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D2.1 Assessment of critical materials and components in FCH technologies

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## Executive Summary

Fuel cell and hydrogen (FCH) technologies are expected to add to decarbonisation of energy and transport sector. One thing among others that prevents FCH commercialization is **recycling and dismantling stage**. There are no lists of critical materials to be treated with special attention, no established pathways for recycling procedures, incomplete legislation and no guidelines.

In order to deliver **reference documentation** and studies about existing and new recycling and dismantling technologies and strategies applied to FCH technologies, the first step is to **identify, describe and classify materials** used in FCH technology considered in the project.

The focus of the current deliverable is set to pure **core FCH technologies** i.e. stack in all considered cases. Balance of plant (BoP) components will be included later in the study, but herein the main goal is assessment of critical materials that are mainly present in core technologies.

To identify materials core technology is broken down to components for each considered technology (PEMFCs, SOFCs, alkaline - AWE and PEM water electrolyzers - PEMWE). Materials in components are considered regarding their **function, location, environmental aspect, costs, and criticality/scarcity** and **used existing recycling technologies**. **Scarcity or criticality of materials** is defined by EU criticality method where all critical materials are classified as combination of their economic importance and supply risk.

The **result** of task 2.1 Assessment of critical materials and components in FCH technologies is **the list of tables with relevant materials in considered core FCH technologies**. List of materials with all accessible data will serve as an input for other tasks in WP2 (Regulatory analysis, critical materials and components identification and mapping of recycling technologies) and further work in other steps of the project.

## Contents

Document Change Control .....	3
Executive Summary.....	4
Contents .....	5
List of Figures.....	6
List of Tables .....	7
Abbreviations.....	8
1. Introduction .....	9
1.1 Study background .....	9
1.2 Goals and targets.....	9
1.3 Methodology in the study .....	9
1.4 Limitations of the study.....	9
2. Overview of the FCH technologies under consideration .....	11
2.1 Solid oxide fuel cells.....	14
2.2 Polymer electrolyte membrane fuel cells.....	16
2.3 Polymer electrolyte membrane water electrolyser.....	17
2.4 Alkaline water electrolyzers.....	19
3. Assessment of materials .....	21
3.1 Hazardous materials waste.....	21
3.2 Scarce or critical materials .....	21
3.2.1 EU Criticality methodology.....	23
3.3 Material value.....	26
4. Materials list and data .....	27
5. Conclusions.....	30
References .....	31

## List of Figures

Figure 1 – Schematic representation of a FC system and its components [5].....	14
Figure 2 – Operational principle of the SOFC [7].....	15
Figure 3 – Operational principle of the PEMFC [11] .....	17
Figure 4 – Basic principle of the PEMEC [12].....	19
Figure 5 – Operational principle of the AWE system [12] .....	19
Figure 6 – The three types of chemical elements [18].....	22
Figure 7 – Presenting the element of hope, the frugal elements and the critical elements [18]....	22
Figure 8 – General scheme of the criticality concept projected into two dimensions [20].....	23
Figure 9 – Visualization of the compound indicator for economic importance [20].....	24
Figure 10 Visualisation of the compound indicator for supply risk as defined by Critical Raw Materials [20].....	24
Figure 11 Scheme of EU criticality methodology [20] .....	25
Figure 12 Updated criticality assessments for the EU for 2013 [20].....	26
Figure 13 EU-20 Critical raw materials [20].....	26

## List of Tables

Table 1 – Hydrogen production methods by primary energy and fuel source [2] .....	11
Table 2 – Typical electrolyser specifications for Alkaline, PEM and SOE [2] .....	11
Table 3 – Typical specifications of most common used fuel cells [4].....	12
Table 4 – List of common material assessment for SOFC [17]–[21] .....	27
Table 5 – List of common material assessment for PEMFC [17]–[21].....	28
Table 6 – List of common material assessment for PEMWE [17]–[21].....	28
Table 7 – List of common material assessment for AWE [17]–[21] .....	29

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## Abbreviations

AWE	Alkaline Water Electrolyser
BoP	Balance of Plant
CAPEX	Capital Expenditures
EOl	End of Life
EPDM	Ethylene Propylene Diene Monomer
FC	Fuel Cell
FCH	Fuel Cell and Hydrogen
FKM	Fluoroelastomer
GDC	Gadolinium Doped Ceria
GDL	Gas Diffusion Layer
HER	Hydrogen Evolution Reaction
LDC	Lanthanum Doped Ceria
LCA	Life Cycle Analysis
LCC	Life Cycle Costs
LCM	Lanthanum Calcium Manganite
LSCF	Lanthanum Strontium Cobalt Ferrite
LSF	Lanthanum Strontium Ferrite
LSGM	Strontium Magnesium doped Lanthanum Gallate
LSM	Lanthanum Strontium Manganite
LSMF	Lanthanum Strontium Manganese Ferrite
MEA	Membrane Electrode Assembly
NBR	Nitrile Butadiene Rubber
OER	Oxygen Evolution Reaction
OPEX	Operational Costs
PEM	Polymer Electrolyte Membrane
PEMEC	Polymer Electrolyte Membrane Electrolyser Cell
PEMFC	Polymer Electrolyte Membrane Fuel Cell
PEMWE	Polymer Electrolyte Membrane Water Electrolyser
PFSA	Perfluorosulphonic Acid
PGM	Platinum Group Metals
PSM	Praseodymium Strontium Manganite
PSMF	Praseodymium Strontium Manganese Ferrite
PSSA	Polystyrene Sulfonic Acid
PTFE	Polytetrafluoroethylene
REE	Rare Earth Elements
SDC	Samarium Doped Ceria
SDZ	Scandium Doped Zirconia
SETIS	Strategic Energy Technologies Information System
SOFC	Solid Oxide Fuel Cell
s-PEEK	Sulfonated Polyether Ether Ketone
YSZ	Yttrium Stabilized Zirconia



## 1. Introduction

### 1.1 Study background

High deployment of FCH technologies is expected in the near future in the EU to decarbonize energy and transport sectors. However, commercialization of FCH technologies (mainly PEM and alkaline electrolyzers as well as PEM and solid oxide fuel cells) is not prepared for full deployment mainly concerning recycling and dismantling stage. The main goal of the project is to deliver the reference documentation and studies about existing and new recycling and dismantling technologies and strategies applied to FCH technologies. One of the key steps in the beginning is the identification of critical materials and components present in FCH technologies, which limit commercialization due to their scarcity or high cost. That leads to increasing of capital expenditures (CAPEX) and operating expenses (OPEX) that represent two basic categories of business expenses in the case of need for replacement considering SETIS materials roadmap for FCH technologies [1]. As the basis to identify new replacement materials, establish recycling and new dismantling processes, logistics to reduce costs and to propose guidelines of the product redesign, it is necessary to conduct a detailed assessment of critical materials and components in FCH products.

In the study all considered FCH technologies are briefly described. Main parts of FCH technologies are identified according to the project definition and the scope of the study. Main focus is given to core FCH technologies. To identify critical materials appropriate assessment of materials was done using EU critically method. Materials are listed in tables, where their location, classification, value, criticality and current dismantling technology are given. In the field of current dismantling technology data are linked to the document from task 2.2 of WP2 Mapping of existing recycling technologies and matching with FCH technologies.

### 1.2 Goals and targets

For each FCH technology considered in the project (PEMFCs, SOFCs, alkaline - AWE and PEM water electrolyzers - PEMWE), a list of most relevant materials are listed. Specific objective was deliver a reference list of critical materials and components in FCH technologies regarding EU criticality method.

The main goal is to provide materials reference tables for each technology considered with specific information: the component, where critical material is located, the name of the material, classification of material or contribution to LCA, value of material or contribution to LCC, current recycling and dismantling procedures.

One of the additional objectives is to provide input data for the task 2.2 of WP2 Mapping of existing recycling technologies and matching with FCH technologies and WP4 Life cycle Assessment.

### 1.3 Methodology in the study

The main approach in the study was the use of data, knowledge and methodology from current state of the art available for FCH technology. The main source of the data and knowledge for the study was partly established by using the methodology developed in the frame of EU funded projects, EU Commission expert groups, relevant scientific and expert papers.

### 1.4 Limitations of the study

The focus of the study is more to core technologies of FCH technology considered in the project (PEMFCs, SOFCs, alkaline and PEM electrolyzers). Materials from BoP will be added later in the study

since BoP components of FCH technologies are regarded as conventional technologies used commonly also outside FCH technologies. Most critical materials are present in core FC technologies, but materials from BoP should not be neglected since there is quite substantial mass of materials used for all BoP components and auxiliary systems.

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## 2. Overview of the FCH technologies under consideration

The main element in FCH technologies considered in the project is hydrogen. As an abundant element, hydrogen can be found in many substances in nature (i.e. fresh and sea water, biomass, hydrogen sulphide, and fossil fuels). In order to produce hydrogen with zero or low environmental impact ("green" hydrogen), all CO<sub>2</sub> and other pollutants must be processed (i.e. separated or sequestered) when hydrogen is extracted from fossil fuels. Thermal, electrical, photonic, and biochemical energy are the primary energy sources to generate hydrogen. Table 1 shows an overview and brief description of hydrogen production methods with their primary energy and material sources [2]. In 2008 almost the complete hydrogen production was based on fossil fuels. The breakdown of the total production is as follows: 49 % natural gas, 29 % liquid hydrocarbons, 18 % coal and 4 % electrolysis and others. The main production technologies within hydrogen production systems are [3]:

- Steam reforming
- Catalytic reforming (refinery)
- Gasification
- Partial oxidation
- Electrolysis.

Table 1 – Hydrogen production methods by primary energy and fuel source [2]

Hydrogen production methods				
Method	Source		Brief description	
	Primary energy	Fuel		
Electrolysis	Electrical	Water	Direct current is used to split water into O <sub>2</sub> and H <sub>2</sub> (electrochemical reaction)	
Plasma arc decomposition		Fossil fuels	Cleaned natural gas is passed through plasma arc to generate H <sub>2</sub> and carbon soot	
Thermolysis	Thermal	Water	Thermal decomposition of water (steam) at temperatures above 2500 K	
Water splitting		Water	Cycling chemical reactions (water splitting into H <sub>2</sub> )	
Biomass conversion		Biomass		Thermocatalytic reaction
Gasification				Conversion of the biomass into syngas
Reforming				Conversion of biofuels into H <sub>2</sub>
Photo catalysis	Photonic	Water	Water is split into H <sub>2</sub> by using the electron hole pair generated by the photocatalyst	
Dark fermentation	Biochemical	Biomass	Biological systems are used to generate H <sub>2</sub> in the absence of light	
High temperature electrolysis	Electrical + Thermal	Water	Electrical and thermal energy are used together to drive water splitting at HT	
Coal gasification		Coal	Conversion of coal into syngas	
Fossil fuel reforming		Fossil fuels	Fossil fuels are converted to H <sub>2</sub> and CO <sub>2</sub>	
Bio photolysis	Photonic+Biochemical	Biomass + Water	Biological systems are used to generate H <sub>2</sub>	
Photo fermentation			Fermentation process activated by exposure to light	
Artificial photosynthesis			Chemically engineered systems mimic photosynthesis to generate H <sub>2</sub>	

Currently the most basic industrial process for almost pure hydrogen production is water electrolysis, and its significance is expected to increase in the future. Water electrolysis is based on the movement of electrons which are supported by an external circuit. Electrolyser based on alkaline, polymer electrolyte membrane (PEM), and solid oxide electrolysis (SOE) are the key electrochemical hydrogen production technologies and are summarized in Table 2. Technology considered for hydrogen production and further analysis of the critical materials in this project are PEM and alkaline water electrolyzers.

Table 2 – Typical electrolyser specifications for Alkaline, PEM and SOE [2]

Hydrogen production methods			
	Alkaline	PEM	SOE
Technology maturity	State of the art	Demonstration	R&D
Operating cell temperature / °C	60 - 80	50 - 80	900 - 1000
Operating cell pressure / bar	< 30	< 30	< 30
Current density / A/cm <sup>2</sup>	0.2 - 0.4	0.6 - 2.0	0.3 - 1.0
Cell voltage / V	1.8 - 2.4	1.8 - 2.2	0.95 - 1.3
Power density / W/cm <sup>2</sup>	to 1.0	Up to 4.4	/
Efficiency / %	62 - 82	67 - 82	81 - 86
Specific energy consumption / kWh/Nm <sup>3</sup>	4.5 - 7.0	4.5 - 7.5	2.5 - 3.5
Hydrogen production / Nm <sup>3</sup> /h	<760	<30	/
Stack lifetime / hr	<90,000	<20,000	<40,000
System lifetime, / years	20 - 30	10 - 20	/
Hydrogen purity / %	>99.8	99.999	/
Cold start up time / min	15	<15	>60

Fuel cells (FCs) are electrochemical devices that directly convert chemical energy, from a reaction between a fuel and an oxidant, into electrical energy. They are considered as a valuable alternative way of electrical energy production due to two main aspects: the low level of emissions during the process and the high conversion efficiencies. Other important features that make FCs attractive are: modular structure that makes them suitable for different applications, flexibility (i.e. the ability to work with different type of fuels) and silent operation. The basic elements of a typical fuel cell consist of an electrolyte in intimate contact with a porous anode (negative electrode) and a porous cathode (positive electrode). The fuel and oxidant gases flow along the surface of the anode and cathode, respectively, and they react electrochemically in the three-phase-boundary (TPB) region established at the gas-electrolyte-electrode interface. A fuel cell can theoretically produce electrical energy for as long as fuel and oxidant are fed to the porous electrodes. Different fuels can be used, such as hydrogen, ethanol, methanol, or gaseous fossil fuels like natural gas. Solid or liquid fossil fuels need to be gasified first before they can be used as fuel. Oxygen or air can be used as oxidant [4].

Several types of fuel cells have been developed that have the potential to widely reach the consumer markets within a few years. The primary challenges are cost, durability and low level of emissions, which need to be solved by materials selection and design engineering. Although the operating principle is the same for all types of cells, materials used and the operating conditions vary considerably. The different types of FCs can be classified into several categories depending on the combination of type of fuel and oxidant, the type of electrolyte and the temperature of operation. Most commonly classification is made according to the type of electrolyte used. The following types of FCs are commonly known, all named after employed electrolyte material:

- The phosphoric acid fuel cell (PAFC),
- The molten carbonate fuel cell (MCFC),
- The solid oxide fuel cell (SOFC),
- The polymer electrolyte membrane fuel cell (PEMFC).

Each type of FCs has certain characteristics, some of which are listed in Table 3. FCs are complex systems, with a wide range of functions, depending on the specific applications (e.g., stationary, transport, portable).

Thus, any approach to the environmental assessment of FCs needs to take into consideration this variability and to be flexible enough to allow for assessment of the technology at different levels.

**Table 3 – Typical specifications of most common used fuel cells [4]**

	<b>PAFC</b>	<b>MCFC</b>	<b>SOFC</b>	<b>PEMFC</b>
<b>Electrolyte</b>	Phosphoric Acid	Molten Carbonate Salt	Ceramic	Polymer
<b>Typical operating temperature / °C</b>	190	650	1000	80
<b>Fuel</b>	Hydrogen (H <sub>2</sub> ) Reformate	H <sub>2</sub> / CO Reformate	H <sub>2</sub> / CO / CH <sub>4</sub> Reformate	Hydrogen (H <sub>2</sub> ) Reformate
<b>Reforming</b>	External	External / Internal	External / Internal	External
<b>Oxidant</b>	O <sub>2</sub> / Air	CO <sub>2</sub> / O <sub>2</sub> / Air	O <sub>2</sub> / Air	O <sub>2</sub> / Air
<b>Electrical efficiency (HHV) / %</b>	40 - 50	50 - 60	45 - 55	40 - 50

Fuel cells considered in the project are PEMFC and SOFC [5]. For the purpose of the LCA studies and identification of the critical materials of PEMFC and SOFC, two modules or boundary conditions have been identified:

- FC stack,
- FC system.

The FC stack consists of individual cells that are combined in a modular format by electrically connecting the cells to form units with the desired output capacity.

The FC main components are:

- Contact layer,
- Cathode gas distribution layer,
- Catalyst layer,
- Electrolyte.

The FC stack main components are:

- Interconnects (also called bipolar or flow-field plates).
- Sealants,
- Current collectors,
- A number of individual cells,

The FC System as a whole comprises of the stack together with the Balance of Plant (BoP) components (all other blocks alongside the FC stack in Figure 1). The FC stack is terminated by the manifold plate which connects the stack to the BoP. The BoP supplies fuel and air, ensures constant stack temperatures, manages required gas/fluid recycling, and provides infrastructure for start-up and shut-down as well as ancillary systems for total system control and power conditioning. The precise arrangement of the BoP depends largely on the FC type, the fuel choice, and the end use of the system. Specific operating conditions and requirements of individual FC and FC stack designs also determine the characteristics of the BoP. BoP can be classified as the equipment necessary for the operation of the FC (essential BoP, ancillary BoP). The use of the FC system for a special application is not considered (External BoP).

The three elements of the BoP are:

- a) Essential BoP supports all system operating modes such as cold start, cool-down to ambient temperature, standby, power-up from standby, cool-down to standby, load following and emergency shut-down:
  - Air delivery system (blower, compressor, metering, pipe work, humidification, pre- heat),
  - Fuel delivery system (fuel pump/blower, metering, fuel cleaning, fuel processing, humidification, cooling/pre-heat),
  - Thermal management system – air or water cooled (heat exchangers, after/start-up burner, steam generator),
  - Recycle streams (water, fuel, CO<sub>2</sub>, liquid electrolyte).
- b) Ancillary BoP supports power management and system control:
  - Power conditioning (DC-DC, DC-AC inversion),
  - Control system and instrumentation (sensor, hardware, software).
- c) External BoP is application specific and maximizes energy efficiency:
  - Housing/pressure vessels,
  - Waste heat recovery.

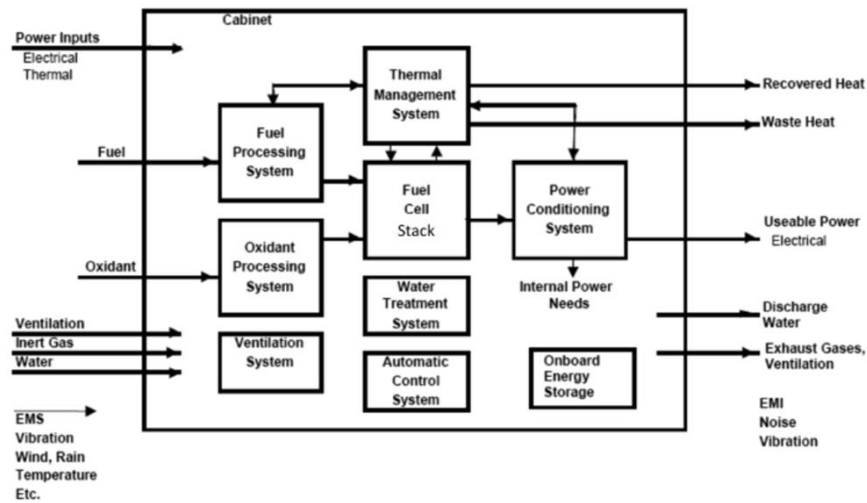


Figure 1 – Schematic representation of a FC system and its components [5]

## 2.1 Solid oxide fuel cells

Solid oxide fuel cells (SOFCs) represent environmentally clean and versatile means of converting chemical energy to electrical energy while providing many advantages over traditional energy conversion systems due to high efficiency, reliability, modularity, fuel adaptability, and very low levels of  $\text{NO}_x$  and  $\text{SO}_x$  emissions. Furthermore, because of their high temperature of operation (750 - 1000 °C), natural gas can be reformed within the cell stack eliminating the need of an expensive, external reformer. The most recent efforts are focused in the development of a so called intermediate temperature SOFC which operates at temperatures between 600 - 800 °C.

The operating principle of the solid oxide fuel cell is illustrated in Figure 2. A SOFC essentially consists of two porous electrodes separated by a dense oxygen ion-conducting electrolyte. Oxidant is reduced at the cathode side and fuel is oxidized at the anode. The difference in oxygen activity of the two gases at the electrodes provides a driving force for motion of the oxide ions in the electrolyte. Oxide ions formed by dissociation of oxygen at the cathode under electron consumption migrate through the electrolyte to the anode where they react with hydrogen to form water and release electrons. The SOFCs must be connected in series in a stack to reach higher voltages necessary for most practical purposes. A stack can in principle comprise any number of cells depending on the desired power, and a fuel cell plant can be designed in modules of stacks in series and parallel connections [6].

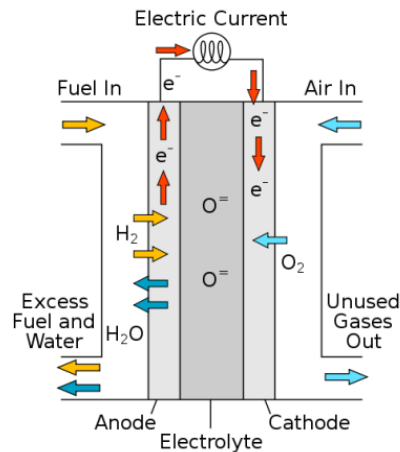


Figure 2 – Operational principle of the SOFC [7]

The electrolyte has to be gas impermeable to avoid direct mixing and combustion of the gases. Oxide materials with fluorite crystal structure such as yttrium stabilized zirconia (YSZ), scandium doped zirconia (SDZ), ceria doped with rare earth elements (REE) e.g. gadolinium (GDC), lanthanum (LDC) or samarium (SDC), and rare earth doped bismuth oxide have been widely investigated as electrolytes for fuel cells. Of these materials, YSZ has been most successfully employed as the electrolyte material for SOFCs exhibiting predominantly ionic conductivity over a wide range of oxygen partial pressures, at operating temperatures of 800 - 1000 °C. Strontium and magnesium doped lanthanum gallate (LSGM) was discovered more recently and has an ionic conductivity similar to that of doped ceria and it has higher oxygen-ion conductivity than conventional YSZ between 600 - 800 °C and negligible electronic conductivity. LSGM is currently considered as one of the most promising electrolyte materials for intermediate temperature SOFCs [8].

The anode must be stable in the reducing environment of the fuel, should be electronically conducting and must have sufficient porosity to allow the transport of the products of fuel oxidation away from the electrolyte/fuel electrode interface. SOFC anodes are fabricated from composite powder mixtures of electrolyte material (i.e. YSZ, GDC or SDC) and nickel oxide (the nickel oxide subsequently will be reduced to nickel metal prior to operation) [9]. Nickel is a well-known SOFC anode material, and acts as the fuel side electro catalyst and current collector. Nickel-based cermet with the electrolyte YSZ is the most widely used anode at present. Ni has also been chosen as an anodic material due to its high electrical conductivity and stability under chemically reducing and part reducing conditions. The presence of nickel can be used with advantage as an internal reforming catalyst, and provides a mechanism for internal fuel reforming directly on the anode.

The cathode is the SOFC electrode where electrochemical reduction of oxygen occurs. SOFC Cathodes have to show high electronic and ionic conductivity, sufficient thermal and chemical stability at high temperature in air as well as good compatibility with the electrolyte. It should have sufficient porosity to facilitate transport of molecular oxygen from the gas phase to the air electrode/electrolyte interface. To satisfy the requirements of cathode material, perovskite structured lanthanum strontium manganite (LSM) and lanthanum calcium manganite (LCM) are most commonly used as they offer excellent thermal expansion matches with zirconia electrolytes and provide good performance at operating temperatures above 800 °C. For intermediate temperature SOFCs, alternative perovskite-structured ceramic electrode materials can be used. These include lanthanum strontium ferrite (LSF), lanthanum strontium cobalt ferrite



(LSCF), lanthanum strontium manganese ferrite (LSMF), praseodymium strontium manganite (PSM), and praseodymium strontium manganese ferrite (PSMF).

Interconnection serves as the electric contact to the air electrode and also protects the air electrode material from the reducing environment of the fuel on the fuel electrode side. The requirements of the interconnection are most severe of all cell components and include the following:

- nearly 100% electronic conductivity,
- stability in both oxidizing and reducing atmospheres at the cell operating temperature since it is exposed to air (or oxygen) on one side and fuel on the other side,
- low permeability for oxygen and hydrogen to minimize direct combination of oxidant and fuel during cell operation
- a thermal expansion close to that of the air electrode and electrolyte,
- non-reactivity with the air electrode and the electric contact material (e.g. nickel).

To satisfy these requirements, doped lanthanum chromite is used as the interconnection material. The conductivity is enhanced as lower valence ions (e.g., Ca, Mg, Sr, etc.) are substituted on either the La<sup>3+</sup> or the Cr<sup>3+</sup> sites.

The sealing development for SOFC can be classified into rigid and compressive seals [10]. Rigid seals require small load when compared with compressive seals during operation and have an excellent hermetic property. The typical of rigid seals are glasses, glass ceramics and braze sealants. Compressive seals require a load application to seal during operation. The most common materials of compressive seals are both non-metallic and metallic. Non-metallic seals are typically made from minerals (mica, vermiculite, etc.) or are ceramic based while metallic are made from noble metals such as silver, gold and platinum.

## 2.2 Polymer electrolyte membrane fuel cells

The primary components of the PEMFC are an ion conducting electrolyte, a cathode, and an anode, as shown schematically in Figure 3. Together, these three are often referred to as the membrane electrode assembly (MEA). Hydrogen fuel is processed at the anode where electrons are separated from protons. The protons pass through the membrane to the cathode side of the cell while the electrons travel in an external circuit, generating the electrical output of the cell. On the cathode side the protons and electrons are combined with oxygen to produce water, which is expelled as the only waste product; oxygen can be provided in a purified form, or extracted at the electrode directly from the air. The electrolyte serves as a barrier to gas diffusion, but will let protons migrate across it.

Accordingly, the half reactions occurring on the anode (1) and cathode (2), respectively, can be written as:



The overall chemical reaction of the PEMFC can be written as:





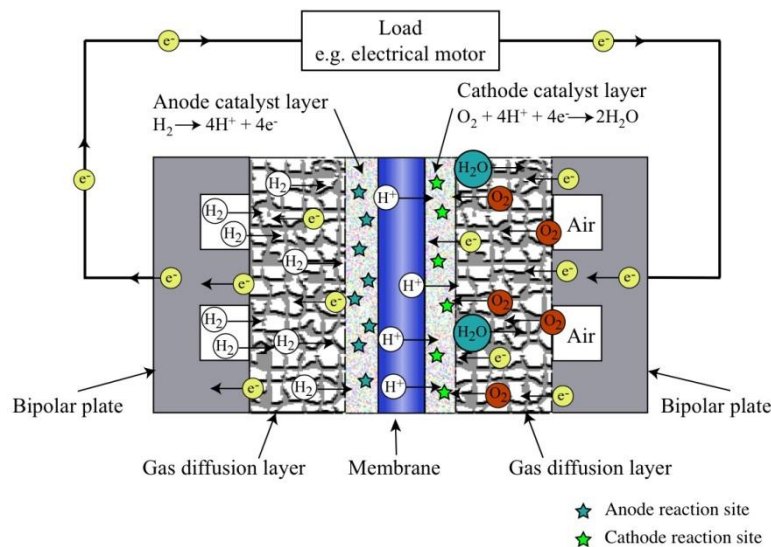


Figure 3 – Operational principle of the PEMFC [11]

The gases are supplied or extracted via distribution channels on the flow-field plates, also known as bipolar plates or interconnects, which are positioned on either side of the MEA. Their role is also to serve as current collectors, and hence, must be highly electrically conductive. The bipolar plates are normally made from graphite composites or stainless steel materials.

The electrochemical reactions take place on the electrodes which are made from porous gas diffusion layer (GDL) normally from carbon cloth or carbon paper. The catalytic layer is applied onto the GDL and consists from a carbon support material on which a platinum or Pt-alloy catalyst is embedded.

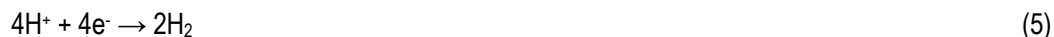
Materials used for electrolytic membranes are normally sulfonated polymers which are capable of holding sufficient water content and, consequently, allow high proton conductivity. Most commonly perfluorosulphonic acid (PFSA) is used (e.g. Nafion®), and recently as a lower cost alternative also sulfonated polyether ether ketone (s-PEEK) and polystyrene sulfonic acid (PSSA).

Generally PEMFCs operate at atmospheric pressure and temperatures between 60 - 80 °C. However, a higher pressure up to 3 bar and the use of various composite membrane materials allows the water-based PEMFCs to operate at temperatures up to 130 °C. A variant which operates at elevated temperatures is known as the high temperature PEMFC (HT PEMFC). By changing the polymer electrolyte from being water-based to a mineral acid-based system, using phosphoric acid ( $H_3PO_4$ ), the HT PEMFCs can operate at temperatures of up to 200 °C.

### 2.3 Polymer electrolyte membrane water electrolyser

PEMWE is a process just reverse of a PEMFC process. Water is split into oxygen, protons and electrons on the anode electrode by applying a DC voltage higher than a thermo-neutral voltage of 1.482 V. Protons pass through the PEM and on the cathode electrode combine with electrons to form hydrogen. Here, the passage of protons through the membrane is also accompanied by water transport (electroosmotic drag). The reactions occurring on the anode (4) and cathode (5), respectively, can be written as:





And the overall chemical reaction of the PEMWE can be written as:



PEMWE can operate at much higher current densities than the AWE. This reduces the operational costs and potentially the overall cost of electrolysis. The low gas crossover rate of the PEM (yielding hydrogen with high purity), allows for the PEMWE to work almost under a full nominal power density range (10 - 100%). This is due to the fact that the proton transport across the membrane responds quickly to the power input, not delayed by inertia as in liquid electrolytes. As discussed above, in AWE operating at low load the rate of hydrogen and oxygen production reduces while the hydrogen permeability through the diaphragm remains constant, yielding a larger concentration of hydrogen on the anode (oxygen) side thus creating hazardous and less efficient conditions.

Nevertheless, problems related to higher operational pressures, such as cross-permeation phenomenon, are also present in PEMWE. Also, the corrosive acidic regime provided by the PEM requires the use of distinct materials. These materials must not only resist the harsh corrosive low pH condition (pH ~ 2), but also sustain the high applied over voltage, especially at high current densities. Corrosion resistance applies not only for the catalysts used, but also current collectors and separator plates.

The PEM electrolyser cell (PEMEC) is similar to the PEMFC and consists of typical components such as the PEM and porous electrodes, flow fields, current collectors and separator plates, end plates, manifolds. However, certain components made from carbon materials, such as catalyst support, porous electrode structures (carbon fibre paper or carbon cloth) and bi-polar plates, which are commonly used in the PEMFC, cannot be used on the oxygen (anode) side of the PEMWE. The high overvoltage imposed at the anode side and high concentration of oxygen, would overtime promote the oxidation of carbon or graphite materials to CO<sub>2</sub>. PEMWE therefore primarily use metallic components (porous structures, flow fields and separator plates) made from Ti, Ti-alloys or coated stainless steel.

Ruthenium and Iridium show the best catalytic properties for the oxygen evolution reaction (OER), but Ir is preferred due to greater corrosion resistance. The cathode catalyst for the hydrogen evolution reaction (HER) is typically platinum or platinum alloys.

In PEMWE, thin PFSA (Nafion®) membranes are typically used as a solid electrolyte. Similar than in PEMFC the s-PEEK polymer is considered to be a cheaper substitute because it is an easy membrane forming material with a relatively high strength. s-PEEK also has a fairly high proton conductivity but the membranes tend to swell excessively or even dissolve at elevated temperature.

Conventional PEMECs normally run under current densities ranging from 0.6 - 2 A cm<sup>-2</sup> and voltages between 1.8 - 2.4 V. Normal operating temperatures vary between 50 - 80 °C, and the pressures of up to 30 bar are used. Similarly to PEMFCs, individual PEMECs may be stacked into a stack, in order to get the desired output at a reasonable stack voltage.

Varieties of gasket materials are used in PEMWEs (e.g. fluoroelastomer (FKM), ethylene propylene diene monomer (EPDM), polytetrafluoroethylene (PTFE), silicon, etc.)

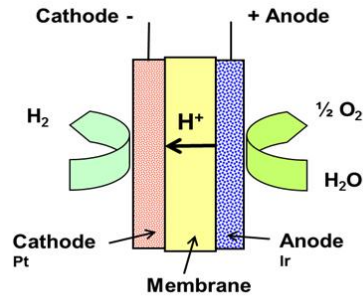


Figure 4 – Basic principle of the PEMEC [12]

## 2.4 Alkaline water electrolyzers

Basic alkaline water electrolysis (AWE) unit consists of an anode, a cathode, power supply, and an alkaline electrolyte, as illustrated in Figure 5. A direct current (DC) is applied to maintain the electricity balance and electrons flow from the negative terminal of the DC source to the cathode at which the electrons are consumed by hydrogen ions (protons) to form hydrogen. In keeping the electrical charge (and valence) in balance, hydroxide ions (anions) transfer through the electrolyte solution to anode, at which the hydroxide ions give away electrons and these electrons return to the positive terminal of the DC source. During the process of water electrolysis, hydrogen ions move towards cathode, and hydroxide ions, move towards the anode. The half reactions occurring on the cathode (7) and anode (8), respectively, can be written as (see Figure 5):



The overall chemical reaction of the AWE can be written as:

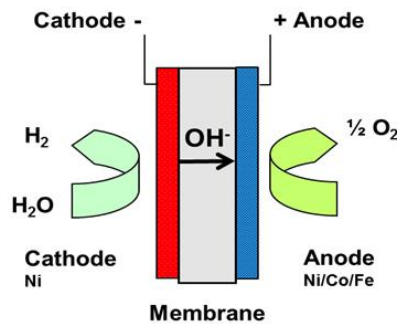


Figure 5 – Operational principle of the AWE system [12]

In order to enhance the conductivity of the solution, electrolytes which generally consist of ions with high mobility are applied in the electrolyser. Potassium hydroxide is preferred over sodium hydroxide due to higher conductivity of electrolyte solution. Most commonly 25–30% alkaline solutions are adopted in commercial electrolyser.

Nickel or Ni-alloys (i.e. Raney Ni) are the most popular electrode material due to dedicated balance amongst the desires for the corrosion resistance, high conductivity, high catalytic effect on

electrochemical reactions, and relatively low cost. To some extent, the electrode itself is a catalyst by affecting the activation energy of the electrochemical reaction. However, doping or coating is often used to obtain a more stable and active electrode. To improve the electro-catalytic activity of the OER Ni-alloys with Co and Li are used or even noble metal oxides ( $\text{RuO}_2$ ,  $\text{IrO}_2$ ). For the HER the platinum group metals (PGM) show the highest activity. Due to synergism in the catalytic behaviour also alloys with non-noble metals such as Mo, Co, and Fe are used for HER.

Gas receivers collect hydrogen and oxygen, which form on and depart from the cathode and the anode, respectively. An ion conductive diaphragm (membrane) prevents the gases from mixing while the ions are still allowed to move through the electrolyte solution. The first commercialized membrane was asbestos which was popular in the early stage. Due to poor corrosion resistance in strong alkaline environment at elevated temperatures and seriously adverse health effect, asbestos was gradually replaced by other materials, mainly by polymers such as PFSA, arylene ethers (e.g. PEEK) and PTFE. Typical materials used for gaskets include graphite, nitrile butadiene rubber (NBR), aramid fibres, and also PTFE.

Conventional AWEs normally run under current densities ranging from  $0.1 - 0.4 \text{ A cm}^{-2}$  and voltages between 1.8 - 2.2 V. Depending on the end use of the hydrogen, the pressure at which the electrolyser operates could be higher than atmospheric pressure. The elevated pressure cells operating at 3.5 MPa reduce the bubble sizes, minimizing ohmic loss due to bubbles, but increase the proportions of dissolved gas and require a more durable diaphragm. Normal operating temperatures vary between 70 - 90 °C, however, the higher the operating temperature, the more stringent demands for the structural integrity of diaphragm and gaskets materials are required.

### 3. Assessment of materials

In this section three criteria are defined which are later used for material classification. These criteria include hazardousness, scarcity or criticality, and price or value of the materials.

#### 3.1 Hazardous materials waste

Simply defined, a hazardous waste is a waste with properties that make it dangerous or capable of having a harmful effect on human health or the environment. Hazardous waste is generated from many sources, ranging from industrial manufacturing process wastes to batteries and may come in many forms, including liquids, solids gases, and sludges.

In this project, the analysis of the most commonly used materials in FCH technologies, different sources to determine material classification were used: The Priority List of Hazardous Substances [13]–[15] and report from Robert A. Goyer and Thomas W. Clarkson about toxic effects of metals [16].

#### 3.2 Scarce or critical materials

Recent disruptions in the industrial supply of certain exotic technology metals have focused new attention on a well-known sustainability issue: resource scarcity. Concern has been voiced over the limits in the future availability of special raw materials, such as REE, PGM and other exotic elements. Those elements are referred to as 'critical' with regard to their high supply insecurity and their economic and technological importance. Critical elements not only enable the design of high-tech products, but are also key constituents of clean or resource-efficient technologies. The current scarcity with regard to technology metals gives new impetus to the discussion about resource-preserving innovation strategies [17].

Resources or materials are considered 'scarce' or 'critical' when there is a high demand from industry combined with a risk to their supply. A more straightforward manner to plot the different elements is shown in Figure 6, in which the probability of a supply disturbance is plotted against the period of availability. In this graph we can distinguish three groups:

- Critical elements
- Frugal elements
- Elements of hope

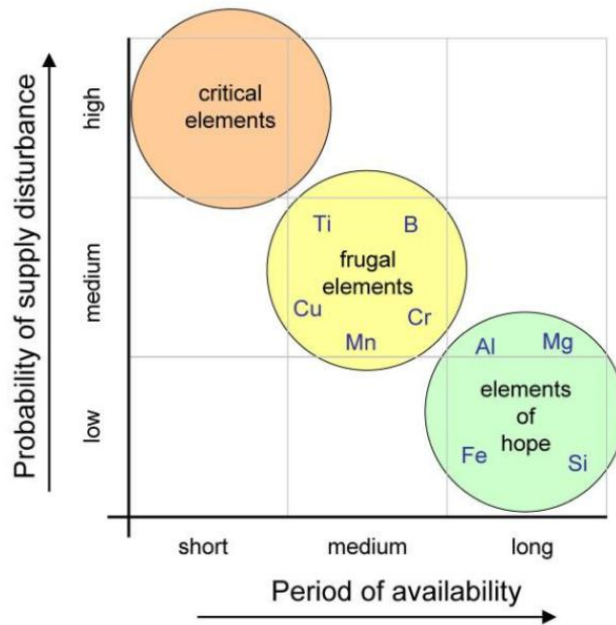


Figure 6 – The three types of chemical elements [18]

Some metal minerals appear to be more critical than indicated by their ratio of reserves against primary production. The study by Diederer [19] showed that several metal minerals suffers from relatively low absolute amounts of reserves and associated low extraction rates, effectively making them non-viable large-scale substitutes for other metals which will be in short supply.

Other metal minerals, like for example manganese, have no acceptable substitutes for their major applications. This is of special interest for those metals which will run out relatively fast at the present course. Even metals with a high ratio of reserves to primary annual production combined with large absolute amounts of reserves and associated extraction rates, can be susceptible to future supply constraints because they are located in just a few geographic locations. An example is chromium which is mainly located in Kazakhstan and southern Africa. Summarizing these considerations, Figure 7 splits a large number of elements into the three described categories [18].

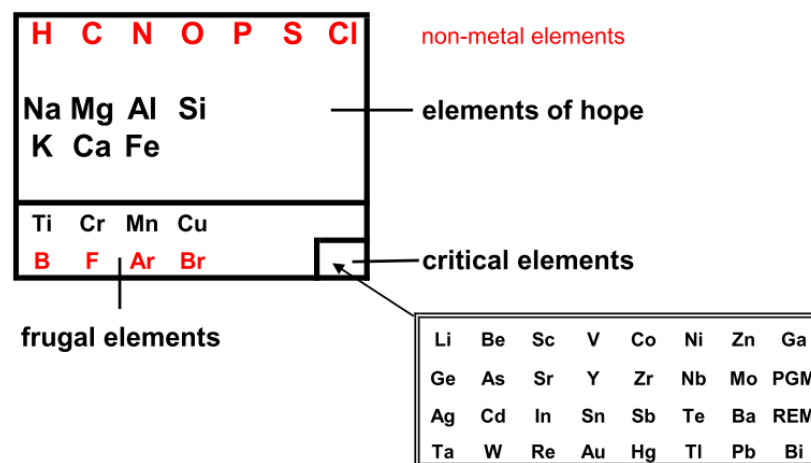


Figure 7 – Presenting the element of hope, the frugal elements and the critical elements [18]

\*PGM = Platinum Group Metals, REM = Rare Earth Metals

**Critical elements:** It is seen that there are over 30 elements that have reached the status of “critical”. Many of these (Zn, Li) are also likely to score high on the impact axis from Figure 6 as they are used in societal critical applications like automotive and battery technology. For these elements it would be advisable to develop some sort of mechanism that ensures that they are used sparsely and only for those applications where they cannot be substituted by other elements.

**Frugal elements:** These types of elements are still less scarce than critical elements but they should be used in a frugal (restrained, austere) manner. As with the critical elements, they should only be applied in mass for applications in which their unique properties are essential. In this way their remaining reserves will last longer (most notably copper and manganese).

**Elements of hope:** These are the most abundant elements available to mankind and can be extracted from the earth's crust, from the oceans and from the atmosphere. They constitute both metal and non-metal elements.

### 3.2.1 EU Criticality methodology

The EU methodology used to assess criticality has a combination of two assessment components[20]:

- Economic importance or expected (negative) impact of shortage,
- Supply risk – Poor governance.

Compound indicators are used for each of these two assessment components; therefore each takes multiple factors into account. The result is a relative ranking of the materials across the two assessment components, with a material defined as critical if it exceeds both the threshold for economic importance and the supply risk shown in Figure 8.

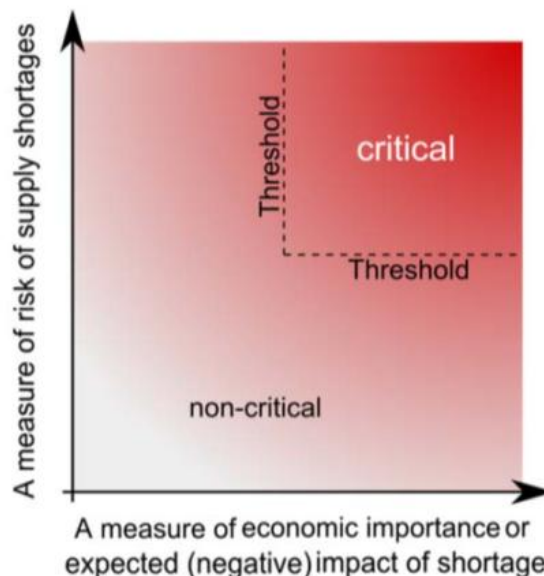


Figure 8 – General scheme of the criticality concept projected into two dimensions [20]



### 3.2.1.1 Economic importance (expected negative impact of shortage)

Measuring the economic importance of a raw material for an economy is a complex task, presenting not only data but also conceptual and methodological difficulties. Because of this, a pragmatic approach was taken when developing the methodology to allow the comparison of non-energy raw materials in a relative ranking. This analysis is achieved by assessing the proportion of each material associated with industrial mega sectors at an EU level (Figure 9). These proportions are then combined with the mega sectors' gross value added (GVA) to the EU's GDP. This total is then scaled according to the total EU GDP to define an overall economic importance for a material.

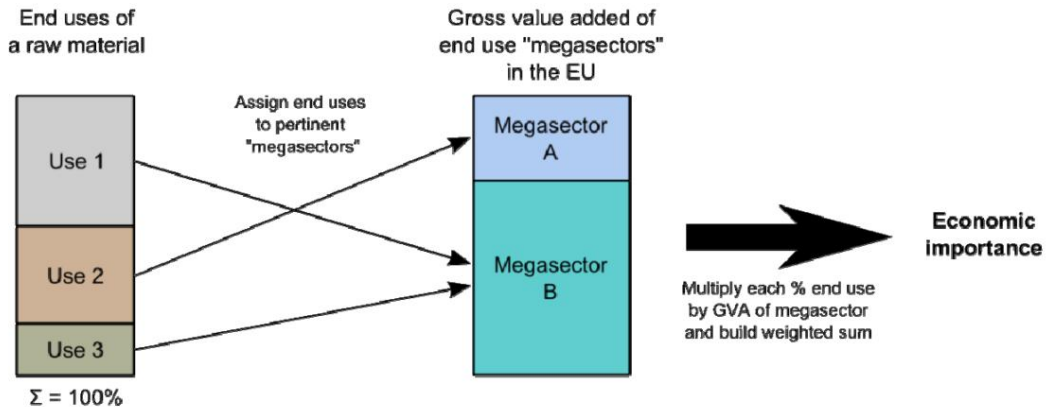


Figure 9 – Visualization of the compound indicator for economic importance [20]

A key feature of the approach is that it is independent of both market size and price of the individual raw materials. Instead it focuses on the benefit these raw materials have for the European manufacturing economy, which can be viewed as more in line with a measure of “impact” [20].

### 3.2.1.2 Supply risk (Poor governance)

Within the methodology, a large influence on supply risk is assumed to be concentrated primary supply from countries exhibiting poor governance because the supply may be interrupted e.g. through political unrest. It should be noted that no direct indicator of geological availability is included within this methodology due to the timescales considered. However, the above mainly applies to primary production, because if any secondary production takes place it does not depend on geology. Therefore, the supply risk is seen to be reduced by the availability of secondary supply from EoL products. Furthermore, the risk is reduced by the existence of options for full substitution (price and performance). The interplay of these individual elements yield a composite indicator for supply risk as is shown graphically in Figure 10 [20].

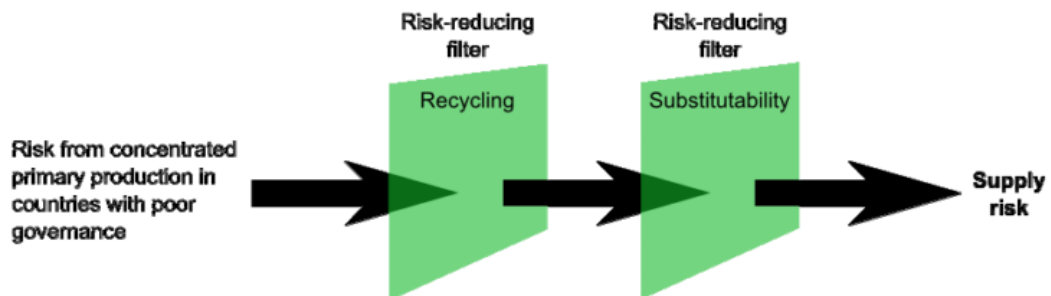


Figure 10 Visualisation of the compound indicator for supply risk as defined by Critical Raw Materials [20]



Therefore the overall supply risks are considered to arise from a combination of several factors, namely:

- a. Substitutability,
- b. EoL recycling rates,
- c. High concentration of producing countries with poor governance.

A scheme of the overall EU criticality assessment methodology for raw materials is shown in Figure 11.

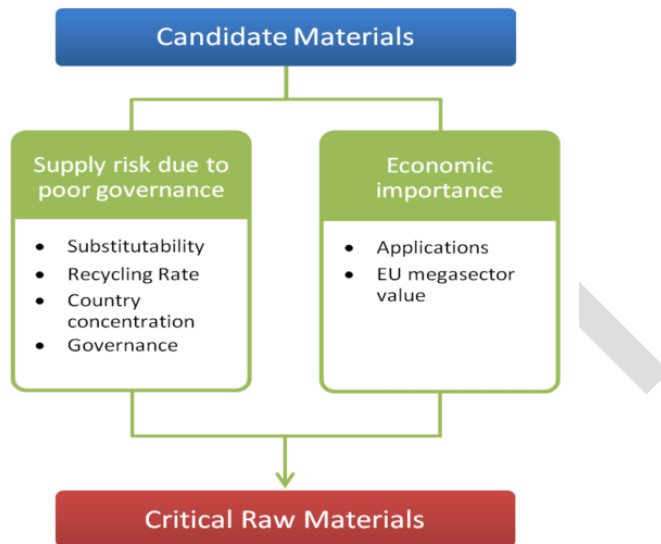


Figure 11 Scheme of EU criticality methodology [20]

### 3.2.1.3 Results of EU Criticality Analysis

Due to Europe's high dependence on imports, there is growing concern about the supply of particular materials. In 2010 the EU published a list of 14 critical raw materials, the so called EU-14, materials on which the European economy depends but which might be at risk of supply disruptions. Supply disruption could be feared if one country exerts a monopoly of supply (e.g. China for REE) or because the mineral is mainly produced in politically or economically unstable regions (e.g. tantalum from the Democratic Republic of Congo). The European Commission have since presented a revised list of Critical Raw Materials. The 2014 list includes 13 of the 14 materials identified in the previous list, with only tantalum moving out of the list (due to a lower supply risk) while six new materials appear on the list. When the EU criticality methodology is applied, to the list of fifty four candidate raw materials, these twenty materials classified as critical are shown in Figure 12 and Figure 13. Critical elements of the EU-20 are: Antimony, Beryllium, Borates, Chromium, Cobalt, Coking Coal, Fluorspar, Gallium, Germanium, Graphite, Indium, Magnesium, Magnesite, Niobium, Phosphate Rock, Platinum Group Metals, Rare Earth Elements (Light), Rare Earth Elements (Heavy), Silicon Metal, Tungsten.

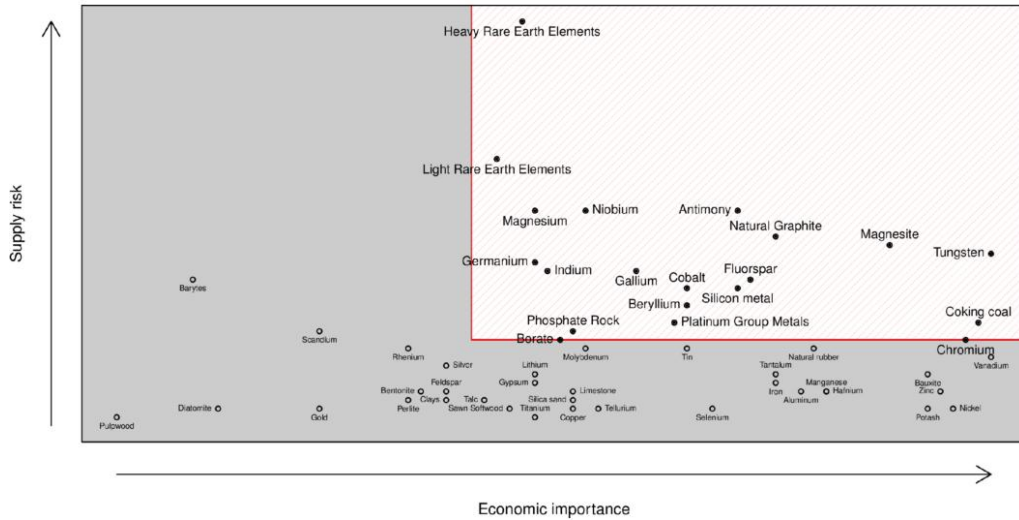


Figure 12 Updated criticality assessments for the EU for 2013 [20]

<b>Antimony</b>	<b>Beryllium</b>	<b>Borates</b>	<b>Chromium</b>	<b>Cobalt</b>	<b>Coking coal</b>	<b>Fluorspar</b>
<b>Gallium</b>	<b>Germanium</b>	<b>Indium</b>	<b>Magnesite</b>	<b>Magnesium</b>	<b>Natural Graphite</b>	<b>Niobium</b>
<b>PGMs</b>	<b>Phosphate Rock</b>	<b>REEs (Heavy)</b>	<b>REEs (Light)</b>	<b>Silicon Metal</b>	<b>Tungsten</b>	

Figure 13 EU-20 Critical raw materials [20]

### 3.3 Material value

The scarcity or criticality of materials is highly connected with material value or price, therefore, prices of elements and their compounds list [21] was used to estimate the material value.

## 4. Materials list and data

In this section the critical components of each individual FCH technology considered in this project are identified. The most commonly used materials used for these components are listed in tables where their material classification, value and criticality are given.

Based on the characteristics of the considered FCH technologies and their core components, described in section 2, the critical materials were identified. The most commonly used materials are listed in separated tables. The properties of the SOFCs, PEMFCs, PEMWEs, and AWEs are given in Table 4, Table 5, Table 6, and Table 7, respectively. Materials are classified according to five different criteria: their function (location) in a component, material hazardousness, material value, scarcity as a material criticality and current recycling and dismantling technologies.

Scarcity or criticality of materials is defined by EU criticality method where all critical materials are classified as combination of their economic importance and supply risk. EU criticality method has two levels, critical and non-critical material. Results of the EU criticality analysis corroborate the methodology used for assessment of the material criticality, where three levels were used to assess the criticality of an individual material (Critical element = High; Frugal elements = Medium, Elements of hope = Low, see Figure 6 and Figure 7).

These lists of materials, with other accessible data, will serve as an input for other tasks in WP2 (Regulatory analysis, critical materials and components identification and mapping of recycling technologies) and further work in other subsequent WPs of the project (i.e. WP4 – LCA for FCH technologies considering new strategies & technologies in the phase of recycling and dismantling).

**Table 4 – List of common material assessment for SOFC [17]–[21]**

Solid Oxide Fuel Cells (SOFC)					
Component	Material	Material classification	Material value	Material Criticality	Current recycling and dismantling technology
Electrolyte	Yttria-stabilised zirconia	Non-hazardous	Medium	High	D2.2. Chapter 7.4
Anode	Nickel-based oxide doped with YSZ	Hazardous (Cat. 1 carcinogen)	Medium	High	D2.2. Chapter 7.3.1.2
	Nickel	Hazardous (Cat. 1 carcinogen)	Medium	High	D2.2. Chapter 7.3.1.2
Cathode	Strontium-doped lanthanum manganite	Hazardous (Irritant)	Medium	High	D2.2. Chapter 7.4
Interconnect	Doped lanthanum chromate	Hazardous (Irritant, harmful)	Medium	Medium-High	D2.2. Chapter 7.4
	Inert metals/alloys	Non-hazardous	High	Medium-High	D2.2. Chapter 7.1
Sealant	Glass/Glass-ceramic	Non-hazardous	Low	Low	D2.2. Chapter 7.4
	Mineral	Non-hazardous	Low	Low	D2.2., Chapter 7.1
	Precious metals	Non-hazardous	High	High	D2.2. Chapter 7.1
Substrate	Ceramic	Non-hazardous	Low	Low	D2.2. Chapter 7.4

**Table 5 – List of common material assessment for PEMFC [17]–[21]**

Polymer Electrolyte Membrane Fuel Cell (PEMFC)					
Component	Material	Material classification	Material value	Material Criticality	Current recycling and dismantling technology
Electrolyte	Perfluorosulphonic acid (PFSA)	Non-hazardous	Medium	Medium	D2.2. Chapter 7.2
	Sulfonated polyether ether ketone (s-PEEK)	Non-hazardous	Medium	Low	D2.2. Chapter 7.2
	polystyrene sulfonic acid (PSSA)	Non-hazardous	Low	Medium	D2.2. Chapter 7.2
	polybenzimidazole (PBI) doped with H <sub>3</sub> PO <sub>4</sub> *	Hazardous (corrosive)	Medium	Low	D2.2., Chapter 7.2
Anode and Cathode - GDL	Carbon cloth or paper treated with hydrophobic agent	Non-hazardous	Low	Low	D2.2. Chapter 7
	Metallic mesh or cloth (e.g. stainless steel)	Non-hazardous	Low	Low	D2.2. Chapter 7.1
Anode and Cathode - Catalyst layer	Platinum or Pt-alloys	Non-hazardous	High	High	D2.2. Chapter 7.3.1.1
	Catalyst support (carbon, metal oxides, carbides, etc.)	Non-hazardous	Medium	Low	D2.2. Chapter 7.3.2.1
Interconnect	Synthetic graphite or graphite composites	Non-hazardous	Low	Medium	D2.2. Chapter 7
	Stainless steel	Non-hazardous	Low	Low	D2.2. Chapter 7.1
Sealant	Thermoplastic	Non-hazardous	Low	Low	D2.2. Chapter 7.2
	Elastomer	Non-hazardous	Low	Low	D2.2. Chapter 7.2

\* used only in HT PEMFC

**Table 6 – List of common material assessment for PEMWE [17]–[21]**

Polymer Electrolyte Membrane Water Electrolyser (PEMWE)					
Component	Material	Material classification	Material value	Material Criticality	Current recycling and dismantling technology
Electrolyte	Perfluorosulphonic acid (PFSA)	Non-hazardous	Medium	Medium	D2.2. Chapter 7.2
	Sulfonated polyether ether ketone (s-PEEK)	Non-hazardous	Medium	Low	D2.2. Chapter 7.2
Catalyst layer - Cathode	Pt or Pt-alloys	Non-hazardous	High	High	D2.2. Chapter 7.3.1.1
Catalyst layer- Anode	Iridium and Ir-alloys	Hazardous (irritant, harmful)	High	High	D2.2. Chapter 7.3.
	Ruthenium and Ru-alloys	Hazardous (toxic, carcinogen)	Medium	High	D2.2. Chapter 7.3.
Anode and Cathode - GDL	Thermally sintered Ti	Non-hazardous	Low	Medium	D2.2. Chapter 7.3.
	Ti or stainless steel mesh	Non-hazardous	Low	Medium	D2.2. Chapter 7.3.
	Synthetic graphite or graphite composites (only possible on cathode side)	Non-hazardous	Low	Medium	D2.2. Chapter 7
Interconnect	Coated titanium or Ti-alloys	Non-hazardous	Low	Medium	D2.2. Chapter 7.3.
Sealant	Thermoplastic	Non-hazardous	Low	Low	D2.2., Chapter 7.2
	Elastomer	Non-hazardous	Low	Low	D2.2., Chapter 7.2

Table 7 – List of common material assessment for AWE [17]–[21]

Alkaline Water Electrolyser (AWE)					
Component	Material	Material classification	Material value	Material Criticality	Current recycling and dismantling technology
Electrolyte	Potassium Hydroxide	Hazardous (corrosive)	Medium	Low	D2.2. Chapter 7
Anode	Precious metals	Non-hazardous	High	High	D2.2. Chapter 7.3.
	Plastic	Non-hazardous	Low	Low	D2.2. Chapter 7.2
Cathode	Raney-Nickel	Hazardous (carcinogen)	Medium	High	D2.2. Chapter 7.3.1.2
	Plastic	Non-hazardous	Low	Low	D2.2. Chapter 7.2
Interconnect	Plastic	Non-hazardous	Low	Low	D2.2. Chapter 7.2
Sealant	Thermoplastic	Non-hazardous	Low	Low	D2.2. Chapter 7.2
	Elastomer	Non-hazardous	Low	Low	D2.2. Chapter 7.2
Diaphragm (membrane)	Asbestos	Hazardous (carcinogen)	Low	Low	D2.2. Chapter 7
	Polymers	Non-hazardous	Medium	Low	D2.2. Chapter 7.2

## 5. Conclusions

In the deliverable D2.1 Assessment of critical materials and components in FCH technologies the list of all relevant materials used in components of considered core FCH technologies are listed in the form of tables. The focus was set to core FCH technologies with BoP components as conventional technology not included. The study was done on the basis of the current state of the art in FCH materials dismantling and recycling area with research based on expert studies and scientific papers as well as current EU legislation.

The list includes the location of the material used in FCH technologies, its function, contribution to environmental aspect (contribution to LCA), value (contribution to LCC), material classification (hazardousness of the material), criticality of material and currently used (if it exists) recycling technology. Criticality or scarcity of the material is the combination of economic importance and supply risk.

From the list of materials for each considered technology (SOFCs, PEMFCs, PEMWEs, and AWEs) some conclusions can be drawn:

- SOFCs materials mainly consist from REE which makes this FCH technology critical from the perspective of the EU states. Also, these materials are classified as rather costly and hazardous.
- PEMFCs materials are mainly low-to-medium in cost with the exception of Pt or Pt-alloy catalysts. Pt and graphite, which is typically used for bipolar plates and represents a significant proportion in weight and volume of the stack, are classified as critical for the EU states. Majority of the materials used in this FCH technology are classified as non-hazardous.
- PEMWEs materials are more expensive compared to the PEMFCs. The OER catalysts are based on REE while the HER catalysts are based on Pt, which means that these materials are also classified as critical and high in costs. The materials are mainly non-hazardous with the exception of the REE used for OER catalysts.
- AWEs materials are mainly low in costs with the exception of both the anode and the cathode catalysts, which are also classified as critical for the EU states. This FCH technology is also classified as rather hazardous since the alkaline electrolyte in liquid form is used. Also, Ni-based catalyst and asbestos diaphragms, used in older types of AWEs, are classified as carcinogen.

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