



Cost-effective PROton Exchange MEmbrane WaTer Electrolyser for Efficient and Sustainable Power-to-H2 Technology

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D2.3 Description of method and parameters with optimized conditions for the CRM recovery from MEAs

WP2 Membrane and MEA development

WP Leader: Dr. Marcelo Carmo/Dr. Meital Shviro (FZJ)
Deliverable Responsible: MONOLITHOS
Deliverable Author(s): Anastasia-Maria Moschovi, Eirini Zagoraiou (MONOLITHOS)



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Table of Content

| | |
|--|-----------|
| Document history | 2 |
| List of Figures | 4 |
| List of Tables | 5 |
| Executive Summary | 6 |
| 1 Introduction..... | 7 |
| 1.1 EoL recycling technologies for CRMs recovery from PEMWE | 7 |
| 1.1.1 MONOLITHOS' hydrometallurgical leaching process | 8 |
| 2 Description of the Membrane Electrode Assembly (MEA)..... | 9 |
| 3 Recycling of CRMs from MEAs..... | 13 |
| 4 Summary | 16 |
| Bibliography..... | 17 |

List of Figures

| | |
|--|----|
| Figure 1. TEM images of the pristine catalysts (a) IrO ₂ and (b) Pt/C. TEM imaging studies performed by Forschungszentrum Julich GmbH (FZJ). | 9 |
| Figure 2. Radiographic series of the development over time in the CCM (Catalyst Coated Membrane), where iridium (Ir) particles detachment is observed. Platinum (Pt) particles in the cathode catalyst layer appear to be more stable, and no catalyst detachment is observed. The electrode side facing the membrane is subjected to extreme stress and faces the most severe delamination. ^[10] | 10 |
| Figure 3. FIB analysis of the catalyst coating: a) and c) Iridium (Ir) layer as anode catalyst; b) and d) platinum (Pt) layer as cathode catalyst. | 11 |
| Figure 4. Two batches of MEAs received by MONOLITHOS for PGMs recovery. | 12 |
| Figure 5. Optical microscopy images of the CLs in MEAs send to MONOLITHOS. | 13 |
| Figure 6. MEA after thermal treatment at 600°C. | 13 |
| Figure 7. MEA after MONOLITHOS' leaching process. | 14 |
| Figure 8. Recycling of Pt from EoL MEAs using MONOLITHOS hydrometallurgical leaching process. | 15 |
| Figure 9. Optical microscopy images of the Nafion membrane after membrane electrode delamination. | 15 |

List of Tables

Table 1. List of MEAs send to MONOLITHOS for hydrometallurgical PGMs recovery..... 12

Executive Summary

Deliverable D2.3 “Description of method and parameters with optimized conditions for the CRM recovery from MEAs” will explore the technical processes and potential pathways for recyclability of the developed CRMs-free and low CRMs content catalysts and MEAs developed in PROMET-H₂ project. Firstly, a short review of the currently available methods to recover CRMs from MEAs will be presented. Consequently, the low cost, environmentally friendly and single step hydrometallurgical leaching process for PGMs recovery developed by MONOLITHOS will be proposed for CRMs recovery from End-of-Life (EoL) MEAs. Different experimental parameters should be explored to describe the optimum conditions for recycling of CRMs (e.g. Pt, Ir, Ru and Ti) from MEAs in high recovery yields. MONOLITHOS succeeded in recovering >99% of Pt content from the first generation of PEMWE EoL MEAs. The present document aims at reporting the main experimental conditions that need to be optimized to design a versatile and environmentally friendly hydrometallurgical leaching process with the highest recovery yields of CRMs from EoL MEAs.

1 Introduction

As the energy demands of the modern world rise increasingly, conventional energy sources, such as fossil fuels, become more and more limited. Hydrogen (H₂) is the simplest and most abundant element in the universe and an ideal source of energy due to its high energy density. Proton Exchange Membrane Water Electrolysis (PEMWE) is a promising technology as a green source of high-purity H₂ production with high efficiency and low energy consumption.

The increased development of PEMWE systems require high amounts of Critical Raw Materials (CRMs) as catalysts (platinum or palladium based catalysts, iridium oxide, ruthenium oxide). State of the art catalysts loading in PEMWE devices is about 0.2-0.5 mgPt/cm² and 2-3mgIr/cm². Due to the low availability and strict cost of CRMs, different pathways are proposed for overcoming commercialization barriers. Recycling of CRMs and high-cost materials from EoL PEMWE devices is one of the most promising solution.

In this report, MONOLITHOS' hydrometallurgical leaching process is presented as a promising method for recycling CRMs from EoL PEMWE in high recovery yields.

1.1 EoL recycling technologies for CRMs recovery from PEMWE

Conventional methods for recovery of PGMs (Platinum Group Metals) from catalytic layers are pyrometallurgy and hydrometallurgy. ^[1] During pyrometallurgical process, thermal treatment of MEAs is carried out at high temperatures without any mechanical pre-treatment. The main drawbacks of the process are the high energy demand and harmful hydrofluoric acid (HF) gas release. On the other hand, hydrometallurgical method exhibits lower energy consumption and is more environmentally friendly than pyrometallurgy. Duclos *et al.*, proposed a hydrometallurgical method to recover Pt from CCMs (Catalyst Coated Membranes), using two different leaching agents, namely H₂O₂/HCl (3 vol.%) and HNO₃/HCl (5 vol.%). ^[1, 2] Although, high Pt recovery efficiency can be achieved (91-93%) under ambient conditions, long reaction time (24h) and further processing to manage the remaining solid waste and hydrochloric acid (HCl) neutralization are required.

Apart from pyrometallurgical and hydrometallurgical processes, novel recovering technologies have also been developed. ^[3] In 2019, M. Carmo *et al.*, proposed a method to recover both noble metal catalysts materials and ionomer membrane separately without any harmful or pollutant emissions from MEAs in PEMWE. ^[4] Recycled electrocatalysts (recovery yield>90%) and membranes can be re-processed and reused for recasting new MEAs.

D2.3 Description of method and parameters with optimized conditions for the CRM recovery from MEAs

Even though, many recycling processes for PGMs and other valuable materials recovery from EoL PEM systems have been addressed, most of them suffer from low recovery yields, high operational cost and negative environmental impact. It is important to note that the existing recovery strategies of PGMs from MEAs are at low TRL (<4) for the time being.

1.1.1 MONOLITHOS' hydrometallurgical leaching process

A single step hydrometallurgical process for PGMs recovery from spent automotive catalytic converters (Three Way Catalysts, TWCs) with high efficiency has been developed by Yakoumis *et al.* [5] According to this method, platinum (Pt), palladium (Pd), and rhodium (Rh) are extracted from spent automotive catalytic powders under mild experimental conditions (70 °C, 2 h) using low acidity reagents (3 M HCl, 4.5 M NaCl, 1% v/v H₂O₂) without any thermal or chemical pre-treatment. The leaching yields obtained 100%, 92%, and 61% for Pt, Pd and Rh, respectively. The management of the solid and liquid wastes is minimized and optimized by the high solid/liquid ratio (70%). Therefore, the mild conditions of the MONOLITHOS' process lead to developing of an environmentally sustainable hydrometallurgical method for the PGMs recycling. This low cost and single step leaching process is a promising method for recycling CRMs from EoL PEMWE.

Taking into account the existing knowledge and also the updated information on characterization, composition and fabrication of both electrocatalysts and MEAs, MONOLITHOS will develop an updated hydrometallurgical leaching process, based on hydrochloric acid and an oxidation mean, in order to recover CRMs (e.g. Pt, Ir, Ru, Ti) from EoL MEAs. During the first year of the project, MONOLITHOS published an article to describe how its method can be applied to the EoL phase of PEMWE to improve techno-environmental and techno-economical performance of CRMs recovery.^[6]

In this report, the information on the potential pathways and the recyclability assessment are addressed. Different experimental parameters (e.g. temperature, concentration of acid, reaction time, oxidation agent) will be studied and elaborated by MONOLITHOS within the project for obtaining the highest recovery yield of CRMs and valuable materials from EoL MEAs.

2 Description of the Membrane Electrode Assembly (MEA)

Formation of the catalyst layers (CLs) by the doctor-blade requires the usage of an appropriate dispersion. The dispersion must be stable during the fabrication and possessing suitable behaviour upon the applied shear force of the doctor-blade. This was achieved by combining the catalyst with the Nafion ionomer while using a suitable mixture out of deionized water, organic alcohols and emulsifier. As anode catalyst IrO_2 from Alfa Aesar was used which possess an Ir content of 85% and a particle size of 6.5 ± 5.3 nm while also agglomerates occurred which were in the range of 17.3 ± 9.8 nm. The BET surface area of IrO_2 was $30 \text{ m}^2 \text{ g}^{-1}$, while for the cathode catalyst Pt/C (HISPEC9100, Johnson & Matthey plc) the BET surface area was $75 \text{ m}^2 \text{ g}^{-1}$.^[7, 8] The used Pt/C catalyst consists of 60 wt. % Pt and 40 wt. % of a not known carbon. The pristine Pt particles size was 3.0 ± 0.8 nm, while the carbon particles range between 25 nm to 50 nm.^[7] Figure 1 shows TEM images of the pristine catalysts used during MEAs fabrication by Forschungszentrum Julich GmbH (FZJ).

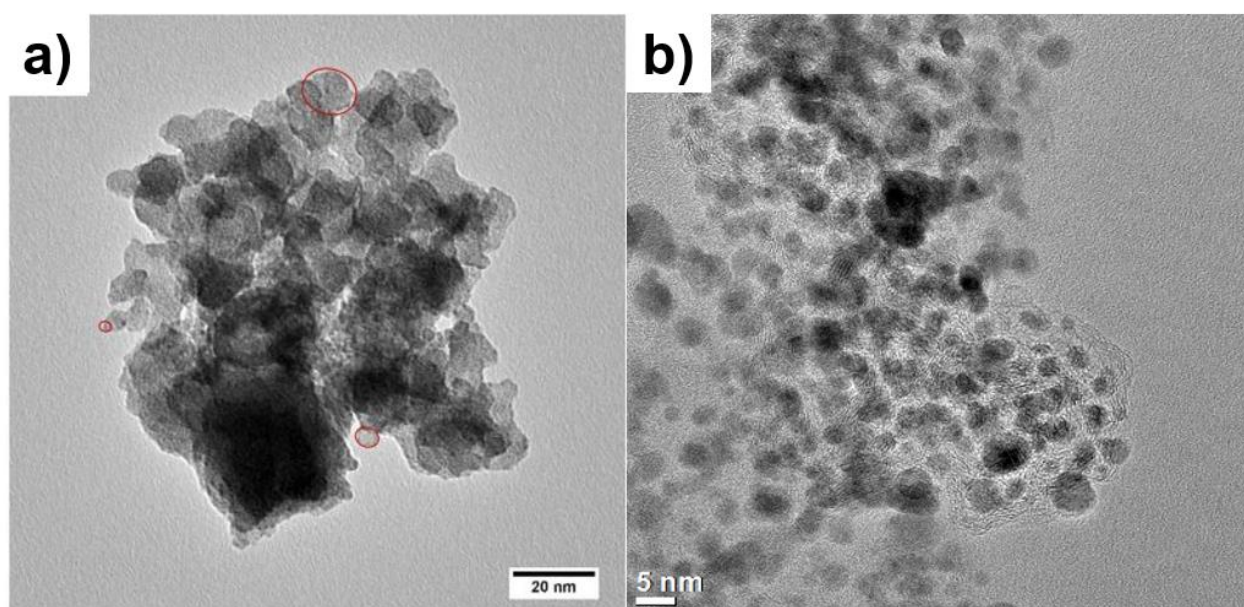


Figure 1. TEM images of the pristine catalysts (a) IrO_2 and (b) Pt/C. TEM imaging studies performed by Forschungszentrum Julich GmbH (FZJ).

The CLs deposited on a PTFE-sheet were used in the decal process after drying. After heating up the assembled CLs together with the N117 membrane, a temperature of $130 \text{ }^\circ\text{C}$ and joining pressure of 1.6 kN cm^{-2} were chosen. The formed Membrane Electrode Assembly (MEA) possessed a membrane thickness of $181 \pm 4 \text{ }\mu\text{m}$, cathode layer thickness of $18 \pm 3 \text{ }\mu\text{m}$ and an anode layer thickness of $5 \text{ }\mu\text{m}$.^[9] The thickness of the CLs is generally due to the loading applied, in case of the anode the

D2.3 Description of method and parameters with optimized conditions for the CRM recovery from MEAs

target loading was $2.2 \text{ mg}_{\text{Ir}} \text{ cm}^{-2}$, while it was $0.8 \text{ mg}_{\text{Pt}} \text{ cm}^{-2}$ for the cathode. The Nafion weight fraction on the anode side was 25 wt. % and inside the cathode layer 20 wt.%. For the hydrometallurgical method applied by MONOLITHOS for the recovery of PGMs, the total MEA size is around 100 cm^2 while the initial electrode area is 25 cm^2 . For the detailed description of the MEA behaviour during operation giving in the following, a different geometric relationship was used, however, the principles are for both MEA geometries the same.

For studying the changes happening to the CLs during operation, in-operando synchrotron radiography was used which showed the catalyst detachment in real-time. The biggest changes can be seen for the anode during operation (Figure 2), while the cathode remained more unchanged. Detachment of the catalysts was due to the blistering of the produced gas, which causes tremendous changes in the initial CL architecture, as can be seen in the images from the post-mortem analysis (Figure 3). However, most of the catalyst detachment occurred after the first 8 hours of operation. After this, no remarkably catalyst detachment occurred. ^[10] For this study a defined measurement protocol was used, which is not the same as used for common electrolysis operation. In principle the mechanism shown, occurs while activation and in the very beginning of a measurement and it extend depends on the CL quality, loading and intermittent operation while activation.

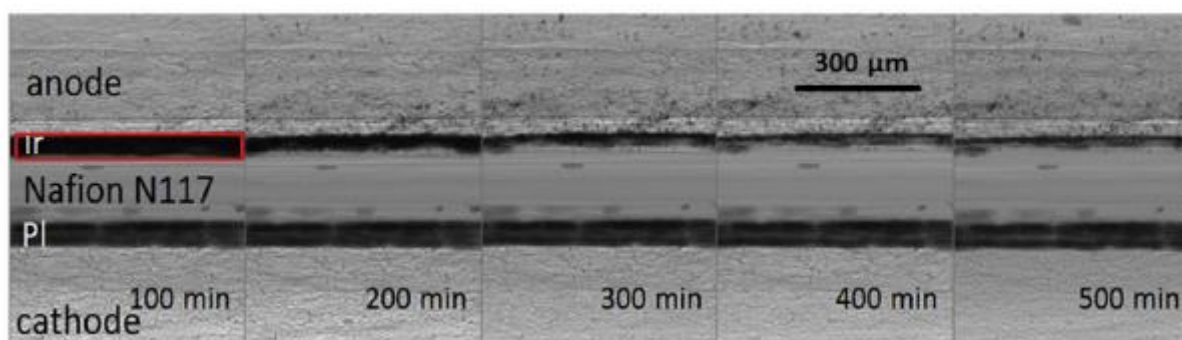


Figure 2. Radiographic series of the development over time in the CCM (Catalyst Coated Membrane), where iridium (Ir) particles detachment is observed. Platinum (Pt) particles in the cathode catalyst layer appear to be more stable, and no catalyst detachment is observed. The electrode side facing the membrane is subjected to extreme stress and faces the most severe delamination. ^[10]

Coupling focused ion-beam (FIB) cutting with scanning electron microscopy allowed to gain insights into the CLs architecture after operation (Figure 3). It can be seen that the cathode layer looked more homogenous than the anode layer. Using image processing software showed that the mean pore diameter was $1.801 \mu\text{m}$ for the cathode and $1.746 \mu\text{m}$ for the anode. However, the Pt particles showed a more elongated shape and a length of nearly 200 nm . ^[10]

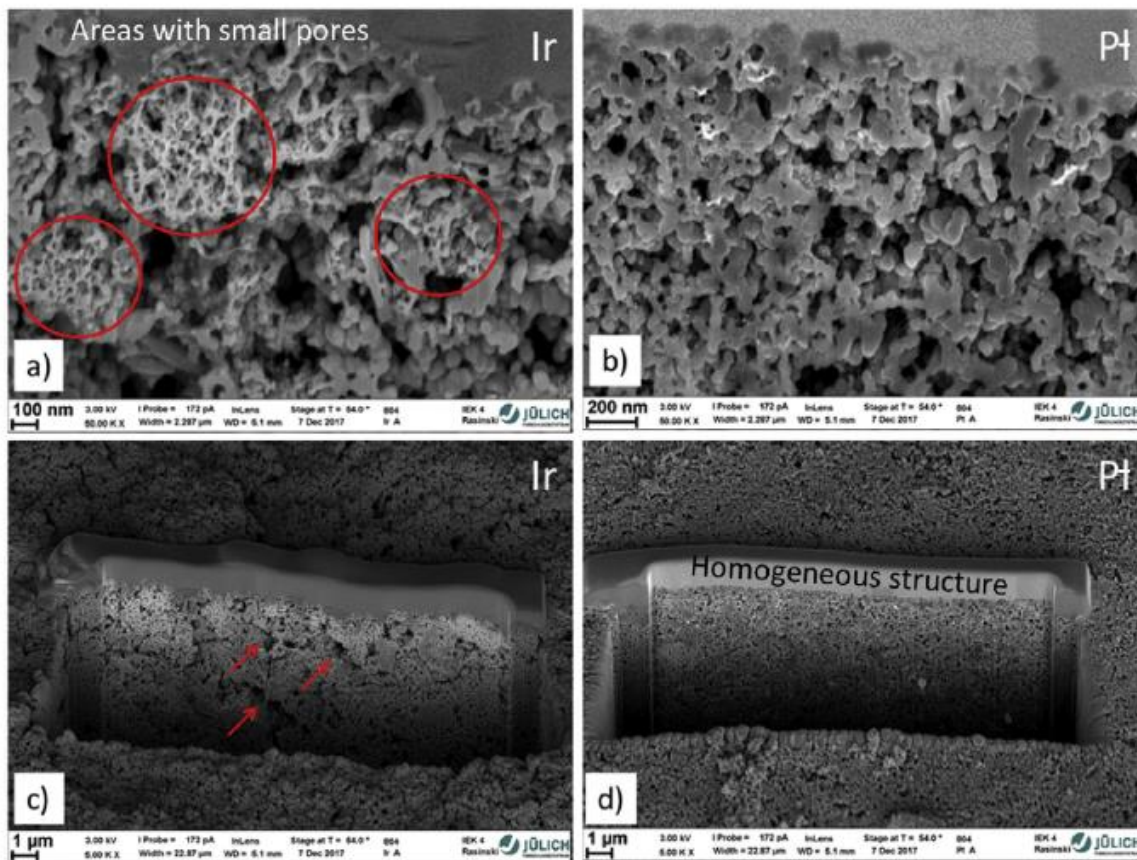


Figure 3. FIB analysis of the catalyst coating: a) and c) Iridium (Ir) layer as anode catalyst; b) and d) platinum (Pt) layer as cathode catalyst.

For testing the hydrometallurgical method applied by MONOLITHOS, several MEAs developed by Forschungszentrum Julich GmbH (FZJ) were chosen as can be found detailed in Table 1 and Figure 4. Mainly high PGMs loaded MEAs were sent to MONOLITHOS because it is more likely that high loaded MEAs are used in industry, while the very low loaded MEAs are used on the research level. Also, most PEM electrolyzers already deployed will use high PGMs loaded MEAs, and therefore recycling of these MEAs should be investigated to prove the feasibility. To test the limits of the recycling process, also very small electrodes were sent (6.25 cm²), Figure 4. We assume that if the PGMs loading becomes too low, then the recycling yields would not be sufficient for the process to be pronounced economically feasible.

Table 1. List of MEAs send to MONOLITHOS for hydrometallurgical PGMs recovery.

| MEA | Anode loading [mg _{Ir} cm ⁻²] | Cathode loading [mg _{Pt} cm ⁻²] | electrode area [cm ²] | Ir [mg] | Pt [mg] |
|------------------|---|---|---|------------|------------|
| MEA20201013_03NU | 2.2 | 0.8 | 25 | 55 | 20 |
| MEA20200922_02NU | 2.6 | 0.8 | 25 | 65 | 20 |
| MEA20200922_01NU | 2.2 | 0.8 | 25 | 55 | 20 |
| MEA20200825_01NU | 0.22 | 0.06 | 6.25 | 1.375 | 0.375 |
| MEA20200723_02NU | 1.03 | 0.85 | 6.25 | 6.4375 | 5.3125 |
| MEA20201029_01NU | 0.24 | 0.05 | 6.25 | 1.5 | 0.3125 |
| MEA20180404_04DH | 2.4 | 0.75 | 25 | 60 | 18.75 |
| MEA20180404_01DH | 2.48 | 0.73 | 25 | 62 | 18.25 |
| MEA20180226_14DH | 2.4 | 0.79 | 25 | 60 | 19.75 |
| MEA20180404_03DH | 2.59 | 0.77 | 25 | 64.75 | 19.25 |
| MEA20171120_06DH | 2 | 0.76 | 25 | 50 | 19 |
| MEA20151105_03DH | 2.19 | 0.84 | 25 | 54.75 | 21 |
| MEA20151105_04DH | 2.33 | 0.78 | 25 | 58.25 | 19.5 |
| MEA20151105_05DH | 2.4 | 0.84 | 25 | 60 | 21 |
| MEA20150914_02DH | 2.19 | 0.82 | 25 | 54.75 | 20.5 |
| MEA20150914_03DH | 2.2 | 0.8 | 25 | 55 | 20 |
| MEA20151105_02DH | 2.28 | 0.84 | 25 | 57 | 21 |
| MEA20201013_01NU | 2.01 | 0.8 | 25 | 50.25 | 20 |



Figure 4. Two batches of MEAs received by MONOLITHOS for PGMs recovery.

3 Recycling of CRMs from MEAs

Before leaching procedure, the CLs' morphology of the received MEAs was studied using optical microscopy technique. Representative optical microscopy images are displayed in Figure 5. According to images obtained, there is no evidence of severe CLs damage (e.g. defects, cracks formation, pits, delamination, etc).

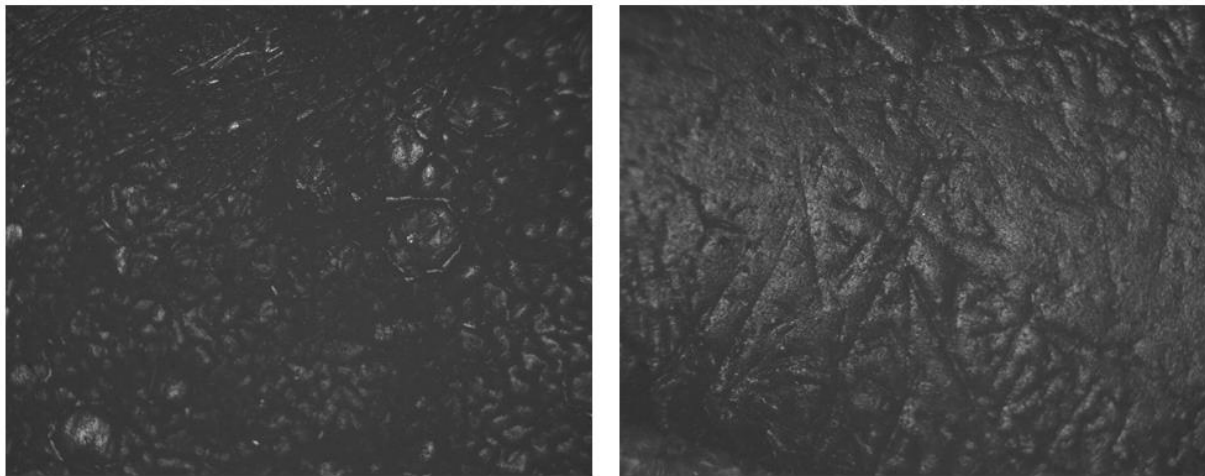


Figure 5. Optical microscopy images of the CLs in MEAs send to MONOLITHOS.

MONOLITHOS studied the recovery of Pt and Ir from the received MEAs using its hydrometallurgical leaching process. For comparison, the recycling of PGMs was also studied after thermal treatment (Figure 6). After calcination at 600 °C and 800 °C, most of the catalytic powder remained in the cup (it was impossible to collect the remaining catalyst).



Figure 6. MEA after thermal treatment at 600°C.

D2.3 Description of method and parameters with optimized conditions for the CRM recovery from MEAs

Due to the low efficiency, high energy demand and hazardous emissions (such as HF) of thermal process, MONOLITHOS proceeded with the recycling of MEAs using its low cost and environmentally friendly leaching process. The used leaching system is based on simple, inexpensive, and inorganic solvents with low acidity, namely 3 M HCl, 4.5 M NaCl, 1% v/v H₂O₂. The use of additional sources of ion chloride helps to avoid the high acidity.

In particular, two approaches were followed: firstly, recycling the entire unit of a MEA and secondly recycling of Pt and Ir from the catalytic powder that obtain after membrane electrode delamination. When MONOLITHOS hydrometallurgical leaching process was performed using the entire unit of a CCM, only a small part of the CLs was delaminated from the Nafion membrane (Figure 7).

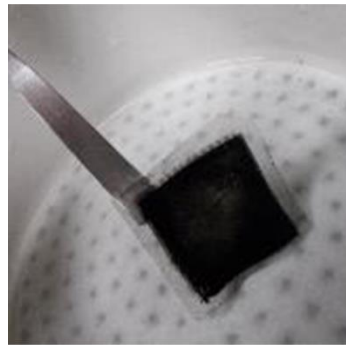


Figure 7. MEA after MONOLITHOS' leaching process.

In order to increase the metal particles that are accessible to the leaching agents, before leaching process, the CCMs were immersed in an alcohol/water mixture to facilitate the separation of the CLs from the membrane. Ultrasonication was used to provide high recovery yield recovery of both the noble metal catalytic materials and the Nafion membrane without the release of hazardous gases. After solvent evaporation, MONOLITHOS hydrometallurgical leaching process was performed to recover Pt and Ir from the remaining catalytic powder (Figure 8). Using XRF analysis, a leaching efficiency higher than 99% was calculated for Pt. Unfortunately, Ir is not accurately determined with XRF MONOLITHOS' instrumentation, and an ICP analysis will be performed in following months, since a new ICP-OES spectrometer will be assessed in MONOLITHOS' facilities.

D2.3 Description of method and parameters with optimized conditions for the CRM recovery from MEAs

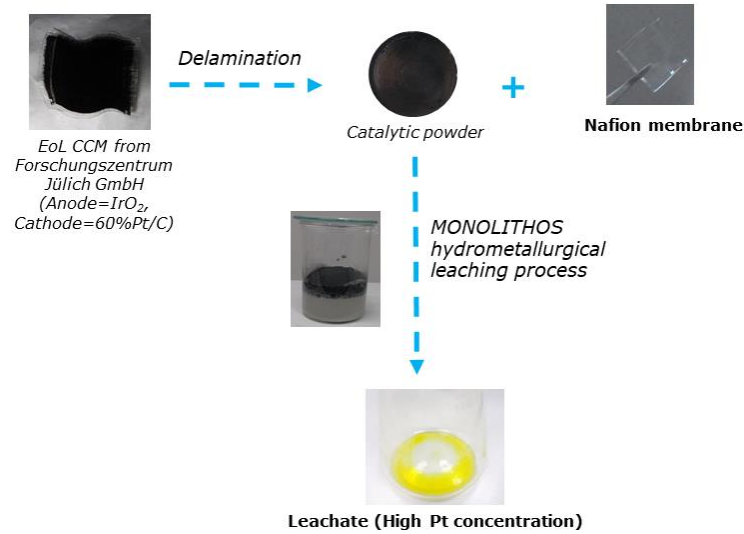


Figure 8. Recycling of Pt from EoL MEAs using MONOLITHOS hydrometallurgical leaching process.

Recycled catalysts can be reused for recasting new MEAs or for other applications. Moreover, Nafion membrane can be regenerated (reactivate the sulfonic groups) and reused in the catalyst layer as ionomer and/or recasting new membranes.

The morphology of recovered Nafion membranes (after membrane electrode delamination) was studied using optical microscopy technique (Figure 9). The deformations (creases) that are mainly observed in the Nafion coated part (catalyst layer was coated on this side) can be probably attributed to the MEA fabrication (e.g. catalysts deposition, MEA assembly by pressing the catalyst coated electrodes with the membrane inside a cell) and/or long-term membrane operation.

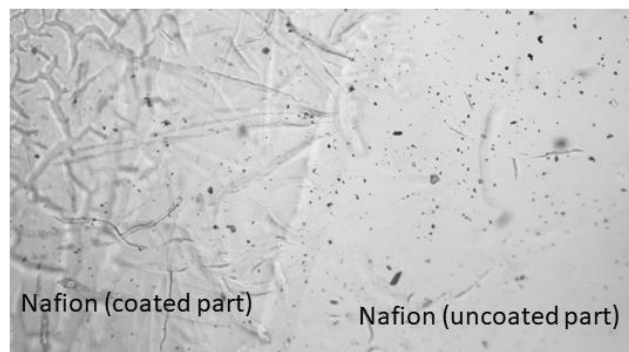


Figure 9. Optical microscopy images of the Nafion membrane after membrane electrode delamination.

4 Summary

The low-cost, single-step, and environmentally friendly hydrometallurgical leaching process developed by MONOLITHOS is a promising method for recycling CRMs from EoL PEMWE. More specifically, the leaching process developed by MONOLITHOS achieved a leaching efficiency of more than 99% for Pt from first-generation EoL CCMs. The experimental conditions such as the type of solvents (mild organic solvents), the solvent ratio, and the electrode detachment/peeling from carbon paper or cloth method (soaking a liquid under stirring or ultrasonication to achieve effective catalyst separation) during membrane-electrode delamination step, as well as the acidity of the HCl solution, the concentration of oxidant and temperature during the leaching process, should be optimized to develop a fast, versatile and environmentally friendly hydrometallurgical process for recycling PGMs, with high yield.

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