Assessment Of The Recycling Concept For Fuel Cell

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Figure 1 - Schematic of PEMFC. Source: Adapted from [12]

Introduction and scope of the project

Over time, progress has always been linked with the growth of requirements for energy. Today, a major part of energy needs has been provided by the combustion of fossil fuels and this has increased the air pollution and the emission of greenhouse gasses, such as CO_2, mainly in urban areas [1]. European Union launched a roadmap for a global climate action to reduce 80% of greenhouse gas emissions by 2050 with respect to the Paris Agreement [2]. Aside from this, the development of resources, environment and economy for the manufacturing industry is a worldwide issue [3].

In this regard, hydrogen technologies play a crucial role in the shift to a low-carbon economy [4]. With that, renewable energy generation is rapidly growing. One of them is the usage of hydrogen fuel cells, which are becoming more promising for various kinds of applications [5]. Furthermore, the studies on the End-of-Life (EoL) Technologies to recover materials spent on the manufacturing processes are extremely important for circular economy, sustainability and maintenance concepts. Based on that, this project aims to evaluate scenarios around recovery materials, chemical processes for valuable metallic components and re-utilization of recovered materials to produce new fuel cells. The project will be divided as follows: I/Literature review, Methods and Key Findings; ii/Final Considerations and Discussions and iii/References.

Literature Review, Methods and Key Findings.

A considerable number of climate change policies focused on the reduction of greenhouse gas emissions (GHG) and fossil fuel consumption are pushing the large-scale deployment of renewable energy sources (RES) and will significantly contribute to the implementation of new objectives of energy supply in Europe and worldwide [6].

In this context, hydrogen storage and generation systems are considered the most promising solutions for producing clean energy. Indeed, hydrogen can be used as a feedstock, fuel, or energy carrier and storage for balancing the supply and demand of electricity [7]. The usage of fuel cells as a novel electricity generation technology compared to the conventional methods has been considered in recent studies in this field [8]. Fuel cell is an electrochemical device in which the chemical energy is directly converted into electrical energy [9]. The core of the fuel cells is the fuel cell stack. It consists of an electrolyte in contact with an anode (negative electrode) and a cathode (positive electrode). The fuel cells are classified in relation to their electrolytes and fuels used as follows [10]:

1. PEMFC (Proton Exchange Membrane or Polymer Electrolyte Membrane Fuel Cell) uses a water-based, acidic polymer membrane as the electrolyte and platinum-catalyzed electrodes. It uses pure hydrogen, but also reformed natural gas, removing carbon monoxide. Its operative temperature is below 100°C / 2. HT-PEMFC (High Temperature PEMFC) is a PEMFC obtained by changing the electrolyte from a water-based to a mineral acid-based system. It operates up to 200°C. / 3. SOFC (Solid Oxide Fuel Cell) consists of two porous electrodes separated by a dense oxygen ion-conducting ceramic membrane as the electrolyte / 4. AFC (alkaline fuel cell) uses an alkaline electrolyte and is fueled with pure hydrogen and oxygen. There are other types of Fuel Cells, to simplify, only those 4 types were exposed. Figure 1 shows a high-level schematic of a PEMFC.

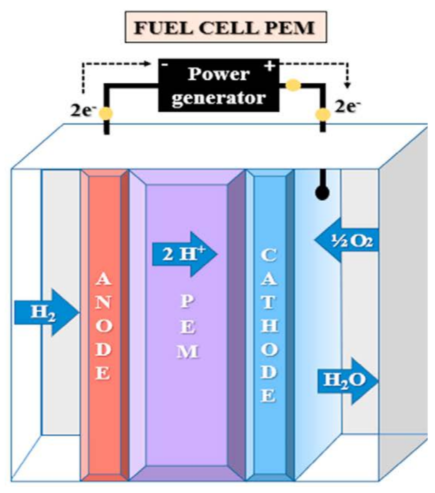

Figure 1: Schematic of PEMFC

The selection of PEMFCs to perform the study on this project is mainly related to the facts that technology has a high maturity level, stable, are already promising power sources, owing to their high-power density, quick start-up, reliability, and portability. This technology shall widespread fast, as PEMFC systems are very versatile and modular considering the wide possible applications range that they could offer from cellular phones to power plants and automotive applications [11].

As previously mentioned, PEMFC is composed of anode, cathode, and electrolyte, those three components form the membrane electrode assembly called MEA. Platinum group metals (PGMs) are the main electrocatalysts used in PEMFC. Since they are **expensive materials**, significant efforts focus on decreasing their loading is being performed. For instance, the Platinum (Pt) loading in PEMFCs has decreased from above 1 g/kW^{-1} in the past decade to around 0.5 g/kW^{-1} nowadays [12]. Novel approaches focus on the use of Pt-free compounds (non-noble metals, alloyed transition metals or alternative noble metals), for which a low price and long-term stability are the main requirements [13]. Electrochemical reactions occur in electrodes where a catalytic layer of Pt is applied on carbon paper. The membrane should be made from a material that has a high proton conductivity such as sulfonated polymers. The following table shows a list of materials commonly used for PEMFC and are classified according to three different criteria [14]. Table (1): List of common materials in PEMFC.

Component	Material	Material classification	Material value	Material Criticality
Electrolyte	Sulfonated polyether ether ketone	Non-hazardous	Medium	Low
	Perfluorosulphonic acid	Non-hazardous	Medium	Medium
	polystyrene sulfonic acid	Non-hazardous	Low	Medium
Anode / Cathode	Carbon cloth/paper treated with hydrophobic agent	Non-hazardous	Low	Low
	Metallic mesh (e.g., stainless steel)	Non-hazardous	Low	Low
Catalyst layer	**Platinum**	**Non-hazardous**	**High**	**High**
Interconnect	Graphite	Non-hazardous	Low	High
Sealant	Thermoplastic	Non-hazardous	Low	Low

Terms used in table (1):

A hazardous material is a material that can be considered dangerous when it is a waste or capable of having a harmful effect on the environment or people's health. The Priority List of Hazardous Substances [15] has been used as a reference. Critical material is a material that has a high demand from industry but there is a risk to its supply. The EU methodology has been used to define the scarcity of material [16]. Material value is related to the price of the material. Materials have been categorized into three different classifications: low-cost materials (price lower than 5 $/kg), high-cost materials (price higher than 500 $/kg), and medium cost materials (5-500 $/kg). The London Metal Exchange has been taken as a reference [17].

In this context, rare materials can play different roles in fuel cell systems. For example, they could be used as catalysts and co-catalysts of electrodes, electrolytes additives, among others. The consumption of rare materials has deployed a wide concern on their high cost, concentrated supply, and resource shortage. A study has shown that 7% of the world's platinum supply will be required for the fuel cell use in the Europe in 2030 [18]. Based on what was exposed above, the evaluation of End-of-Life (EoL) Technologies for some components from a PEMFC is important mainly related to the cost that is directly linked to material criticality. In this context, presenting End-of-Life Technologies is important. Table 2 summarizes the conventional and novel EoL technologies identified for relevant PEMFC stack materials [13]. Table 2 - Recovery Technologies vs Material. Source: Adapted from [13].

Material			Recovery Technologies	
			Current [a]	Novel [b]
Ni; NiO			HTH; HMT	N/A
Ag			HMT	N/A
YSZ			HTH	N/A
Ir			HMT; PMT	TD
Ru			HMT; PMT	TD
Ionomer			N/A	AP; AD
PGM			HMT; PMT	SED; TD; AP
$LaMnO_3$	$LaCrO_3$		N/A	N/A
[a] HTH: Hydrothermal Treatment; HMT: Hydrometallurgical treatment; PMT: Pyro-hydrometallurgical treatment				
[b] TD: Transient Dissolution; AP: Acid Process; SED: Selective Electrochemical dissolution; AD: Alcohol Dissolution				

Current EoL technologies; Hydrometallurgical treatment - The hydrometallurgical pathway involves the dissolution of target elements from solid matrices through caustic or acid attacks [13]. Pyro-hydrometallurgical treatment - When applied to PEMFC systems, pyro-hydrometallurgical treatment involves a calcination process in which GDLs (Gas Diffusion Layers), membranes and electrodes are incinerated [13]. Hydrothermal treatment - Involves the processing of waste materials with steam at relatively elevated temperature and pressure [13]. **Novel EoL technologies;** These technologies focus on the recovery of Platinum while allowing the additional recovery of other relevant materials such as the membrane or the carbon support [13]. Selective electrochemical dissolution - The method is based on the electrochemical dissolution of materials at different voltage and pH windows [13]. Acid process - In contrast to current processes, this pathway allows the efficient recovery of both the PGM and the ionomer from CCM MEAs by using strong acids to oxidize the carbon support followed by separation steps (filtration and centrifugation [13]. Alcohol solvent process - The process in this patent can be understood as a pretreatment allowing the subsequent recovery of the polymer resin in addition to the catalyst [13]. Figure 2 shows a summary of relevant aspects of EoL technologies.

EoL technology[a]	PMT	HMT	HTH	AP	SED	TD
Investment cost	−	+	−	−	+	+
Operating cost	−	+	0	−	0	0
Recovery efficiency	+	−	0	++	+	+
Energy requirements	−	++	−	−	−	++
Hazard/toxicity	−	−	−	−	0	−
Other environmental concerns	−	0	++	−	0	++

[a] PMT: pyro-hydrometallurgical treatment; HMT: hydrometallurgical treatment; HTH: hydrothermal treatment; AP: acid process; SED: selective electrochemical dissolution; TD: transient dissolution.

Figure 2: Summary of aspects of EoL

Despite all the efforts to characterize the best way to recycle platinum from a PEMFC, some other processes/concepts needs to be explored and are closely related to the life cycle cost of a certain component. In order to have a complete view of cost and processes, it is important to detail the most promisor recycling process.

Chemical process – Hydrometallurgical details

The first step is to use a leaching agent such as H_2O_2/HCl to dissolve the platinum.

$$Pt + 2\,H_2O_2 + 6\,HCl \text{ à } H_2PtCl_6 + 4H_2O$$

$$H_2O_2 + 2\,HCl \text{ à } Cl_{2\,(g)} + 2\,H_2O$$

$$2\,H_2O_2 \text{ à } 2\,H_2O + O_{2\,(g)}$$

After that, the filtration step takes place to remove the solid carbon powder from the mixture leaving us with a liquid solution of PtCl This solution can be treated with two different techniques; the first option is by using liquid-liquid extraction process, 15 vol. % Cyanex923/Octanol extractant system with NaOH as a stripping agent seems to be efficient enough to carry out the recovery efficiently. The second option is by using a resin process, Lewatit-MP-62 resin was chosen as an ion exchanger because it is a weak base ion exchanger which makes it easier to regenerate compared to Amberjet 4200 (strong-base ion exchanger). The saturated resin then can be recovered and regenerated using a solution of NaOH. The last step is to precipitate the platinum by treating the solution with ammonium chloride (NH4Cl). The platinum precipitated will be in the form of (NH4)2PtCl6 [19].

Platinum is an important part of PEMFC, because it ensures there is enough catalytic activity in both the anode and at the cathode where the reaction takes place. Because of that we should think about how to utilize the recovered platinum in PEMFC. One of the main reasons behind selecting the above-mentioned recovery process is that its end product Ammonium hexa-chloro-platinate $(NH_4)_2PtCl_6$ has low decomposition temperature and relatively high solubility in water which make it a good precursor to obtain metallic Pt. To further use it in proton exchange membrane PEM fuel cell [20].

Pt/C Preparation: The procedure starts with dissolving the metal in triple-distilled water 1 mg of the precursor for every 1 ml of water. Then this solution will be added to the Vulcan support and stirred continuously. After that, the solution will be washed, filtered, and dried. The resulting powder will then be thermally decomposed by heating at 450°C for 1 hour in order to avoid hydride formation. The reduction process was then carried out in a 10% H_2 in Ar mixture flowing at 450°C. [20]

Some points to consider: i/ Pt from natural ores requires 18,860–254,860 MJ/Kg of metal and 100,000–1,200,000 m^3_{water}/ ton of metal extracted, while recycled Pt needs 1400–3400 MJ/Kg and 3000–6000 m3/ton respectively [16] and ii/ Pt ores usually contain sulfide minerals, which can lead to a dangerous fume in addition to tons of CO2 during the smelting and refining process [21]. Pt recycling is an efficient way to obtain Pt, both from an economic and environmental perspective and it is important for the technological conversion that our planet needs [22].

Concept of Maintenance

Maintenance is one of the life cycles costs of a product. According to [23], systems and/or products are subject to wear and tear, corrosion, contamination, and alterations in the properties of the materials. After a certain period, being used or not, the product's condition may not be the desirable one anymore. Thus, to restore the product to its original status or to maintain its operational condition, a set of actions and resources are necessary [24]. Maintenance is the ability to maintain or restore a system in functioning state, which contains inspections and repairs [25]. As maintenance is typically classified as preventive and corrective. A corrective maintenance's objective is to restore the product after a breakdown (failure occurrence). Preventive maintenance seeks to perform services in pre-defined intervals, aiming at keeping the product operational status at a required level [24]. Overall, the total cost of the system (Ctot) can be divided into capital cost (Ccc), fuel cost (Cfuel), and operation & maintenance cost (CO&M). The contribution of the O&M cost will be assumed constant throughout the system's lifetime, and it is related by the maintenance factor (φ) as a percentage of the total cost. On this case, the factor is about 5% [11]. On the paper, the authors doesn`t show the criteria around the operation and maintenance cost. Assuming that Maintenance Cost will be 50% of 5%, it means, 2.5% of CO&M, seems reasonable for an expected life of 10/15 years as expected by the industry [18]. Despite this questionable assumption performed by the authors of this project, the maintenance cost needs to be broken down even more. On this matter, consider Spare Part cost, Labor Cost (Including repair, diagnostics of failure, work environment, among others) and all the Downtime issues is important as well.

Final Considerations and Discussions

On the transition to a greener energy, hydrogen and fuel cells will have a significant role in modern society. Sustainability is always a major player in this transition, taking a crucial step towards green energy and recycling of components including rare materials. On the other hand, the usage of rare materials will increase rapidly and even more demand will be foreseen. Based on that, the studies related to EoL and new ways to recycle the material are valuable for several reasons passing from Sustainability to reduction on Maintenance cost of components. Based on the study from [14], it gives us some highlights about the process selected. Figure 2 shows that for the hydrometallurgical process, the recovery efficiency and hazard/toxicity are the most sensitive parameters that could be improved. Attached to the good energy consumption value and minimal impact on the environmental aspects, this process is a promisor factor for the scalability of the process. The hydrometallurgical process has several benefits, including low-cost investments, low complexity, and low operation costs. Those aspects will bring a good environment for a reduction on the complete process cost and in consequence, reduction on the parts price (remanufactured parts mainly) by the usage of recycled components/materials. On the threats side for the process selected, the usage of hazard/toxicity components are a point to be checked carefully since some regulation can be in place and make the process hard to be secured. To have more sustainable recycling processes, manufacturers of hydrogen technology should take a part too by making products that have great compatibility with recycling and dismantling processes. This connection between manufacturers and recycling companies is extremely valuable. On one side there are the companies designing the components to reach their goals. On the other side there are companies trying to recover the materials, running in a circular economy and being greener. Those aspects directly impact the life cycle cost, including maintenance and operational costs. In terms of the maintenance cost, some questions must be placed and clarified, for example: What is the level of repair that is possible to be performed on a fuel cell system? Is it possible to replace only a damaged part of MEA? Is there any possibility to rework the MEA after damages? Depending on the level, it is possible to reach more sustainable cost for the components. Defining the level of repairs, it is possible to increase the durability of the complete fuel cell that today is a challenge for some applications. Assuming a possibility to repair only a damage cell, how to secure all the chemical activities? Some other questions on the chemical processes and electrochemistry aspects. How to secure a sustainable environment for usage of hazard/toxicity materials? Furthermore, the technology of Fuel Cells and recycling processes are being increased during the years. Apart from it, some pending points needs to be clarified in order to secure a correct and added value processes to support the environmental aspects and reduction on the cost of maintenance and operations.

References

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