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Identification of the environmental hotspots of a recycling process - Case study of a Pt PEMFC catalyst closed-loop recycling system evaluated via life cycle assessment methodology

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KEYWORDS

Closed-loop recycling process; Life Cycle Assessment (LCA); Proton Exchange Membrane Fuel Cell (PEMFC); Platinum (Pt).

HIGHLIGHTS

- A Pt/C closed-loop recycling process which combines Pt extraction step and synthesis of recycled Pt/C catalyst is reported.

- A closed-loop recycling process for Pt/C electrocatalysts with an efficiency of 96% is reported.

- A life cycle assessment shows that recycling of platinum reduces the environmental burdens related to platinum mining.

- The efficiency of the recycling process is directly linked to a decrease in its environmental impacts.

- Implementation of recycling processes should minimize their energy consumption, especially for the steps using heat.

ABSTRACT

Proton-exchange membrane fuel cell (PEMFC) technology using green H₂ as a fuel to produce decarbonized electricity is considered as a promising substitute for fossil fuels. However, its development is impeded by the use of critical raw materials, such as platinum which catalyzes the hydrogen oxidation and oxygen reduction reactions. In this paper, a novel closed-loop system for the re-manufacturing of platinum-based catalyst electrode from recycled material is developed. Three different recycling alternatives are compared using the life cycle assessment (LCA) methodology. The most promising one, which combines the extraction step with an innovative synthesis of recycled Pt/C catalyst, leads to the manufacturing of an electrochemically active Pt/C catalyst with a highrecovery efficiency of 96 %. Sensitivity analyses display that the recycling processes

significantly relieve the environmental burdens associated with platinum mining and that their efficiencies directly relate to a decrease in environmental impacts.

Introduction

Proton-exchange membrane fuel cells (PEMFCs) are electrochemical devices with potential applications in mobility and stationary energy storage^{1,2}. Within PEMFCs, electricity is produced by converting the chemical energy of a fuel (H₂ gas) into heat and electricity, dispelling only water as a by-product. At the anode of the PEMFC, hydrogen is oxidized to H⁺ ions and electrons, of which the former are transported via a solid polymer electrolyte membrane to the cathode. Here, the H⁺ ions participate in the oxygen reduction reaction for the production of water. The electrons travel through an external circuit generating electricity. These reactions take place inside the membrane-electrodes assembly (MEA), which is the core component of the PEMFC. Typically, the MEA is composed of a proton-exchange membrane (PEM) with electrode layers on each side, both covered by gas diffusion layers (GDLs). H_2 oxidation and O_2 reduction reactions are catalyzed by noble elements such as platinum (Pt) at the anode and cathode electrode layers, respectively. Each MEA is sandwiched between two bipolar plates and the sequential package of MEA and bipolar plates constitutes the stack with a specific voltage. A stack PEMFC is an assembly of multiple PEMFCs connected in series to reach the desired power.

The global environmental benefits of PEMFCs (and other fuel cells) are still being discussed^{3–5}. However, it is known that an electric vehicle powered from a PEMFC has the potential of reducing local transport related pollution, serving as an interesting option in areas where this is a problem. This is due to the absence of harmful exhaust gases produced during the use phase of a PEMFC. Besides the mobility application, PEMFC

technology is also suitable in supplying portable electronic devices, due to its operation at relatively low temperatures.

Recent decades have shown an increasing interest in the research, development and small-scale industrialization of PEMFCs, driven by their environmental benefits⁶. To date, several countries are developing H₂ technologies^{7,8}. However, PEMFCs require Pt-based catalysts for both the hydrogen oxidation and oxygen reduction electrochemical reactions. Pt is largely used in the automotive sector for the catalytic conversion of exhaust gases. Its world reserves are estimated to last over 100 years. However, the potential fuel cell (FC) developments are not yet included in these estimations⁹. Even though 60 to 70 % of Pt is currently recycled at end-of-life (EoL), the recycled Pt represents only 23 % of industry supply, thus its recycling is far away from compensating for the current consumption⁹. Moreover, considering both the supply risks related to mines locations (South Africa and Russia) and their economic importance, the European Commission classifies all platinum group metals as critical raw materials¹⁰.

Although H₂ production contributes the most to environmental impacts during the life cycle of the FC, many studies also present the significant impact of Pt^{11-16} .

EoL steps are often considered as non-essential from a design phase point of view while among environmental concerns they are fundamental to maximize the reuse and recycling efficiency of the materials. Moreover, determining their environmental performance contributes to facilitating future process improvements¹⁶. Three different PEMFC recycling approaches have been developed by our research team at a lab scale to recover and re-use the Pt catalyst. Previously, Duclos *et al.* developed two hydrometallurgical alternatives based either on solvent extraction or resin sorption using

polyol synthesis as the final step of the closed-loop Pt/C catalyst recycling¹⁵. Carbonbased extraction (CBE) recycling process inspired by the work of Seok *et al.*¹⁷ using a synthetic protein was developed later on as an interesting alternative to the former two approaches. This paper focuses on the environmental evaluation of the CBE recycling process based on the LCA methodology and its comparison to the two previously developed closed-loop recycling alternatives¹⁵.

1 Life cycle assessment methodology applied to PEM fuel cells

LCA is a standardized methodology^{18,19}. It assesses the potential environmental impacts of products, processes or services. All input and output materials, energy and waste flows are identified and evaluated regarding several environmental impact categories. Four steps, detailed hereafter, are mandatory when performing an LCA:

- Step 1: Definition of the objectives and the scope of the study determination of the LCA framework (definition of goals, functional unit (FU), impact categories, assessment methods, allocations and EoL rules, etc.);
- Step 2: Inventory analysis collection of inputs and outputs;
- Step 3: Impact assessment linking of the above-mentioned flows to the impact categories;
- Step 4: Interpretation overall cross-cutting analysis.

All the methodological choices related to the LCA part of the study are detailed and discussed in the electronic supplementary information (ESI) (Annex 1).

1.1 State of the art of PEMFC LCAs

Taking into account the context of the development of the PEMFC technology, i.e. the decarbonation of energy production and supply, some attention is already paid to the evaluation of its environmental impacts using the LCA approach. The most relevant FC environmental studies are discussed here, while special attention is given to the EoL aspects. Additional information can be found in Table A1.a, section A1 of the ESI which provides details on the analyzed products, boundaries and used functional unit of the study.

As FCs are often included in larger systems, several LCA studies not only address the FCs, but also include the surrounding elements, such as the FC vehicle (FCV). For example, Evangelisti *et al.* investigated manufacturing, H₂ use and EoL stages based on 'currently used technologies in specialized industries'¹³. They compared an FCV both to a battery electric and an internal combustion engine propelled vehicle, where the data was taken from commercial databases (ecoinvent 3.1 and internal database of GaBi7 software) associated to the LCA software tools. It was shown that for an FCV, the manufacturing stage was predominant in terms of environmental impacts, with a large contribution coming from the manufacturing of the PEMFC stack.

Focusing exclusively on the PEMFC, Notter *et al.* detailed all used processes and constituting elements of a 10 kW high temperature PEMFC unit with multiwalled carbon nanotubes as carbon support for Pt nanoparticles, including the use phase and the recycling *via* a pyrometallurgical process²⁰. They showed that using recycled Pt reduced the manufacturing impacts to 15 % of the initial value. Simons and Bauer evaluated the impact of the manufacturing, use and EoL stages of a PEMFC in 2010 and made a projection for 2020 for a 1 kW peak power PEMFC system¹¹. Here again, MEA, the critical

stack component, has the largest impacts contribution regarding the FC production and disposal. Stropnik *et al.* considered the entire Life Cycle (LC) of a PEMFC: manufacturing, use and EoL¹⁴. The FU used is '1 kWh of energy, which means 1 kWh of produced electricity'. They showed that Pt use has a strong contribution to all investigated impacts of the manufacturing step. Regarding the overall LC, the manufacturing phase is sometimes higher, sometimes lower than the use phase, depending on the use scenario and the share of renewable energies in the energy mix¹⁴. Furthermore, the EoL treatment may reduce the overall impacts by 24 %¹⁴. Similarly, Mori *et al.* have recently demonstrated that Pt accounts for 63.5% of the total carbon footprint (1160 kg CO₂ eq.) for the production of a 48kW_{el} PEMFC stack¹⁶. A high relative contribution was also found for all other assessed environmental indicators, excluding freshwater eutrophication¹⁶. The authors also demonstrated that, at stack level, significant impact reductions ranging from 29 to 54% could be achieved with a lower Pt loading and if recycled Pt is used as the catalyst instead of primary sourced Pt¹⁶.

Duclos *et al.* focused on the production and the EoL stages of a Pt/C based MEA¹². They evaluated two EoL scenarios (incineration of virgin Pt based MEA *vs.* recycled Pt based MEA) and investigated four recycling alternatives with the ambition to determine the main environmental burdens associated with the MEA production and its recycling. Their FU covers the manufacturing and the recycling of a 25 cm² single cell MEA. It was demonstrated that the HCI/H₂O₂ based leaching combined with the ion exchange resin separation provided a more sustainable alternative for the recovery of Pt compared to the use of solvent extraction or HCI/HNO₃ based leaching. In a more recent study, they investigated the recycling of a PEMFC containing a bimetallic catalyst at the cathode side

(Pt₃Co/C), including the synthesis of a recycled catalyst and its testing in a single cell PEMFC¹⁵. The framework was similar, and the FU was described as 'recycling a PEMFC MEA containing the Pt₃Co/C catalyst at the cathode and having a global Pt loading of 0.6 mg Pt cm⁻² into a new MEA having the Pt/C catalyst at the cathode and a global Pt loading of 0.6 mg Pt cm⁻²'. In both studies, the Pt recycling brought significant reductions to the overall environmental impacts compared to the use of primary Pt.

The recycling process and its inventory carried out by Duclos et al. was further used by Lotric et al.²¹. Their recent work focused on the LCA of several hydrogen technologies, centering on EU critical raw materials and EoL strategies. The source of decrease in environmental impact came from the avoidance of virgin materials in closed-loop and the reduction in energy in open-loop recycling systems. The greatest contribution to this decrease originated from the avoidance of virgin materials, especially PGMs which have a significant environmental impact in the material production phase. The negative effect of the absence of PGM recycling is observed in all studied technologies. However, it is more evident in the case of technologies that include platinum (PEM water electrolyzers and PEMFCs).

Typically, LCAs of PEMFC systems do not include performance degradation during fuel cell operation, although it is known that it can negatively influence the system durability and its hydrogen consumption²². Stropnik at al. developed a semi-empirical model, that includes the degradation effects caused by different operational regimes (dynamic and stationary). They demonstrated that the use of existing life cycle inventory (LCI) models (not including the degradation effects) underestimate the environmental impacts²³.

1.2 Inventory analysis & assessment of the formers LCAs

Most studies are based on secondary data. The use of the ecoinvent database is recurrent. However, primary data and/or the construction of new sets from databases are often used by authors in the field^{11–15,20,24–30}.

Three assessment methods are traditionally used in the PEMFC literature, i.e. CML (Centrum Milieukunde Leiden), ReCiPe and ILCD 2011 (International reference Life Cycle Data system). It is important to note that the IPCC 2013 is used in both the CML and ReCiPe methods to calculate the global warming potential impact. Priorities of authors regarding the assessment methods and assessed impact categories are detailed in section A1 of the ESI (Table A1.b).

The available literature is specific regarding the categories of impacts that should be assessed. There is a consensus in both sets of studies to include global warming potential (GWP), photochemical oxidation (Phot. Oxid.), freshwater ecotoxicity (FW-Ecotox.), eutrophication potential (Eutro. Pot.), abiotic depletion (AD) and acidification potential (Acid. Pot.) impact categories. The ozone layer depletion (OLD) is also often included in these LCAs. The main reasons explaining the choice of these impact categories are detailed in the ESI (Annex 1).

1.3 LCA interpretation

When performing an LCA, several hypotheses are made to test the robustness of the study²⁴. A survey made in the LCA community reports on multiple key issues that LCA practitioners commonly deal with³⁰:

completeness analysis.

- consistency analysis.
- sensitivity analysis.
- scenario analysis.
- uncertainty calculation.
- parameter variation.

For example, Duclos *et al.* performed sensitivity analyses regarding the transport and energy mix to evaluate the influence of these parameters on the final results¹⁵. Similarly, Evangelisti *et al.* carried out sensitivity analyses on specific components (i.e. stack, H₂ tank, etc.) and parameter variation (i.e. Pt loading), comparing the consistency with other published studies¹³. Others ensured the data quality was based on a qualitative evaluation regarding temporal, technological, geographical and completeness criteria²⁷.

LCAs of PEMFCs are well described and codified in literature to date. However, recycling processes of FCs are less investigated, thus being the topic of this paper. A closed-loop recycling process for the manufacturing of new electrodes catalyst based on recycled platinum is developed and compared with previous studies in the light of LCA methodology.

2 Materials and Methods

Three alternative methods were designed for the recycling of Pt from MEAs. The experimental procedures and main results are given in the following paragraphs. The two recycling processes developed by Duclos *et al.* are first briefly recalled^{12,15}. Furthermore, the carbon-based extraction (CBE) process is described, and the experimental achievements are presented.

2.1 Recycling of Pt/C by a hydrometallurgical approach based on ion exchange or solvent extraction and polyol synthesis.

We have previously developed and optimized a closed-loop process for the recovery of Pt and Pt/C synthesis for their direct reuse within a PEMFC^{12,15}. This process combines a hydrometallurgical approach and a modified polyol synthesis route. Moreover, two alternatives for Pt recycling have been studied and compared:

- A solvent extraction method composed of the following steps: leaching with an H₂O₂/HCl mixture, solvent extraction with Cyanex 923 (a liquid phosphine oxide blend used as an extractant for various metals) in octanol, and back extraction based on NaOH stripping.
- An ion exchange resin method composed of the following steps: leaching with an H₂O₂/HCl mixture, sorption with Lewatit MP-62resin (a weakly basic, macroporous anion exchange resin with tertiary amine groups), and desorption with an NaOH solution.

The process can also be adapted to Pt and Co separation in the case of a presence of Pt₃Co catalyst in the entry flow of used MEAs. The alkaline solutions containing dissolved Pt ionic species have been directly used as entrants for the polyol synthesis. More detailed information on the optimization and process developments can be found in Duclos *et al.* (2017) and Duclos *et al.* (2020)^{12,15}. The detailed flowsheets of each simulated step can be found in the ESI (Figures A2.2.a and A2.2.b) of this paper.

A high-performing Pt/C catalyst (with a 20 wt% loading of Pt on the carbon) was synthesized using the ion exchange resin-based route combined with polyol synthesis¹⁵.

However, the corresponding LCA study revealed several weaknesses in the developed approach. These were associated with the multiplication of subsequent separation steps, leading to Pt losses in each step of the protocol, resulting in non-negligible Pt losses (in the range of 20 %) over the entire process. These losses were compensated for by using primary Pt to maintain the Pt quantity constant within the system (in accordance with the FU chosen). The primary Pt additional supply was consequently responsible for the main impacts contribution in several impact categories (abiotic depletion, acidification potential, freshwater ecotoxicity). These results demonstrate a prevailing need for a reduction in the number of separation steps, justifying the use of a new recycling method.

Moreover, compared to the recycling process, the polyol synthesis generated higher impacts (of several orders of magnitude). The synthesis scored particularly high in the global warming potential category due to the use of electricity and the end-of-life of used solvent (ethylene glycol). This presents a second argument for developing an alternative recycling process where both recycling and synthesis steps are combined.

2.2 Recycling of Pt/C by carbon-based extraction process

The carbon-based extraction (CBE) process was investigated as an alternative closedloop recycling pathway that differs significantly from our previous methods. The main objective was to improve the Pt recovery efficiency by minimizing the number of experimental steps as previously discussed. As in our previous work¹⁵, the CBE scenario does not allow to access the Pt salt intermediate state and leads directly to Pt/C particles as a final product. The new pathway fully detailed in the ESI (Annex 2 - Section A2.1) was inspired by the work of Seok *et al.*, who used a simple and bio-friendly method to prepare dopamine-induced Pt and N-doped carbon@silica hybrids¹⁷. In the presented work, polydopamine is used as the reducing agent of Pt salt and as a precursor for the nitrogen functionalization of the carbon support. Polydopamine, which is the polymerized form of dopamine, is commonly found in mussels' adhesive proteins. This biomolecule has recently attracted a lot of attention from the scientific community due to its interesting adhesive properties. In the present work, this polymer is first deposited on the carbon support, allowing the impregnation of Pt salts which are further reduced into Pt nanoparticles *via* the catechol functional groups of polydopamide. These groups are converted into quinone groups during the reduction process. The three main steps of the CBE recycling process are hereafter described.



Figure 1 - Detailed scope of CBE recycling process

Step 1 – MEA leaching (optional step).

MEA leaching was performed in the same way as in Duclos *et al.* using a 3% H₂O₂/HCl mixture¹⁵. Spent MEAs of 25 cm², with a final Pt loading of 0.63 mg Pt.cm⁻² (determined experimentally) were used. The MEAs were provided by an industrial partner, however neither the ageing conditions nor the initial loading is communicated for reasons of confidentiality. After the leaching step, the Pt concentration in solution was analyzed to

be 760 mg/L, which corresponds to a leaching efficiency of 97%, in accordance with Duclos *et al.*¹⁵.

Step 2 – Coating the carbon support with polydopamine (Pdop@VC).

Polydopamine (Pdop) was used to coat the Vulcan carbon (VC) support. VC particles were first dispersed in a solution made of tris-acetate buffer (pH 8.5), distilled water and ethanol and the obtained mixture was sonicated. One milligram of dopamine hydrochloride was then added, and the solution was again sonicated. The obtained mixture was magnetically stirred for 24 hours. During this step the dopamine gently polymerized and covered the VC particles. The obtained Pdop@VC particles were separated by centrifugation and washed with deionized water.

Step 3 – Depositing Platinum nanoparticles.

Finally, the Pt leachate from step 1 was diluted with H₂O and ethanol. 6M NaOH solution was added to basify the medium to a pH of 6 (necessary for chloride precipitation). The sodium chloride (NaCl) precipitate was filtered off, thus removing excess chloride ions detrimental to the Pt nanoparticles' electrocatalytic activity³¹. Pdop@VC (step 2) particles were added and the suspension was sonicated with stirring for 24 hours to impregnate the PtCl₆²⁻ ions onto the Pdop@VC support. The ions were then reduced into Pt nanoparticles by the hybrid support itself. The particles are further designated as Pt@Pdop@VC particles. As in the previous protocol based on the polyol synthesis (section 2.1), a platinum loading of 20 wt% was targeted.

The synthesized Pt@Pdop@VC particles were then removed by filtration, washed with water and dried for 6 hours. Pt/C was finally obtained by the thermal degradation of the polymer at 250°C for 2.5 hours in a furnace. This step was mandatory in order to achieve

an electrochemically accessible Pt surface. It is also important to note that the thermal degradation of polydopamine led to nitrogen functionalization of the carbon support, beneficial to its durability in PEMFC application³².

3 Insights into the life cycle assessment model

This next section provides detail on the framework of the LCA model, including the definition of the goals, the scope of the study, and the chosen functional unit and study boundaries. The inventory analysis is presented and the choice of assessment method is explained. Finally, the obtained results are analyzed.

The following sub-sections detail the methodology adopted to evaluate the environmental impacts of the CBE recycling process inspired by Seok *et al.*¹⁷ and its comparison with alternative processes developed by Duclos *et al.*¹⁵.

3.1 Goals and scopes

Several objectives drove this study:

- The evaluation of the environmental impacts associated with the production and EoL of an aged PEMFC MEA, recycled *via* the CBE recycling process.
- The comparison of EoL alternatives from an environmental point of view and the evaluation of various Pt recycling strategies at a lab scale.
- The facilitation of orientating research activities towards efficient recycling processes for MEAs in PEMFCs.

The undertaken LCA is a gate-to-gate study, which consists in MEA manufacturing and EoL phases (the operation phase is not the focus of this study).

Figure 2 summarizes the scope of objective 1, including the study boundaries and the main inlets and outlets for the aged PEMFC MEA. Three main parts are described: the initial Pt/C production from primary raw materials (orange frame); the MEA production (red frame); and the CBE recycling process including the treatment of all MEA components (green frame). Accordingly, the environmental impacts of the MEA were estimated by considering the catalyst and MEA production, and its end-of-life treatment, without accounting for the use phase. The hydrogen use was excluded from the study as explained in the introduction section. The LCA results were based on a hypothetical collection rate of 100 %. Regarding the EoL, the hypotheses are the same as in Duclos *et al.*¹⁵: The catalyst layers deposited on the membrane were treated according to the studied recycling scenario alternative. Wastewaters were treated in a wastewater treatment plant, spent solvents followed a specific treatment, and Nafion[®] was incinerated. For the GDL, PTFE was incinerated as well as other wastes. For the gasket, the PET was considered as recycled material.



Figure 2 - Scope of the CBE recycling process for used Pt/C MEA

Furthermore, the study compared the CBE recycling process with the solvent and resinbased alternatives coupled to polyol synthesis (objective 2) from Duclos *et al.*¹⁵. System boundaries varied between the processes. They are described in Figure 4 and in Figures A2.2.a and A2.2.b of the ESI. The last objective (objective 3) was based on a cross-functional approach. It is discussed in detail in the section named, 'Sensitivity analyses and limitations of the study'.

The FU considered in this study was the 'EoL recycling and recovery of one kilogram of Pt at the end of the recycling process'. Based on the targeted Pt loading of 20 %, the functional unit corresponded to 5 kg of Pt/C particles composed of 1 kg of Pt and 4 kg of C. The entry Pt quantity was fixed to 1 kg. Therefore, in the case of losses during the recycling process, the lost Pt was replaced by an equivalent quantity of primary Pt. The reference flow is 42.6 kg in mass or 66.497 in number of MEAs entering the EoL scenario. This FU facilitated the analyses as it encompasses the studies related to objectives 1 and 2. It is easily comparable to Duclos *et al.* studies^{12,15}, which state that it can be easily correlated to the electrical power at a stack scale, based on the power density' (near 0.7 W cm⁻²). To do so, the Pt particles that are recycled must present satisfactory morphological and electrochemical characteristics to manufacture new MEAs with equivalent characteristics.

Finally, an attributional LCA was carried out in this study as a lab-scale recycling process without any large-scale decision to support it. The SimaPro v8.4 software has been used to perform the analysis, using SimaPro PhD license.

3.2 Inventory analysis

Most of the inputs and outputs were transposed using the ecoinvent v3.3 database, using 'allocation, recycled content' data. Three different approaches were adopted when data was missing, depending on the situation. If it concerned a process absent from the ecoinvent database, the input and output elementary flows were modelled using direct measurements (as detailed in section A3.1 of the ESI). This was the case for the electric consumption of the devices used. If the concern was related to a chemical reagent, the 'life cycle tree' approach was employed. This consisted of building the reagent from its basic precursor substances for which available life cycle data can be accessed and used, representing the situation in a realistic manner³³. For example, this approach has been adopted for tris-acetate buffer modelling. When we weren't able to model it, we used data from another database, double checked the impacts with literature and carried-out sensitivity analysis, such as in the case of H₂PtCl₆. All the data modeled in SimaPro is available in sections A3.2 and A3.3 of the ESI. For data that was built, a deeper analysis using pedigree matrix is given in section A4 of the ESI.

Melideo *et al.* proposed 'not to use a cut-off but to clearly state which parts of the inventory are included and excluded and to interpret properly the results and discuss limitations'²⁵. To that extent, several hypotheses were made to perform the current LCA due to unknown or incomplete data. They are addressed in the discussion section and are detailed in section A6.2 of the ESI.

3.3 Choice of the impact assessment methods

To relate with previous studies (see section A1 of the ESI), the CML IA baseline V3.04 method was used, and the results were compared with the ReCiPe 2016 midpoint H v1.0 method (see section A5 of the ESI). According to the literature section, seven carefully selected potential environmental impact categories were considered: acidification potential; abiotic depletion; eutrophication potential; fresh water ecotoxicity potential; global warming potential; ozone layer depletion potential; photochemical oxidation potential.

4 Results

The achieved efficiency of the CBE Pt nanoparticles synthesis step was 99 %. Combining the leaching (97 %) and the synthesis (99 %) efficiencies, the overall efficiency was particularly high (96%) compared to our previous work (around 85 %).

4.1 Characterization and Electrochemical performance of the recycled Pt/C catalysts

The three recycled Pt/C catalysts were characterized by transmission electron microscopy (TEM). Representative images are displayed in Figure 3 and compared with a Pt/C reference material purchased from Tanaka (Pt/TKK). The morphological characteristics of the Pt/C recycled *via* ion exchange resin alternative are closely alike to the benchmark catalyst in terms of the Pt particle size and the degree of agglomeration. The particle size of the Pt/C obtained by the carbon-based extraction (CBE) process is slightly superior (between 2 and 4 nm in average) but the Pt nanoparticles are homogenously dispersed on the carbon support. Alternatively, the catalyst corresponding to the solvent extraction method is more dissimilar to the commercial one due to the presence of large nanoparticles coexisting with smaller ones. These results agree with

the electrochemical characterization results shown in Figure 3. The four catalysts have been tested for the oxygen reduction reaction (ORR), the cathodic reaction in a PEMFC. The resin-based Pt/C catalyst presents ideal morphological and electrochemical characteristics with a high ORR performance in terms of both mass and specific activity. The Pt/C solvent catalyst and CBE based catalyst exhibit a lower specific surface area compared with the Pt/C resin and references due to the presence of larger particles in the two samples. This translates to a lower ORR mass activity (normalized by the mass of Pt deposited on the electrode) for these two recycled catalysts. It is important to note that the specific activity of the Pt/C CBE catalyst (normalized by the Pt electrochemical surface area) was in the same order of magnitude as the reference catalyst, confirming the interest of this synthesis route. Additionally, the marginally lesser ORR mass activity at the beginning of life should be compensated in terms of stability upon PEMFC operation since larger crystallites are less prone to dissolution/redeposition degradation mechanism³⁴.



Figure 3 Transmission Electron Microscopy (TEM) images of Pt/C catalysts synthetized via different recycling methods compared to a commercial TKK catalyst (top) and Electrochemical characterizations - Variations of Pt specific surface area determined via CO stripping coulometry a) ORR specific activity b) and ORR mass activity c) for the

electrocatalysts evaluated in this work. b) and c) were measured at E = 0.95 V vs. RHE from the ORR kinetic currents in O₂-saturated 0.1 mol.L⁻¹ HClO₄ after correction for Ohmic drop and mass transport. Other conditions: Pt loading of 20 μ g cm⁻², potential sweep rate of 0.005 V.s⁻¹, ω of 1600 rpm, increasing potential sweep from 0.20 to 1.05 V vs the RHE, and T of 25 ± 1°C.

4.2 Comparison of the environmental impacts of the recycling methods

This section first presents the environmental impacts of the CBE recycling process, the first objective of this study. Detailed results of the 11 and 17 impact categories of the CML and ReCiPe methods, respectively, are provided in section A5 of the ESI. A comparison with the results of Duclos *et al.*¹⁵ was afterwards carried out. Results are discussed step by step in separate sections.

4.2.1 Determination of the CBE recycled catalyst synthesis impacts

Before analyzing the results, it should be highlighted that the impact of the CBE synthesis of Pt/C catalyst alone was assessed in first time, i.e., the benefits of Pt recovery are not included yet. The CBE Pt/C synthesis is composed of three main steps (H₂PtCl₆ solution production, Pdop@VC particles production and waste streams treatment), and the details are schematically explained in Figure 4. To compare the impacts of the CBE synthesis with the polyol synthesis studied previously, only the blocks corresponding to the Pdop@VC particles production and the waste treatment impacts are assessed first.



Figure 4 - Detailed scope of the CBE recycling process

Figure 5 is built the basis of simulation results using the inventories available in Tables A3.2.a to A3.2.1 of the ESI. All impact categories, except for photochemical oxidation formation, are dominated by the electricity consumption relative to the different heating steps used within the CBE synthesis. Waste generation and treatment contribute significantly only to the GWP (27 %) impact category and they represent less than 16 % of the impacts for other impact categories. The use of chemicals, especially ethanol, corresponds to 14-23 % of the impacts generated for abiotic depletion, GWP, acidification potential and eutrophication potential. However, they contribute up to 57 % for the photochemical oxidation formation category.



Figure 5 - Impacts of the Carbon-based extraction synthesis of Pt/C catalyst used to extract and refabricate Pt/C electrocatalyst- w/o savings

As in the previous paragraph, we again focus on the section related to the CBE synthesis of the recycled Pt/C catalyst of Figure 4. The main difference is the inclusion of the Pt recycling avoided impacts (in green in Figure 6). Figure 6 is built on the basis of simulation results using results from Figure 5 and Table A3.2.m of the ESI. Complete results are given in Annex 5. When primary Pt used for PEMFC production is replaced by Pt recycled via CBE process, this means that the corresponding quantity of primary Pt will not be mined and extracted. The associated impacts will thus be considered as "avoided" (i.e. as environmental benefits = damaged that will not be caused) and will be given an opposite sign to impacts that are created. This was achieved by comparing the impact of the production of primary Pt (corresponding to the quantity of Pt recovered by the CBE process) to the impact of the CBE catalyst synthesis. The higher of both values was put equal to 100% and considered as reference, while the corresponding % of the second value was determined according to the rule of three. The CBE catalyst synthesis coupled to a previous leaching step produces a secondary raw material (recycled Pt/C) with a remarkably high efficiency (up to 96 % of initial Pt/C quantity) as mentioned in the section 2.2., It will thus avoid the use of primary Pt in future production cycles. It should also be highlighted that chemicals and processes from Figure 4 have been merged for clarity. They are labelled: 'Chemicals for CBE processes' and 'CBE processes'.



Figure 6 - Impacts of the Carbon-based extraction synthesis used to extract and refabricate Pt/C electrocatalyst - with savings

In Figure 6, all environmental burdens related to the CBE process will be given, as explained above, positive sign and are thus plotted in the upper part of the figure. The avoided impacts associated to the fact that primary Pt is not used are considered as environmental benefits. They are given a negative sign and are plotted in the lower part of the figure. In this manner, it is possible to emphasize the benefits (if any) of the developed recycling process. Unavoidably, each recycling process itself produces environmental impacts related to the consumption of chemical products and electricity and the produced emissions (solid waste, liquid effluents and gaseous emissions such as VOC, GHG etc.). In this study, the environmental burdens associated with CBE synthesis (use of chemicals, recycling processes and generated wastes) are non-negligible (superior to 20%) for global warming, freshwater ecotoxicity, photochemical oxidation

formation and eutrophication potential. Moreover, the savings due to Pt recycling only compensate approximately 50 % of the burdens of the CBE synthesis for the global warming category. Although the quantity of greenhouse gases (GHG) associated with the primary Pt production is rather high, the CBE synthesis seems to lead to more GHG emissions, certainly due to the electricity consumption of the heating step and spent solvents treatment. In addition, for the ozone layer depletion category, the CBE recycling process generated 28 times more environmental burdens which mainly come from the electricity consumption in steps which require heating. The treatment of waste streams generated throughout the recycling process also affects global warming, while the consumption of chemicals impacts both the global warming and ozone layer depletion categories. Finally, it is important to note that Pt recycling leads to more avoided impacts than burdens (detailed in Figure 6) in five studied impact categories: abiotic depletion, freshwater ecotoxicity, photochemical oxidation formation, acidification potential and eutrophication potential.

4.2.2 Comparison of several recycling alternatives vs. the use of primary Pt

In this subsection, the impacts of the three different recycling methods are compared with the reference scenario based on the use of primary Pt (designated as the ref. sc. in Figure 7). The reference scenario corresponds solely to the production of 1 kg of primary Pt. Its transformation into Pt/C was not taken into account, using the hypothesis that this transformation has negligible impacts compared to the extraction and the production of primary platinum. Moreover, as previously highlighted in section 3.1, the inlet quantity of Pt was made equivalent to its outlet quantity. Thus, when losses appeared within the

recycling process, the lost quantity of metal was replaced with a primary Pt addition. For coherence, the supplementary primary Pt was transformed by simulations into its H₂PtCl₆ form as explained in Figure 4. The additional inlet flow - labelled H₂PtCl₆ solution (addition) - was introduced into the system prior to the synthesis step with leaching solution (for CBE synthesis) or the solution originating from the resin or solvent separation methods. The proportion of both Pt flows was adjusted according to the losses generated in the separation process (as described in Figure A2.2.a and A2.2.b and Tables A3.3.b to A3.3.e in the ESI). This facilitated the comparison of the three alternative methods under the same experimental conditions and boundaries, highlighting the differences between the recycling processes.



Figure 7 - Comparison of the impacts generated by the three recycling processes studied with a reference scenario based on the use of primary Pt (Primary Pt vs Solvent vs Resin vs CBE recycling process)

All three recycling approaches present environmental advantages regarding five of the seven studied impact categories (abiotic depletion, freshwater ecotoxicity, photochemical oxidation formation, acidification potential and eutrophication potential). These range from 65 to 92 % of impacts reduction compared to the reference scenario based on the use of primary Pt. Recycling consequently appears to be a promising alternative. It is important to note that the CBE recycling process is the least impacting with regards to the abiotic depletion, the photochemical oxidation formation, the acidification potential and the eutrophication potential compared with the solvent or resin recycling alternatives. These advantages are due to several factors such as limited number of steps, limited amount of chemicals used, improved efficiency or a combination of the above. The improvements vary from 116 to 212 % and from 150 to 258 % for the CBE recycling alternative with respect to the solvent and resin ones. However, for the freshwater ecotoxicity impact category, although the benefit is substantial compared to the reference scenario (around 65 %), the CBE recycling process displays inferior results to those of Duclos et al.¹⁵; respectively 59 and 73 % worse than the resin and solvent recycling processes. These results are strongly related to the use of heat during the recycling operations and, thus, the electricity consumption.

For global warming, the CBE recycling process score is similar to the reference scenario. However, the solvent and resin processes have lower impacts than the reference scenario by 17 and 40 %, respectively. Such differences are again linked to the use of electricity for heat production within the CBE recycling operations.

For the ozone layer depletion potential impact category, the three recycling alternatives surprisingly lead to significantly more environmental burden than without the recycling

process. The primary Pt extraction seems to emit a negligible amount of substance affecting this impact category compared to the use of electricity needed to recycle it at its EoL. The CBE recycling process is the most impacting process, exceeding the reference score by more than 1200 %.

To decrease the impact of the CBE recycling process in Global Warming and Freshwater Ecotoxicity impact categories, in comparison with the previously developed recycling alternatives¹⁵, the main hotspot to work on is the energy consumption. The first actions could involve decreasing either the temperature or the duration of the process. Alternatively, other sources of energy or more efficient equipment could be used. When upscaling to an industrial level, economies of scale would improve the process efficiency for the CBE recycling alternative. The resin sorption and solvent extraction recycling processes would also improve in their efficiencies for the same reasons.

4.2.3 <u>Environmental impacts of the MEA's life cycle including the CBE recycling</u> process as the EoL treatment and Pt closed-loop recycling

Focusing on the environmental impacts of the MEA all along its lifecycle: i.e. from primary raw materials extraction up to the end of the recycling process (including losses) and raw material being either returned to the market or reused in the same application as indicated in Figure 2. The use of H₂ is not included as previously explained. The MEA modelling was inspired by Duclos *et al.*¹² and was adapted to fit the model used in our study. Namely, the modification of Pt weight used to manufacture the electrodes (see Table A3.3.a of ESI) was carried out. In Figure 8, the chemicals, generated waste and electricity used in the CBE recycling process are again grouped together for clarity (in

green or textured green). The Pt leaching step is again included in the analysis together with the primary Pt supplemented to mitigate the losses generated within the recycling process (stream designated as H₂PtCl₆ solution in Figure 4, see Table A3.2.m in the ESI for mass balances). Moreover, the production and EoL treatment of other elements of the MEA (such as the gasket, membrane, GDL, etc.) are now included and assessed. The upper part of the figure 8 gathers thus together the impacts of MEA production and the impacts associated to the end-of-life treatment of its components (gasket, membrane, GDLs ...) including the CBE recycling process for Pt/C recycling. The lower part of the figure emphasizes the potential savings related to the Pt closed-loop recycling via the CBE process. For five impact categories (abiotic depletion, freshwater ecotoxicity, photochemical oxidation formation, acidification potential and eutrophication potential), the use of primary Pt for the production of the initial electrodes (see Figure 2 for explanation) represents the majority of the impacts generated (between 60-91 %). They are thus counterbalanced by the savings related to the recycling of Pt due to the CBE process efficiency of 96 %. However, for GWP, the CBE recycling process represents 48 % of the generated environmental impacts, 21 % for the use of primary Pt and 30 % for the use of other MEA components (particularly Nafion®), while the recycling benefits remain around 21 %. Moreover, for ozone layer depletion, Nafion[®] contributes a substantial 93 % of the environmental impacts. While we showed in Figure 7 that the impact of CBE recycling operation within this category (0.025 kg CFC-11 eq) as 12 times higher than the impact of Pt extraction, it appears that it has almost no contribution to this category compared to Nafion[®] (1.24 kg CFC-11 eq) on the entire LC scale.



Figure 8 - Impacts of the LC of the MEA following Carbon-based extraction recycling process used to extract and refabricate Pt/C electrocatalyst - with savings

It can thus be concluded that the CBE recycling process strongly reduces the environmental burden during the lifecycle of an MEA for the following impact categories: abiotic depletion, freshwater ecotoxicity, photochemical oxidation formation, acidification potential and eutrophication potential. However, as highlighted previously, the CBE recycling process does not significantly influence the ozone layer depletion impact category; the majority of the impacts come from the use of Nafion[®]. Nafion recycling should thus also be addressed in order to decrease the impacts of the PEMFC technology. Although less attention has been given to this topic compared to Pt recycling, some works can be found^{35–44}. However, the proposed recycling processes generally

entailed harmful/toxic solvents and/or energy-intensive conditions. Their impacts should be thus assessed in details to understand correctly the benefits that Nafion recycling could bring, but this is out of the scope of the present study.

As mentioned in the discussion, the CBE recycling process scores significantly high in the GWP impact category (48 % of the total environmental burden of the lifecycle (use of H₂ excepted) of an MEA). The share of responsibilities for such an increase are: the electricity consumed in the CBE recycling process (48 %), the generated waste (27 %) and the treatment of used chemicals (25%). Improving the energy efficiency and optimizing the CBE recycling process are keys to reducing the impacts within the GWP category as well as other impacts categories. Nevertheless, the waste management and the use of chemicals must also be considered to reduce them. Upscaling from a laboratory-scale experiment to industrial scale has the potential for improvements in the reduction of impacts due to the economy of scales. However, attention must be paid to the electricity consumed in the CBE process, the waste generated and the treatment of used chemicals. Meanwhile, the environmental avoided impacts due to the use of recycled Pt represent only 21 % of the environmental burden within the GWP category, which does not compensate for them. Several sensitivity analyses have been tested in section A6 of the ESI. The conclusions are presented in section 'Sensitivity analyses and limitations of the study'.

5 Sensitivity analyses and limitations of the study

5.1 Sensitivity analyses regarding the CBE recycling process

Several sensitivity analyses have been carried out and the main results are subsequently given. Regarding the MEA, 'carbon fibers' data used in the GDL was not available in the ecoinvent database. In general, data of the fibers are scarce. A module from the IDEMAT database was used in this work as was done in Duclos *et al.*¹⁵. A sensitivity analysis using data from Khanna *et al.*⁴⁵ (ESI section A6.1) was thus performed. Compared to our initial MEA, results display an increase in impact of 35 % regarding global warming, 12 % for photochemical oxidation formation, and less than 8 % regarding the five other impact categories. As the overall contribution of the impacts of the GDL increase, the contribution of the CBE recycling process proportionally decreases.

Furthermore, the following hypotheses were tested: (1) the exclusion of glassware and cleaning; (2) machine and firm depreciation exclusion; and (3) the size of the wastewater treatment plant. Our simulations confirmed that there was no value in including them as they contributed insignificantly to the impacts, as shown in sections A6.2.1, A6.2.4 and A6.2.5 of the ESI.

Regarding electricity consumption, the French energy mix was considered for the performed simulations. However, it is mainly based on nuclear power and as the electricity consumption has a strong influence on the results obtained (see Figure 5 and Figure 6), three other energy mixes were evaluated (i.e. Germany, Europe and the United States). The comparison is available in Figure A6.2.6, section A6.2.7 of the ESI. It was found that the energy mix composition does not significantly affect the MEA manufacturing. Regarding the CBE recycling process, there is no significant difference in both the abiotic depletion and ozone layer depletion impact categories. Nevertheless,

there are slight differences regarding the CBE savings for Photochemical Oxidation Formation and Acidification Potential categories (up to 20 %, for the US mix). The differences are always in favor of the reference scenario (French energy mix). For the global warming category, the impacts of the CBE recycling process represent around 30 % of the total impact for the French energy mix. Moreover, the impacts of CBE recycling process increase by 400 % to 550 % when using alternative energy mixes for the global warming category. Regarding freshwater ecotoxicity and eutrophication potential impact categories, results are even more contrasted. The reference scenario (French energy mix) leads to environmental savings (-35 % and -67 % of the overall MEA impacts, respectively), while the other energy mixes lead to an increase of +18 to +66 % for freshwater ecotoxicity and +48 to +142 % for eutrophication potential impact categories, depending on the energy mix. It is worth highlighting that the differences vary significantly upon altering the electricity mix. Environmental burdens may appear and potential savings may switch to potential burdens in some impact categories.

5.2 Sensitivity analyses regarding the comparison of different recycling alternatives

Two remaining hypotheses were evaluated in section A6 of the ESI and are detailed hereafter. Using a new set of measurements, the manufacturing of one kg of Pt from polyol synthesis was considered to require around 20 GJ of electricity instead of 120 GJ (as mentioned in Duclos *et al.*¹⁵) However, the results detailed in section A6.2.2 of ESI signify that this difference (from 20 to 120 GJ) only has a small influence on the Global Warming impact category (around 19 %). It presents a significant influence on the Ozone

Layer Depletion potential and a negligible influence (less than 15 %) on the five other impact categories. The polyol synthesis is the only step that has a noticeable effect on the OLD category with approximately +400 % impact when moving from 20 GJ to 120 GJ.

Secondly, we investigated the different ways of simulating the H₂PtCl₆ solution as a created module. Results display no significant difference when considering both stoichiometric and life cycle tree modeling, nor when nitrogen dioxide emissions are considered as wastes or coproducts. The only significant difference comes from the origin of Pt (primary sources, polyol synthesis 20 GJ or 120 GJ) as highlighted before. The graphs, tables and modeling details are available in section A6.2.3 of the ESI.

5.3 Limits of the study

Several elements are limiting regarding the results obtained within this study. Firstly, although uncertainties of the measurement of electricity consumption were reported (see ESI, section A.3.1), they were not taken into account during the LCA. The uncertainties related to chemicals have not been considered, due to the lack of reliable data. Moreover, the CO₂ and NO_x emissions of step L7 in the CBE protocol (see Figure 1) were not included due to the inability to quantify them experimentally. Thirdly, some of the chemical data that was created was based on less recent articles^{46,47}. Current manufacturing processes are likely to involve different reactions and/or experimental conditions. Furthermore, some chemicals reported were not considered due to the lack of available data in databases or an inappropriate description in the references. This concerns 'PLP', 'TPL' enzymes and the quantity of sodium sulfate, in addition to the heating process for dopamine hydrochloride (see Figure A3.2.b in ESI) as mentioned in Lee *et al.*⁴⁸.

Throughout this paper, we aimed to provide the clearest possible view of our hypotheses and modeling decisions. Consistency was double-checked and explained for each created data (life cycle tree or stoichiometric modeling) and for several hypotheses (20 vs 120 GJ and MEA vs model leachate). Several sensitivity analyses were performed to evaluate the strengths and weaknesses of the LCA (carbon fibers, cleaning and glassware hypothesis, machine & firm depreciation inclusion, wastes management and the origin of the energy mix). Several scenarios were analyzed (aged MEA vs three versions of model leachate as well as several energy mix origins) to evaluate the influence of potential varying parameters.

6 Conclusion & perspectives

The carbon-based extraction process developed at a lab scale to recycle Pt nanoparticles from an aged PEMFC MEA shows an impressive recycling efficiency (approx. 96 %). The environmental impacts of this recycling pathway were estimated to confirm or refute its potential interests. The LCA reports the environmental burdens to come predominantly from steps requiring heat, (thus consuming electricity) while smaller contributions come from the use of ethanol and the generation of waste streams that must afterwards be treated. The benefits of Pt recycling outweigh the environmental burden for five impact categories (abiotic depletion, freshwater ecotoxicity, photochemical oxidation, acidification potential and eutrophication potential). However, the impacts are not counterbalanced for the global warming and ozone layer depletion potentials. For these latter two impact categories, the overall benefits of Pt recycling are less important than the impacts generated by the CBE recycling process. When including the impacts of the

entire MEA (including the Nafion[®] membrane), results do not significantly change, excluding the global warming and ozone layer depletion potential categories. The use of Nafion[®] strongly increases these impacts, of which they are not compensated for by the benefits of Pt recycling. This underlies the necessity to recycle the Nafion[®] membrane and the ionomer from the catalyst layer. Nafion[®] contributes to more than 93 % of the ozone layer depletion and 28 % of the global warming impact categories.

The comparison of the CBE recycling process with the former Pt recycling processes developed by Duclos *et al.*¹⁵. and with a reference scenario based on the use of primary Pt presents an improved performance regarding four of seven studied impact categories (abiotic depletion, photochemical oxidation, acidification potential and eutrophication potential) from -37 to -67 % compared with Duclos *et al.*¹⁵ and from -81 to -92 % of the reference scenario value. However, the large consumption of energy in the heating steps entailed a lesser efficiency in the CBE recycling process compared to previous processes regarding global warming, ozone layer depletion and freshwater ecotoxicity. Nevertheless, it provides a better option than no recycling for freshwater ecotoxicity. Moreover, the process is equivalent to the 'no recycling' scenario for global warming and is significantly more impacting than the others for the ozone layer depletion potential. However, the latter two impact categories must be put into perspective with the environmental burdens related to the MEA production which are more notable than those of the CBE recycling process.

The LCA results show several advantages in favor of the CBE recycling process. This recycling scenario is appropriate to recycle Pt from aged MEAs of PEMFCs and maximizes the recovery efficiency. However, to be fully satisfactory, particularly regarding

the global warming impact, it is necessary to optimize the energy consumption related to the heating steps of the protocol.

Chemical engineering perspectives related to the process upscale should focus primarily on the optimization of the steps involving heating as they are responsible for the majority of created impacts. For example, coupling some of the steps (e.g. the drying and annealing steps) could improve overall results. The recycling of Nafion[®] components could also lead to an improvement in the environmental efficiency of the PEMFC technology.

LCA perspectives are twofold. In the short-term, this study could be integrated into a larger one including the entire fuel cell system for a vehicle and the use of H₂. In other ways, a mid-term perspective could be to move from lab-scale to an industrial level for the reevaluation of the environmental burdens associated with each component, strictly evaluating the best option.

ASSOCIATED CONTENT

Supporting Information.

All the data that was used to perform the LCA and all completed results are available in the electronic supplementary material.

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Author Contributions

Tom Bauer collected the experimental data, performed the LCA modelling, and paper writing.

Kiranpal Singh developed and implemented the CBE synthesis process and helped with its description for the LCA modelling.

Guillaume Mandil participated in the funding acquisition, supervised the LCA modelling and revision and brought guidance regarding the previous works. Lenka Svecova participated in the conceptualization of the study, in the funding acquisition and supervised the LCA modelling namely with regards to the previous works. She also supervised the writing of the paper.

Laetitia Dubau participated in the funding acquisition, the conceptualization of the study. She supervised the development of the CBE synthesis and performed some of the electrochemical experiments and TEM imaging. She also supervised the writing of the paper.

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Notes

Any additional relevant notes should be placed here.

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ABBREVIATIONS

General abbreviations

CBE Carbon-Based Extraction

CML _____Centrum Milieukunde Leiden

EoL _____End-of-Life

ESI _____Electronic Supplementary Information

FC _____Fuel Cell

FCV _____FC vehicle

FU _____Functional Unit

GDL _____Gas Diffusion Layer

ILCD _____ International reference Life Cycle Data system

kWh kiloWatt.hour

LCA _____Life Cycle Assessment

LC....Life Cycle

MEA _____Membrane-Electrode Assembly

PEM _____Proton-Exchange Membrane

TEM _____Transmission Electron Microscopy

ORR _____Oxygen Reduction Reaction

Impact Categories abbreviations

AD _____Abiotic Depletion

- Acid. Pot. _____Acidification Potential
- Eutro. Pot. _____Eutrophication Potential
- FW-Ecotox. Freshwater Ecotoxicity
- GHG _____Greenhouse gases
- GWP _____Global Warming Potential
- HT _____Human Toxicity
- M-Ecotox. Marine Ecotoxicity
- OLD _____Ozone Layer Depletion potential
- PM Forma Particulate Matter Formation
- Phot. Oxid. Photochemical Oxidation Formation
- T-Ecotox. Terrestrial Ecotoxicity

Chemical abbreviations

- H₂_____Hydrogen
- H₂PtCl₆_____Hexachloroplatinate
- NaCl _____Sodium chloride

NaOH _____Sodium hydroxide

Pdop Polydopamine

Pt _____Platinum

VC _____Vulcan carbon

HCI _____Hydrochloric acid

H₂O₂ Hydrogen peroxide

HNO₃_____Nitric Acid

NO₂ Nitrous oxide

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