



Recovery of Platinum and Ruthenium from PEM Electrodes via Hydrometallurgical Approach

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Abstract

The recovery of platinum group metals (PGMs) from secondary sources is becoming increasingly relevant from an economic and environmental perspective. There are many studies on the extraction of precious metals using hydro- or pyrometallurgical treatment. Most publications focus on the recycling of these metals from catalytic converters. However, less information is available regarding the recycling of PGMs from electrocatalysts, which are important for the achievement of the decarbonization goals of the European “Green Deal.” This paper focuses on the hydrometallurgical approach for Pt and Ru recycling from the proton exchange membrane (PEM) electrode, as those elements are commonly applied to promote a hydrogen-based economy. The proposed recycling scheme contains pre-treatment, leaching, volatilization, and precipitation steps. A parametric study (e.g., reagent concentration, additives, temperature, leaching time, solid-to-liquid ratio, and stirring rate) concerning the above process steps is presented. Leaching tests demonstrated high recovery yields for both metals, achieving 90% for Pt and 82% for Ru, after 4 h of leaching at 75 °C in 4 M HCl with the addition of 1.5 M AlCl₃ as an alternative chloride ion source. Two approaches were followed for Pt/Ru separation: (i) Ru volatilization and (ii) selective Pt precipitation. In the volatilization step, the use of 1 M Na₂S₂O₈ as an oxidizing agent enabled complete Ru recovery (up to 100%) within just 1.5 h. Various acids were evaluated as trapping media to produce different Ru precursors. For selective Pt precipitation, the addition of 5 M NH₄Cl to the bi-metallic leach solution resulted in up to 96% Pt recovery within 30 min, while Ru precipitation was minimal (~3%). The obtained PGM salts produced by this recycling procedure have been reused as precursors to manufacture a new PtRu electrocatalyst, enabling in this way the circularity of the studied elements.

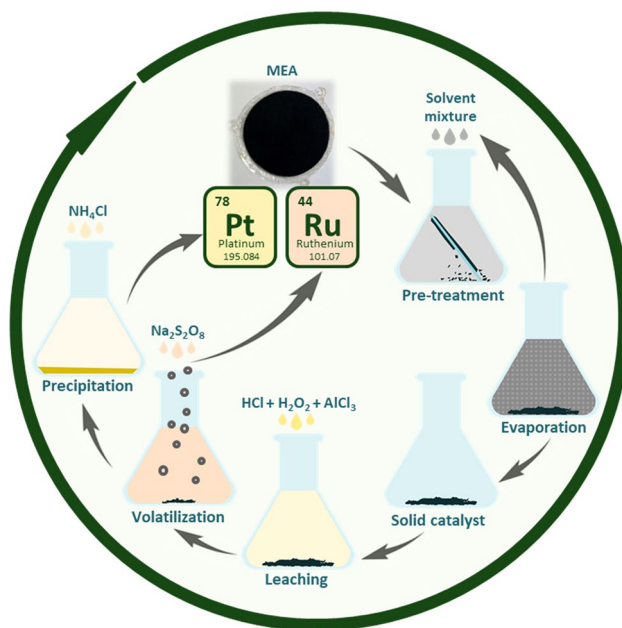
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Graphical Abstract



Keywords Platinum · Ruthenium · Recycling · Hydrometallurgy · Electrocatalyst · PEM electrode

Introduction

Platinum group metals have high technological importance due to numerous fields of applications, such as the automotive industry, refining of metals, medical treatment, and other sectors [1]. The catalytic properties of the PGMs are presently exerting a positive impact on the environment through their application as automotive catalysts and electrocatalysts. The combined catalytic properties of Pt, Ru, and Ir are relevant for producing HER (hydrogen evolution reaction) and OER (oxygen evolution reaction) electrocatalysts for converting renewable energy to hydrogen and “in reverse” for producing electricity [2, 3], without any direct carbon emissions. The produced hydrogen and oxygen can be used directly for fuel cells to replace fossil fuels or find an array of alternate industrial applications, including using hydrogen as fuel or reductant [4, 5]. The increasing deployment of hydrogen technologies is expected to lead to a significant rise in the quantities of end-of-life (EoL) electrolyzers, including PEM, solid oxide (SOEC), and alkaline (AWE) units in the near future. With projections estimating global electrolyzer capacity to reach 40 GW by 2030 [6], the first significant wave of EoL electrolyzers is likely to emerge after this time. Moreover, the size of the resulting stream to be recycled will depend on the installed electrolyzer capacity and operational lifespan, which will vary across different electrolyzer technologies.

PEM-based fuel cells and electrolyzers have numerous advantages over other fuel cell and electrolyzer technologies, the most notable of which are fast start-up times, high power density, and good response to variable operation [7, 8]. However, due to the acidic environment present in PEM-based systems, precious metals, in particular PGMs, are needed to ensure high activity and stability of the catalysts [2, 3]. To achieve this, the continuous development of catalysts with enhanced properties is investigated by altering support materials, introducing dopants, and changing the composition of the active species and reducing PGM content [9–12].

Despite the reduced emissions resulting from PGM usage, their production and refining are not without any environmental impact. Only about 3–10 g of PGMs are present per ton of copper- or nickel-containing ores, thus the primary metallurgical recovery of PGMs is linked to the production of the above base metals and involves ore flotation, smelting, converting, and treatment/refining of formed residue (i.e., anode slime) in many steps to produce pure metals [13]. Therefore, economic and environmentally friendly ways associated with the recycling of material streams to recover these metals are needed. Furthermore, the development of recycling technologies for PGMs is also of high importance, since PGMs are considered critical raw materials for the European Union [14], and primary PGM production is limited to a small number of countries, predominantly in South Africa and Russia [13]. In this context, to ensure process

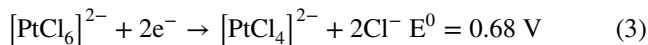
sustainability and aid resource security, the total production-recycling loop needs to be considered to provide the input for predicting the material behavior, design the catalyst where the PGMs are deployed, and consider the re-usage of respective recovered materials.

This study aims to develop a hydrometallurgical route for the separation of PGMs from spent PEM electrodes. Hydrometallurgy is preferred over pyrometallurgy, where PGMs are typically collected in a copper-molten phase, primarily due to lower emissions formed during treatment [15]. Pyro-processing of PEM electrodes can cause the release of toxic gases and volatile species as the result of the combustion of C-support materials and F-containing membranes [15, 16]. Secondly, the hydrometallurgical treatment requires lower energy consumption due to milder process temperatures combined with high recovery yields and selectivity [17]. Generally, the recycling scheme proposed within this study consists of two main stages supplemented by several material treatments to follow the circular hydrometallurgical principles [18]. During the first stage, the metal incorporated on the support material is transferred into solution. The dissolution of PGMs is an essential step of the recovery process, as it has the greatest impact on the overall efficiency of the recycling scheme. The next step involves separating PGMs from the solution with subsequent treatment to recover high-purity salts.

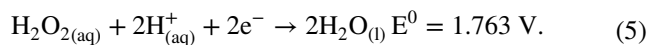
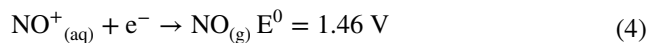
Most published studies have been dedicated to the recovery of PGMs from spent automotive catalysts which mainly consist of Pt, Pd, and Rh [19–22]. However, very few studies were focused on the recovery of PGMs from the spent electrocatalysts of fuel cells or electrolyzers, which contain mainly Pt, Ir, and Ru [15, 23, 24]. This study advances the ongoing efforts to recycle PEM-electrocatalysts with different PGM compositions and catalyst support materials [25, 26]. In this work, the process parameters for the hydrometallurgical processing of PtRu-based electrocatalyst will be optimized to maximize yields while utilizing benign chemicals and minimizing their consumption.

The primary hydrometallurgical step, leaching, exploits the action of chemical agents (i.e., lixivants) capable of transferring metals from a solid material to an aqueous solution through metal complex formation. The lixiviant action can be unselective or selective and will determine whether it requires further purification steps or not. For PEM electrolyzers, the recycling process is more complex due to supporting materials (e.g., membrane, gas diffusion layer (GDL), and support nanoparticles), which can impair the leaching efficiency [26]. For the dissolution of PGMs from the spent catalysts, alkaline (e.g., NaOH, NaCN) or acidic (e.g., HCl, H₂SO₄, HNO₃) mediums are commonly applied [27, 28]. Leaching reactions harness the combined action of a complexing agent that forms stable complexes with the metals dissolved into a solution. The higher the stability of

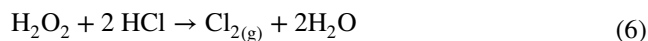
the complex, the easier the oxidation of the metal. The use of halides as a complexing agent, mainly chlorides, is an often described leaching strategy owing to the decrease in the reduction potential of PGM chloro-complexes compared to the redox potential of PGMs without the halide addition [29]:



In order to effectively dissolve PGMs in hydrochloric acid, the presence of an oxidizing agent is necessary. The oxidizing agent ensures the oxidation of the metal to an ionic form, and the acid concentration must be sufficient to enable the complexation reaction with metal ions. A wide range of oxidation agents has been proposed in the literature to improve the leaching of PGMs (e.g., O₃, H₂O₂, HNO₃, HClO) [27, 28, 30]. Due to its high efficiency, leaching with aqua regia is one of the most commonly used hydrometallurgical methods for PGM recovery. Nevertheless, the usage of aqua regia produces a wide variety of byproducts and toxic fumes. In the past years, hydrogen peroxide received huge attention as an effective additive for enhancing the leaching process of PGMs [23, 31, 32]. Considering that the reduction potential of hydrogen peroxide is even higher than that of nitrosyl ion generated in aqua regia, high leaching yields are expected [29, 33]:



From an environmental point of view, the advantage of this system is the elimination of nitrogen compounds emitted compared to leaching with aqua regia. However, the use of hydrogen peroxide in hydrochloric acid instead of nitric acid is accompanied by the emission of chlorine gas, which needs to be considered in an industrial process due to its high toxicity and corrosivity:



Several studies have already described that hydrogen peroxide can effectively replace nitric acid in a hydrochloric medium during platinum leaching. For instance, the use of 10 HCl:1 H₂O₂ at a temperature of 80 °C for the leaching of the monometallic (Pt/Al₂O₃) automotive catalytic converter

allowed to achieve 95% of Pt leaching efficiency [34]. The use of different additives to the H_2O_2 -HCl system was also tested to increase the leaching efficiency of Pt. The NaCl and HCl mixture, for example, allows to decrease the acidity, corrosivity, and leads to an effective PGM dissolution by using 3 M HCl, 4.5 M NaCl, and 1 vol% H_2O_2 to leach Pt from spent automotive catalyst with 100% efficiency at 70 °C for 2 h [32]. Similar results were also published by our research team, reaching up to 100% leaching efficiency for Pt and slightly lower 91%, for Ru [26]. The dissolution of Ru is more challenging and the mechanism to explain the ruthenium leaching behavior is not completely understood. Chemically Ru is very resistant, and in air, the surface of the metal is usually covered by a RuO_2 layer, which prevents further oxidation. The dissolution of Ru can take place in the presence of a strong oxidizing agent, such as fluorine and chlorine at temperatures above 300 °C, or leaching with aqua regia with the addition of HF [35]. Furthermore, it is more difficult to obtain reliable data on ruthenium due to the presence of a large amount of the formed complexes in its several oxidation states [36]. Among all, the oxidation states (III), (IV), and (VIII) are the most common for ruthenium [35, 37], which strongly depends on the applied conditions (e.g., acid concentration and temperature). In hydrochloric acid, numerous hydroxo- and aqua-chlorocomplexes are known for Ru (III) such as $[\text{RuCl}_6]^{3-}$, $[\text{RuCl}_5(\text{H}_2\text{O})]^{2-}$, $[\text{RuCl}_4(\text{H}_2\text{O})_2]^-$, and $[\text{RuCl}_3(\text{H}_2\text{O})_3]$, and for Ru (IV): $[\text{RuCl}_6]^{2-}$, RuOHCl_5^{2-} , $[\text{Ru}_2\text{OCl}_{10}]^{4-}$, $[\text{Ru}_2\text{OCl}_9(\text{H}_2\text{O})]^{3-}$, $[\text{Ru}_2\text{OCl}_8(\text{H}_2\text{O})_2]^{2-}$ and other species [35, 38].

Due to the volatile nature of the Ru complex in its highest oxidation state (VIII), a distillation of RuO_4 is the most efficient separation method. The volatilization of ruthenium tetroxide can occur from the solution with an oxidizing agent (e.g., O_3 , HNO_3 , HClO_4 , NaBiO_3 , KMnO_4 , $\text{K}_2\text{Cr}_2\text{O}_7$) [36, 39–43], or by heating the Ru-containing solid in an oxidizing atmosphere at high temperatures (above 600 °C) [44, 45]. The application of a strong oxidizing agent in the solution is a fast and energy-efficient way for ruthenium oxidation, however, concentrated acid, prolonged time, and elevated temperatures are required for RuO_4 distillation [40, 42, 43]. The formed gaseous ruthenium tetroxide can be trapped by a suitable absorbing medium such as hydrochloric acid [46], nitric acid [47], sodium hydroxide [48], paraffin oil [49], or other suitable solutions.

For Pt separation from the leaching liquor, many techniques can be applied, such as solvent extraction, ion exchange, and precipitation, among other processes [19, 23, 30, 50, 51]. Selective precipitation is a widely employed method in the refining of multimetallic solutions, which is based on the addition of compounds able to form low-soluble complexes with selected metal cations. The formed PGM salts can serve as a precursor for electrocatalysts production [51–53]. The application of recycled PGMs to fabricate

Table 1 Composition of PEM electrode

Material	Composition, %	
	Calculated	Analyzed
Pt (PtRu alloy NPs)	22.1	20.8
Ru (PtRu alloy NPs)	11.1	10.6
Carbon NPs	11.1	16.1*
Carbon substrate	41.0	37.0
Nafion®	14.7	–

*Total C content was determined, to which carbon NPs and Nafion® ionomer contribute

electrocatalysts is expected to significantly decrease costs for PEM technologies and ensures a closed-loop recycling system.

This study presents a novel recycling scheme for PEM electrodes, encompassing the entire process from electrode pre-treatment to the reuse of PGMs in electrode fabrication. A key advancement lies in the application of alternative media, specifically salts, to significantly reduce the acidity of the used solutions, thus offering a more environmentally friendly and efficient approach for PGM extraction. Given the increasing reliance on Ru in the production of electrocatalysts for PEM electrolyzers [10, 25, 54–56], this study addresses the gap in understanding its recycling efficiency and extraction yield from this type of material. Two separation strategies, precipitation and volatilization, were evaluated to recover Pt and Ru from bi-metallic leach solutions. The precipitation process demonstrated versatility by enabling selective separation of Pt and Ru or their co-precipitation, which could be tailored to specific application needs. Alternatively, volatilization introduced a novel approach for Ru recovery, allowing the direct separation of Ru as various Ru-complexes under mild operating conditions. These alternative methods for PGM recovery provide a direct pathway to produce high-value precursors for electrocatalyst manufacturing, thus contributing to more sustainable and efficient recycling processes for PEM electrodes.

Experimental

Materials

The following chemicals were used for experiments and analyses: HCl (37%, VWR), HNO_3 (69%, Merck), H_2O_2 (30%, Merck), $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$ (99%, Alfa Aesar), H_2SO_4 (95–97%, Merck), $\text{Na}_2\text{S}_2\text{O}_8$ (99%, Merck), $\text{K}_2\text{S}_2\text{O}_8$ (99%, VEB Jenapharm—Laborchemie Apolda), $(\text{NH}_4)_2\text{S}_2\text{O}_8$ (99.8%, VWR Chemicals), NH_4Cl (99.8%, Merck), NaOH (98%, Merck), NaNO_3 (99.5%, VWR Chemicals), $\text{C}_2\text{H}_5\text{OH}$ (99.9 + %, EMSURE® ACS), $\text{CH}_4\text{O}_3\text{S}$ (Methanesulfonic

acid (MSA) 98%, Sigma-Aldrich), $C_2H_2O_4 \cdot 2H_2O$ (Oxalic acid dihydrate 99%, Merck), $C_5H_8O_2$ (Acetylacetone 99 + %, Merck) and N,N' -diphenylthiourea (for synthesis, Merck), $C_2H_6O_2$ (Ethylene glycol, technical $\geq 98.0\%$, VWR), $(NH_4)_2PtCl_6$ (Ammonium hexachloroplatinate (IV), Pt 43.4% min, Thermo Scientific), $(NH_4)_2RuCl_6$ (Ammonium hexachlororuthenate (IV), Ru 28.4% min, Thermo Scientific).

Electrode Manufacture and Pre-treatment

The electrode used for the testing of the Pt and Ru recovery was produced by the Danish Technological Institute (DTI, Denmark) by spray-coating a commercial carbon cloth with polytetrafluoroethylene (PTFE)-bonded carbon microporous layer (MPL) (W1S1005, Fuel Cell Store) with a commercial PtRu catalyst (HiSPEC 12100, Alfa Aesar) supported on carbon, with a loading of $18 \text{ mg}_{PtRu}/\text{cm}^2$. The composition of the catalyst-coated electrode is shown in Table 1. The calculated values were obtained based on the weighted amount of the dry material utilized during the production of the electrode, while the analyzed values were obtained after the alkaline fusion of the electrode. Carbon and sulfur contents were determined using the ELTRA CS-580 analyzer.

The electrode material was pre-treated with a solvent–water mixture to separate the PGM-containing catalytic layer from the substrate. The details of the pre-treatment step were described elsewhere [26]. In this step, the PGMs are concentrated in the form of solid particles in the isopropanol–water mixture. After evaporation of the solvent, the catalytic layer was recovered as a solid (henceforth denoted as “solid catalyst”) and was further utilized for the leaching experiments.

The alkaline fusion with a mixture of 1 NaNO_3 :5 NaOH at 600°C was applied for the determination of the PGM content of the solid catalyst, i.e., the feed to the leaching process. First, 0.1 g (± 0.001 g) of the material was added to a zirconium crucible, and then 0.2 g of NaNO_3 and 1.0 g of NaOH were added. Next, the crucible covered by the lid was placed in a muffle furnace for 2 h at 600°C . After the crucible was cooled down to room temperature, the material was dissolved in a boiling 6 M HCl solution. The PGM concentration was determined by an inductively coupled plasma optical emission spectrometer (ICP-OES, Varian Agilent 725-ES). The metal content in the solid catalyst after substrate separation step was determined to be 33.0% and 16.8% for Pt and Ru, respectively. This solid catalyst was used for leaching and volatilization tests.

Leaching

The leaching step was carried out in a 50 mL Erlenmeyer flask with the mass of the solid catalyst 0.1 g (± 0.001 g).

To evaluate the influence of the solid-to-liquid (S/L) ratios 1, 2.5, and 4 g/L, different masses (0.16 g and 0.04 g) with regard to the liquid phase (40 mL total volume) were applied. The experiment was performed on the stirring and heating plate (Wiggins WH620). The temperature (55, 65, and 75°C) and stirring rate (200, 500, and 800 rpm) were varied.

Series of hydrochloric acid solutions were prepared and pre-heated before the experiment in the beaker. In the case of additive addition, the solution of hydrochloric acid with the corresponding concentration of the salt (1.5 M $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$) was prepared and pre-heated before the experiment. The pre-heated solutions were transferred to the flask containing the solid catalyst. Next, the oxidizing agent (H_2O_2) was added in different dosages. The experiment was performed for 4 h, and hourly 1 mL samples were taken, filtered, and then Pt and Ru content were analyzed by ICP-OES.

The leaching rate of PGMs was calculated according to the following equation:

$$R \% = \frac{c \times V}{W \times m} \times 100, \quad (8)$$

where R (%)—the leaching recovery percentage of metal (Pt or Ru); c (mg/L)—the concentration of metal ion (Pt or Ru) in the leach liquor; V (L)—the leach liquor volume; W (mass %)—the content of Pt or Ru in the sample, and m (mg)—the mass of the sample.

The experimental error of this step was determined through the repetition of the same experiment five times. The base-case leaching conditions were 4 M HCl with 5 vol% H_2O_2 , at S/L ratio: 2.5 g/L, 75°C , and 500 rpm. The determined experimental error at these conditions was 2.6% for both Pt and Ru.

Separation of Pt and Ru

After Pt and Ru were dissolved into the solution as chloro-complexes, they needed to be separated from the solution. Two approaches were tested to separate these metals: volatilization of ruthenium and precipitation of platinum.

For the volatilization experiments, solid catalyst after separation of the substrate or concentrated leach solution with the concentration of Pt = 6804 mg/L and Ru = 3265 mg/L were applied. In each experiment, the persulfate salt ($\text{Na}_2\text{S}_2\text{O}_8$, $\text{K}_2\text{S}_2\text{O}_8$, or $(\text{NH}_4)_2\text{S}_2\text{O}_8$) in the form of a solid was added to a 100 mL three-necked round-bottom flask, to achieve the concentration of 1 M in the final volume of 45 mL, which was adjusted with concentrated H_2SO_4 (to reach 1.5 M) and deionized water. Afterward, the temperature was maintained at 60°C , and the stirring rate was adjusted to 600 rpm. Next, the material was added, when the desired temperature was reached. As the trapping medium

for RuO_4 capture, several acidic solutions (HCl , HNO_3 , MSA , or $\text{C}_2\text{H}_2\text{O}_4$) were applied (100 mL total volume). Ammonium chloride and acetylacetone were also tested as an absorption medium; however, it was not as sufficient as the other tested trapping medium for RuO_4 . For the stepwise addition test, 4.5 ml of the freshly prepared 2 M $\text{Na}_2\text{S}_2\text{O}_8$ solution was added hourly to the reaction flask. The progress of the ruthenium volatilization process was verified by taking the 1 mL samples from the trapping solution. The concentration of Ru in the solution was determined by an ultraviolet–visible spectrometer (UV–VIS, Mettler Toledo UV5) using $\text{N,N}'$ -diphenylthiourea as an indicator [57]. The determined analytical error was 1.3%.

The precipitation process was carried out by adding an ammonium chloride solution (2 mL of NH_4Cl , 0.5 M–7 M) to the 2 mL leach solution (with different concentrations of PGMs) under vigorous stirring (300 rpm) at room temperature. The precipitation of the 45 mL solution obtained after the volatilization (free of ruthenium) was also tested using 4 mL of 5 M NH_4Cl , for 2 h at 300 rpm. To define the error of the precipitation experiments, the same experiment using 2 mL of leaching liquor ($\text{Pt} = 407 \text{ mg/L}$ and $\text{Ru} = 183.05 \text{ mg/L}$) and 2 mL of 3 M NH_4Cl was performed five times (300 rpm, 30 min). The determined experimental error at these conditions was 0.6%.

Results and Discussion

Leaching

Before the leaching tests, the separation of the catalytic layers, which consist of PtRu catalyst and a Nafion® ionomer, from the substrate was successfully performed by treating the electrode with an isopropanol–water mixture. This separation step enabled the simple processing of the PGM-containing material and was more advantageous for the leaching procedure. The hydrophobic PTFE-treated carbon cloth and the ionomer cover make metal recovery directly from the untreated electrode material complicated because the chemical coating inhibits the contact between metal particles and reagents [26]. Therefore, the separation of the catalytic layer from the substrate can concentrate the PGM particles, thereby simplifying the PGM extraction by a subsequent hydrometallurgical route.

Effect of H_2O_2 Dosage

The hydrochloric acid-based solution was used to leach the PtRu catalyst at a temperature of 75 °C. The addition of H_2O_2 as an oxidant to the reaction mixture has been proposed as an alternative to the traditional aqua regia system [23, 32]. The effect of hydrogen peroxide dosage and

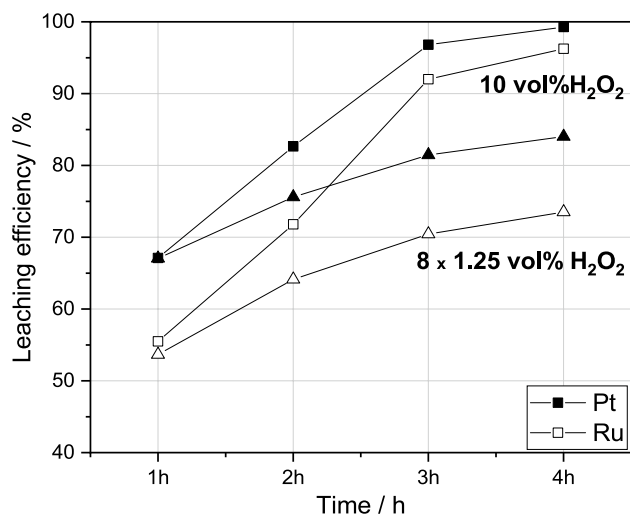


Fig. 1 Effect of one-time (10 vol%) and stepwise addition ($8 \times 1.25 \text{ vol\%}$) of H_2O_2 to HCl -based leaching solution on the leaching yields of Ru and Pt ($T: 75 \text{ }^\circ\text{C}$, 500 rpm, 8 M HCl , S/L ratio: 2.5 g/L)

hydrochloric acid concentration for this system has been discussed in our previous work, demonstrating that the optimum hydrogen peroxide dosage for leaching solutions lies in the range 5–10 vol% [26]. A further increase in the dosage of hydrogen peroxide up to 20 vol% was studied in this work but did not improve the leaching efficiency of PGMs (only 71% for Ru and 77% for Pt). Such a trend was also found in other studies [24, 31], which may be due to the decomposition of the hydrogen peroxide leading to a dilution of the solution. Therefore, to mitigate the decomposition of H_2O_2 , the stepwise addition of the oxidizing agent was tested instead of the one-time addition at the beginning of the experiment in 8 M HCl solution. Figure 1 illustrates that for both Pt and Ru, the addition of the total H_2O_2 volume at the beginning of the experiment makes the leaching curve steeper, which means that the metal dissolution occurs faster. As a result, the stepwise addition did not lead to an increase in leaching yields (74% for Ru and 84% for Pt) in comparison to single addition (96% for Ru and 99% for Pt). It can also be concluded that the amount of H_2O_2 is not a limiting factor at the beginning of the leaching process since the leaching yields after 1 h are nearly the same in both cases. However, the concentration of H_2O_2 was approximately 7.3 times higher when it was added all at once (0.977 M) compared to stepwise addition (0.134 M).

Effect of Chloride Ion Concentration

The primary role of the hydrochloric acid in solution is the formation of the chloro-complexes, which decreases the

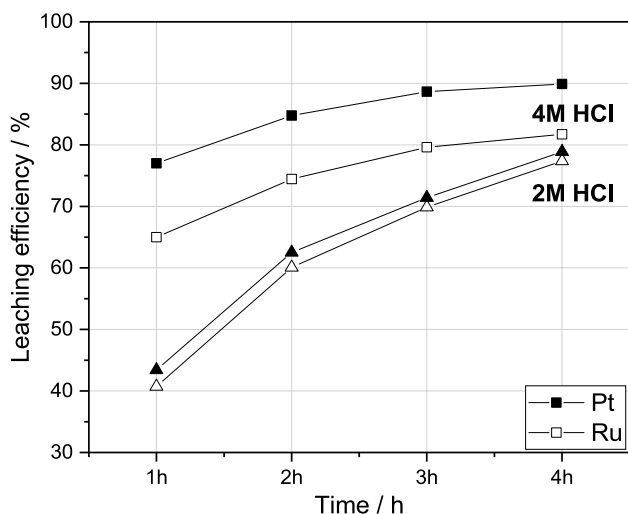


Fig. 2 Leaching yields of Ru and Pt obtained at different HCl concentrations with 1.5 M AlCl_3 (T: 75 °C, 5 vol% H_2O_2 , S/L ratio: 2.5 g/L)

reduction potential of PGMs. Therefore, it is also possible to use chloride salts to enable the formation of chloro-complexes and reduce the acid concentration in the leaching solution [26, 32, 58]. In this work, the effect of HCl concentration (2 and 4 M) with the same concentration of AlCl_3 (1.5 M) optimized previously [26] was tested. As observed in Fig. 2, even using 2 M HCl, relatively high leaching yields were achieved, 77% for Ru and 79% for Pt after 4 h. At higher HCl concentration, the leaching yields are consequently higher: 82% for Ru and 90% for Pt for the same experimental duration. These results also evidenced that AlCl_3 can replace or limit the use of concentrated acids. With the addition of AlCl_3 , the HCl concentration can be lowered to 2 or 4 M compared to Fig. 1, where the HCl concentration is equal to 8 M, while obtaining satisfactory leaching efficiencies, and the usage of chloride salts decreases the corrosivity of the leaching liquor and makes this lixiviant more attractive for industrial applications.

Effect of Temperature

The influence of the reaction temperature on metals dissolution was examined (Fig. 3). As expected, the decrease in the temperature (75 °C, 65 °C, and 55 °C) decreases the leaching efficiency. Higher temperatures facilitate the leaching process and enhance the dissolution rate of PGMs. After 4 h of leaching at 75 °C, the leaching efficiencies of 82% for Ru and 90% for Pt were achieved. Temperatures above 75 °C were not studied due to the fast decomposition of H_2O_2 and evaporation of lixivants, while increasing the leaching energy requirement. However, maximum recovery

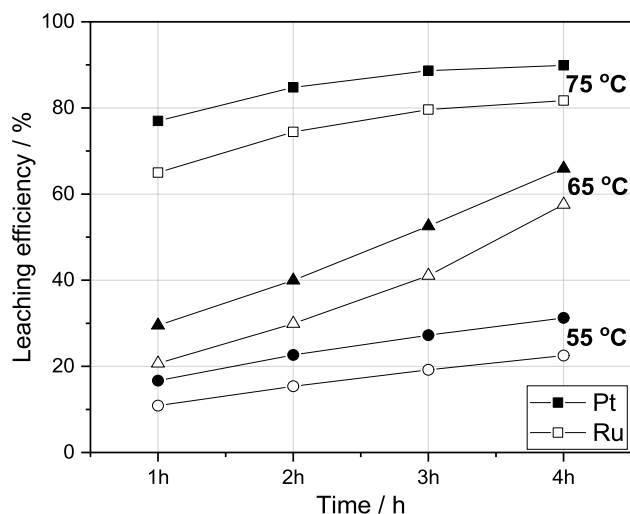


Fig. 3 Leaching yields of Ru and Pt obtained at different temperatures (4 M HCl and 1.5 M AlCl_3 , 5 vol% H_2O_2 , S/L ratio: 2.5 g/L)

can be further enhanced by extending the reaction time or optimizing other process parameters.

Effect of Stirring Rate

The influence of the stirring rate on the PGM leaching efficiency is displayed in Fig. 4. The increase in the stirring rate from 200 to 500 rpm increases the dissolution of Pt and Ru. However, when the stirring speed is further increased, the yields decrease. Fan et al. [59] pointed out, for another leaching system, that a decrease in the leaching efficiency can originate from the simultaneous rotation of liquid and solid, thus not increasing the relative velocity between them and leading to a worse mixing between these two phases.

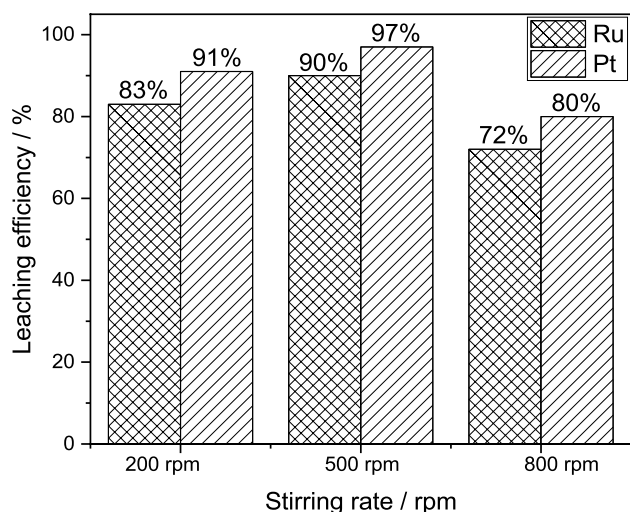


Fig. 4 Leaching yields of Pt and Ru at different stirring rates (T: 75 °C, 8 M HCl, 5 vol% H_2O_2 , S/L ratio: 2.5 g/L, time: 4 h)

The above reasoning can explain the drop of leaching efficiency at 800 rpm compared to 500 rpm.

Effect of Solid-to-Liquid Ratio

Besides agitation and temperature, another parameter that can affect the leaching yields is the solid-to-liquid ratio. This ratio refers to the mass of material leached by a defined volume of liquid. The increase in the leaching efficiency with the increase of the S/L ratio from 1 to 2.5 to 4 g/L was observed (Fig. 5). The obtained results indicated that no optimum was reached when increasing S/L ratio to 4 g/L. The further increase of the S/L ratio was not possible, due to the limited availability of the material for the tests. Although this trend can be considered unusual, it has also been observed in other studies using a similar leaching system [31, 32]. Nonetheless, it should be noted that under the experimental conditions implemented, all cases should correspond to conditions where solution saturation is not reached (abundant solution). The increase in leaching efficiency could be also attributed to the surface reactions [24] on the grain, and as the amount of solids increases, the collisions between the particles increase, leading to the exposure of fresh surfaces.

Volatilization and Capture of Ru

After the leaching process, the obtained solution was filtered to remove the undissolved catalyst, leaving an aqueous solution containing Pt and Ru in a chloride matrix. Quantitative recovery of Ru was achieved from the leaching solution using a two-step strategy entailing a first oxidation-volatilization step and a second reduction-trapping step. The volatile nature of Ru (VIII) is an advantageous property for its separation from other PGMs present in a material.

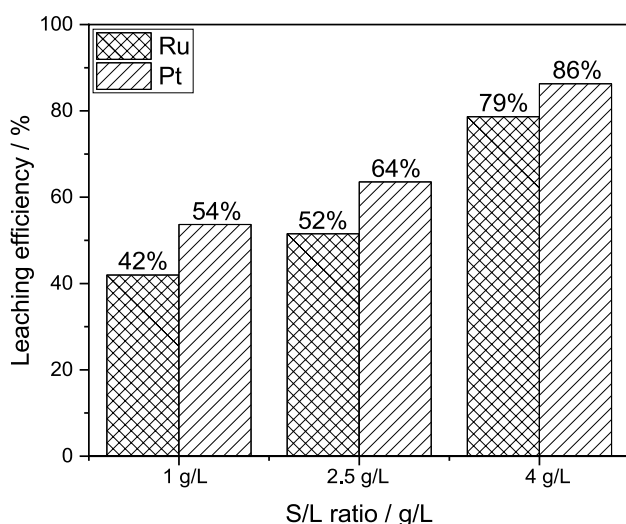
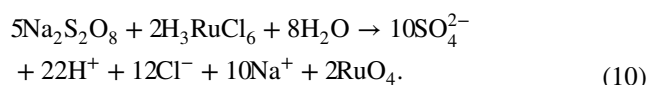
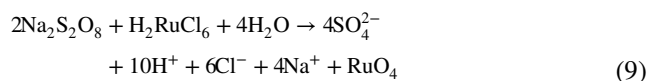
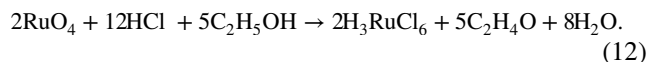
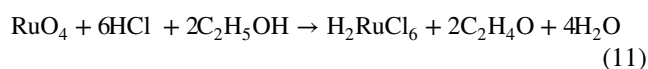


Fig. 5 Effect of S/L ratio on the leaching efficiencies of Ru and Pt (8 M HCl, T: 65 °C, 5 vol% H₂O₂)

Previous studies mentioned the use of nitric acid to promote Ru volatilization [40]. However, preliminary experiments indicated that even when applying 80 °C, the volatilization of Ru from aqueous leach concentrate with nitric acid was not as efficient as other tested oxidants (only 10% separation yield after 5 h). In contrast, using Na₂S₂O₈, at 60 °C, 100% volatilization of Ru from the leach concentrate was achieved. Therefore, due to the high standard reduction potential of Na₂S₂O₈ ($E^0 = 2.01$ V), this reactant was applied to promote ruthenium oxidation by the proposed reactions:



As shown in the equations above, persulfate salt was used as an oxidant to convert different ruthenium species in acidic medium to ruthenium tetroxide. The formed gaseous RuO₄ was then trapped by the absorbing medium possibly following the proposed reactions, reducing RuO₄ to Ru (III) and Ru (IV) chloride species:



Attempts were made to optimize the parameters of the oxidizing mixture (temperature, time, concentrations of Na₂S₂O₈ and H₂SO₄) and trapping solution (concentration and type of the acids, concentration of ethanol) to increase the Ru recovery yield. The optimal conditions for the Ru volatilization from the aqueous leach concentrate were defined as 1 M Na₂S₂O₈ with 1.5 M H₂SO₄ for 1.5 h at 60 °C. The HCl-based trapping medium consisted of 4 M HCl and 5 vol% ethanol, however, the concentration of organic acids in the trapping solution was not optimized, as this research is still in progress.

Effect of Different Persulfate Salts

The influence of the different persulfate salts on the ruthenium recovery yield was investigated. It was demonstrated that Ru volatilized with 100% efficiency through oxidation with Na₂S₂O₈ after already 1.5 h (Fig. 6) in the HCl-based trapping solution (with 5 vol% ethanol). When K₂S₂O₈ was used, the yield of 100% after about 1.5 h was also obtained, while with (NH₄)₂S₂O₈, a low yield of about 13% after 2 h was observed. In the (NH₄)₂S₂O₈ and K₂S₂O₈ cases, the additional advantage of using these oxidants was revealed, i.e., that they both allow separating Pt in the form of precipitate ammonium or potassium hexachloroplatinate (IV)

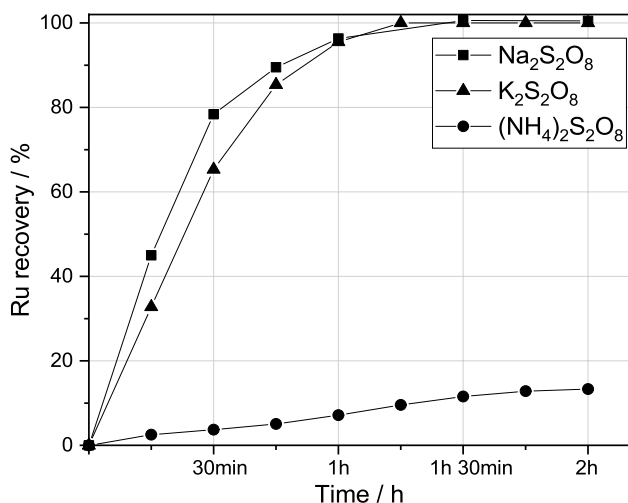


Fig. 6 Volatilization efficiency of Ru from the 5 ml of leach solution with the initial concentration of Pt 6804 mg/L, Ru 3265 mg/L at T: 60 °C, and 600 rpm in a total reaction volume of 45 ml

((NH₄)₂PtCl₆ or K₂PtCl₆) in parallel to Ru volatilization. However, the recovery yield of Ru using (NH₄)₂S₂O₈ was found to be low, likely due to the formation of sludge after mixing the reagents. In contrast, K₂S₂O₈ proved to be a more effective reagent for the simultaneous separation and recovery of Pt and Ru. Nonetheless, the use of potassium may cause impurities during the preparation of the Pt sponge. Therefore, Na₂S₂O₈ was chosen as the best performing oxidation agent for Ru volatilization.

Combined Leaching and Oxidation Step

The efficiency of the Ru volatilization was also tested by using the solid catalyst without the previously applied leaching step (as it was performed in Section “Effect of different persulfate salts”). In this process, the metals should be simultaneously leached and Ru volatilized in the same reaction solution. Based on the obtained results, it was observed that the leaching of the solid catalyst with Na₂S₂O₈ is the limiting step for the Ru separation (Fig. 7), compared to the volatilization of Ru from the concentrated leach solution (Fig. 6). Furthermore, since the thermal decomposition of persulfate salt can occur at elevated temperatures [60], the hourly stepwise addition of Na₂S₂O₈ (20% from initial concentration) was investigated. However, the addition of the fresh salt solution did not affect the volatilization behavior of Ru and it reached the efficiency of around 43% in both cases (Fig. 7).

Effect of Trapping Solution

Furthermore, the influence of different trapping mediums was tested to obtain Ru-complexes valuable for practical

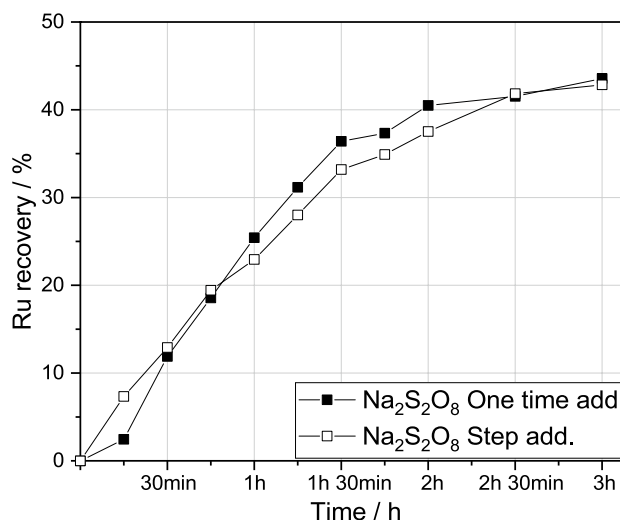


Fig. 7 Comparison of the Ru volatilization efficiency from solid catalyst applying 1 M Na₂S₂O₈ (initial concentration) with hourly addition of Na₂S₂O₈ (20% from the initial concentration) (m: 0.1 g, T: 60 °C, and 600 rpm in a total reaction volume of 45 ml). Trapping medium: 4 M HCl with 5 vol% ethanol

applications. If hydrochloric acid is used as a trapping medium, ruthenium chloride (most probably as RuCl₃·xH₂O) can be recovered, which has been found to be useful in many fields, especially for the synthesis of the heterogeneous catalyst [61–63]. However, other ruthenium complexes (e.g., ruthenium (III) acetylacetonate Ru(acac)₃) can also be used as a precursor for catalyst fabrication [64].

In our previous work, it has been shown that not only hydrochloric or nitric acid [42, 65, 66], but also other acids such as sulfonic and carboxylic acids can serve as an absorption medium for RuO₄ [67]. In this study, the trapping efficiency of oxalic acid and methanesulfonic acid for Ru was evaluated (Fig. 8). The results indicated that these acids could sufficiently capture RuO₄, however, the lower Ru recovery yield (in the range of 40–43%, Fig. 8) compared to that of the concentrated leaching liquor (up to 100%, Fig. 7) is attributed to the low leaching rate of Ru from the solid catalyst in the reaction flask. The recovery of Ru from the leach liquor concentrate by applying these acids as the trapping media would also lead to the high (up to 100%) volatilization efficiencies, however, in this section, we were aiming to study the combined step using the solid catalyst as the starting material. In addition, sulfuric acid, nitric acid, ammonium chloride solution, and acetylacetone were also tested as a trapping medium but did not lead to the complete capture of RuO₄. Therefore, their use as a trapping medium is not recommended. The wide accessibility and low price of hydrochloric acid make it preferred for large-scale applications. However, the possibility to use other mediums opens new pathways for the preparation of halide-free precursors for the manufacture of Ru-containing catalysts. Thus, the

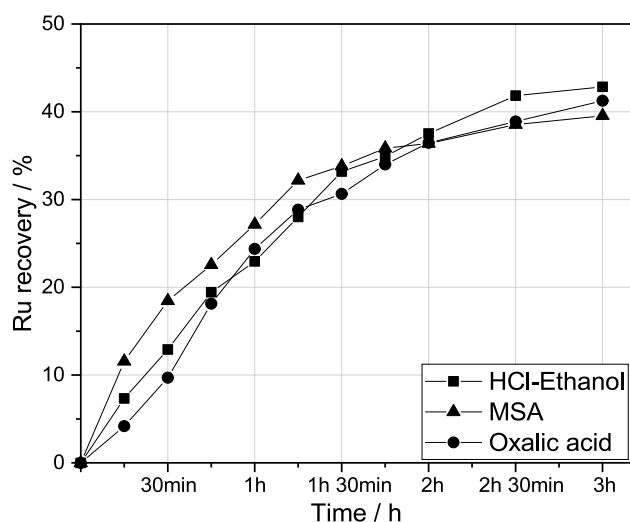


Fig. 8 Volatilization efficiency of Ru from the solid catalyst applying different trapping solutions (m: 0.1 g, T: 60 °C, and 600 rpm in a total reaction volume of 45 mL)

recovery process can be adjusted to the desired ruthenium complex, depending on the final application field.

Precipitation of Pt

Precipitation tests were performed with the HCl-based leach solutions to investigate the effect of NH_4Cl concentration and PGM content on the Pt and Ru precipitation behavior. Currently, no information is available in the published literature regarding the co-precipitation of Pt and Ru from the solution. Therefore, it was of interest to develop a better understanding of the effect of process conditions on the precipitation efficiencies of PGMs, specifically focusing on the precipitation behavior of Pt, and whether it will be possible in this way to efficiently separate it from Ru without an additional volatilization step. Platinum can be recovered in the solid state by precipitation of ammonium hexachloroplatinate ($(\text{NH}_4)_2\text{PtCl}_6$) using ammonium chloride as a precipitation agent.

Direct Precipitation from the Leach Solution

The main process variables (PGM concentration, ammonium chloride concentration, and precipitation time) were tested to achieve high precipitation efficiency (Table 2). The results indicated that after 30 min, most of the Pt was already precipitated, regardless of the concentration of Pt in the initial leach solution. After 24 h, the recovery of Pt was almost not affected, while the Ru precipitation increased. The initial PGM concentration in the system significantly affects the precipitation efficiency of Ru. The lowest precipitation efficiency was observed with the lowest PGM content in

Table 2 Precipitation yields of Pt and Ru depending on their initial concentration in the leachate and the precipitation time

PGM concentration	Time	Ru, %	Pt, %
C_{Ru} : 59 mg/L C_{Pt} : 124 mg/L	30 min 24 h	0 0	69 72
C_{Ru} : 183 mg/L C_{Pt} : 407 mg/L	30 min 24 h	3 18	96 99
C_{Ru} : 501 mg/L C_{Pt} : 864 mg/L	30 min 24 h	34 67	93 96

3 M NH_4Cl used as precipitating agent

the leachate. To ensure high product purity, it is essential to minimize the precipitation time. Prolonged reaction time can lead to co-precipitation of Ru, resulting in contamination of the formed platinum salt. In such cases, preliminary removal of Ru by volatilization is advisable.

Effect of NH_4Cl Concentration

The influence of the precipitation agent concentration was also tested. The concentration of NH_4Cl was varied in the range 0.5 M–7 M (Fig. 9). With increasing NH_4Cl concentration, the solubility of the platinum complex decreases, and the precipitation efficiency increases. Because of the lower solubility of the Pt complex, it was possible to selectively precipitate Pt with only a limited co-precipitation yield (below 10%) of Ru. According to Lai et al. [45], $(\text{NH}_4)_2\text{RuCl}_6$ has lower solubility than $(\text{NH}_4)_3\text{RuCl}_6$. This indicates that Ru (IV) must be the most predominant species precipitating. Furthermore, with the NH_4Cl concentration of

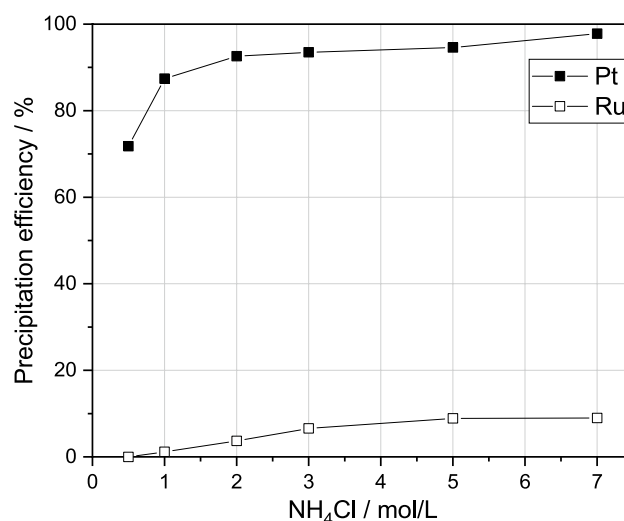


Fig. 9 Precipitation efficiencies of Pt and Ru depending on NH_4Cl concentrations (initial concentration of Ru 183 mg/L and 407 mg/L of Pt in solution, at 300 rpm for 30 min)

0.5 M, it was possible to precipitate about 72% of Pt within 30 min, while no Ru precipitated. For the selective precipitation of Pt, the concentration of NH_4Cl should not exceed 2 M. This ensures minimal Ru precipitation and achieves high purity of the platinum salt. Alternatively, to streamline the process and enhance material circularity, the leach solution with a predefined composition can be precipitated, allowing for the direct formation of a specific Pt-to-Ru ratio suitable for catalyst synthesis.

It is worth emphasizing that the precipitation from the solution left after volatilization (described in Section “Volatilization and capture of Ru”) has also been successfully carried out. This approach of precipitation after volatilization is important as it increases the purity of the obtained salt because only Pt in the solution will precipitate, solving the issue with Ru co-precipitation.

Reuse of the Recovered Material for Electrode Production

In order to assess the quality of the recovered material, a patented solvothermal synthesis developed by DTI [68] for the deposition of Pt-based catalysts on carbon [69] was adapted for the salts used in this work, namely, $(\text{NH}_4)_2\text{PtCl}_6$ and $(\text{NH}_4)_2\text{RuCl}_6$. The commercial salts for both elements were acquired from Thermo Scientific, in order to have a reference for the outcome of the synthesis to compare with the recovered materials. The metallic loading of both the commercial ($(\text{NH}_4)_2\text{PtCl}_6$ with metal content 43.4% and $(\text{NH}_4)_2\text{RuCl}_6$ —28.4%) and the recovered (Pt content 42.3%, Ru—30.6%) salts was determined by ICP-OES, and this value was used to establish a recipe for the synthesis of PtRu nanoparticles on carbon support (Ketjenblack EC-300 J, AkzoNobel). The targeted outcome was an alloy of $\text{Pt}_{0.5}\text{Ru}_{0.5}$ with a metallic loading on carbon of 50 wt%. The precursor salts were dissolved in stoichiometric amounts in deionized water, while the carbon support was dissolved in ethanol

with 1 vol% ethylene glycol. The precursor and support flows were matched to the desired outcomes, pressurized to 300 bar, and mixed with a pre-heated water flow at 450 °C and 300 bar, targeting a mixing temperature of 250 °C. After flowing through the heated portion of the solvothermal flow reactor, which was kept at 250 °C, the product was cooled down and tapped, before being cleaned by centrifugation for 4 times at 15300xg in deionized water and dried in a ventilated oven at 85 °C overnight.

The products were characterized by TGA (TGA, TA Instruments TGA Q500) to determine the metal loading, which was, respectively, 39% with the commercial precursors and 34% with the recovered precursors. Scanning electron microscopy (SEM, Carl Zeiss XB-1540 EsB) equipped with an energy-dispersive X-ray spectroscopy system (EDX, Oxford X-Max 50 mm² SDD) and ICP-OES were used to determine the elemental composition. Specifically, the atomic Pt:Ru ratio was found to be 61:39 with the commercial precursors, and 67:33 with the recovered precursors. SEM images (Fig. 10) show slight agglomeration of the particles, independently of the nature of the precursor salts. Finally, X-ray diffraction (XRD, Malvern Panalytical Empyrean with a Cu source) was used to analyze the crystal structure of the catalyst nanoparticles, as shown in Fig. 11. Peak broadening shows a generally smaller crystallite size in comparison with the commercial catalyst used in the original electrode, but the presence of shoulders on the main peaks suggests the presence of a portion of non-alloyed metallic Pt and Ru. Moreover, the carbon support used for the synthesis also exhibits additional peaks between 20° and 30° in comparison to the commercial catalyst.

While the synthesis outcome did not exactly match the planned values, this was true for both the synthesis with the commercial salts and the recovered salts and simply indicates that a synthesis procedure optimization, possibly with different types of precursor salts and supports, is necessary, which was out of the scope of this work. Specifically, the

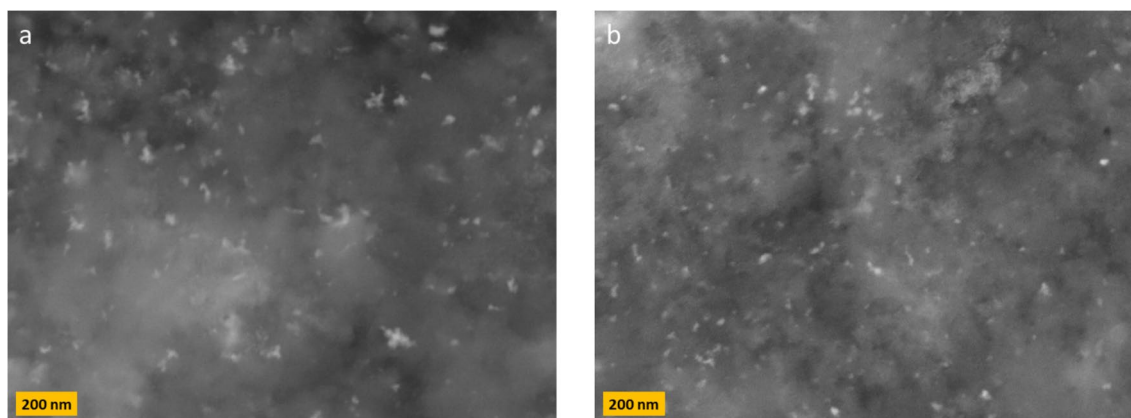


Fig. 10 SEM images of **a** the catalyst synthesized with the commercial precursor salts, and **b** the catalyst synthesized with the recovered salts

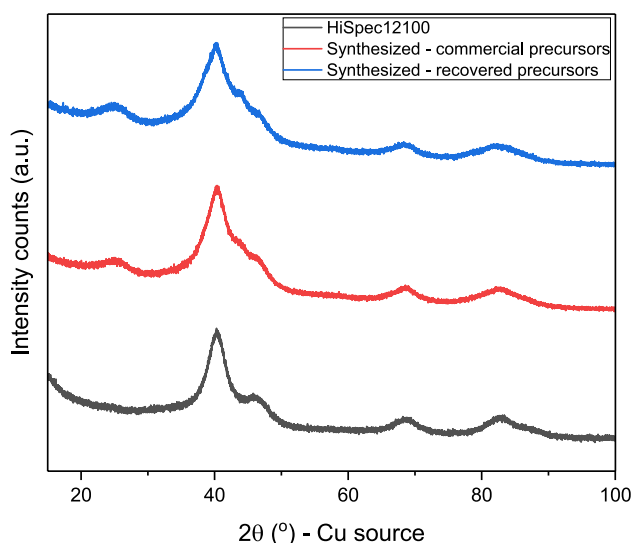


Fig. 11 XRD patterns acquired using a Cu source of the synthesized supported catalysts versus the commercial reference catalyst

optimal parameters for tuning the reduction rate of the Pt and Ru precursors to obtain alloyed nanoparticles would need to be found. The synthesis performed with recovered precursor materials resulted in a similar product as the one performed with commercially available precursors, which indicates a high quality of the recovered material.

Recycling Strategy for PtRu-Based Electrocatalyst

The presented results demonstrate that the proposed hydrometallurgical approach is efficient for recovering PGMs from spent PEM electrodes. The developed recycling strategy includes several steps as follows:

1. Pre-treatment of the electrode material (or MEA) for separation of the PGMs from the carrier material (substrate), thus producing a solid residue.

2. Leaching of the solid residue to dissolve PGMs.
3. Volatilization of Ru for its separation from other PGMs.
4. Precipitation of PGMs with ammonium chloride.

The proposed flow-sheet diagram for the separation of Pt and Ru from the electrode material is shown in Fig. 12.

The proposed hydrometallurgical process for the electrodes consists of several steps: pre-treatment, leaching, volatilization, precipitation steps, and the capture of chlorine gas evolved during the process. First, the separation of the electrocatalyst from the substrate needs to be performed. The proposed method involves extracting the catalytic layer from the carrier material by the alcohol–water mixture. The pre-treatment step is of great importance not only for the hydrometallurgical process but also for potential pyrometallurgical treatment (e.g., using a metal collector phase for PGM pre-concentration), as it eliminates the emission issue of hazardous F-containing gases. The substrate can be recycled to the fabrication stage of the electrocatalyst. Solvents from the separation step can be reused by evaporation from the catalyst suspension and condensation as a clean solution, thus, minimizing alcohol consumption in the recycling scheme. After separation, the solid residue will be subsequently treated with the leaching solution. In this case, an unselective leaching step with an HCl-based medium described in Section “Leaching” is performed. Optimizing the leaching process has resulted in a significant reduction in the hydrochloric acid concentration (up to 4 M) by adding the chlorides (salts) required for PGMs leaching. The addition of H_2O_2 as an oxidant in the leaching step results in the formation of Cl_2 , which must be considered in the process and captured accordingly to ensure safe processing (e.g., captured with an ammonium carbonate solution). In the next step, the volatilization with $\text{Na}_2\text{S}_2\text{O}_8$ and capture of RuO_4 will be performed to separate Ru from Pt, which is also present in the leach solution in the form of a chloro-complex (described in Section “Volatilization and capture of Ru”). The chlorine gas evolved during the oxidation of Ru can be collected and reused in the same way as during

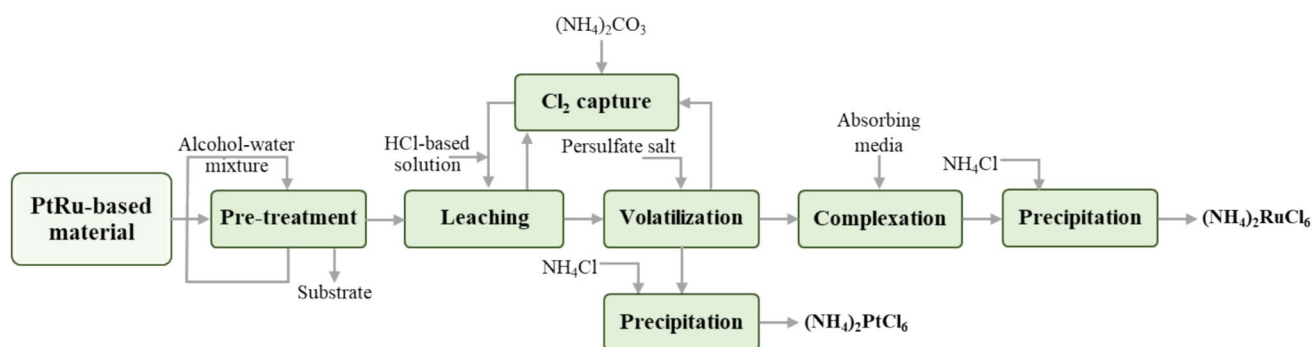


Fig. 12 Proposed flow-sheet diagram for the hydrometallurgical processing of the PtRu-based material

the leaching step. In the next step, the precipitation with ammonium chloride (Section “[Precipitation of Pt](#)”) takes place to obtain high-purity salts, which can then be used for electrocatalyst production described in Section “[Reuse of the recovered material for electrode production](#).” As part of the research project, the proposed scheme is undergoing further development and refinement to minimize processing steps and reagent consumption and follow the zero-waste concept.

Conclusions

A novel hydrometallurgical route for the separation of PGMs from spent PEM electrodes was developed. It has been shown that HCl–H₂O₂-based leaching system is useful for high recovery rates of PGMs even at mild conditions (75 °C for 4 h). Furthermore, the acidity of the leaching solution can be decreased without impairing the efficiency of PGM recovery by applying widely accessible salt additives, such as AlCl₃. Thus, the recovery rates of about 90% and 82%, for Pt and Ru, respectively, were reached by applying 4 M HCl with 1.5 M AlCl₃ after 4 h at 75 °C. The influence of important operating variables on the leaching yield of PGMs was studied. Further refining steps are needed to separate Pt and Ru from each other. Several options for PGM recovery, such as volatilization and precipitation, were successfully tested. Numerous persulfate salts were tested to define their activity for the volatilization of ruthenium as ruthenium tetroxide. Potassium and sodium persulfates showed nearly the same efficiency for the Ru volatilization: in both cases, 100% of Ru was recovered after about 1.5 h. Even when not applying Ru volatilization, high purity of Pt precipitate was achieved by adjusting the NH₄Cl concentration below 2 M in a selective precipitation step. Increasing the concentration of PGMs decreases the separation degree of Pt and Ru even if a low NH₄Cl concentration is applied. The precipitation time and concentrations of metals and NH₄Cl influence both yield and degree of purity immensely. Hence, it seems optimal to precipitate Pt after Ru volatilization and recover the metal salts with ammonium chloride separately. The recovered ammonium salts ((NH₄)₂PtCl₆ and (NH₄)₂RuCl₆) were directly used as precursors for electrocatalyst synthesis and demonstrated comparable performance to those synthesized from commercial salts. Finally, a recycling scheme has been proposed based on the aforementioned experimental findings.

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Declarations

Conflict of interest The authors declare that they have no conflicts of interest.

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