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Matthieu Gras, Lucien Duclos, Nicolas Schaeffer, Vijetha Mogilireddy, Lenka Svecova, et al.. A Comparison of Cobalt and Platinum Extraction in Hydrophobic and Hydrophilic Ionic Liquids: Implication for Proton Exchange Membrane Fuel Cell Recycling. ACS Sustainable Chemistry & Engineering, 2020, 8 (42), pp.15865-15874. 10.1021/acssuschemeng.0c04263 . hal-02995459

HAL Id: hal-02995459

<https://hal.univ-grenoble-alpes.fr/hal-02995459>

Submitted on 9 Nov 2020

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A comparison of cobalt and platinum extraction in hydrophobic and hydrophilic ionic liquids: implication for Proton Exchange Membrane Fuel Cell recycling

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Keywords

Recycling; Fuel cells; Metal ion separation; Ionic liquids; Closed loop; Process evaluation

Abstract

Starting from a real Proton Exchange Membrane Fuel Cell (PEMFC) leachate, separation of the strategic metals platinum(IV) and cobalt(II) was carried out using two distinct strategies applying ionic liquids (ILs), either *via* solvent extraction (SX) or acidic aqueous biphasic system (AcABS). The versatility of ILs and their ability to provide original solutions to common issues in the field of used device recycling is illustrated, with both approaches critically compared. The highly hydrophobic tetradecylpyridinium bis(trifluoromethanesulfonyl)imide ([C₁₄pyr][NTf₂]) was synthesized and applied to the separation of Pt/Co. This solvent was able to selectively extract over 98% of Pt(IV) from the PEMFC leachate in one step while leaving Co(II) in the aqueous phase and exhibited the highest reported partition of Pt(IV) in a [NTf₂]-based IL. In a second approach, the AcABS based on the fully water-miscible tributyltetradecylphosphonium chloride ([P₄₄₄₁₄][Cl]), HCl and water, is compatible with the concentrated nature of the leachate and extracts both platinum(IV) and cobalt(II) quantitatively. In a second stage, a selective precipitation step enabled the recovery of platinum(IV) in the form of an organometallic complex whilst leaving the co-extracted cobalt(II) in solution. This work represents the

first utilization of an AcABS for the recycling of a real waste technological object. These two different types of ILs in both cases resulted in an efficient separation of Pt(IV) from Co(II), using two very different pathways. The merit and transferability of each approach is critically compared, and suggestions are made as to the suitable condition range for each technique.

Introduction

Ionic liquids (ILs), defined as low melting salts below an arbitrary threshold of 100 °C, were extensively studied over the last two decades for the extraction and separation of various metals from aqueous phases.¹⁻⁴ Much of this interest stems from the versatile solvation environment they offer, allowing for the extraction of both neutral and ionic complexes and a greater number of metal extraction mechanisms.⁵ Furthermore, through careful modification of the cation and anion moieties, the physico-chemical properties of the resulting IL can be tailored to a specific separation application.⁶ Due to this design versatility, ILs are often referred to as “designer solvents”.¹ Finally, the ability of ILs to simultaneously act as metal extractants and as the second apolar phase removes the necessity for volatile and flammable organic diluents, potentially improving the environmental footprint of the process.

Two conceptually different approaches are often proposed for metal extraction based on the IL hydrophilicity, namely solvent extraction (SX) using hydrophobic ILs and aqueous biphasic system (ABS) using hydrophilic ILs. Solvent extraction, which involves the preferential partition of a solute between two immiscible phases, is the industrially preferred hydrometallurgical separation option due to its operational ease and flexibility.⁷ The choice of IL is restricted by the hydrophobic requirement, containing either a perfluorinated anion or long alkyl chains or a combination of both. Such ILs were successfully applied towards the extraction of numerous transition metals⁸⁻¹¹ as well as gold¹²⁻¹⁴ and platinum group metals^{12,14-16} for example. ABS are ternary systems composed of water and two solutes with varying hydration energies, in this case one of the solutes being an IL. When combined in the correct proportions, two immiscible - yet reversible - aqueous phases are formed: an IL-rich phase and a phase enriched in the second solute. ABS is often touted as a more environmentally benign alternative to SX as (i) the extraction occurs between two aqueous phases, (ii) lower quantities of IL are required, and (iii) hydrophilic ILs are generally less toxic and more biodegradable than their hydrophobic counterpart.^{3,17} However, the range of possible ABS is limited by the lack of reported biphasic region at low pH conditions for most systems as the traditional salting-out agents are alkaline in nature (e.g. carbonate or phosphate salts) whilst acids are known to induce a salting-in effect.^{3,18-20} Our group recently proposed a new acidic ABS (AcABS) that overcomes the presented limitations of ABS at the low pH typical of common leach solutions.²¹ In AcABS, a suitable hydrophilic IL is salted-out by the acid inherently present in the leach solution, allowing for the design of an integrated platform for a “one-pot” hydrometallurgical treatment. Compared to the studies using neutral ABS for metal

extraction,²² AcABS avoid metal hydrolysis, a crucial factor for the extraction of certain metal such as platinum.

Whilst both SX and ABS/AcABS have their respective advantages that are often used as justification for the selection of one approach over another, there is a lack of studies that allows their direct comparison. In this work two IL-based processes, a SX one using the hydrophobic tetradecylpyridinium bis(trifluoromethanesulfonyl)imide ($[C_{14}pyr][NTf_2]$) IL and an AcABS one using the hydrophilic tributyltetradecylphosphonium chloride ($[P_{44414}]Cl$), were applied and compared for the recovery of metals from waste proton exchange membrane fuel cells (PEMFC). PEMFC are electrochemical devices able to convert chemical energy into electrical energy.^{23,24} Despite their use limited to highly specific applications,²⁵ PEMFC remain an important area of research activity due to their potential.²⁴⁻²⁹ Most notably, the electrode material forming the membrane electrode assembly (MEA) is composed of highly valuable Pt_3Co nanoparticles deposited onto a carbon substrate.³⁰⁻³¹ Since both platinum and cobalt were identified as critical metals by the European Commission,³² finding alternative and sustainable ways of recycling these metals is of the utmost importance to valorize PEMFC technologies in a circular economy context. Platinum is one of the most expensive metals on the market at approximately 27900 \$.kg⁻¹ in 2019 whilst the price of cobalt has wildly fluctuated over the last three years, peaking in 2018 at over 94 \$.kg⁻¹ before falling to an average of 37.4 \$.kg⁻¹ in 2019.³³

With the dual aim of establishing a clear comparison of the merit of IL-based SX vs. AcABS whilst addressing the critical separation and recovery of Pt(IV) and Co(II), SX and AcABS processes based on $[C_{14}pyr][NTf_2]$ and $[P_{44414}]Cl$ respectively were developed. Although the separation of Pt(IV) from Co(II) was recently demonstrated using conventional SX with Cyanex 923 diluted in octanol,³¹ this separation is not reported using ionic liquids. In a first instance, the single element extraction of Co(II) and Pt(IV) using $[C_{14}pyr][NTf_2]$ or $[P_{44414}]Cl$ is studied with respect to HCl concentration. Based on the results, the separation of these two metal ions from real leachate samples from a MEA of a real PEMFC cathode materials using SX or AcABS is disclosed. An efficient Pt(IV)/Co(II) separation is obtained for $[C_{14}pyr][NTf_2]$ whilst Pt(IV) is selectively recovered by precipitation following extraction of both metals in $[P_{44414}]Cl$. Finally, a critical discussion on the merit of both approaches is presented. To the best of our knowledge, the obtained platinum distribution ratio in $[C_{14}pyr][NTf_2]$ is the highest reported so far for an IL based on $[NTf_2]^-$ anion, and this work presents the first application of AcABS to the recycling process of used devices such as PEMFC electrodes.

Results and Discussion

Metal extraction from synthetic solutions

To better appreciate how metal complexation influences the extraction efficiency in both IL-based SX and AcABS, the extraction of Pt(IV) and Co(II) was studied as a function of HCl concentration with the results presented in **Figure 1** and summarized in **Table 1**. In all cases, the HCl molarity is the initial aqueous phase concentration before addition of the IL. Extraction using [C₁₄pyr][NTf₂] was carried out between 1 and 12 mol.L⁻¹ HCl and the results are presented in **Figure 1A**. The extraction yield (%E) using [C₁₄pyr][NTf₂], distribution coefficient (D_M) and the platinum/cobalt separation factor (α_{Pt/Co}) were calculated according to the following equations:

$$\%E1 = \frac{([M]_{aq,0} - [M]_{aq,f})}{[M]_{aq,0}} \times 100 \quad (1)$$

$$D_M = \frac{[M]_{IL,f}}{[M]_{aq,f}} \quad (2)$$

$$\alpha_{Pt/Co} = \frac{D_{Pt}}{D_{Co}} \quad (3)$$

Where the subscript *aq* and *IL* denote the respective phase and [M]₀ and [M]_f the metal concentrations in mol.L⁻¹ before addition of the IL and after extraction respectively.

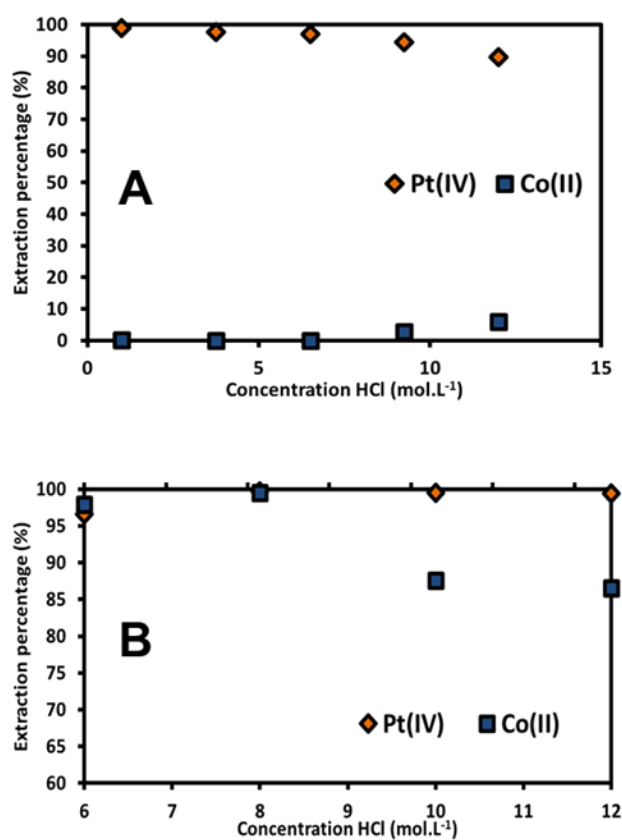


Figure 1. Influence of HCl concentration on extraction efficiency of metals from single element solutions (metal concentration of 1.0x10⁻² mol.L⁻¹) using (A) [C₁₄pyr][NTf₂] and (B) [P₄₄₄₁₄]Cl-HCl-

H₂O AcABS. The HCl molarity is the initial aqueous phase concentration before addition of the IL. Color code - platinum(IV) in orange diamonds and cobalt(II) in blue squares. In figure 1B, at 8 mol.L⁻¹ HCl, orange diamond is hidden by blue dot. Extraction yields for Pt(IV) and Co(II) are not reported below 6 mol.L⁻¹ HCl because [P₄₄₄₁₄]Cl is miscible in aqueous solutions under such conditions.

Results indicate that Pt(IV) is extracted by [C₁₄pyr][NTf₂] in the entire HCl concentration range. A smooth decrease of the extraction yield is observed with the increasing HCl concentration, ranging from 99.0 % to 89.6 % at 1 and 12 mol.L⁻¹ HCl respectively. Such a decrease was previously assigned to the co-extraction of HCl and the resulting change of the physico-chemical properties of the IL phase by acid extraction.¹⁶ In contrast, Co(II) was not extracted using [C₁₄pyr][NTf₂] at HCl concentrations below 6.5 mol.L⁻¹ (%E_{Co} < 0.1 %). Under these conditions, Pt(IV) is effectively separated from Co(II) with $\alpha_{\text{Pt/Co}} > 1000$. At higher concentrations of HCl, namely 9.25 and 12 mol.L⁻¹, 2.7 and 5.9 % Co(II) are respectively co-extracted resulting in a drop in the extraction selectivity.

Table 1. Influence of HCl concentration and extraction system ([C₁₄pyr][NTf₂] and [P₄₄₄₁₄]Cl) on the extraction efficiency of platinum(IV) and cobalt(II) and their separation from single element solutions.

[C ₁₄ pyr][NTf ₂]					
[HCl] (mol.L ⁻¹)	1.0	3.7	6.5	9.3	12.0
%E _{Pt(IV)}	99.0	97.7	96.9	94.5	89.6
D _{Pt(IV)}	100.1	41.7	33.7	18.6	9.78
%E _{Co(II)}	<0.1	<0.1	<0.1	2.7	5.9
D _{Co(II)}	<0.01	<0.01	<0.01	0.03	0.06
$\alpha_{\text{Pt/Co}}$	>1000	>1000	>1000	620	163
[P ₄₄₄₁₄]Cl					
[HCl] (mol.L ⁻¹)	6.0	8.0	10.0	12.0	
%E _{Pt(IV)}	96.6	99.7	99.5	99.4	
D _{Pt(IV)}	15	282	317	542	
%E _{Co(II)}	97.9	99.5	87.6	86.5	
D _{Co(II)}	24	169	41.5	22.3	
$\alpha_{\text{Pt/Co}}$	0.61	1.67	7.64	24.3	

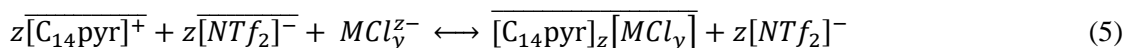
Compared to SX, the study of metal extraction with HCl concentration in AcABS is restricted by the extent of the biphasic region at a given temperature. All extractions were performed at 50 °C due to the greater HCl composition range available (≥ 6 mol.L⁻¹ HCl) with increasing temperature conferred by

the presence of lower critical solution temperature (LCST).³⁴ The selected mixture points for the [P₄₄₄₁₄]Cl-HCl-H₂O AcABS are based on previously reported phase diagrams,³⁴ with the metal distribution for varying HCl concentration presented in **Figure 1B** and **Table 1**. Contrary to SX where no change in phase volume was observed after water saturation of the IL, the change in volume of the aqueous phases in AcABS upon addition of the IL means the extraction yield is calculated according to equation (4).²¹

$$\%E2 = 100 \times \left(1 - \frac{[M]_{low} V_{low}}{[M]_0 V_{initial}} \right) \quad (4)$$

where [M]_{low} represents the concentration in mol.L⁻¹ of the metal ion in the lower phase after extraction. V_{initial} and V_{low} are the volumes in L of the mixture before and after extraction in the lower phase, respectively. As in the SX system, Pt(IV) is extracted above 95% for all AcABS compositions. Due to the experimental uncertainty related to the phase volumes, 95 % extraction can be considered as nearly quantitative. This is in agreement with recent results from our group.²¹ In contrast to the [C₁₄pyr][NTf₂] system, Co(II) is well extracted in the AcABS, with the final extraction efficiency varying with the HCl concentration. A maximum Co(II) extraction of 99.7% is observed for 8 mol.L⁻¹ HCl and decreases thereafter to 86.5% for 12 mol.L⁻¹ HCl. Considering the efficient extraction of Co(II) and Pt(IV) in AcABS for all tested HCl concentrations, direct separation in one stage is not feasible with α_{Pt/Co} ≤ 25.

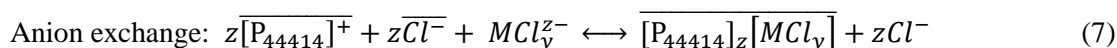
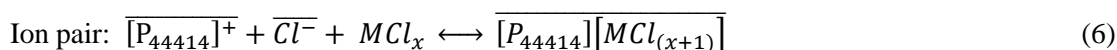
Both Pt(IV) and Co(II) are known to form various chlorometallate complexes as a function of chloride concentration. In the HCl concentration range 1 to 12 mol.L⁻¹ HCl, Pt(IV) is present as the anionic PtCl₆²⁻ complex.^{16,35} In contrast, Co(II) is predominantly under the form of a positively charged or neutral cobalt(II) complex containing H₂O and 1 or 2 Cl⁻ anions for HCl concentrations below 6 mol.L⁻¹. At HCl concentrations 8 mol.L⁻¹ and above, Co(II) can form anionic chlorocobaltate(II) complexes such as CoCl₃⁻ and CoCl₄²⁻ when the [Co]/[H₂O] ratio is low.³⁶⁻³⁸ The transition from cationic to anionic cobalt complexes can be visually observed as the solution color gradually shifts from red for [Co.6H₂O]²⁺ to blue for the negatively charged cobaltate(II) complexes. Relating the metal speciation to the partitioning results for SX and AcABS in **Figure 1**, cationic Co(II) is not extracted into [C₁₄pyr][NTf₂] but is slightly extracted as the tetrachlorocobaltate(II) complex. Extraction of negatively charged complexes (MCl_y^{z-}), such as PtCl₆²⁻ or CoCl₄²⁻, in hydrophobic IL with fluorinated anions occurs via anion exchange and the formation of a hydrophobic ion-pair¹⁶ with the cation of the IL according to equation (5).



The upper bar refers to the species in the IL phase. The hydrophobicity of the IL component ion strongly influences the prevalent extraction mechanism by determining the extent of ion-exchange. Transfer of a hydrophobic ion to the aqueous phase, and *vice versa* for the transfer of a hydrophilic ion to the IL phase, is thermodynamically unfavourable due to the differences in hydration energies. This explains

the inability of [C₁₄pyr][NTf₂] to extract metals when in their highly solvated cationic form due to an extremely unfavourable cation exchange mechanism. Conversely, the hydrophobic [NTf₂]⁻ anion suppresses the exchange of anionic metal complexes with higher energies of solvation, the latter being typically related to the charge density of the complex. This explains why due to its small size and high solvation energy, extraction of Co(II) as CoCl₄²⁻ is low whilst the more charge diffused PtCl₆²⁻ is quantitatively extracted from 1 mol.L⁻¹ HCl.³⁶⁻⁴⁰ According to equation (5), one expects the more hydrophobic the cation, the lower the solubility of the resulting [C₁₄pyr]₂[PtCl₆] complex in water and the higher the extraction yield. In fact, the extraction efficiencies reported using [C₁₄pyr][NTf₂] are one order of magnitude greater than those reported in the homologous systems based on the more hydrophilic 1-octyl-3-methylimidazolium or 1-octylpyridinium cations.^{12,14,16}

As the AcABS shares a common anion between the acid and IL, metal extraction can proceed via a simplified version of Eq. (5) either through ion-pair or anion-exchange reaction:



Due to the sole presence of Pt(IV) as PtCl₆²⁻ in the studied HCl concentration range, Pt(IV) extraction proceeds exclusively by anion exchange according to equation (7) to form the complex [P₄₄₄₁₄]₂[PtCl₆²⁻]. In contrast, Co(II) extraction can proceed either by ion pair or anion exchange depending on the total system chloride concentration. The variation in Co(II) extraction with HCl concentration is attributed to the change in Co(II) speciation as a function of the [Metal]/[Ligand] ratio. A maximal Co(II) extraction of 99.5% is obtained for 8 mol.L⁻¹ HCl before decreasing for [HCl] ≥ 10 mol.L⁻¹. At 8 mol.L⁻¹ HCl, CoCl₃⁻ as the predominant cobalt species in solution is then gradually replaced by the more charge dense CoCl₄²⁻ at higher concentrations of HCl.^{8,21,22,36-40} However, as the listed HCl concentration corresponds to that of the initial aqueous phase concentration before addition of the IL, the total system chloride concentration is in fact diluted when considering the total system volume. As such, extraction most likely proceeds via an ion-pairing mechanism, equation (6), and the extraction of the CoCl₂ species to the IL phase in accordance with that found for Co(II) partition from chloride media with other basic extractants.³⁸ The drop in Co(II) extraction for [HCl] ≥ 10 mol.L⁻¹ is therefore assigned to the increasing presence of anionic chlorocobalt species and the resulting change in the predominant extraction mechanism from ion-pair to anion-exchange. The obtained extraction behavior corresponds with previous studies detailing the extraction mechanism of Co(II).^{8,21,22,38} Even for 12 mol.L⁻¹ HCl, the selectivity of the Pt(IV)/Co(II) separation is far inferior to that obtained in the [C₁₄pyr][NTf₂] system.

Extraction of platinum and cobalt present in MEA materials

Based on the extraction results from synthetic solution, IL-based SX and AcABS separation were applied to the separation and recovery of the critical metals Co(II) and Pt(IV) from the MEA materials of a real PEMFC. We previously showed that 12 mol.L⁻¹ HCl with 3 vol.% H₂O₂ as oxidant could dissolve 99% and 95% of Co(II) and Pt(IV) respectively from PEFMC, with this leachate serving as the basis of this work.³⁰⁻³¹ Three different leachate compositions with different metal to HCl concentration ratios, referred to as A, B and C and listed in **Table 2**, were studied to probe the influence of metal speciation on the extraction selectivity. Leachate A corresponds to the final leachate, whilst leachate B and C correspond to leachate A diluted two-folds with either 12 mol.L⁻¹ HCl or H₂O. Extraction results for all three leachates using [C₁₄pyr][NTf₂] and [P₄₄₄₁₄]Cl are presented in **Figure 2**. The composition of the upper and lower phases obtained mixing the ionic liquid with leachate A, B and C can be found in the supplementary information file.

Table 2. Composition of the real PEMFC leachates used in separation experiments.

Leachate	[HCl] (mol.L ⁻¹)	[Co(II)] (mol.L ⁻¹)	[Pt(IV)] (mol.L ⁻¹)
A	12.0	1.2x10 ⁻²	4.8x10 ⁻³
B	12.0	6.0x10 ⁻³	2.4x10 ⁻³
C	6.0	6.0x10 ⁻³	2.4x10 ⁻³

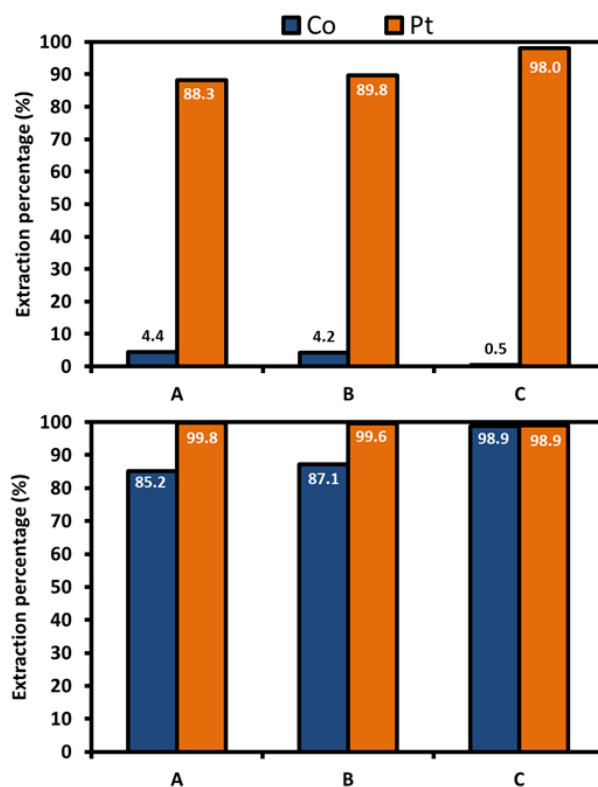
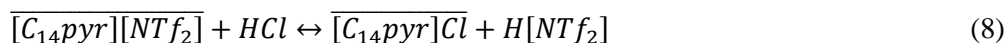


Figure 2. Extraction efficiency of metals from a PEMFC leachate using [C₁₄pyr][NTf₂] (top) and [P₄₄₄₁₄][Cl] (bottom). Initial aqueous phase composition corresponds those listed in **Table 2**. Color code - platinum(IV) in orange and cobalt(II) in blue.

In both IL systems, extraction of metals from real leachates are comparable to those obtained from synthetic solutions for a given HCl concentration. This suggests that any potential other compound present in the PEMFC matrix does not affect the extraction of platinum and cobalt. It is important to highlight that an electrode is not only composed of metal/C but also contains Nafion® as a binder. The latter can swell under the influence of an aqueous solution and adsorb some metallic salts.³¹ Leachate A and B present similar extraction behavior in each respective system. The concentration of metals under the tested conditions, far from the theoretical stoichiometric limit set by equations (5) to (7), has thus little influence on the extraction yield at this acid concentration. Leachate A was diluted with ultra-pure water by a factor of two, yielding leachate C ([HCl]= 6 mol.L⁻¹). In line with the evolution of Pt(IV) and Co(II) speciation with HCl concentration, a decrease in the HCl concentration results in an opposite Pt(IV)/Co(II) separation behavior in the [C₁₄pyr][NTf₂] and [P₄₄₄₁₄][Cl] systems respectively. In the [C₁₄pyr][NTf₂] system, extraction yield of Pt(IV) increased to 98.6 wt% while Co(II) extraction decreased below 1.0 %, resulting in an efficient separation of both metals. In contrast, Co(II) and Pt(IV) are quantitatively extracted from leachate C using AcABS, with the system presenting no separation selectivity for Pt(IV) and Co(II) under the tested conditions.

An important aspect to determine the economic and environmental viability of any IL-based process is the loss of the IL components during extraction. This in turn would hinder the complete recycling of the IL whilst its dissipation increases the toxicity impact. As such, the aqueous solubility of [C₁₄pyr]⁺, [NTf₂]⁻ and [P₄₄₄₁₄]⁺ in pure water and in synthetic leachate with the same composition as leachate B and C was determined at 50 °C with the results presented in **Table 3**. The aqueous solubility of [C₁₄pyr]⁺ was measured in solutions containing no metals due to the overlap of the [C₁₄pyr]⁺ and PtCl₆²⁻ UV-vis peaks. Solubility kinetics of the [C₁₄pyr][NTf₂] performed in pure water is presented in **Figure 3**. [C₁₄pyr][NTf₂] is continuously solubilizing in water until a plateau observed after 150 hours stirring reaching a value of 0.19 mmol.L⁻¹. This solubility is among the lowest solubilities in water reported so far and is mostly due to the increased length of the alkyl chain.^{19,41,42} For comparison, the solubility of 1-butyl-3-methylimidazolium and 1-octyl-3-methylimidazolium bis(trifluoromethanesulfonyl)imide ILs in water is of 16 mmol.L⁻¹ and 2.5 mmol.L⁻¹ respectively.^{19,42} However, it was shown that changes in solubility could occur depending on the nature of the aqueous phase; most notably an increase in the solubility of aromatic IL cations was observed with increasing acid concentrations.^{18-20,42} A similar salting-in behavior is reported here, with the solubility of [C₁₄pyr]⁺ increasing by almost two orders of magnitudes to 9.7 mmol.L⁻¹ in 12 mol.L⁻¹ HCl solution (leachate B). The ion-pair extraction mechanism

for PtCl_6^{2-} in $[\text{C}_{14}\text{pyr}][\text{NTf}_2]$ proposed in Eq(5) suggests the aqueous release of two $[\text{NTf}_2]^-$ anions to the aqueous phase to preserve charge neutrality. Considering quantitative extraction of PtCl_6^{2-} from synthetic leachates B and C ($[\text{Pt(IV)}] = 2.4 \text{ mmol.L}^{-1}$), this would entail the release of 4.8 mmol.L^{-1} of $[\text{NTf}_2]^-$ to the aqueous phase. Results in **Table 3** indicate a greater than expected aqueous $[\text{NTf}_2]^-$ concentration. This difference is attributed to the formation of the water-soluble $\text{H}[\text{NTf}_2]$ for high Cl^- to $[\text{NTf}_2]^-$ ratio as described in equation (8),^{18-20,42} highlighting a more complex $[\text{NTf}_2]^-$ partition behavior than equation (5) simply suggests.



In contrast, the solubility of the quaternary phosphonium $[\text{P}_{44414}]^+$ cation decreases with increasing HCl concentration, from fully miscible in water to practically immiscible in 12 mol.L^{-1} HCl. This is to be expected based on the mechanism of AcABS formation and the salting-out effect of HCl for ILs containing bulky quaternary phosphonium or ammonium cations.^{34,43}

Table 3. Aqueous solubility of the IL component studied after contacting for 150 h and 50°C with synthetic leachate B and C (BDL – Below detection limit). The experimental detection limit for quantitative NMR is 5 mol%.

System	[HCl] (mol.L^{-1})	$[\text{C}_{14}\text{pyr}]^{+b}$ (mmol.L^{-1})	$[\text{NTf}_2]^-$ (mmol.L^{-1})	$[\text{P}_{44414}]^+$ (mmol.L^{-1})
Water ^a	0.0	0.19	BDL	Fully miscible
Leachate B	12	9.7 ± 1.9	8.9 ± 1.4	BDL
Leachate C	6	3.8 ± 0.6	6.2 ± 0.9	15.5 ± 2.0

^a Measured at 25°C ; ^b Measured in the absence of metal cations.

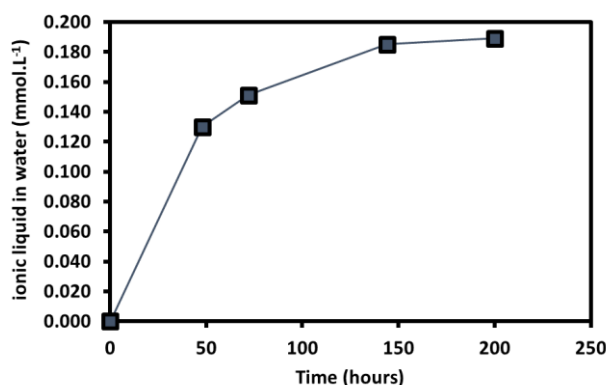


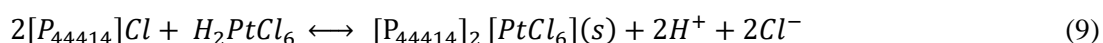
Figure 3. Solubility of $[\text{C}_{14}\text{pyr}][\text{NTf}_2]$ in water at 25°C .

Selective precipitation of platinum from cobalt in AcABS

The difference in Co(II) extraction and Pt(IV) separation selectivity between the [C₁₄pyr][NTf₂] and [P₄₄₄₁₄][Cl] based systems (**Figures 1-2**) entails the development of two separate methodologies. In the case of SX using [C₁₄pyr][NTf₂], Pt(IV) is selectively extracted to the IL phase, leaving Co in the aqueous solution. Pt(IV) can be subsequently recovered from the IL phase by stripping using an acidified thiourea or thiosulfate solution,^{44,45} or through its reductive precipitation by hydrazine addition⁴⁶ as was previously detailed for IL-based SX.

In the AcABS, the quantitative extraction of both Co(II) and Pt(IV) implies the need for an additional selective stripping step compared to the SX separation. Following extraction of Co(II) and Pt(IV) from real leachate C using AcABS, the phases were separated and the [P₄₄₄₁₄][Cl]-rich phase carefully isolated. The isolated [P₄₄₄₁₄][Cl]-rich phase was subsequently diluted with 0.3g of 1 mol.L⁻¹ HCl. Such a choice was made in order to fulfill four criteria: cobalt ion is found in solution under the form of a neutral or positive aquocobalt(II) complex, Pt(IV) remains under the form of a [PtCl₄]²⁻ anion, [P₄₄₄₁₄][Cl] is fully miscible in the resulting aqueous solution and that the latter would be as small as possible.

The resulting solution became turbid and an orange precipitate could be observed. Previous works showed that Au(III), Pt(IV) or Pd(II) can be recovered by precipitation through the addition of a water-soluble IL under mildly acidic conditions as an insoluble IL-metallate complex containing the IL cation and a negatively charged complex AuCl₄⁻, PtCl₆²⁻ or PdCl₄²⁻.¹³⁻¹⁴ Moreover, the precipitate of 1-octylimidazolium hexachloroplatinate was also found to exhibit a red-orange color. In line with these previous reports, the orange color of the bottom phase obtained in this study corresponds to the presence of a salt containing PtCl₆²⁻ and the cation of the IL. The precipitation can thus be represented according to equation (9):¹⁴



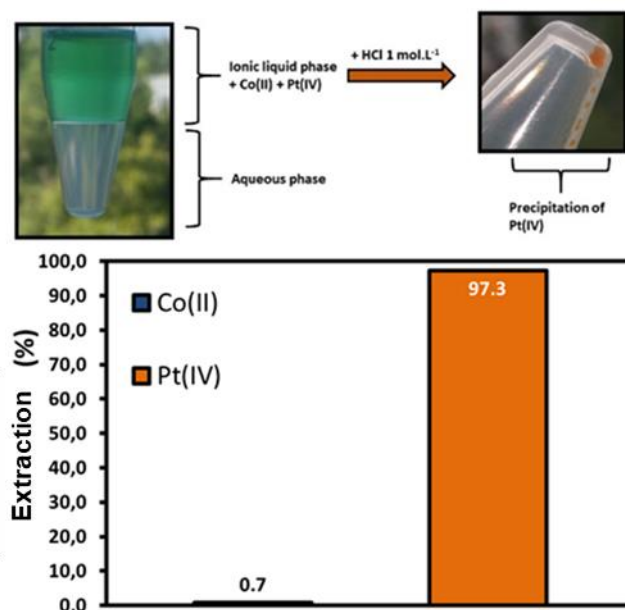


Figure 4. (Top) Snapshots of the platinum precipitation in the $[P_{44414}]Cl-HCl-H_2O$ AcABS. (Bottom) Quantification of the precipitation of platinum(IV) in the $[P_{44414}]Cl-HCl-H_2O$ AcABS after extraction from leachate C.

Snapshots of the platinum precipitate as well as the analysis of the aqueous phase after precipitation are highlighted in **Figure 4**. Chemical analysis of the precipitate and the residual solution following precipitation confirms that more than 97% of Pt(IV) is precipitated whilst cobalt quantitatively remains in the aqueous phase and is not affected at all by the precipitation of $PtCl_6^{2-}$. Under the experimental conditions, the aqueous solution exhibited a red color due to the shift of Co(II) from an anionic complex to a cationic one ($[Co(H_2O)_6]^{2+}$) during dilution. No insoluble precipitate between $[P_{44414}]^+$ and a positively charged or neutral cobalt complex is thus expected to occur. In other words, the selective precipitation of platinum is due to stronger complexation constants of Pt(IV) towards chloride ligands than those of Co(II).⁴⁰ At this point, it is worth noticing that precipitation of Pt(IV) following the extraction of both metal ions is necessary for a successful process. Indeed, a direct precipitation of Pt(IV) starting from leachate C and using $[P_{44414}]Cl$ in order to form a hydrophobic salt such as described in eq. (9) is not possible because under such conditions, $[P_{44414}]Cl$ is indeed not miscible with water, hence leading to an extraction of $[PtCl_4]^{2-}$. Overall, this enables the complete separation of platinum from cobalt in a simple two-step process using AcABS.

Recycling of $[P_{44414}][NTf_2]$

With the general objective of designing a sustainable process for recycling Co(II) and Pt(IV) from PEMFC membranes using ionic liquids, implies investigating on the reusability of an IL used for separating metal ions. Recycling of [NTf₂]-based ionic liquids have already been reported elsewhere, generally using a stripping step in order to remove the metal ions extracted towards the IL.⁴⁴⁻⁴⁸ The main recycling concern raised in this work is therefore related to the reusability of the AcABS. Only one instance of such a study for AcABS was reported very recently by our group.⁴⁷ As a proof of concept, a similar method for recycling [P₄₄₄₁₄]Cl is presented here.

At the end of the separation process, [P₄₄₄₁₄]Cl is present in an aqueous phase containing Co(II) and HCl. Results are collected in Table 4. IL recycling implies to remove Co(II) and separate the ionic liquid from the aqueous solution. To that end, a first stripping step for precipitating Co(II) out from the aqueous phase was first investigated. A solution containing 4 M NaOH was added to the aqueous phase containing both Co(II) and [P₄₄₄₁₄]Cl in order to reach a pH of 10. The solution was then stirred for 60 minutes. Precipitation of over 98 % Co(II) under the form of a brown solid, cobalt(II) hydroxide was then observed.

In a second step, ionic liquid [P₄₄₄₁₄]Cl was removed from the aqueous solution by using its abilities to form an ABS in presence of NaCl. NaCl was added to the resulting aqueous phase in order to obtain a mixture containing 10 wt% NaCl. In agreement with previous reports,⁴⁹ a biphasic system was then obtained. The upper phase was found to contain [P₄₄₄₁₄]Cl and 15.7 wt% water, as measured using a Kirl-Fisher titration method. The purity of the ionic liquid obtained by this method was confirmed by ¹H and ³¹P NMR as shown in the supplementary information file. Finally, the ionic liquid phase was used with a new sample of leachate C, as presented in the article. Extraction of Co(II) and Pt(IV) was successful and extraction yields of 98.1 ± 0.5 % and 99.3 ± 1.1 % for Co(II) and Pt(IV) were respectively obtained. Overall, this proves that sustainable processes for separating Co(II) and Pt(IV) using [P₄₄₄₁₄]Cl can be elaborated.

Table 4. Stripping of Co(II) at the end of extraction cycle 1, recovery of [P₄₄₄₁₄]Cl and extraction of metal ions from leachate C in extraction cycle 2.

	Recovery of Co(II)	Recovery of [P ₄₄₄₁₄]Cl	Extraction cycle 2
Conditions	pH 10 (Add NaOH)	10 wt% NaCl	[P ₄₄₄₁₄]Cl / leachate C
Recovery	98% Co(II)	99 % [P ₄₄₄₁₄]Cl	98.1 ± 0.5 Co(II) 99.3 ± 0.5 Pt(IV)

AcABS and SX for the recovery of metals from waste matrices: a comparison

Two processes for Pt(IV) and Co(II) extraction from real PEMFC leachates were developed based on two ILs with opposite properties: a hydrophobic $[C_{14}pyr][NTf_2]$ and a hydrophilic $[P_{44414}][Cl]$. Important contributions were made in both processes: (i) quantitative Pt(IV) extraction was achieved in a fluorinated IL and (ii) AcABS was for the first time applied to the recycling of strategic metals from real wastes by simply adding the IL to a real leachate solution. To close the process, the isolated metallic cations can easily be precipitated as salts by increasing the pH using NaOH or Na_2CO_3 .⁴⁷ Co(II) can also be reduced by electrodeposition to a metallic form both in aqueous solution as well as from the $[P_{44414}][Cl]$ -rich phase.^{48→49} A conceptual flow diagram for the recycling of cobalt and platinum from PEMFC by either SX or AcABS is presented in **Figure 5**. The full blue and red lines surround the various stages used in this work for the separation of metals by hydrophilic and hydrophobic ILs, respectively. The dotted black line represents the solvents recycling.

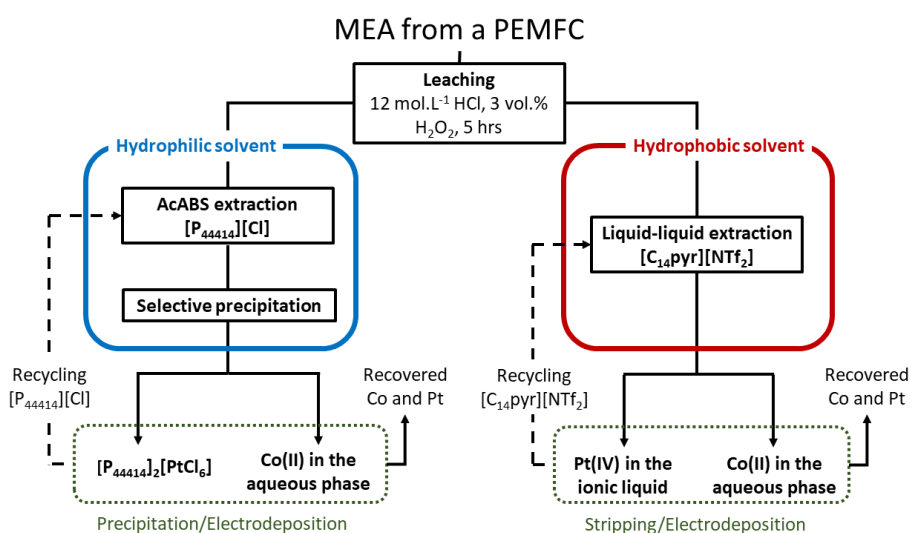


Figure 5. Flow sheet for the recycling of cobalt and platinum from a PEMFC using a hydrophobic ionic liquid or an AcABS extraction step.

A comparison of the proposed processes is here discussed based on process complexity, separation efficiency, price and potential environmental impact. A summary of the discussion is available in **Table 5**. Due to the lack of significant co-impurities present in the PEMFC waste matrix both processes present quantitative separation of Pt(IV) from Co(II). However, the ability of the hydrophobic $[C_{14}pyr][NTf_2]$ to selectively extract Pt(IV) directly from the leach solution across a broad range of HCl concentrations (1 to 12 mol.L⁻¹ HCl, **Figure 1**) is a significant advantage. Conversely, the range of AcABS is restricted by the extent of the biphasic region for a given temperature. Whilst the biphasic domain can be increased

either through raising the temperature³⁴ or addition of NaCl,^{48→49} this does imply increased control of the separation conditions and therefore increased operational costs.

Table 5. Comparison of the developed SX and AcABS processes for Pt(IV) and Co(II) extraction from real PEMFC leach residues based on [C₁₄pyr][NTf₂] and a [P₄₄₄₁₄]Cl respectively.

Criteria	[C ₁₄ pyr][NTf ₂] (SX)	[P ₄₄₄₁₄]Cl (AcABS)
Operational limit	Independent of HCl concentration	Temperature and HCl concentration dependent
Process simplicity	Simple	Simple
Process flexibility	Inflexible	Flexible
Selectivity	Selective for Pt(IV)	Non-selective
Extraction mechanism	Ion-pair/anion-exchange	Ion-pair/anion-exchange
Loss of IL component	Increases with HCl concentration and metal extraction	Decreases with HCl extraction
IL toxicity	Very toxic	Toxic
IL cost	Expensive to very expensive	Expensive

An important benefit of AcABS is that all system components are water soluble with both phases containing a considerable quantity of water. This overcomes one of the major issues associated with ILs: their viscosity. Performing the extraction in aqueous media significantly improves the mass transfer properties of the system, with the viscosity of the [P₄₄₄₁₄]Cl system under experimental conditions below 50 cP.³⁴ The viscosity of the [P₄₄₄₁₄]Cl-rich phase was shown to increase to 629 cP following extraction of a concentrated Co(II) solution due to the formation of the [P₄₄₄₁₄][CoCl₃] and [P₄₄₄₁₄]₂[CoCl₄] complexes.⁴⁹ Even after extraction, viscosity in AcABS are still lower than that of the water-saturated trihexyltetradecyl phosphonium chloride before extraction ([P₆₆₆₁₄]Cl, around 830 cP),⁸ the hydrophobic counterpart to [P₄₄₄₁₄]Cl. Finally, the water-soluble nature of AcABS allows for the direct precipitation of PtCl₆²⁻ without the need of an additional stripping stage as in conventional SX. Alternatively, AcABS can provide a tailored electrodeposition environment by variation in the ionic strength, acidity and water content of the media suitable for metals with reduction potentials within the limit imposed by hydrogen evolution.⁴⁹ However, the usability of the precipitated [P₄₄₄₁₄]₂[PtCl₆] complex remains to be seen, an additional purification step is most likely required to separate and recover the IL cation and Pt(IV).

In both separation systems, metal extraction proceeds via an ion-pair/anion-exchange mechanism. The greater hydrophobicity of the [NTf₂]⁻ anion does confer a certain selectivity, restricting the extraction

to poorly hydrated anionic complexes of low charge densities, such as $[\text{PtCl}_6]^{2-}$. In contrast, the extent of separation in $[\text{P}_{44414}]\text{Cl}-\text{HCl}-\text{H}_2\text{O}$ AcABS solely depends on the metal cation – chloride complexation constant of differing metals: metals with high to medium complexation constants such as Pt(IV), Fe(III), Co(II) or Mn(II) were reported as extracted whilst Ni(II) was not.^{21,49} This suggests that the $[\text{C}_{14}\text{pyr}][\text{NTf}_2]$ -based process could be more robust to the presence of common metallic impurities like Fe(III). A non-negligible impediment to extraction using $[\text{C}_{14}\text{pyr}][\text{NTf}_2]$ is the partial loss of the $[\text{NTf}_2]^-$ anion (Eq(5) and **Table 3**) to the aqueous phase during extraction to charge balance the incoming PtCl_6^{2-} anion. Loss of the $[\text{NTf}_2]^-$ anion is both costly and not sustainable. $[\text{NTf}_2]^-$ is consistently identified as a clear (eco)toxicological hazard across a range of trophic levels whilst its complex synthesis process is reflected in the high cost of the precursor salt.^{17,50} Loss of the IL cationic moiety to the aqueous phase also presents a significant toxicity hazard potential due to the lipophilicity conferred by the cation tetradecyl alkyl chain.¹⁷ As the $[\text{C}_{14}\text{pyr}]^+$ and $[\text{P}_{44414}]^+$ cations present opposite solubility trends with acid concentration, the $[\text{C}_{14}\text{pyr}][\text{NTf}_2]$ system appears best suited in dilute HCl solutions whilst AcABS excels in concentrated HCl solution.

Finally, the question of the price of such solvents remains a strong issue as they can be 5 to 20 times more expensive than molecular solvents.⁵⁰⁻⁵² A direct cost comparison between these two ILs will not be attempted here because such a comparison would be very questionable as these are still produced on a batch scale. Nevertheless, regardless of the IL cation, a severe impediment to the application of fluorinated ILs is the price of the $\text{Li}[\text{NTf}_2]$ precursor used during the metathesis reaction. With regards to the cation, $[\text{P}_{44414}]^+$ is more expensive than $[\text{C}_{14}\text{pyr}]^+$ due to the greater anticipated price of the phosphine precursors compared to pyridine as well as the lower alkylation yields due to steric hindrance. By performing the extraction in aqueous media, lower quantities of ILs are required in AcABS compared to SX as water represents a significant proportion of the IL-rich phase. Whilst the economic feasibility of IL processes is improved by the extensive recycling of the IL phase,⁵² it remains largely dependent on the market price of the target metals and their recovered purity.

Conclusions

Two distinct approaches, a SX process and an AcABS process based on the hydrophobic $[\text{C}_{14}\text{pyr}][\text{NTf}_2]$ and hydrophilic $[\text{P}_{44414}]\text{Cl}$ respectively, are developed and assessed for the recovery of the critical metals Pt(IV) and Co(II) from real PEMFC leachates. These two different types of ionic liquids have proven to lead in both cases to an efficient separation of Pt(IV) from Co(II), using two very different pathways. An efficient Pt(IV)/Co(II) separation is obtained for $[\text{C}_{14}\text{pyr}][\text{NTf}_2]$ whilst Pt(IV) is selectively recovered by precipitation following extraction of both metals in $[\text{P}_{44414}]\text{Cl}$. This once again proves the versatility of ionic liquids, and their ability to provide original solutions to common issues in the field of used devices recycling. Comparison of the two processes suggests that their applicability is primarily

determined by the effluent acidity due to the increased loss of the IL. $[P_{44414}]Cl$ AcABS appears better suited to concentrated HCl solutions whilst $[C_{14}pyr][NTf_2]$ excels under more dilute conditions. The lower energy of solvation of $[NTf_2]^-$ from $[C_{14}pyr][NTf_2]$ compared to the Cl^- from $[P_{44414}]Cl$ suppresses the exchange of anionic metal complexes with higher energies of solvation, thereby conferring a greater selectivity to $[C_{14}pyr][NTf_2]$. However, loss of the $[NTf_2]^-$ anion during extraction negatively impacts the extraction process, something that is avoided in the more tunable AcABS process. Ultimately, the feasibility of IL processes is dependent on the market price of the target metals and their recovered purity.

Experimental

A detailed description of the chemicals and instruments used in this work as well as the experimental protocol followed can be found in the Supplementary Information. This includes the $[C_{14}pyr][NTf_2]$ synthesis protocol and the characterization by 1H -NMR (Figure S1), thermogravimetric analysis (Figure S2) and by differential scanning calorimetry (Figure S3) of the obtained IL.

Metal extraction from ideal solutions

In a first instance, the extraction of Co(II) and Pt(IV) from model leach solution containing variable concentration of HCl was studied in the $[C_{14}pyr][NTf_2]$ and $[P_{44414}]Cl$ -HCl- H_2O systems respectively. $[P_{44414}]Cl$ has the form of a white waxy solid and is fully water soluble for all compositions but forms a reversible biphasic system in the presence of HCl. For all extraction experiments from model solutions, the concentration of metals was of $1.0 \times 10^{-2} \text{ mol.L}^{-1}$. Typically, 2 g of $[C_{14}pyr][NTf_2]$ or 1 g of $[P_{44414}]Cl$ was mixed with 2 mL of an aqueous solution. The tubes were placed in a rotator installed in a heat chamber in order to control the temperature. All extraction experiments were performed at 50 °C. After 3 hours of agitation, the aqueous phases were carefully separated from the hydrophobic ionic liquid and were analyzed by AAS. In the case of AcABS, both the IL- and acid-rich phase were analyzed by atomic absorption spectrophotometry (AAS) as all components are water soluble. Quantification of the water content in the IL-rich phase at 25 and 50 °C under the tested conditions was reported in a previous work.²¹ All extraction percentages (equations (1) and (4)) were given with an error of ± 1 and 5 % for %E1 and %E2 respectively. The loss in accuracy for AcABS extractions is due to the experimental uncertainty associated with the accurate measurement of phase volume.

Leaching, separation and precipitation of metals from PEM fuel cell

The Membrane Electrode Assembly was prepared by the LITEN department from CEA Grenoble, France, and is composed of a proton exchange membrane (PEM) surrounded by two catalytic layers and two gas diffusion layers. Nafion® was used as polymer electrolyte for the PEM membrane.

Leaching of the MEA was performed according to an optimized procedure previously published.³⁰⁻³¹ Briefly, 16 cm² of MEA was treated with 200 mL of aqueous solution containing 3 vol.% H₂O₂ in HCl 12 mol.L⁻¹. The leaching step was carried out at 25°C for 5 hours. After that, the obtained leachate solution was filtered in a Büchner funnel and analyzed by AAS; concentrations of 1.2x10⁻² and 4.8x10⁻³ mol.L⁻¹ for platinum(IV) and cobalt(II) were respectively measured in agreement with the reference study.^{30,31} The extraction of metallic ions from solutions A, B and C (composition given in **Table 2**) using [P₄₄₄₁₄]Cl or [C₁₄pyr][NTf₂] was carried out following the same procedure as that detailed in the preceding subsection using model solutions. The inherent acid concentrations in all leachates was sufficient to yield a biphasic system in the [P₄₄₄₁₄]Cl-HCl-H₂O AcABS. The precipitation of Pt(IV) from the loaded IL-rich phase in AcABS was adapted from a previous work.²⁵ Briefly, following extraction of metals from leachate C using the [P₄₄₄₁₄]Cl-HCl-H₂O AcABS, the IL-rich phase (corresponding to the upper phase) was carefully separated and cooled down to 25°C. To this, 0.3 g of HCl 1 mol.L⁻¹ was added to induce the selective precipitation of Pt(IV). The metal content of the IL-rich phase before and after precipitation was analyzed by AAS to determine the extent of precipitation.

Conflicts of interest

Authors declare no conflicts of interest.

Acknowledgements

Authors would like to acknowledge labex CEMAM, Rhône-Alpes region and EIT InnoEnergy H2020 for financial support. We are also grateful to the LITEN team from CEA, Grenoble for providing the PEMFC. N.S. acknowledges the project CICECO-Aveiro Institute of Materials, UIDB/50011/2020 & UIDP/50011/2020, financed by national funds through the FCT/MEC and when appropriate co-financed by FEDER under the PT2020 Partnership Agreement.

Supporting information

Chemicals, instruments and measurements, synthesis and characterization of [C₁₄pyr][NTf₂], composition of phases in AcABS formed using leachate A, B and C, ¹H NMR and ³¹P NMR spectra for [P₄₄₄₁₄]Cl

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