Recycling of Critical Raw Materials from Hydrogen Chemical Storage Stacks (PEMWE), Membrane Electrode Assemblies (MEA) and Electrocatalysts

A M Moschovi, E Zagoraiou, E Polyzou and I Yakoumis
MONOLITHOS Catalysts and Recycling Ltd. 83, Vrilissou Str., 11476 Polygono, Athens, Greece
E-mail: yakoumis@monolithos-catalysts.gr

Abstract. The increase in energy demands for the establishment of a modern digital era has resulted in the significant limitation of the energy sources. The depletion of energy reserves drew attention to alternative renewable energy sources that can satisfy the energy requirements in an environmentally friendly way. Hydrogen is an ideal chemical energy storage. Proton exchange membrane water electrolysis (PEMWE) is a promising technology as a green source of high-purity hydrogen. For that reason, PEMWE devices are already used in aerospace to produce oxygen for the crew on the Space Stations. The use of Critical Raw Materials (CRMs, especially Pt and Ir) and high cost materials in the PEMWE systems compromises their economic feasibility. It is necessary to implement End-of-Life (EoL) strategies that optimise the recovery of CRMs within feasible and environmentally friendly processes. In this paper an overview of the existing technologies for recycling of Membrane Electrode Assemblies and electrocatalysts from PEMWE systems are revealed. MONOLITHOS has developed a novel optimized hydrometallurgical method for high PGMs recovery from spent automotive catalysts. This work aims to describe how this method can be applied to the EoL phase of PEMWE to improve techno-environmental and techno-economical performance of CRMs recovery.

1. Introduction
Technological advantages have led to improved quality of life, increasing the earth’s population and consequently energy demands. Almost 90% of consumed energy is provided by fossil fuels [1]. Fossil fuels are considered as non-renewable energy sources and become scare progressively. The dependency of a country on fossil fuel as main power source can lead to serious economic and political issues. In addition, fossil fuels consuming produce greenhouse gases causing air pollution and global warming. The European Union targets for 2030 aims in reducing greenhouse gas emission by 40% with respect to 1990, increase the renewable share in energy consumption at least to 32% and improve the energy efficiency at least to 27% [2]. According to the above a rapid transition moving from fossil to sustainable fuels is required to meet the increased energy demands.

Renewable Energy Sources (RES) based on solar or wind energy have been used to produce renewable energy with minimal environmental impact and economic cost [3]. However, they cannot guarantee the undisturbed energy production because of unstable weather conditions. Electrochemical
energy storage of hydrogen (H₂), is a promising option with the potential to provide low-carbon energy for all sectors of the economy.

1.1. Fuel Cell and Hydrogen (FCH) technologies
Hydrogen is one of the most promising clean, efficient and sustainable energy carrier. Hydrogen technology, having many attractive properties as high energy density (140 MJ/kg), can be produced from renewable and sustainable sources and its energy can be distributed continuously. A series of applications (industrial, transport/mobile, portable, stationary energy applications) including power generation in periods of increased demand, supplementation of the natural gas grid for increased efficiency, vehicle fueling or use as a feedstock for green generation of chemicals can be covered with H₂. Environmentally friendly electrochemical conversion of H₂ in fuel cells produces energy and water as byproduct, without carbon dioxide (CO₂) emissions. The environmentally friendly byproducts are the main reason for the development of Fuel Cell and Hydrogen (FCH) technologies.

The replacement of fossil-based technologies by FCH systems are considered a pathway to reduce the dependence on fossil fuel, since these devices enable a low carbon energy economy, allowing the use and storage of renewable energy in form of H₂ (figure 1). FCH technologies belong to clean technologies and offer a significant reduction in CO₂ and NOx emissions. In a fuel cell, H₂ is consumed to produce energy, (figures 1a & 1b). On the other hand, in a water electrolyzer, energy is consumed to produce H₂ (figures 1c & 1d).

FCH technologies are proven and established in aerospace. For example, an Advanced Closed Loop System (ACLS) which recycles CO₂ on the Space Station into O₂ has been developed by European Space Agency (ESA) for human spaceflight [4]. In ACLS, CO₂ exhaled by astronauts is used to produce water (Sabatier reaction). This water then is used to produce oxygen (by electrolysis) for the crew on the Space Station.

1.2. H₂ production in Proton Exchange Membrane Water Electrolyzer (PEMWE)
Hydrogen production from water is an attractive route for costless renewable electricity. Water is abundant on earth’s surface and can be used to meet the H₂ needs required for the sustainable production of fuels and chemicals. Among the water splitting technologies, electrolysis is the most efficient and mostly extensively studied [5]. In water electrolysis, water splits into H₂ and O₂ by supplying electrical energy. In a water electrolyzer, the latter reaction is divided into two sub reactions that take place on the anode and cathode respectively, which are separated by a solid or liquid electrolyte, (figure 2). Catalysts are used in both electrodes, to increase reactions rates. The main advantages of H₂ production through electrolysers are low emissions, high efficiency, low energy consumption, easy start and stop recycling and easy transport. The main disadvantages are low scale application, limited lifetime, high cost (electrolyte, critical metal materials) and sensitivity towards impurities in the water.
1.3. Main components of a PEMWE

The major PEMWE component is the membrane electrode assembly (MEA), (figure 3a). MEA consists of the proton conductor polymer membrane sandwiched between two porous electrical conducting electrodes. Solid poly sulfonated membrane (commonly Nafion™ from Chemour) with typical thickness of 60-200 μm is used as an electrolyte [7]. These membranes have unique properties such as high strength and efficiency, high oxidative and thermal stability, good durability, high proton conductivity and low electron conductivity. The hydration of the membrane should be preserved, so as for the proton conduction to be favored. Therefore, heat and water management systems are critical processes to ensure efficient operating conditions. On both sides of the membrane, thin electrodes (10 μm thick) are directly bonded to the surface. The SoA catalysts for PEMWE are platinum (Pt) or palladium (Pd) at the cathode and iridium oxide (IrO2) or ruthenium oxide (RuO2) at the anode [8]. Iridium is typically used for water oxidation, due to its high corrosion resistance. The MEA is clamped between two electrically conductive porous transport layers (PTLs). The transport layers are typically made of carbon paper and sintered titanium (Ti) foam or felt (280 μm thick) on the cathode and the anode side, respectively [9]. PTLs are responsible for effective mass transport and heat/water management and ensure electrical conductivity.

De-ionized water is supplied to the anode side of the cell by a flow field separator plate and diffused via current collector. Current collectors enable an electric current to flow between the electrodes and flow field plates, (figure 3a). Due to severe acidic operational conditions and high overvoltage and concentration of O2 at the anode side, metallic separator plates and current collectors are primarily used in PEMWE devices. Typically, Ti-based materials show outstanding strength, high thermal conductivity, low permeability, high electrical conductivity and corrosion resistance [8]. However, after long operation under high anodic potentials, Ti corrodes and an inert insulating oxide layer is formed. Thus, protection of the titanium plates using precious metal Pt and Ir coatings are used. At the cathode side a graphite flow field is usually used to transport H2 via current collector.

In order to achieve the desired electric power, multiple MEA are interconnected by bipolar plates (BPPs), (figure 3b). Bipolar plates’ surface is designed with a set of channels that have the dual function of reactant delivery and coolant handling. A bipolar plate electrically connects adjacent cells, uniformly distributes H2O and gases, separates oxygen in anode of one cell from the H2 in cathode of the adjacent cell, removes heat from active areas and provides mechanical support to the MEA. Bipolar plates should exhibit low surface contact resistance, excellent corrosion resistance, high electrical and thermal conductivity, low gas permeability, good mechanical strength, low weight and low cost. BPPs are generally made of graphite, polymeric compounds or carbon-polymer composites.
Titanium, aluminum and metal alloys, such as Cr-Ni steel, are also considered suitable given their high electrical conductivity and good mechanical properties. However, due to corrosion conditions, metallic bipolar plates need to be coated [10].

For potential leaks to be prevented and ensure an optimal compression between the layers, gaskets (made up of silicon, Teflon™, rubber, etc.) are interposed. The PEM stack is mechanically supported by two thick end plates, (figure 3). Due to the operating temperature and the presence of humidity, the materials that are used for end plates should exhibit high electrical insulation, high thermal conductivity, stability and rigidity, and corrosion resistance. Therefore, end plates are typically made of Al or steel.

2. Recycling CRMs from PEMWE

In terms of sustainability and environmental impact, PEMWE is considered as most promising system for high pure efficient H₂ production from renewable energy sources. However, the increased development of PEMWE devices require high amounts of critical raw materials (CRMs) as electrocatalysts and corrosion coatings (Pt, Ru, Ir) and high cost materials (Ti) as BPPs and PTLs, (table 1). For example, 1 MW PEMWE requires about 1.5 kg of Ir catalyst and annual production of Ir is about 3-4 tons.

| Catalyst (mg/cm²) | Porous transport layer (mg/cm²) | Bipolar plates (mg/cm²) |
|------------------|---------------------------------|-------------------------|
| Anode 2-3 (Ir)   | 5 (CRMs-coated Ti)              | 0.02-0.04 (CRMs on Ti)  |
| Cathode 0.2-0.5 (Pt) | 5 (CRMs-coated Ti)              | 0.02-0.04 (CRMs on Ti)  |

CRMs are identified in the EU according to two main aspects: 1) economic importance and 2) risk of supply disruption [12]. The value chain of CRMs is not fully and homogeneously covered by European industry. China is the principal global supplier of CRMs. To address the growing concern of securing CRMs for the EU economy, the Commission launched the European Raw Materials Initiative in 2008 [13]. One of the priority actions of the Initiative was to establish a list of CRMs at the EU level. The Commission established the first list in 2011 which contained 14 CRMs. After that, the list is revised every three years. In 2020, the list has been expanded to 30 materials [14].

The coronavirus pandemic has revealed Europe’s dependencies in certain products, critical materials and value chains. For example, China is the main supplier for CRMs used into batteries, making European carmakers reliant on Chinese suppliers. As the pandemic triggers transport disruption between western capitals and China, and due to the lack of mineral deposits in Europe, there is an urgent need to secure the supply of vital materials. In order to reduce Europe’s dependency on external importers, exploration, investment and improved recycling processes must be developed [15].

The most challenging barrier for PEMWE to overcome and become sustainable, is the reduction of their cost without their performance to be compromised. Despite the significant progress in the last decade [11], economic issues still hamper their commercialization. In this respect, environmentally sustainable approaches to recover CRMs from PEMWE should be considered. The transition from a
linear to a circular economy, where the value of CRMs is maintained in the markets for as long as possible, is a crucial parameter to develop a sustainable, low carbon and competitive EU economy.

2.1. Conventional methods

Nowadays, the simplest process with a negligible environmental impact contains mechanical steps to recycle a PEMWE stack such as the disassembly of the stack into its individual components [3]. Recycling of the MEA and BPPs from PEMWE systems is challenging because specialized recycling processes are required, (table 2). The recovery of precious metals and membrane from the MEA can be achieved by shredding the used MEA and delaminate the different layers [3].

| Components       | Material | Critical aspect | Recycling technologies |
|------------------|----------|-----------------|------------------------|
| Anode            | Ir, Ru   | Cost, hazard    | HMT\(^a\), PMT\(^b\)  |
| Cathode          | Pt       | Cost            | HMT\(^a\), PMT\(^b\), SED\(^d\), TD, AP\(^e\) |
| Electrolyte      | Ionomer  | Cost, hazard    | N/A, AD\(^f\), AP     |
| Bipolar plates   | Ti       | Cost            | HMT\(^a\), N/A        |

\(^a\) HMT: hydrometallurgical technology. \(^b\) PMT: pyrometallurgical technology. \(^c\) TD: transient dissolution. \(^d\) SED: selective electrochemical dissolution. \(^e\) AP: acid process. \(^f\) AD: alcohol dissolution.

Conventional methods for recovery Pt, Ru, Ir and Ti from composite materials are pyrometallurgy and hydrometallurgy [3]. According to pyrometallurgical method thermal treatment of the materials is carried out in a high-temperature furnace to bring about physical and chemical transformation and enable recovery of valuable metals. In pyrometallurgy processing mechanical pre-treatment is not required and high recovery rates can be achieved. However, it is energy vorous, quite expensive and release highly toxic and corrosive hydrofluoric acid gas.

On the other hand, hydrometallurgy, is the SoA process for Platinum Group Metals (PGMs) recovery. Hydrometallurgical method chemical reactions are carried out in aqueous or organic solvents for metal recovery. The process consists of the following general steps: (i) leaching, (ii) solution concentration, purification and precipitation, and (iii) metal recovery/refining [17]. A mixture of strong acid and oxidizing agent is usually used as leaching agent. Aqua-regia (HCl/HNO₃=3/1) is known to be the best reagent to recover PGMs supported on carbon substrate from spent catalysts and in the most cases allows Pt recovery >95% [18]. After leaching, filtration of the PGMs containing solution is took place to separate solid carbon particles from dissolved metals.

In the solution concentration and purification step, PGMs anions in solution are separated by different techniques. Sulfides, hydroxides and carbonates are widely used for metals precipitation [19]. Pt can be precipitated as (NH₄)₂PtCl₆ salt using NH₄Cl and reused with carbon powder for new catalysts to be recycled [17]. A refining step is required in order to achieve high purity metals in separate solutions. Hydrometallurgical process exhibits higher selectivity, lower energy consumption and more environmentally friendly with respect to pyrometallurgical method. The main drawback of the method is the use of large volume of solvents and the generation of toxic wastewater.

Platinum group metals can be extracted from the catalytic layers of PEMWE with leaching process. However, pre-treatment to delaminate the layers of the MEA is mandatory. On the other hand, in case of PGMs extraction with pyrometallurgy, pre-processing is not required [16]. Although, pyrohydrometallurgy exhibits higher recovery efficiency than hydrometallurgy, safety and environmental issues raise, due to demanding and severe working conditions.
Recycling methods for Ti recovery could provide an important cost reduction in PEMWE technology. Ti which is not a natural element, is normally produced by Kroll process. In general, Ti can be recovered through conventional existing processes based on physical separation (size reductions and magnetic separation). However, when Ti is combined with other elements, a more complex recovery method is required. Main disadvantages of the latter method are the large material and energy expenditures for the process and remain of Ti in the processed materials. Chloride and fluoride recycling technologies can also be used for Ti recovery.

2.2. Novel methods

Recycling of precious electrocatalysts (Pt, Ir) used in PEMWE systems using the above existing methods is usually inefficient or essentially nonexistent due to design constructions, unavailable recycling technologies and the thermodynamics of separation [20]. Duclos et al. [17], proposed hydrometallurgy to recover Pt from catalyst coated membrane (CCM) MEA of a PEM fuel cell system. A series of leaching solutions and separation techniques were examined, obtaining 76% of Pt recovery yield. However, further processing is required to manage remaining solid waste and HCl neutralization.

However, apart from pyrometallurgical and hydrometallurgical processes for CRMs recovery from MEAs, novel recovering technologies has also been developed [16]. The designing of a single process where the entire unit of the stack is subjected to, in order for the precious metals and other valuable materials to be recovered, is highly desirable. Novel methods usually show advanced technical, economic and environmental performance. Selective electrochemical dissolution method is proposed for Pt and carbon support recovery from cathodic compartment of MEAs [21]. Although, high purity Pt is recovered in high yield under mild conditions, reconditioning of carbon support is required in order to be reused. Acid process is proposed for Pt and membrane recovery from MEAs [22]. The main advantages of the method are high Pt recovery yield and low pollution emissions. However, acid process is a time-consuming method and high pH conditions are also required. Recently, M. Carmo et al. [23], proposed ultrasonication to recover both noble metal catalysts materials and ionomer separately without any harmful and pollutant emissions from MEA in PEMWE. The membrane free from catalysts is separated, dried and reused to fabricate new MEAs. Pt and Ir are separately recovered and reused. This is an environmentally friendly and fast process and high recovery yield (>90%) can be achieved.

2.3. MONOLITHOS’ method

Although last decades many novel recycling methods for PGMs recovery from MEAs are addressed, most of them suffer from low recovery yields, negative environmental impact and high operational cost. A single step hydrometallurgical method for PGMs (Pt, Pd, Rh) recovery from spent automotive catalytic converters has been developed by Yakoumis et al., (figure 4) [24].

![Figure 4. Novel hydrometallurgical method of MONOLITHOS for PGMs recovery from spent automotive catalysts [24].](image-url)
An automotive catalytic converter is adapted to the exhaust gas pipe of an internal combustion engine in order to convert toxic gases (CO, HC, NO\textsubscript{x}) into less harmful ones (CO\textsubscript{2}, H\textsubscript{2}O, N\textsubscript{2}) (figure 5). According to Yakoumis et al. [24] single step method, Pt, Pd and Rh are extracted from spent automotive catalytic powder under mild experimental conditions (70 °C, 2 h) using low acidity reagents (3 M HCl, 4.5 M NaCl, 1% v/v H\textsubscript{2}O\textsubscript{2}) and without any thermal pre-treatment or chemical reduction. This method results in recovery rates for Pt, Pd and Rh, namely 100%, 92% and around 60%, respectively. According to Yakoumis et al.’ study [24], a batch of more than 20 commercial spent catalyst samples has been mechanically pre-processed (i.e. sorted, decanned, milled, ground, homogenized and characterized), in order for a 20 kg sample of homogenized fine spent catalytic powder to be derived and to be used for the process optimization. The leaching parameters were optimized by studying HCl molarity of the leaching solution (3-12 M), Cl\textsuperscript{-} anion source (NaCl, AlCl\textsubscript{3}), oxidizing agent concentration and balance of Cl\textsuperscript{-} sources (3/4.5). The recovery rates of the PGMs have been validated through X-ray fluorescence spectroscopy analysis (XRF), where the equipment used has been successfully calibrated to measure low PGM concentrations with high accuracy for all three PGM elements.

![Figure 5. Automotive catalytic converters.](image)

Replicating the application of Yakoumis et al. [24], recycling technique to CRMs recovery from MEAs and the entire stack without disassembly is promising, since the technique is capable in recovering CRMs simultaneously from PEMWE, MEAs and electrocatalysts. Considering the special features of each component the method can be utilized to recover Pt, Ir, Ru and Ti from PEMWE. The experimental conditions such as acidity of HCl solution, the concentration of the oxidizing agent and the solid/liquid ratio should be optimized, in order to design a versatile and environmentally friendly hydrometallurgical method with the highest recovery yield of CRMs from the stack, without being disassembled. X-Ray fluorescence (XRF) spectroscopy will be used for recovery yield validation.

3. Conclusions

The growth of required energy and the increase in fossil fuel resource depletion, have led to the development of alternatives systems for sustainable production of fuels and green energy. H\textsubscript{2} is proposed as a promising alternative source of energy. Eco-friendly and high purity H\textsubscript{2} production by PEMWE has attracted great scientific attention as an effective option to reduce greenhouse gas emissions. PEMWE systems have been already used to produce oxygen for the crew on the Space Stations. Nowadays, the increased development of PEMWE devices that require high purity CRMs (Pt, Ir, Ru, Ti), together with the low availability of these metals compromise their economic feasibility. In this regard, there is an emergency need for an efficient, low cost and environmentally friendly recycling EoL strategy for the recovery of CRMs and high cost materials from PEMWE. The low cost, single step hydrometallurgical process for PGMs recovery developed by MONOLITHOS Ltd. [24] is a promising method for simultaneously CRMs recovery from PEMWE stacks, MEAs and electrocatalysts. In particular, different experimental parameters will be explored to describe the
optimum conditions for recycling of Pt, Ru, Ir and Ti, in high recovery yields from MEAs and the entire stack without disassembly.

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