively separate molecules of different shapes and sizes. This selectivity can also be exploited in catalysis applications. Besides the shape and size, the acidy of a zeolite is also tunable.

In summary, zeolites have

- high surface area
- dimensionality of micropores
- molecular confinement in pores
- separation of molecules by size, shape etc
- possibility to house tunable catalyst centers

MOFs - What are they?

Metal–organic frameworks (MOFs) consist of metal clusters (secondary-building units, or SBUs) coordinated to organic ligands (linkers) that together can form complex 3D network structures. MOFs are an attractive class of materials due to their ultrahigh porosity (up to 90 % of their volume is empty space) and

high internal surface area (¿6000 m^2/g, that is four times the size of an NHL regulation ice hockey rink). As the identity of both the organic linkers and the inorganic clusters can be varied, MOFs have highly tunable structures, which is one of their main advantages.

The choice of SBUs and linkers is responsible for crystal structure of the resulting MOF, which determines its physical and chemical properties e.g. pore size and surface area. Examples of well-known MOF structures (See Figure 1 from ref [1], figure was removed from document due to copyright).

Using pristine MOFs for hydrogen production and storage is hampered by their poor electrical conductivity and low stability. The efficiency of MOFs can be enhanced by strategies such as addition of dopants, addition of functional groups into the organic ligands, and defect engineering. The high price of MOFs is another disadvantage. Although the SBU clusters and organic linkers themselves are inexpensive, the MOF synthesis yields are typically low, which severely increases the cost.

The main applications explored for MOFs in hydrogen production and storage are:

- In electrocatalysis, as starting materials or catalysts
- For photo HER as photocatalysts, supports, or starting materials for heterojunction structures
- As storage medium for hydrogen

Further Reading:

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