

Sustainable SoluTions FOR  
recycling of end-of-life Hydrogen  
technologies



## Deliverable D1.5

Pilot-scale plant (TRL5) based on 3 recycling  
technologies for PEMFCs

### Document Details

Due date	31/12/2023
Actual delivery date	20/12/2023
Lead Contractor	HRD (IDO-Lab)
Version	V1_OD (IDO-Lab)
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Input from	CEA
Reviewed by	CEA, Environment Park and University of Ljubljana

### Document Details

<input checked="" type="checkbox"/> PU – Public
<input type="checkbox"/> CO - Confidential, only for members of the consortium (including the EC)



This project has received funding from the Fuel Cells and Hydrogen 2 Joint Undertaking (now Clean Hydrogen Partnership) under Grant Agreement No 101007216. This Joint Undertaking receives support from the European Union's Horizon 2020 Research and Innovation program, Hydrogen Europe and Hydrogen Europe Research.



## Abbreviations

AB	Advisory Board
AD	Alcohol Dissolution
AEL	Alkaline Electrolysis
BMIM-Cl	Butyl-methyl-imidazolium chloride
BMIM-TFSI	1-Butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide
BPP	Bipolar Plate
CCM	Catalyst Coated Membrane
CL	Catalyst layer
CRM	Confocal Raman Microscopy
CRMs	Critical Raw Materials
EoL	End-of-Life
GA	Grant Agreement
GDE	Gas Diffusion electrode
GDL	Gas Diffusion Layer
GPC	Gel Permeation Chromatography
HMT	Hydrometallurgical Process
HRD	Hensel Recycling Deutschland
HTEL	High Temperature Electrolysis
HTH	Hydrothermal Treatment
ICP-OES	Inductively Coupled Plasma Optical Emission Spectrometry
IL	Ionic liquids
LCA	Life Cycle Assessment
LCC	Life Cycle Costing
MEA	Membrane Electrode Assembly
NMR	Nuclear Magnetic Resonance
NP	Nanoparticle
PFSA	Perfluorosulfonic acid
PEMFC	Polymer Electrolyte Membrane Fuel Cell
PGMs	Platinum Group Metals
Pt	Platinum
TGA	Thermal gravimetric analysis
US	Ultrasound Bath
WE	Water Electrolysers
WP	Work Package



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# 1 Introduction

The recovery of CRMs traditionally is being carried out by means of pyrometallurgy. Although this represents a heavy burden for the environment due to the high generation of CO<sub>2</sub>, it has been proved to be the most efficient method to gain back PGMs.

However, Pt and Pt alloys (Pt + Co, Pt + Ru and Pt and Ir in WE) are to be found on PFSA-based carriers, which incineration may cause harmful emissions and would also completely destroy the ionomer membrane.

Being the ionomer itself an interest element to recover and being this goal part of the BEST4Hy project, the investigation of hydrometallurgical and alcohol-dissolution-based techniques makes sense and covers the scope of this deliverable.

## 2 Pilot-scale plant (TRL5) based on 3 recycling technologies for PEMFCs

### 2.1 Hydrometallurgical process (HRD)

#### 2.1.1 Concept, technology, methodology

HRD proposes a hydrometallurgical process consisting of a series of steps to recover Pt from pure CCMs as solid [NH<sub>4</sub>]<sub>2</sub>PtCl<sub>6</sub> salt, ammonium hexachloroplatinate. An efficient technology has already been studied and described by “L. Duclos et al”<sup>1</sup>, which was then adopted by HRD/IDO-Lab and scaled up at TRL5.



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<sup>1</sup> L. Duclos, L. Svecova, V. Laforest, G.Mandil, P.-X. Thivel, “Process development and optimization for platinum recovery from PEM fuel cell catalyst”, Hydrometallurgy 160 (2016) 79–89

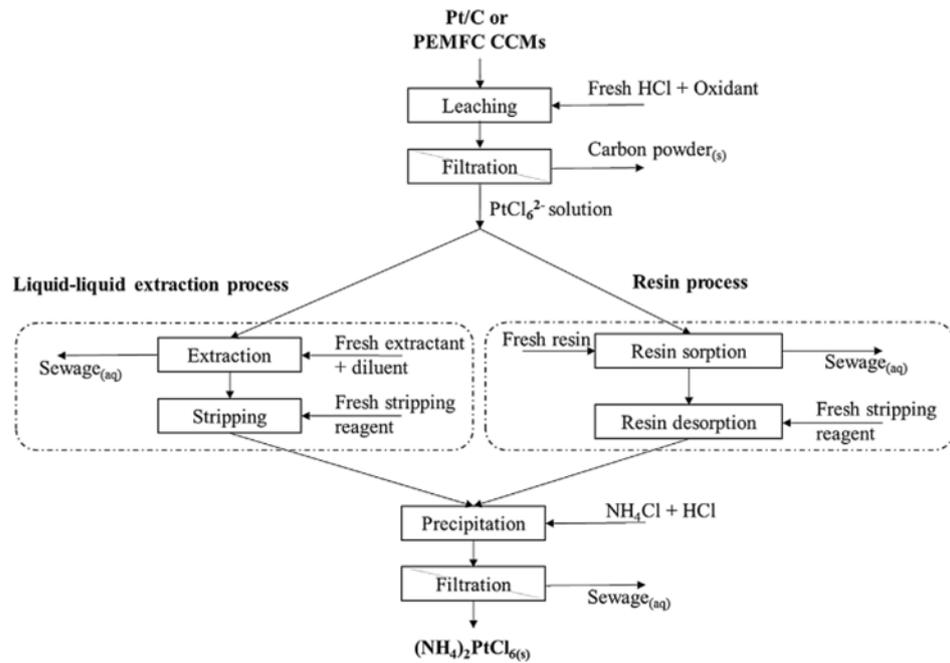
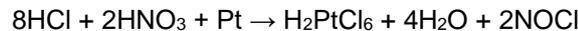


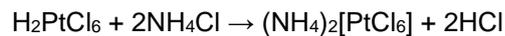
Figure 1 Graphic Description of the Duclos et al. Process

The first step is the leaching process of pure CCMs, where the following reaction takes place in aqua regia:



Due to the fact that Pt is in solution, it is possible to determine the Pt concentration using ICP-OES. This value is considered when calculating the theoretical yield of the Pt salt by mass balance.

The  $\text{PtCl}_6^-$  is then precipitated to Pt-salt with a saturated ammonium chloride solution:



The Figure 2 below shows the workflow of the laboratory scale platinum recovery process at IDO-Lab.

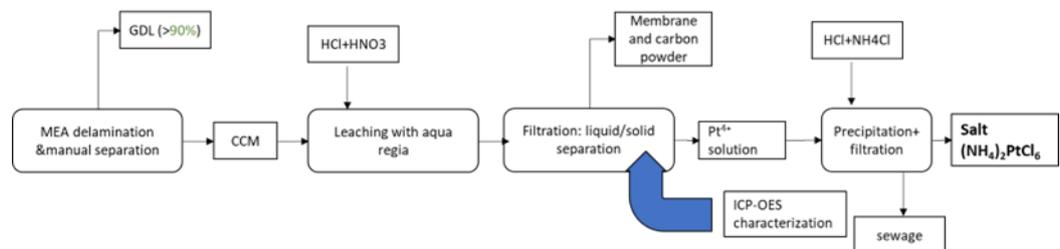


Figure 2 HMT process at IDO-Lab



## 2.1.2 Laboratory optimization

After adjusting parameters, such as batch size, filtration techniques and choice of filter paper, the HMT process was optimized, and high yields of Pt were achieved at TRL3 scale. During the evaluation of the process, these high yields were increased once more, in average reaching 93%, as the table hereunder shows.

Stack	Cell type	initial weight (g)	Leaching	Filtration	Pt-conc. in solution	Precip.	Vac. Filtr.	Pt salt in g	yield in %
<b>NM5-366-240</b>	<b>A (200 h)</b>	<b>103,13</b>						<b>20,2 (total)</b>	<b>93% (average)</b>
Batch#5.1	only CCM	28,87	400 mL	Blue ribbon	9,24%	150 mL	0,2 µm	5,291	87,2
Batch#5.2	only CCM	34,31	400 mL	Blue ribbon	8,46%	150 mL	0,2 µm	6,374	96,5
Batch#5.3	only CCM	39,95	400 mL	Blue ribbon	9,19%	150 mL	0,2 µm	8,026	96,1

Table 1: Evaluated Pt salt results of batch #5 after laboratory optimization.

Task 1.1.2 of WP1, the topic of laboratory optimization dealt with in the first 14 months. The obtained Pt-salt samples were sent to CEA to be further processed there. According to WP2 the Pt precursor was used for the Pt/C catalyst synthesis.

## 2.1.3 TRL5 pilot plant

According to the goal of the WP1, the pilot plant to scale up the evaluated HMT process was set up on the premises of IDO-Lab. For this purpose, a reactor vessel with a volume of 2 litres was installed, which is connected and controlled by an *ad-hoc* software. “Hei-Control PRO” is a software that allows connecting different devices with each other in one interface. You can monitor and control the entire network of devices from one dashboard, even remotely. A reactor can be equipped with useful tools and applications that are necessary during a whole process. Some relevant parameters to be mentioned are:

- Temperature control: not only the ambient temperature can be observed, but the temperature of the recirculating chiller can also be useful to monitor the reaction.
- pH sensors
- Stirrer: the stirrer can be programmed, e.g., if you want to stop stirring at a certain time of the current reaction.
- Pump: installation of a peristaltic pump if you want to feed your reactor continuously.



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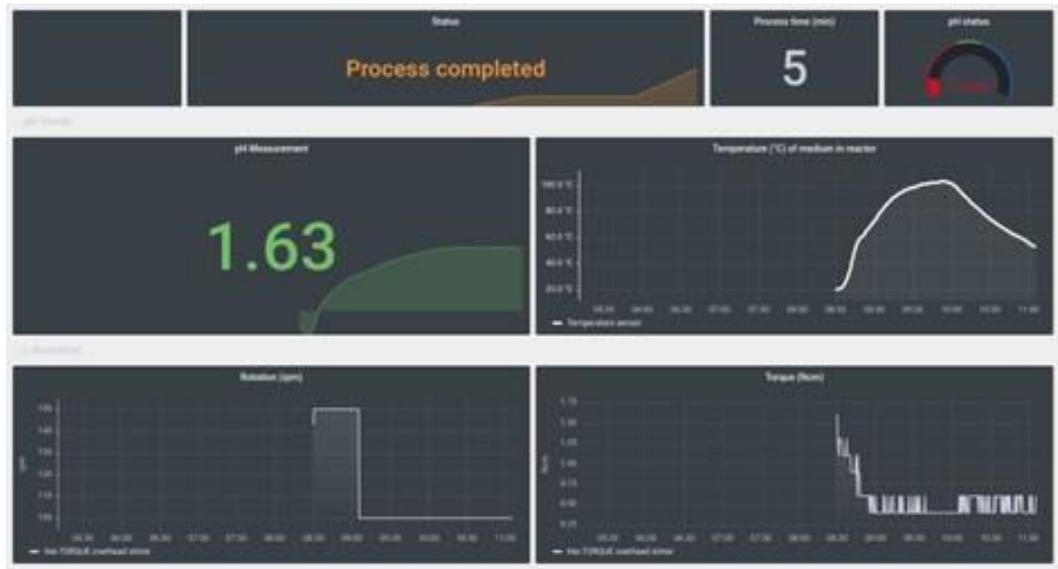


Figure 3: Dashboard of "Hei-Control software"



Figure 4: Pilot plant of the Hydrometallurgical Process



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### 2.1.3.1 Results at TRL5 level

The size of the 2 litre-reactor vessel allows to treat significantly more material, which also has got a positive effect on the Pt yield (>90%), even above the goal (~ 80%) set in the GRANT Agreement. It was also assessed that Pt recovery is not influenced by the age or operative hours of the cells treated.

Results of the evaluation of the HMT process at TRL5 scale were presented at the M30 GA Meeting. Three batches were realized with optimised conditions to show the repeatability.

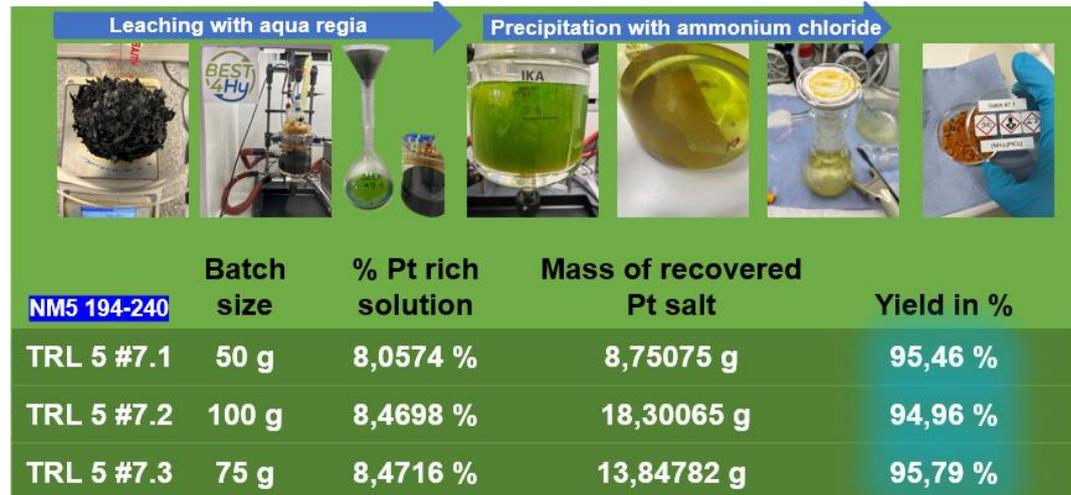


Figure 5: Results of batch #7 at TRL5 scale



Figure 6: recovered Pt as ammonia hexachloroplatinate from batch #7.3

### 2.1.4 Conclusions and perspectives

The hydrometallurgical process presented by HRD/IDO-Lab in this project at TRL5 scale shows how the recovery of platinum as Pt salt works in close-loop. For an open loop scenario, use in other applications is possible, for example, in the semiconductor industry or electroplating. In any case, either close or open loop, the most relevant aspect in favour is that CRMs like platinum will be recycled and reintroduced in the industry in a more



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sustainable way. For instance, the carbon footprint reduction in case of recycled Pt/C, which is reimpregnated into the catalyst layer, is 57%<sup>2</sup>.

## 2.2 Ionomer recovery by alcohol dissolution (HRD)

### 2.2.1 Concept, technology, methodology

HRD proposes a novel technology based on Alcohol Dissolution (AD) for the extraction and re-use of both the precious metals and the ionomer in PEMFC. The process consists of an AD process at high temperature and pressure autoclave reactor. Conventional PEMFCs technologies for recovery, such as HMT and High Temperature Treatment (HTH), which is an incineration process, succeed in salvaging Pt, but no other valuable materials as, for instance, the ionomer membrane. Moreover, the high content of fluoropolymer perfluorosulfonic acid (PFSA) generates emissions of fluorine and hydrofluoric acid processed in HTH. Hydrogen Fluoride (HF) gas is toxic to humans, animals, and plants, and shows also high corrosivity.<sup>3</sup> For all these reasons, the alternative process of AD was identified.

The objective of this task is to demonstrate the high recovery yield % of ionomer (80%), together with the recovery of Pt/C ink (80% of Pt). Traditional processes, as hydrometallurgical and pyrometallurgical, allow to effectively separate only Pt. As already described in D1.1, the development of the ionomer recovery technique by alcohol dissolution (AD) represents a very important milestone of the BEST4Hy project.

The extreme heterogeneity of the ionomer, with many different producers and a variety of products, makes it more difficult to identify the best process methodology.

For instance, Figure 2 reports the very different structure of two commercial ionomers: long side chain - Nafion™ (Chemours) and short side chain - Aquivion® (Solvay).



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<sup>2</sup> Life cycle assessment of platinum recycling from aged PEMFC membrane electrode assembly, University of Ljubljana

<sup>3</sup> Zuber et al, in Recycling of Precious Metals from Fuel Cell Components, Umicore AG&Co KG, Hanau, Germany

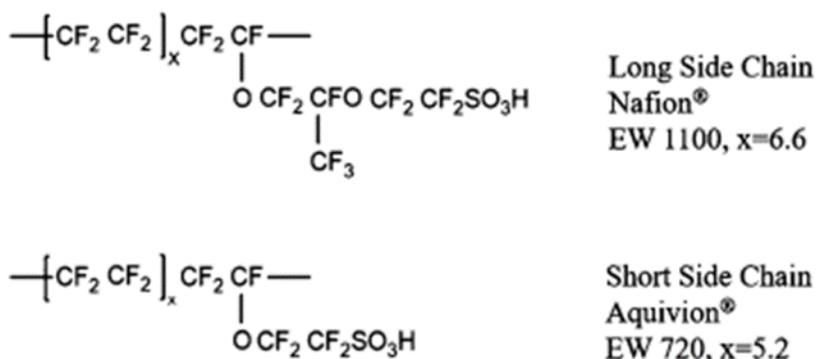


Figure 7 Nafion and Aquivion perfluorinated sulfonic acid ionomer structures<sup>4</sup>

Furthermore, it is also necessary to take into consideration the complex degradation of the polymer during PEMFC stack operation, i.e., effects linked to the ambient conditions that generate mechanical degradation (due to relative humidity cycling, damaging during MEA manufacturing) and chemical degradation (due to low relative humidity, high temperature and high cell voltage). Membranes can be contaminated by ionic species, which might come from metal bipolar plates, humidifiers, tubing materials, air, and dissolution and repositioning of Pt catalyst (Pt band inside of ionomer membrane). The sulphonate sites have a stronger affinity to metal ions, except Li<sup>+</sup>, than for protons, leading to exchange of the protons by the metal ion when present, and this effect can result in partial drying out of membrane, thus, also reducing the proton conductivity. Bruijn et al. studied that during fuel cell operation, the Nafion™ crystallinity changes, especially at relatively dry conditions. It is believed that a high crystallinity corresponds to open ion-channels, and dehydrated, collapsed channels correspond to a decrease in crystallinity.

The AD process developed by HRD and IDO-Lab consists of an alcohol dissolution in a high temperature and pressure autoclave reactor, which is fed with pure CCM in an alcohol/water mixture, followed by different separation steps to split the ionomer solution from Pt/C. Therefore, the mixture is transferred in a laboratory centrifuge, the ionomer

<sup>4</sup> Performance Comparison of Proton Exchange Membrane Fuel Cells with Nafion and Aquivion Perfluorosulfonic Acids with Different Equivalent Weights as the Electrode Binders, Ting Li, Jiabin Shen, Guangying Chen, Shaoyun Guo, and Guangyou Xie; ACS Omega 2020, 5, 28, 17628-17636.



solution is removed by mechanical separation (e.g., decanting) and it is then filtered to guarantee high quality of ionomer - and prevent any particles in the solution.

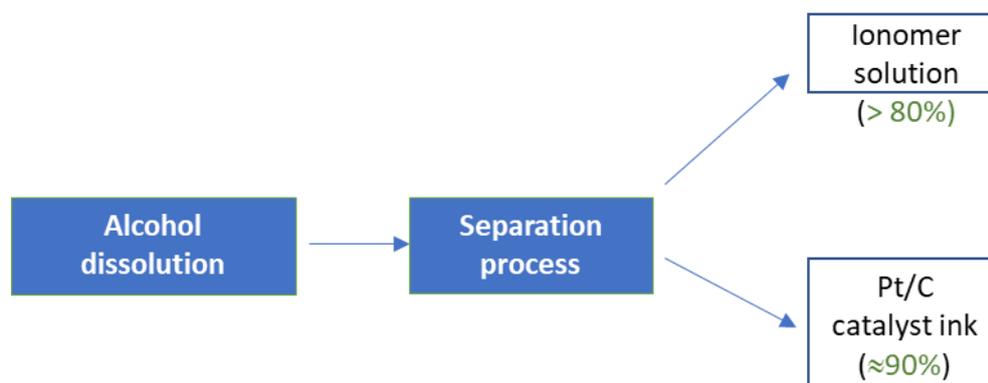


Figure 8: Scheme of IDO-Lab AD process

The ionomer recycled, delivered in solution, will be evaluated by CEA by incorporating it in a catalytic ink using as reference a commercial catalyst to manufacture a MEA. The comparison of the *in-situ* performance on a single cell between this MEA and a reference MEA manufactured with commercial catalyst and ionomer dispersion will permit to characterise the impact of the recycled ionomer material. For this, it is crucial to know the concentration of the ionomer before incorporating and the ratio of the solvent.

The viscosity of the ionomer solution could be measured with a rheometer. After that, the ionomer will be tested incorporating the commercial catalyst at MEA level. Again, the (wt) % of ionomer in the dispersion is an important parameter to know for ink formulation as the ratio of the solvents. To get this information, external labs with the right lab equipment to do organic analysis have been contacted. In addition to the possibility of structure elucidation, it should be clarified whether it is possible to determine the concentration. At this moment the ionomer can only be identified, but not quantified.

The involvement of Solvay (as internal Advisory Board member) has helped the consortium at the beginning of this phase to identify the ionomer material present in the solution prepared by IDO-Lab, adding some meaningful information (degradation, contamination, lower quality).

The degradation of the ionomer chain via backbone rupture can be detected via gel permeation chromatography (GPC) and the C-HSO<sub>3</sub> cleavage via Solid-state NMR spectroscopy and MAS and/or titration.

## 2.2.2 Laboratory optimization

The process was developed by first identifying the best solvent and then the steps required to separate ionomer and the Pt rich component.



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In the experimental documentation of “Solubilization of Nafion™”<sup>5</sup> the investigation of solubility of Nafion membrane is described by using different alcoholic solvents. This was the first approach at IDO-Lab to observe the dissolution behavior of the sample, which was a mixture of CCM and GDL. Since only ionomer components are soluble in alcohol, this technology showed as promising for a clear separation of ionomer and ink.



*Figure 9: Dissolution tests with different alcoholic solvents*

In his study, Wegg also describes that the dissolution of Nafion™ improves at high pressure and high temperature. Therefore, further attempts were made using pressure vessels for the microwave. A measurement of vapour pressure in the reactor during the reaction could not be made because there was no pressure sensor for these parts.

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<sup>5</sup> Wegg, Benjamin. 2002. „Solubility Studies of the Nafion® Perfluorosulfonated Ionomer”



Figure 10: Dissolution tests using pressure vessels.

Even with very limited volume per vessel, an improvement in solubility of the sample was evident.

Two alcoholic solvents were compared with each other. Both solutions showed the same results after the process. Because methanol is a toxic solvent, ethanol should be chosen for future experiments. Economically speaking ethanol is also better than methanol, being cheaper.

Solvent	Solubility	Comment
Methanol	✓	toxic
Ethanol	✓	more ecofriendly

Table 2: Solubilities of different alcoholic solvents on CCM

The next challenge was the separation of the fractions: Pt/C ink and ionomer solution. Two different filtration steps were tested as shown in Figure 9. The conventional filtration technique with a blue-ribbon filter paper was unsuccessful because the ink ran through the filter paper. Another separation technique is the vacuum filtration. Cellulose filter papers with different mesh sizes were used. The filtration steps often failed due to filter clogging hence the opportunity of a pre-filtration step was evaluated. Soon, contact was established with manufacturers to obtain corresponding offers for a laboratory centrifuge. The aim is to separate the coarse part so that clogging is prevented during vacuum filtration.

Filter	result	Comment
Blue ribbon	x	
Cellulose 0.2 $\mu\text{m}$	x	Vacuum filtration
Cellulose 0.45 $\mu\text{m}$	✓	Vacuum filtration

Table 3: Choice of filter paper and filtration techniques

### 2.2.3 TRL5 pilot plant

IDO-Lab optimized reliable, cost-effective, and efficient operating procedures by choosing parameters like ethanol/water mixture as solvent at TRL3. Temperature and time parameters were chosen so that the experiments ran most efficiently. These optimized routines and operating procedures fed the design of the pilot plant, consisting of a low-



pressure reactor and a laboratory centrifuge with some accessories to treat from small to larger volumes.

The reactor should be built taking the following parameters into account:

- Size / volume (proportional to number of cells to be treated at the same time)
- Temperature (heating: up to 200°C)
- Pressure (see Table 5)
- Compatibility with used solvents
- Easy to handle for the operator
- Stability

Since the pressure of the solvents could not be measured during the lab scale processes, experimental chemistry data estimating the pressure of ethanol at specific temperatures were used here. Accordingly, the reactor should be able to withstand a pressure of about 10 bar when working in the range of 100°C – 150°C. Offers were obtained from various manufacturers.



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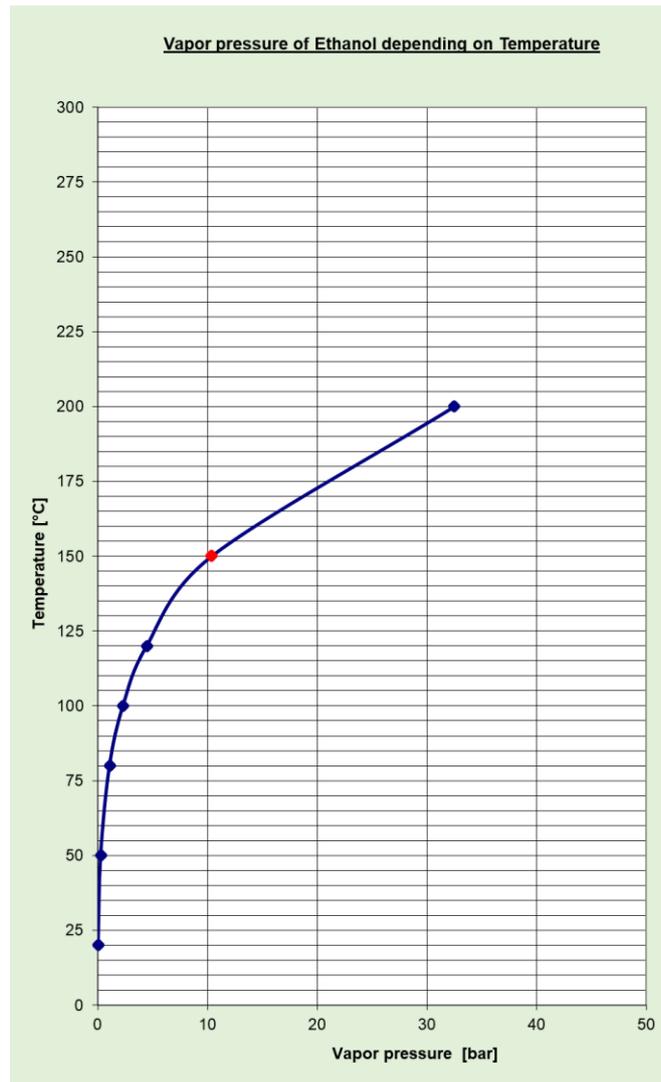


Table 4: Vapor pressure of ethanol (Dr. H. Thies, Ciba Geigy, 30.01.1987)

The centrifuge had already been selected and ordered according to appropriate criteria, e.g., cooling system, volume and type of solvent. Finally, hereafter the scheme of the TRL5 scale-up process plant which has been built up at IDO-Lab seat:

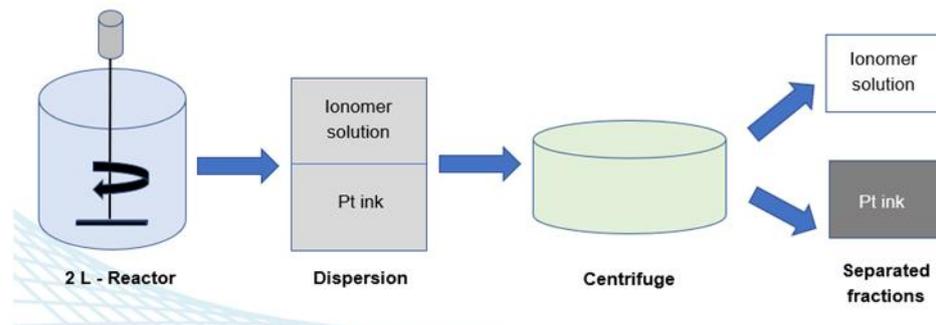


Figure 11: TRL5 scheme of AD process

The following structure could be realized:

### Low Pressure Reactor NR-3000

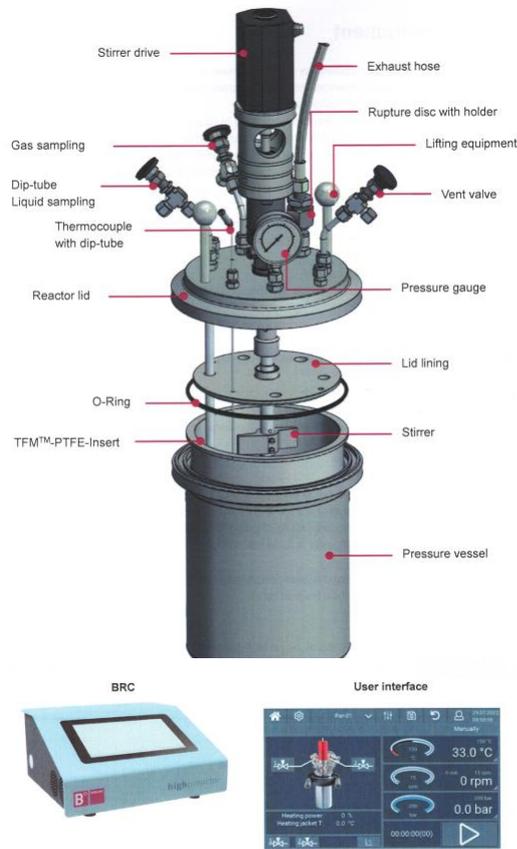


Figure 12: Low-pressure reactor NR-3000 and BRC Controller

The pressure laboratory reactor is employed as a reaction vessel for chemical effects and material tests which are performed under excess pressure. Increased pressure can be produced by the addition of gases or by heating the reaction solution in the sealed vessel. Pressure and temperature sensors are available to track the progression of temperature and pressure in the unit. These also allow the progression of values to be recorded by a PC as well as displaying them on a digital temperature and pressure monitor.

The BRC process controller can be used universally as a regulator for loads up to a power consumption of 3000 W. The control parameters of the PID controller can be freely programmed for different temperature ranges.

### Centrifuge Allegra V-15R



Figure 13: Centrifuge Allegra V-15R

The Beckman Coulter Allegra V-15R refrigerated centrifuge is a bench top centrifuge that can be used for the separation of components using relative centrifugal force. It can be equipped with different rotors.



With different type of rotors, a wider range of centrifugation application is possible. The large swinging-bucket has a maximum capacity of 3000 mL, which is also the capacity of the low-pressure reactor, up to a maximum speed of 4700 rpm. If higher G-force is needed, the fixed angled rotor will allow higher rotation (max. 11360 rpm), but it has a maximum capacity of only 400 mL. Both rotors can be used up to 4°C with a density rating of 1,2 g/mL at maximum speed.



Figure 14: AD Pilot plant at IDO-Lab

### 2.2.3.1 Results at TRL5 level

The results from the AD process at IDO-Lab could be confirmed and evaluated. Like the process described for batch #8.2, it was possible to separate the ionomer from the ink with the same parameters. Moreover, the initial weight of 100 grams shows that the aimed batch size was reached.

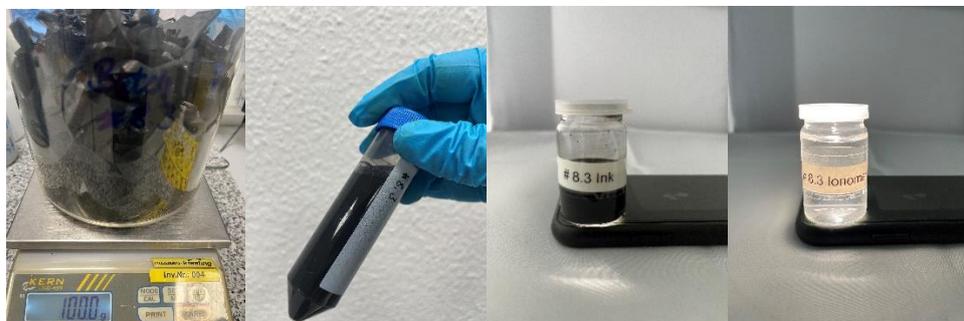


Figure 15: Batch #8.3: from initial weight to the separated fractions Pt ink and ionomer solution

The F-NMR spectra of the obtained ionomer solution show the expected signals for the ionomer type, even after recycling.

An example how a F-NMR of an ionomer should look like was given. A figure from literature Journal of Polymer Science shows the chemical shift and signals where ionomers can be detected at.



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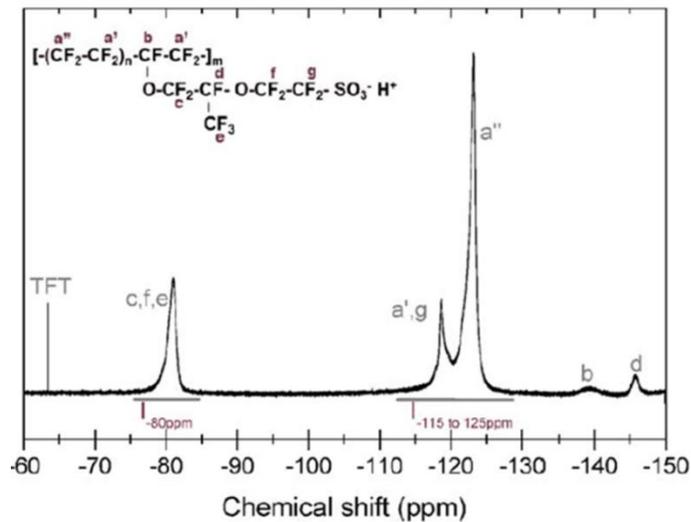


Figure 16: Chemical shift: example F-NMR spectrum of an ionomer, figure from literature *Journal of Polymer Science, Part B: Polymer Physics* 2016, 54 2210-2222

Accordingly, there are main peaks at 80 ppm and from 115 ppm to 125 ppm. Fortunately, exactly these peaks can be clearly seen on each spectrum of all samples.

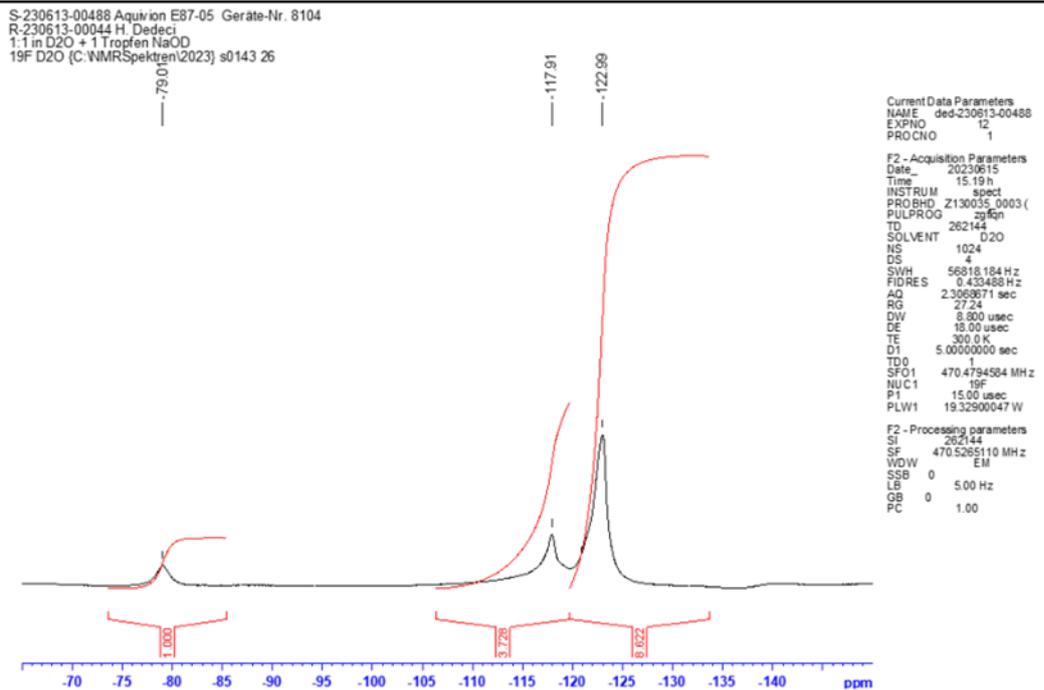
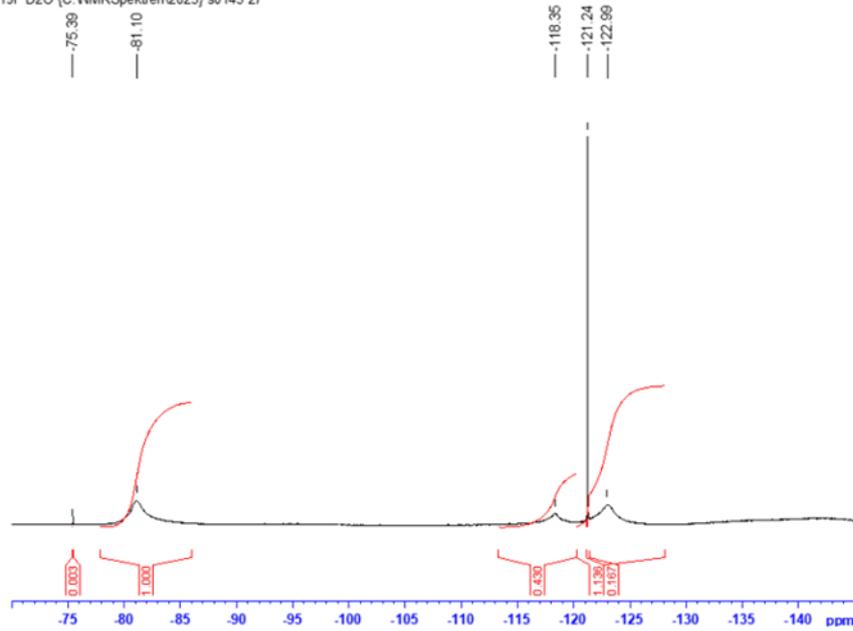


Figure 17: F-NMR spectrum of sample #1: Aquivion (reference material)



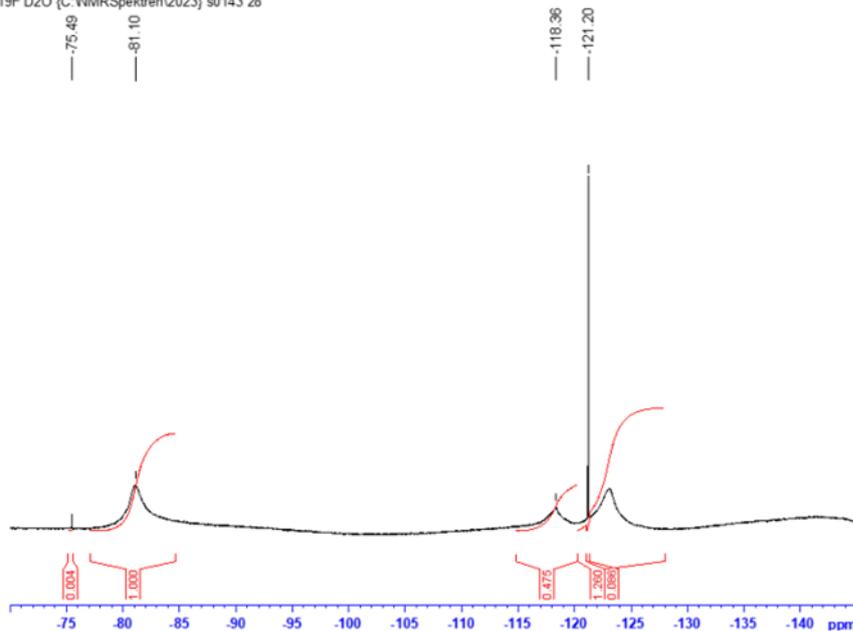
S-230613-00486 #8.1a Geräte-Nr. 8104  
R-230613-00044 H. Dedeci  
1:1 in D2O + 1 Tropfen NaOD  
19F D2O (C:WMRSpektren(2023) s0143 27



Current Data Parameters  
NAME ded-230613-00486  
EXPNO 10  
PROCNO 3  
F2 - Acquisition Parameters  
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Time 6.25 h  
INSTRUM spect  
PROBHD Z130035\_0003(  
PULPROG zgpgn  
TD 262144  
SOLVENT D2O  
NS 1024  
DS 4  
SWH 56818.184 Hz  
FIDRES 0.433488 Hz  
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RG 34.25  
DVI 8.800 usec  
DE 18.00 usec  
TE 300.0 K  
D1 5.0000000 sec  
TD0 1  
SFO1 470.4794584 MHz  
NUC1 19F  
P1 15.00 usec  
PLW1 19.3290047 W  
F2 - Processing parameters  
SI 262144  
SF 470.5265110 MHz  
WDW EM  
SSB 0  
LB 5.00 Hz  
GB 0  
PC 1.00

Figure 18: F-NMR spectrum of sample #2: Batch #8.1

S-230613-00487 #8.2a Geräte-Nr. 8104  
R-230613-00044 H. Dedeci  
1:1 in D2O + 1 Tropfen NaOD  
19F D2O (C:WMRSpektren(2023) s0143 28



Current Data Parameters  
NAME ded-230613-00487  
EXPNO 10  
PROCNO 1  
F2 - Acquisition Parameters  
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PULPROG zgpgn  
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DS 4  
SWH 56818.184 Hz  
FIDRES 0.433488 Hz  
AQ 2.3068671 sec  
RG 34.25  
DVI 8.800 usec  
DE 18.00 usec  
TE 300.0 K  
D1 5.0000000 sec  
TD0 1  
SFO1 470.4794584 MHz  
NUC1 19F  
P1 15.00 usec  
PLW1 19.3290047 W  
F2 - Processing parameters  
SI 262144  
SF 470.5265110 MHz  
WDW EM  
SSB 0  
LB 0.30 Hz  
GB 0  
PC 1.00

Figure 19 F-NMR spectrum of sample #3: Batch #8.2

For further detailed investigations, an improvement of experimental conditions would be helpful (e.g., higher sample temperature, variation of concentration and pH value etc.) With sharper signals, a more detailed analysis applying line fitting may be feasible.

Another way to characterize the ionomer is infrared (IR) spectroscopy, which is the most widely used analytical technique. Ion exchange properties are used for assignment of



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ionomer peaks, such as (C – C), (CF<sub>2</sub>), (C – O – C) or (SO<sub>3</sub><sup>-</sup>) bands.<sup>6</sup> Four samples were prepared and characterized by an external organic lab, ASO (Analytical Service Obernburg):

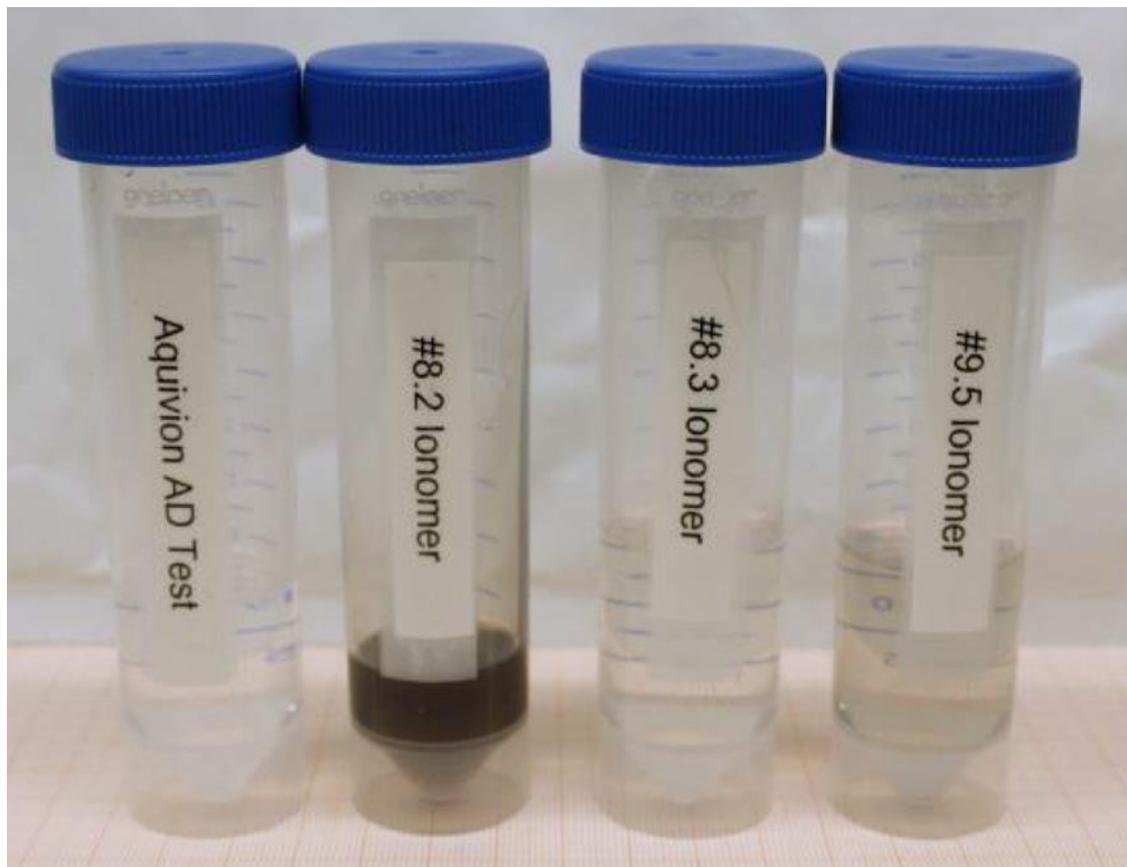


Figure 20 Prepared samples for IR spectroscopy

The following spectra show detected molecule bands and the presence of each ionomer.

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## 1. Aquivion AD Test

virgin membrane which went through the whole AD process (SOLVAY® ionomer)

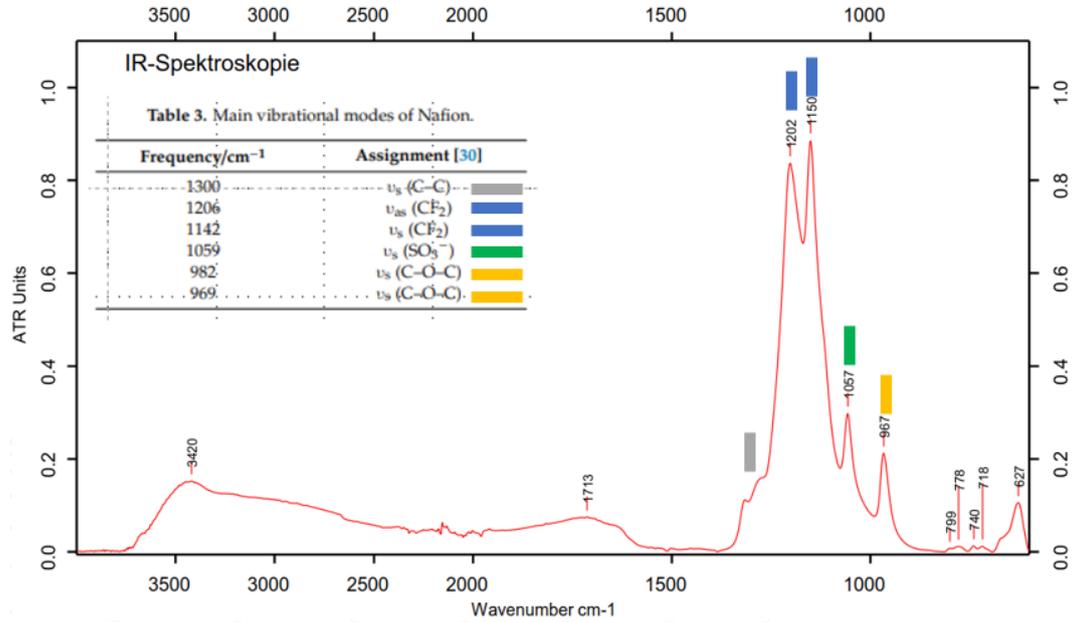


Figure 21 IR spectrum of Aquivion AD Test

## 2. #8.2 Ionomer (from PEM-FC)

product after AD process and evaporation of water and alcohol (Nafion® ionomer)

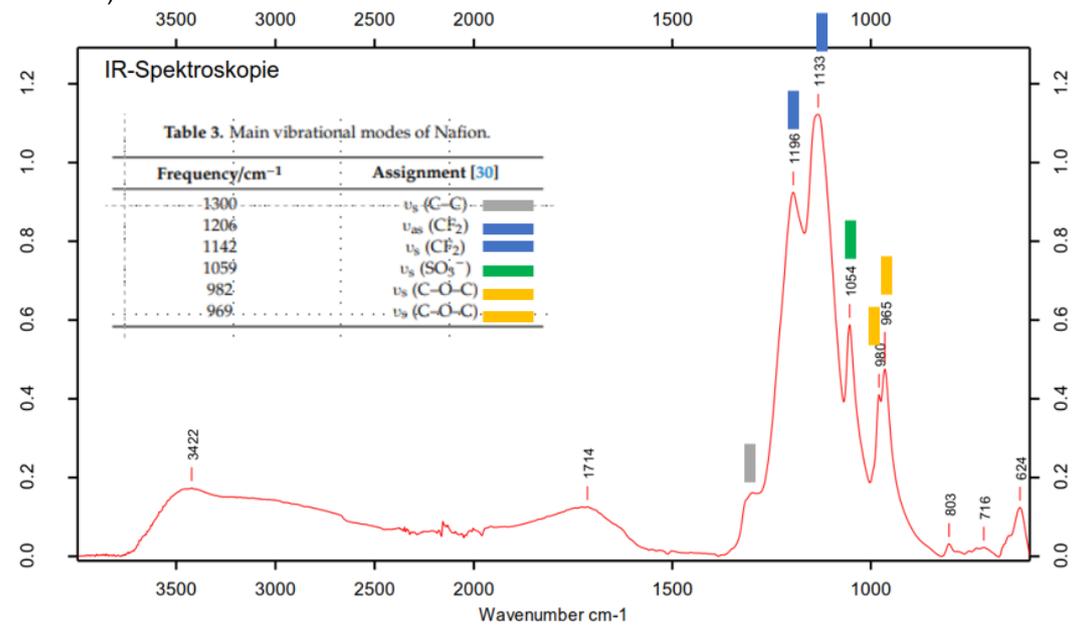


Figure 22 IR spectrum of #8.2 ionomer (from PEM-FC)

3. **#8.3 Ionomer (from PEM-FC)**  
 same as #8.2 except evaporation

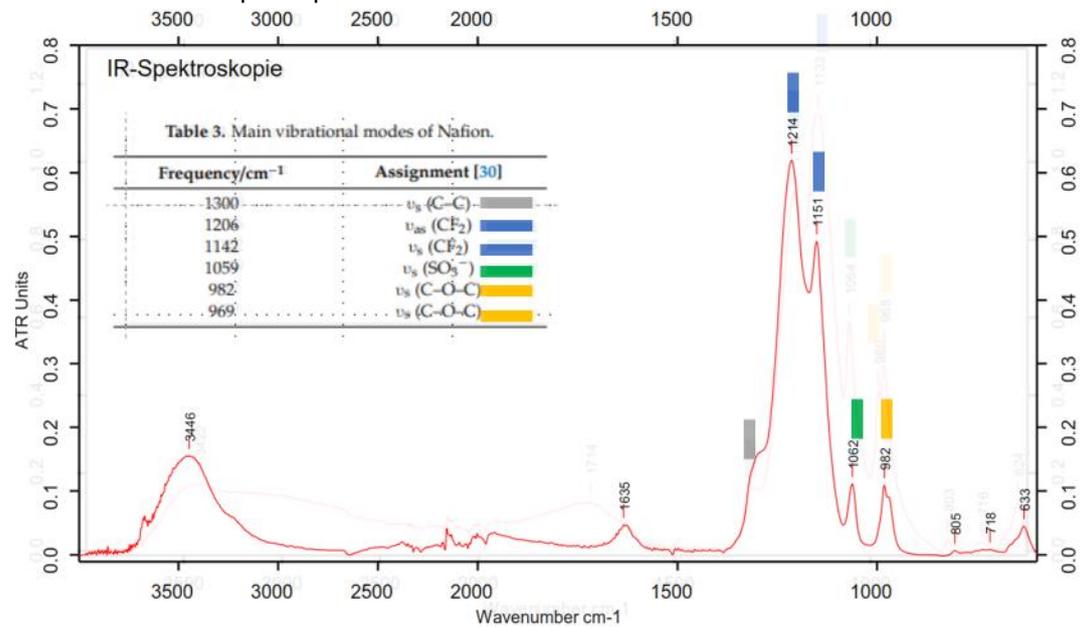


Figure 23 IR spectrum of #8.3 ionomer (from PEM-FC)

4. **#9.5 Ionomer (from PEM-WE)**  
 solution after AD process (Nafion® ionomer)

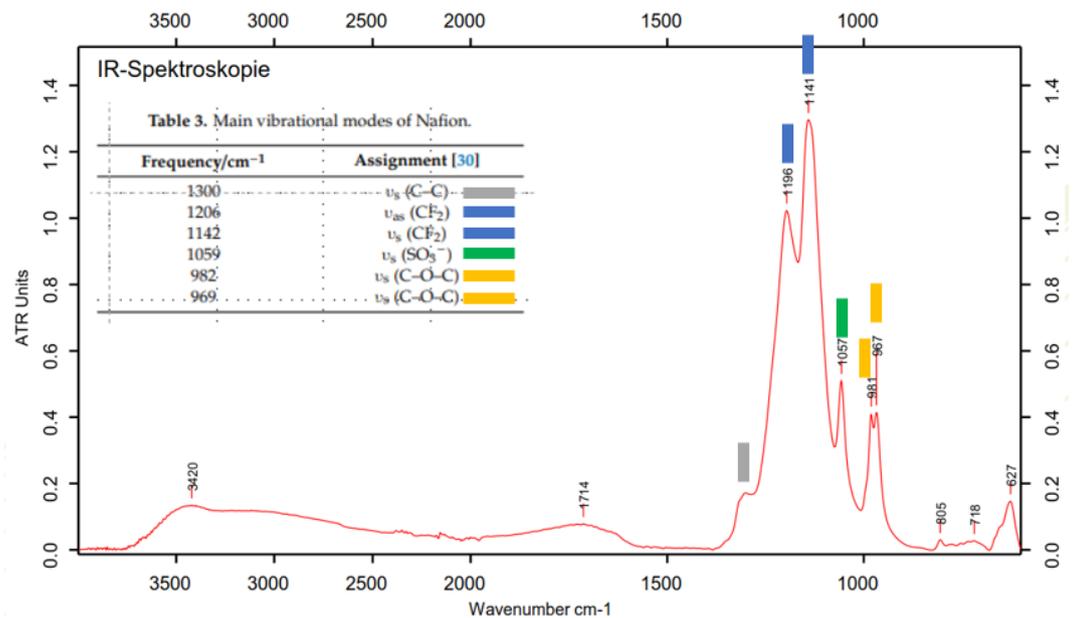


Figure 24 IR spectrum of #9.5 ionomer (from PEM-WE)

A further analytical technique was kindly provided and recommended: Confocal Raman Microscopy (CRM). CRM allows quantification of the EW of PFSA and is a robust method in measuring parameters such as membrane thickness, swelling and water uptake. A study on the ionomer properties of PFSA membranes with CRM was published in the Journal of

Membrane Science.<sup>7</sup> The feasibility was evaluated with the reference sample “Aquivion AD Test”, which CRM spectrum is shown in Figure 25. A reference spectrum for the tested Aquivion ionomer was found in literature.<sup>8</sup>

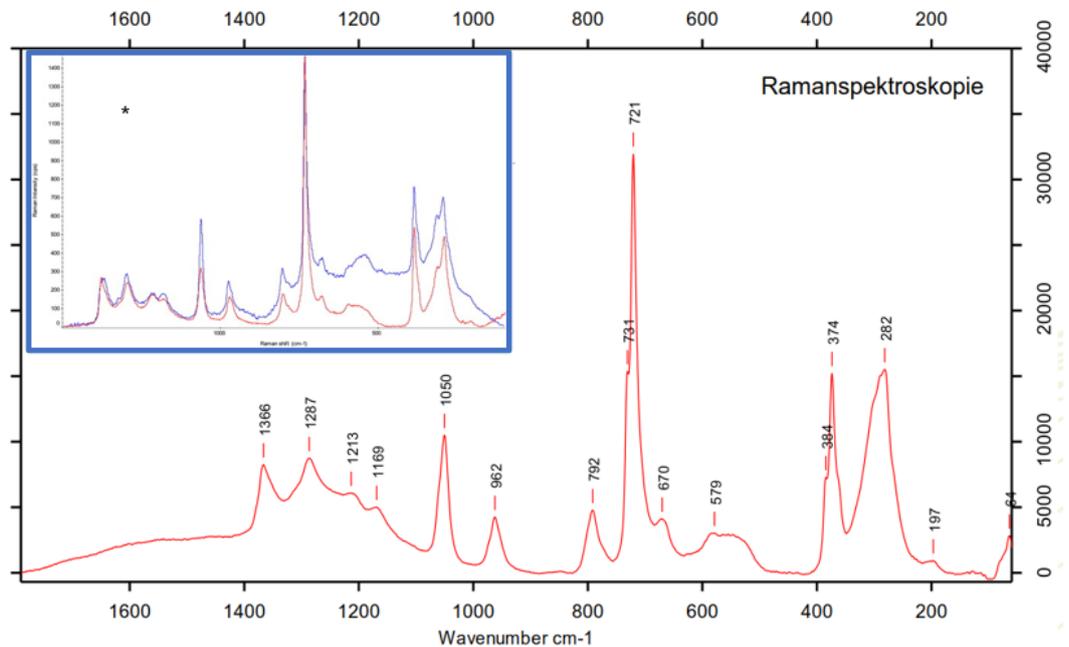


Figure 25 CRM spectrum of Aquivion AD Test and reference spectrum from literature

<sup>7</sup> Maximilian Maier, Dunia Abbas, Miriam Komma, Muhammad Solihul Mu'min, Simon Thiele, Thomas Böhm, A comprehensive study on the ionomer properties of PFSA membranes with confocal Raman microscopy, *Journal of Membrane Science*, Volume 669, 2023, 121244, ISSN 0376-7388, <https://doi.org/10.1016/j.memsci.2022.121244>. (<https://www.sciencedirect.com/science/article/pii/S0376738822009899>)

<sup>8</sup> Stefano Radice, Claudio Oldani, Luca Merlo, Massimiliano Rocchia, Aquivion® PerfluoroSulfonic Acid ionomer membranes: A micro-Raman spectroscopic study of ageing, *Polymer Degradation and Stability*, Volume 98, Issue 6, 2013



The collected PGM containing ink from Batch #8.2 was processed as described in the HMT part until a platinum-concentrated solution was obtained and characterized by ICP-OES.



Figure 26 HMT route of recovered PGM ink from AD process and final products, showing the initial material (CCM), PGM solution, ionomer solution and recovered carbon from CCM)

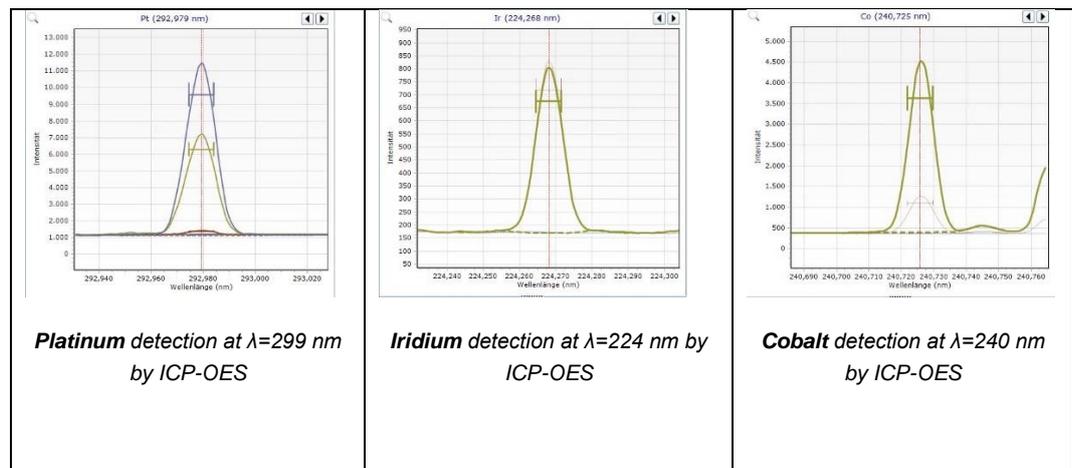


Figure 27 Characterization of PGM ink by ICP-OES

### 2.2.3.2 Patent

Back in June 2023, a patent attorney was contacted and the decision to have our method patented made - for the moment within Germany, but possibly in the next future in other countries, too. On this basis, BEST4Hy will have the opportunity to go beyond the SoA, paving the way for a well-established and cost-effective recovery of valuable materials from PEMFCs devices. Moreover, HRD will be one of the first Recycling Centres to study and implement the technology, so to improve the process and make it more solid from an industrial point of view.



This project has received funding from the Fuel Cells and Hydrogen 2 Joint Undertaking (now Clean Hydrogen Partnership) under Grant Agreement No 101007216.



## 2.2.4 Conclusions and perspectives

Hensel Recycling and IDO-Lab have developed a novel technology that allows two PEMFC membrane components to be separated from one another using an alcohol dissolution process in a low-pressure reactor at TRL5 scale. In this way, in addition to the Platinum ink, the ionomer is also recycled in a cost-effective and environmentally friendly manner, because of the absence of oxidizing acids or high temperatures which leads to corrosive fluorine emissions. Public and political interest focus on the topic of ionomer since the EU ban on PFAS is being discussed. In addition, the recovery of the carbon described above produces hardly any waste in the entire recycling process.

The technology could be further developed to better investigate and understand the following aspects:

- Selection of other solvents (e.g., isopropanol or butanol), which can lead to better separating conditions.
- Use of industrial centrifuges, which reach higher G-forces as this might allow a one-step separation of the ionomer from the ink.
- Centrifugation tests on virgin materials for comparison
- Reuse of solvent after dissolution process

The last point would lead to the use of a rotary evaporator to recover the solvent and put it back into the process. This mechanism is shown in Fig. 15.

Recycling of Catalyst-Coated-Membranes components (Platinum and Ionomer)

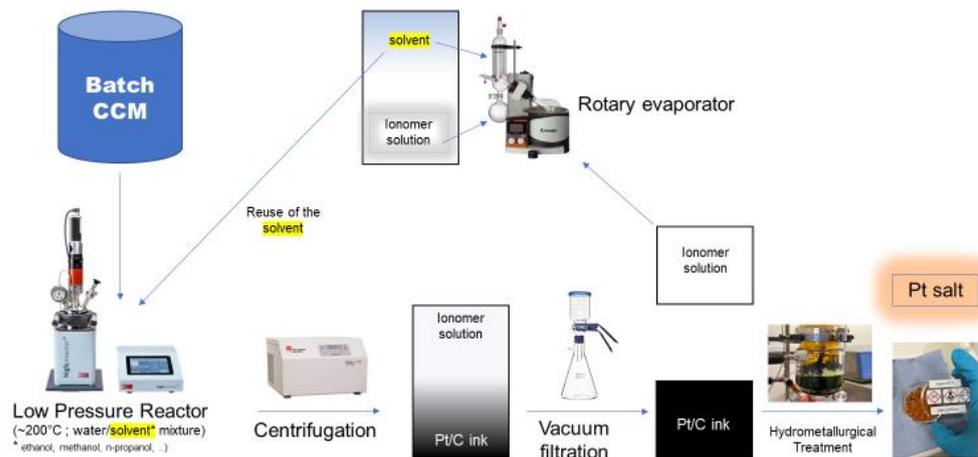


Figure 28: Recycling of CCM components and reuse of the solvent



This project has received funding from the Fuel Cells and Hydrogen 2 Joint Undertaking (now Clean Hydrogen Partnership) under Grant Agreement No 101007216.

## 2.3 Electroleaching and electrodeposition to recover metallic Pt

### 2.3.1 Concept of the process

Innovative Pt recovery ways are needed to avoid the pollutant and toxic emissions of gas and effluents, generated through pyrometallurgical and hydrometallurgical Pt recovery paths. In the following task, CEA Liten propose an efficient non-toxic recovery process for Pt from end-of-life and scraps PEMFC material. The one-step process proposed in a patent [1] was developed and optimized to enable the simultaneous Pt electroleaching and electrodeposition in ionic liquid mixture implying 1-Butyl-3-methylimidazolium chloride (BMIM Cl) and 1-Butyl-3-methylimidazolium trifluoromethanesulfonate (BMIM TFSI). The electroleaching of Pt directly from the catalyst coated membrane (CCM) was enabled using metal mixed oxide mesh anodes to ensure the full contact of the Pt nanoparticles with both the anode and the electrolyte. The almost complete electroleaching was obtained by adapting several parameters such as chloride concentration, platinum ions concentration, temperature, and process duration. A one-step recovery of Pt was developed, directly from CCM to ionic liquid in sustainable and safe ionic liquid mixture as electrolyte.

#### 2.3.1.1 Presentation of patent

The developed process is based on the existing proof of concept described in the patent EP3263744 A1 2018-01-03. Pt nanoparticles are electrochemically leached at the anode, forming platinum and chloride complexes, and zero-valent platinum is electrochemically deposited at the cathode of the same electrochemical cell. The oxidation and reduction reactions occur in a mixture of ionic liquids as electrolyte, selected for its ability to complex platinum and sufficient fluidity to enable an adequate speed for the circulation of chemical species.

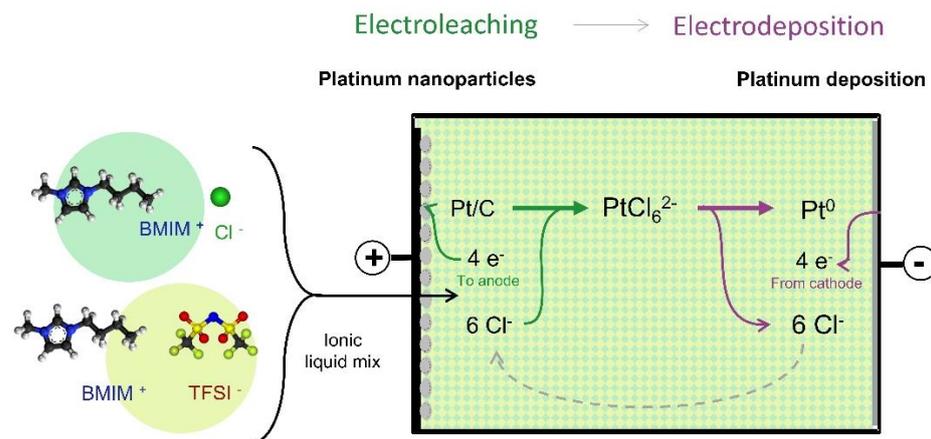


Figure 29: Scheme of simplified electrochemical leaching and deposition process operating mode



### 2.3.1.2 Process application and challenges on real material

There are mainly two types of membrane electrode assemblies (MEA): the catalyst coated membranes (CCM) where the catalyst layer (CL) is coated on the membrane, and catalyst coated substrates (CCS), for which the CL is coated on the gas diffusion layer (GDL), forming a gas diffusion electrode (GDE). Depending on the type of MEA, the application of the electrochemical lixiviation/deposition process will require several development steps.

## 2.3.2 Development of a pilot-scale platinum recovery process in the laboratory

### 2.3.2.1 Results obtained at laboratory scale

On a laboratory scale (4g of electrolyte and 16 mg of CCM material), we were able to demonstrate that simultaneous electroleaching and electrodeposition of platinum had been possible in the mixture of ionic liquids, at the anode and cathode respectively. Optimisation of the parameters to achieve greater than 95% Pt recovery from the CCM in the ionic liquid was achieved after parameter adjustment.

We applied a potential ranging from 0.25V to 2.5V. The optimum is around 2.0 V.

The minimum temperature required for the process is 80°C, to allow homogeneous mixing of ionic liquids. This was swept between 80 and 130°C. Tests carried out at 80 and 90°C resulted in lower electro-leaching yields than those obtained at 100°C. Above 100°C, the TLC was detached from the DSA before the end of the 30 min required to compare the experiments.

The increase in chloride concentration improves electroleaching but the effects on electrodeposition must be attentively considered: the increase in chloride anion concentration reduces the potential required for electrodeposition. A concentration of 1 M was chosen, allowing an electroleaching and electrodeposition potential within the electrochemical window allowed by the mixture of ionic liquids.

Therefore, a potential of 2.0 V (vs Ag+/Ag), applied to the anode, in a mixture of BMIM TFSI and BMIM Cl ionic liquids at 1M chloride and 100°C were identified as the optimum parameters for platinum recovery. The duration of the process depends on the CCM surface to be treated.

### 2.3.2.2 Set up of pilot scale electrochemical Pt recovery

PEMFC containing GDE are less developed and the main PEMFC composition mainly implies CCM. Therefore, an anode system, adapted for the recovery of Pt from CCM was developed. For this aspect, we focused the material prospecting to stainless materials to enable platinum electroleaching directly from CCM (scraps or end-of-life material). To ensure a large coverage of the CCM surface, a mesh material was considered. A Dimensionally Stable Anode (DSA) composed of metal mixed oxides (MMO) was used to test the possibility to electroleached platinum from CCM material.



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### 2.3.2.3 Preparation of the anode

The MEA is first manually dismantled (Figure 30) and separated into 2 GDL and one CCM. 6 MEAs are manually dismantled to recover 6 CCM and 12 GDLs. Only 6 GDLs are used for the functioning of the pilot-scale electrochemical process (Figure 31).

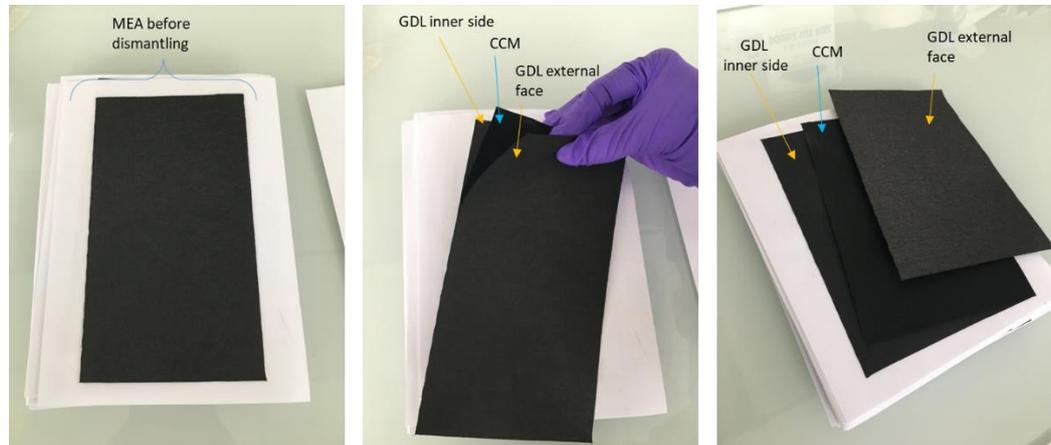


Figure 30 : MEA manual dismantling and separation into 1 CCM and 2 GDLs

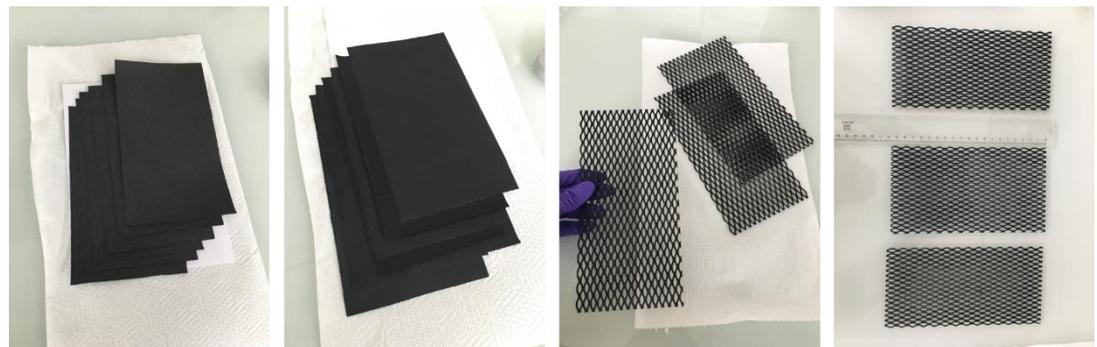


Figure 31 : Photographs of raw material used for pilot-scale process operation from left to right: 6 CCMs; 6 GDLs and the 3 DSA grids.

The CCM are bonded onto the DSAs. On each DSA, 2 CCM are bonded with a resin (Figure 32). Around 24 hours are required for the resin to dry. The anode containing 2 CCM and one DSA is presented on Figure 33.

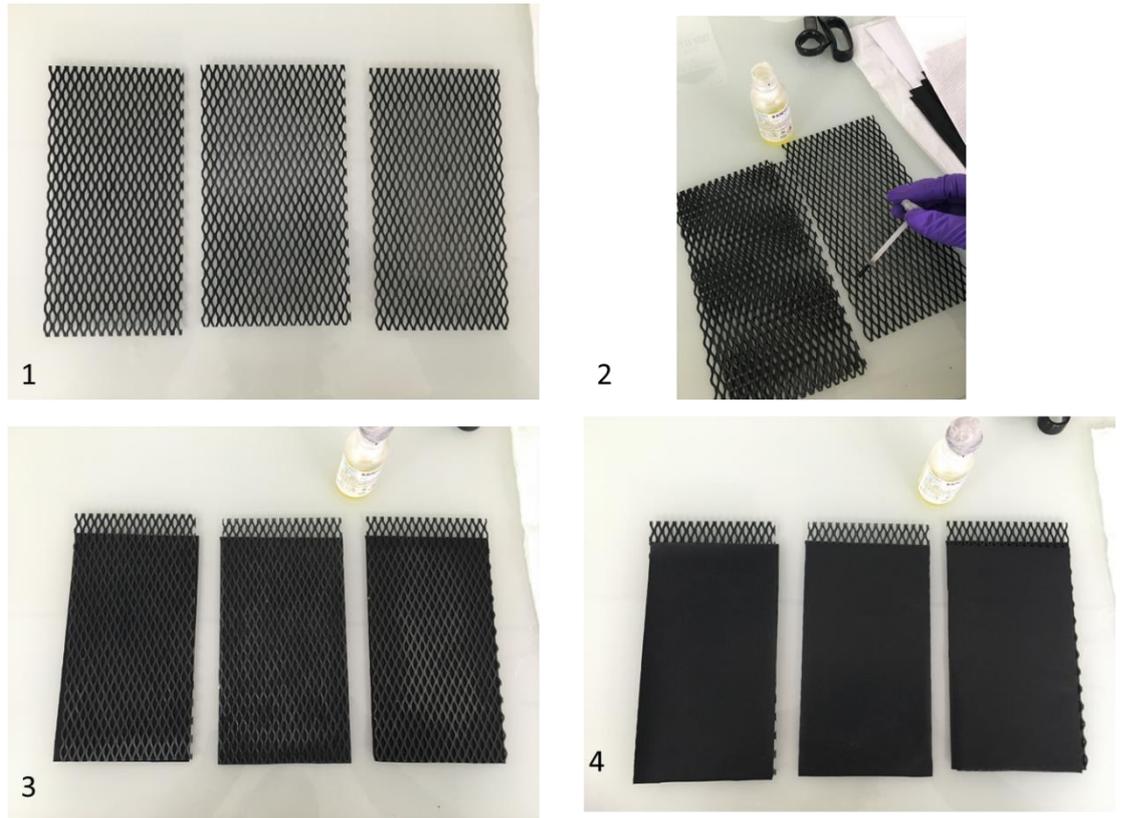


Figure 32 : Photographs of steps for bonding CCM to DSA: 1-presentation of 3 DSA without CCM; 2- brush application of resin on DSA at different grid points; 4- DSAs with CCM on one side; 4-DSAs with CCM on both sides



Figure 33: photographs from different angles of a DSA with CCM on both sides

The reactor used to carry out the pilot-scale process consists of a glass vessel measuring 245 x 135 x 240 mm.

The reference electrode is composed of a silver wire in composite ionic liquid BMIC with the exact same composition as the electrolyte of the cell medium.

### 2.3.2.4 Electroleaching from CCM material

The process of recovering platinum by electrochemical leaching at the CCM and recovery by electrodeposition at the cathode (GDL) was proven at laboratory scale. The laboratory scale treatments allowed for the recovery of platinum from CCM samples of approximately 15 mg. Scaling up, initiated at 150 mg, was continued for a set of 6 CCMs, i.e. about 6.15 g, and is presented here.

The electroleaching of CCM was obtained by bonding the CCM on the electrode with a resin. At 100°C, in ionic liquid with 1 M of chloride anions and with a potential of 2.0 V (vs Ag/Ag<sup>+</sup>) for 11 hours, the electroleaching of Pt was clearly observed from the CCM.

The simultaneous electroleaching and electrodeposition of platinum (ELED) was obtained at 100°C at 2.3 V (vs Ag/Ag<sup>+</sup>).

Initial tests of electrochemical platinum recycling at the 5 L scale required adjustments to the planned set-up, before operating in a similar manner at the 3 mL and 150 mL scales. The adjustments required relate to the contact between the CCM and the dimensionally stable anode (DSA), i.e. the electrode in the form of a grid that allows conduction of electrons from the CCM to the positive terminal of the potentiostat.

The assembly is shown in Figure 34 and shows the alternation of the anodes and cathodes which correspond to the working electrode and the counter electrode respectively.

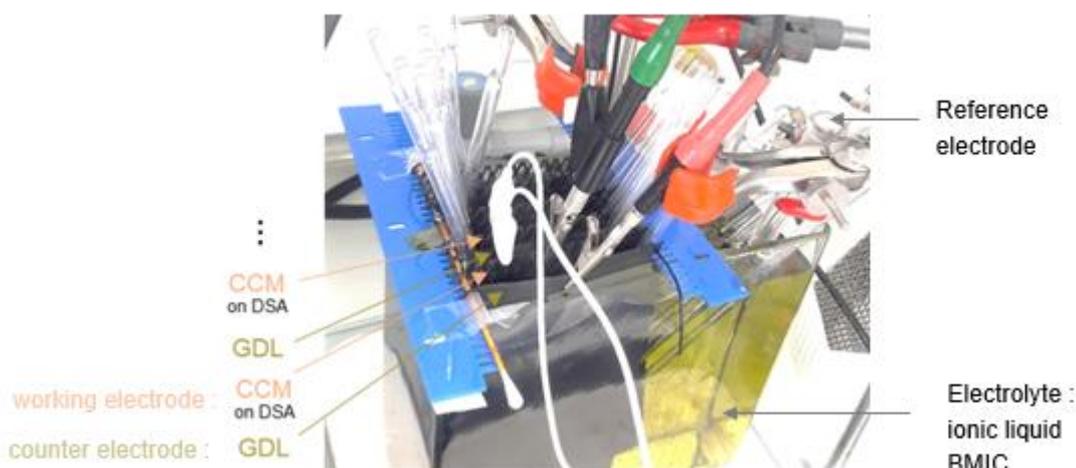


Figure 34 : Photograph of the set-up of the 5 L pilot scale Pt recovery process by electrochemistry



Adjustments to the stirring speed were necessary. Indeed, too much stirring led to the rippling of the CCMs stuck to the DSAs, causing disturbances in the current measurement. Parts of the CCM peeled off during the platinum recovery experiment, directly affecting the current intensity but also the final electroleaching yield. Only a part of the CCM was properly bonded and after 5 hours, a maximum of 70% of Pt recovery was obtained, leading to a plateau and no further Pt was recovered from this set up. As conclusion, the efficiency of bonding of CCM to the grid is paramount and determines the effectiveness of the recovery.

Therefore, the drying time of one hour for a small surface of DSA (3 cm<sup>2</sup>) is not sufficient in the case of CCMs of 150 cm<sup>2</sup>. A 24-hour resin drying time at ambient temperature was applied for the platinum electroleaching of the CCMs. This time allowed the CCMs to remain in contact with the DSA for several hours, the total duration of the treatment.

After adjusting the anode preparation and stirring speed, 6 CCMs could be treated and 95% of the platinum could be recovered. The electroleaching profile indicates that approximately 11 hours are required to recover 95% of the platinum contained in the 6 CCMs and less than 2 hours were required to electroleach more than 70% of Pt from the 6 CCMs as observed by the kinetics of the reaction presented on Figure 7.

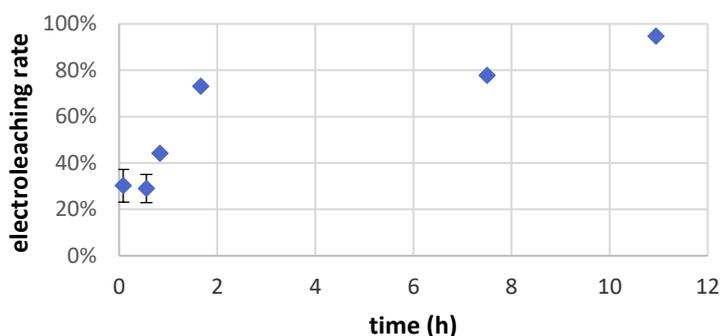


Figure 7: Electro-leaching kinetics of platinum from 6 CCM in 5L BMIM TFSI electrolyte with 1M of chlorides, at 100 °C with mechanical stirring at  $E=2.0$  V (vs  $Ag^+/Ag$ ).

The electroleaching of the platinum led to the release of approximately 600 mg of platinum resulting in a platinum concentration of less than 1 mM. However, in laboratory scale tests (3 mL of ionic liquid and 3 cm<sup>2</sup> of CCM), platinum deposition requires a minimum platinum concentration in solution estimated at 7 mM. Electrodeposition would require the electroleaching of approximately 10 g of platinum, equivalent to 100 CCMs. This would require at least 178 hours for a platinum electrodeposition experiment. An alternative would be the leaching of pure platinum, a platinum plate of 7 g which costs several thousand euros. Scaling up electroplating is therefore complicated to set up and will not be presented in this study. The proof of concept for electrodeposition was demonstrated at the 3 mL laboratory scale. On a larger scale and as perspective, the recovery of platinum from platinum plates should be considered so that the deposited metal is progressively detached at the cathode.



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### 2.3.3 Conclusions and perspectives

CEA Liten propose a new process of simultaneous electroleaching of Pt from CCM and electrodeposition of Pt on GDL. The work done during the project enabled to set up of the process for both GDE and CCM. The process was first optimized at lab scale through process development and parameters exploration. It was also developed at 5 kg pilot scale.

The operating parameters of the simultaneous electroleaching-electrodeposition process of platinum from the CCM to the recycled GDL have been studied. A concentration of 1 M of chlorides, at 100°C, at a potential of 2 V (vs Ag<sup>+</sup>/Ag) in direct current and without pretreatment of the CCM were retained. For a surface of 29 cm<sup>2</sup>, between 4 and 5 hours are necessary to recover all the platinum in the electrolyte.

For a surface of 1800 cm<sup>2</sup>, 11 hours were necessary to transfer 95% of the platinum from 6 CCM treated in parallel, to the electrolyte.

The process is robust and can be applied for fresh to end-of-life CCM or GDL material.

The electrolyte is composed of a composite ionic liquid which is intended to be reused several times. The sustainability of the process was studied. An interaction between the ionic liquid cation BMIM and the ionomer long chains from the CCM was identified but does not seem to affect the process as more than 8 electroleaching cycles can be performed in the same ionic liquid, despite the interaction formed after the second cycle.

At lab scale, platinum is electrodeposited simultaneously to the electroleaching from a concentration close to 10 mM of Pt dissolved in the electrolyte with a deposition rate of 0.1 mg/h. Simultaneous electroleaching and electrodeposition were proven on a laboratory scale, on 3 cm<sup>2</sup> of CCM. At a pilot-scale of 5 L, the electroleaching step of platinum was demonstrated on 6 CCMs treated simultaneously. As a perspective, the electrodeposition should be studied and carried out with a platinum plate as electrode in order to consider the electrodeposition of platinum directly on the plate with progressive release of platinum pieces as it accumulates.

The recovery of platinum by electrochemical means in a single step is innovative. The environmental benefits of this recycling method are currently being studied by BEST4Hy partners. The aim is to understand the environmental impact, through energy and material consumption assessment, and to compare it with other ways of obtaining platinum, whether from mining or other recycling processes.

## 3 References

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