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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 ($[\text{C}_{14}\text{pyr}][\text{NTf}_2]$) 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 $[\text{NTf}_2]$ -based IL. In a second approach, the AcABS based on the fully water-miscible tributyltetradecylphosphonium chloride ($[\text{P}_{44414}]\text{Cl}$), 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

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

36

37 **Introduction**

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

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

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

69 Whilst both SX and ABS/AcABS have their respective advantages that are often used as justification
70 for the selection of one approach over another, there is a lack of studies that allows their direct
71 comparison. In this work two IL-based processes, a SX one using the hydrophobic tetradecylpyridinium
72 bis(trifluoromethanesulfonyl)imide ($[C_{14}pyr][NTf_2]$) IL and an AcABS one using the hydrophilic
73 tributyltetradecylphosphonium chloride ($[P_{44414}]Cl$), were applied and compared for the recovery of
74 metals from waste proton exchange membrane fuel cells (PEMFC). PEMFC are electrochemical
75 devices able to convert chemical energy into electrical energy.^{23,24} Despite their use limited to highly
76 specific applications,²⁵ PEMFC remain an important area of research activity due to their potential.²⁴⁻²⁹
77 Most notably, the electrode material forming the membrane electrode assembly (MEA) is composed of
78 highly valuable Pt₃Co nanoparticles deposited onto a carbon substrate.³⁰⁻³¹ Since both platinum and
79 cobalt were identified as critical metals by the European Commission,³² finding alternative and
80 sustainable ways of recycling these metals is of the utmost importance to valorize PEMFC technologies
81 in a circular economy context. Platinum is one of the most expensive metals on the market at
82 approximately 27900 \$.kg⁻¹ in 2019 whilst the price of cobalt has wildly fluctuated over the last three
83 years, peaking in 2018 at over 94 \$.kg⁻¹ before falling to an average of 37.4 \$.kg⁻¹ in 2019.³³

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

97

98 **Results and Discussion**

99 **Metal extraction from synthetic solutions**

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

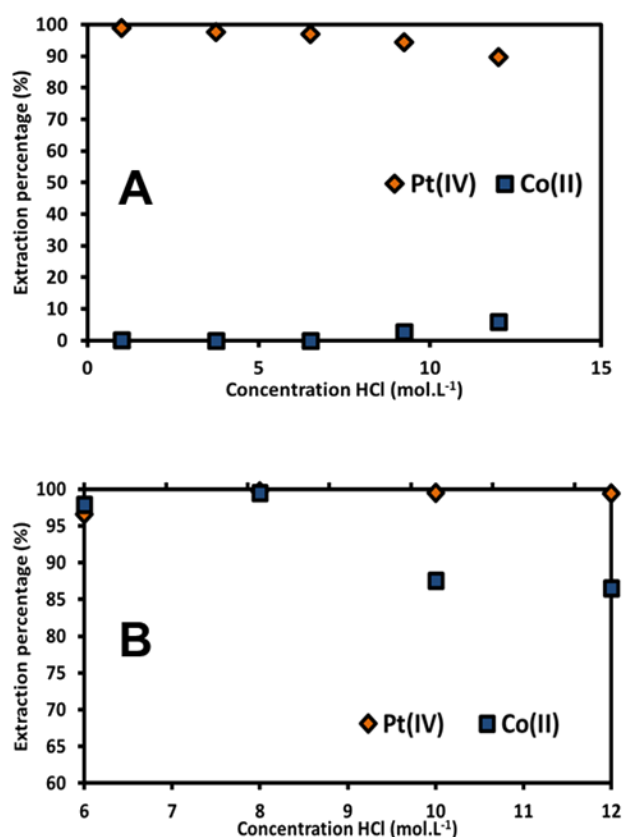
$$107 \quad \%E1 = \frac{([M]_{aq,0} - [M]_{aq,f})}{[M]_{aq,0}} \times 100 \quad (1)$$

$$108 \quad D_M = \frac{[M]_{IL,f}}{[M]_{aq,f}} \quad (2)$$

$$109 \quad \alpha_{Pt/Co} = \frac{D_{Pt}}{D_{Co}} \quad (3)$$

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

112



113

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

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

120

121 Results indicate that Pt(IV) is extracted by [C₁₄pyr][NTf₂] in the entire HCl concentration range. A
 122 smooth decrease of the extraction yield is observed with the increasing HCl concentration, ranging from
 123 99.0 % to 89.6 % at 1 and 12 mol.L⁻¹ HCl respectively. Such a decrease was previously assigned to the
 124 co-extraction of HCl and the resulting change of the physico-chemical properties of the IL phase by
 125 acid extraction.¹⁶ In contrast, Co(II) was not extracted using [C₁₄pyr][NTf₂] at HCl concentrations below
 126 6.5 mol.L⁻¹ (%E_{Co} < 0.1 %). Under these conditions, Pt(IV) is effectively separated from Co(II) with
 127 $\alpha_{\text{Pt/Co}} > 1000$. At higher concentrations of HCl, namely 9.25 and 12 mol.L⁻¹, 2.7 and 5.9 % Co(II) are
 128 respectively co-extracted resulting in a drop in the extraction selectivity.

129

130 **Table 1.** Influence of HCl concentration and extraction system ([C₁₄pyr][NTf₂] and [P₄₄₄₁₄]Cl) on the
 131 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	

132

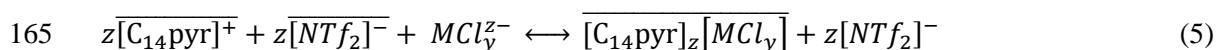
133 Compared to SX, the study of metal extraction with HCl concentration in AcABS is restricted by the
 134 extent of the biphasic region at a given temperature. All extractions were performed at 50 °C due to the
 135 greater HCl composition range available (≥ 6 mol.L⁻¹ HCl) with increasing temperature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

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

$$142 \quad \%E2 = 100 \times \left(1 - \frac{[M]_{low} V_{low}}{[M]_0 V_{initial}} \right) \quad (4)$$

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

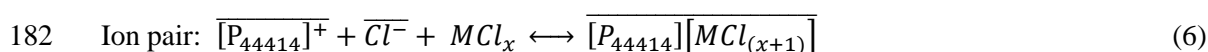
152 Both Pt(IV) and Co(II) are known to form various chlorometallate complexes as a function of chloride
 153 concentration. In the HCl concentration range 1 to 12 mol.L⁻¹ HCl, Pt(IV) is present as the anionic
 154 PtCl₆²⁻ complex.^{16,35} In contrast, Co(II) is predominantly under the form of a positively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



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

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

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



184 Due to the sole presence of Pt(IV) as PtCl₆²⁻ in the studied HCl concentration range, Pt(IV) extraction
 185 proceeds exclusively by anion exchange according to equation (7) to form the complex [P₄₄₄₁₄]₂[PtCl₆²⁻
 186]. In contrast, Co(II) extraction can proceed either by ion pair or anion exchange depending on the total
 187 system chloride concentration. The variation in Co(II) extraction with HCl concentration is attributed
 188 to the change in Co(II) speciation as a function of the [Metal]/[Ligand] ratio. A maximal Co(II)
 189 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
 190 ¹ HCl, CoCl₃⁻ as the predominant cobalt species in solution is then gradually replaced by the more
 191 charge dense CoCl₄²⁻ at higher concentrations of HCl.^{8,21,22,36-40} However, as the listed HCl concentration
 192 corresponds to that of the initial aqueous phase concentration before addition of the IL, the total system
 193 chloride concentration is in fact diluted when considering the total system volume. As such, extraction
 194 most likely proceeds via an ion-pairing mechanism, equation (6), and the extraction of the CoCl₂ species
 195 to the IL phase in accordance with that found for Co(II) partition from chloride media with other basic
 196 extractants.³⁸ The drop in Co(II) extraction for [HCl] ≥ 10 mol.L⁻¹ is therefore assigned to the increasing
 197 presence of anionic chlorocobalt species and the resulting change in the predominant extraction
 198 mechanism from ion-pair to anion-exchange. The obtained extraction behavior corresponds with
 199 previous studies detailing the extraction mechanism of Co(II).^{8,21,22,38} Even for 12 mol.L⁻¹ HCl, the
 200 selectivity of the Pt(IV)/Co(II) separation is far inferior to that obtained in the [C₁₄pyr][NTf₂] system.

201

202 **Extraction of platinum and cobalt present in MEA materials**

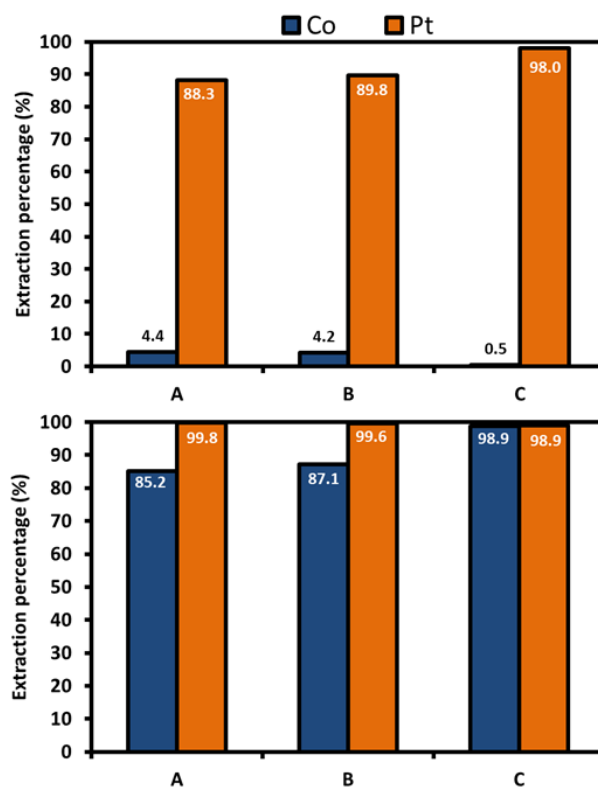
203 Based on the extraction results from synthetic solution, IL-based SX and AcABS separation were
 204 applied to the separation and recovery of the critical metals Co(II) and Pt(IV) from the MEA materials
 205 of a real PEMFC. We previously showed that 12 mol.L⁻¹ HCl with 3 vol.% H₂O₂ as oxidant could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

214

215 **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

216



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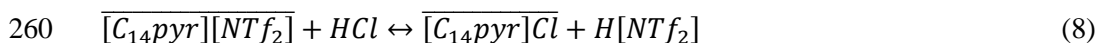
218 **Figure 2.** Extraction efficiency of metals from a PEMFC leachate using [C₁₄pyr][NTf₂] (top) and
219 [P₄₄₄₁₄]Cl (bottom). Initial aqueous phase composition corresponds those listed in **Table 2**. Color code
220 - platinum(IV) in orange and cobalt(II) in blue.

221

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

237 An important aspect to determine the economic and environmental viability of any IL-based process is
238 the loss of the IL components during extraction. This in turn would hinder the complete recycling of
239 the IL whilst its dissipation increases the toxicity impact. As such, the aqueous solubility of [C₁₄pyr]⁺,
240 [NTf₂]⁻ and [P₄₄₄₁₄]⁺ in pure water and in synthetic leachate with the same composition as leachate B
241 and C was determined at 50 °C with the results presented in **Table 3**. The aqueous solubility of [C₁₄pyr]⁺
242 was measured in solutions containing no metals due to the overlap of the [C₁₄pyr]⁺ and PtCl₆²⁻ UV-vis
243 peaks. Solubility kinetics of the [C₁₄pyr][NTf₂] performed in pure water is presented in **Figure 3**.
244 [C₁₄pyr][NTf₂] is continuously solubilizing in water until a plateau observed after 150 hours stirring
245 reaching a value of 0.19 mmol.L⁻¹. This solubility is among the lowest solubilities in water reported so
246 far and is mostly due to the increased length of the alkyl chain.^{19,41,42} For comparison, the solubility of
247 1-butyl-3-methylimidazolium and 1-octyl-3-methylimidazolium bis(trifluoromethanesulfonyl)imide
248 ILs in water is of 16 mmol.L⁻¹ and 2.5 mmol.L⁻¹ respectively.^{19,42} However, it was shown that changes
249 in solubility could occur depending on the nature of the aqueous phase; most notably an increase in the
250 solubility of aromatic IL cations was observed with increasing acid concentrations.^{18-20,42} A similar
251 salting-in behavior is reported here, with the solubility of [C₁₄pyr]⁺ increasing by almost two orders of
252 magnitudes to 9.7 mmol.L⁻¹ in 12 mol.L⁻¹ HCl solution (leachate B). The ion-pair extraction mechanism

253 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
 254 the aqueous phase to preserve charge neutrality. Considering quantitative extraction of PtCl_6^{2-} from
 255 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
 256 $[\text{NTf}_2]^-$ to the aqueous phase. Results in **Table 3** indicate a greater than expected aqueous $[\text{NTf}_2]^-$
 257 concentration. This difference is attributed to the formation of the water-soluble $\text{H}[\text{NTf}_2]$ for high Cl^-
 258 to $[\text{NTf}_2]^-$ ratio as described in equation (8),^{18-20,42} highlighting a more complex $[\text{NTf}_2]^-$ partition
 259 behavior than equation (5) simply suggests.



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

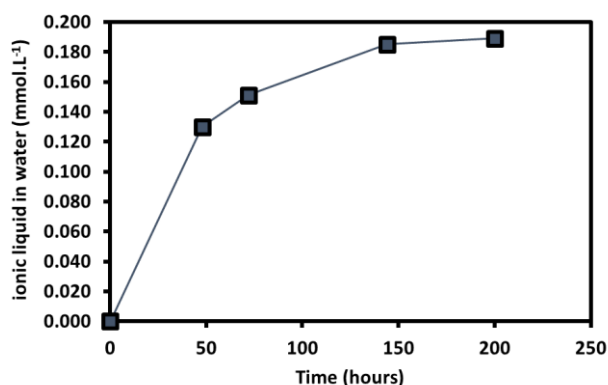
265

266 **Table 3.** Aqueous solubility of the IL component studied after contacting for 150 h and 50°C with
 267 synthetic leachate B and C (BDL – Below detection limit). The experimental detection limit for
 268 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

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

270



271

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

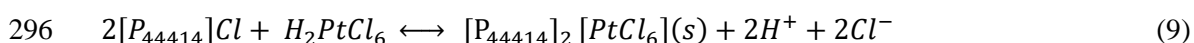
273

274 Selective precipitation of platinum from cobalt in AcABS

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

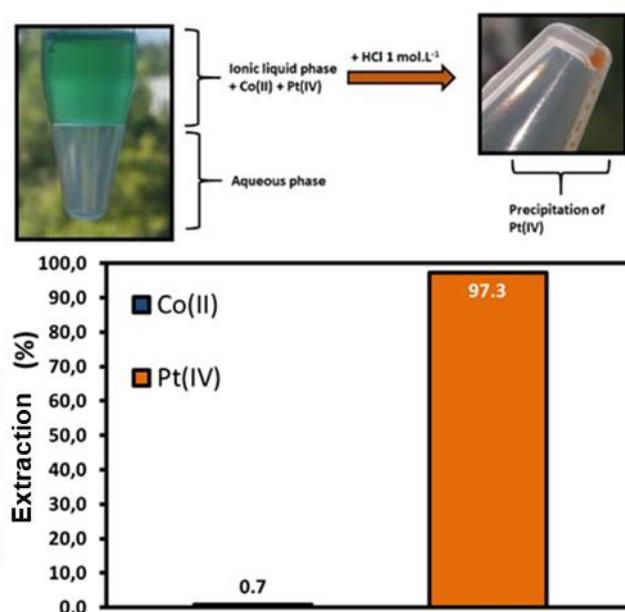
281 In the AcABS, the quantitative extraction of both Co(II) and Pt(IV) implies the need for an additional
282 selective stripping step compared to the SX separation. Following extraction of Co(II) and Pt(IV) from
283 real leachate C using AcABS, the phases were separated and the [P₄₄₄₁₄]Cl-rich phase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

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



297

298



299

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

303

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

318

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

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

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

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

344

345 **Table 4.** Stripping of Co(II) at the end of extraction cycle 1, recovery of [P₄₄₄₁₄]Cl and extraction of
 346 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)

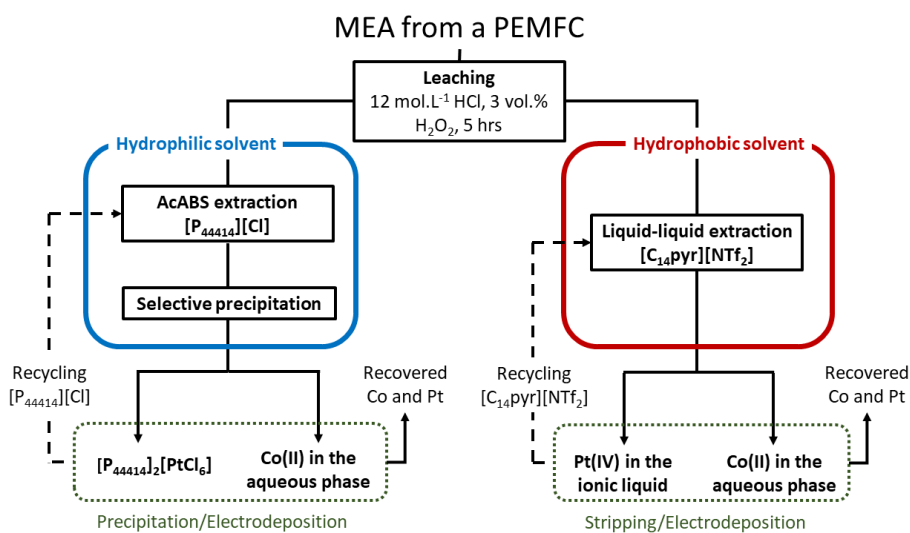
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348

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

350 Two processes for Pt(IV) and Co(II) extraction from real PEMFC leachates were developed based on
351 two ILs with opposite properties: a hydrophobic [C₁₄pyr][NTf₂] and a hydrophilic [P₄₄₄₁₄][Cl]. Important
352 contributions were made in both processes: (i) quantitative Pt(IV) extraction was achieved in a
353 fluorinated IL and (ii) AcABS was for the first time applied to the recycling of strategic metals from
354 real wastes by simply adding the IL to a real leachate solution. To close the process, the isolated metallic
355 cations can easily be precipitated as salts by increasing the pH using NaOH or Na₂CO₃.⁴⁷ Co(II) can
356 also be reduced by electrodeposition to a metallic form both in aqueous solution as well as from the
357 [P₄₄₄₁₄][Cl]-rich phase.^{48→49} A conceptual flow diagram for the recycling of cobalt and platinum from
358 PEMFC by either SX or AcABS is presented in **Figure 5**. The full blue and red lines surround the
359 various stages used in this work for the separation of metals by hydrophilic and hydrophobic ILs,
360 respectively. The dotted black line represents the solvents recycling.

361



362

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

365

366 A comparison of the proposed processes is here discussed based on process complexity, separation
367 efficiency, price and potential environmental impact. A summary of the discussion is available in **Table**
368 **5**. Due to the lack of significant co-impurities present in the PEMFC waste matrix both processes present
369 quantitative separation of Pt(IV) from Co(II). However, the ability of the hydrophobic [C₁₄pyr][NTf₂]
370 to selectively extract Pt(IV) directly from the leach solution across a broad range of HCl concentrations
371 (1 to 12 mol.L⁻¹ HCl, **Figure 1**) is a significant advantage. Conversely, the range of AcABS is restricted
372 by the extent of the biphasic region for a given temperature. Whilst the biphasic domain can be increased

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

375

376 **Table 5.** Comparison of the developed SX and AcABS processes for Pt(IV) and Co(II) extraction from
 377 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

378

379 An important benefit of AcABS is that all system components are water soluble with both phases
 380 containing a considerable quantity of water. This overcomes one of the major issues associated with
 381 ILs: their viscosity. Performing the extraction in aqueous media significantly improves the mass transfer
 382 properties of the system, with the viscosity of the [P₄₄₄₁₄]Cl system under experimental conditions below
 383 50 cP.³⁴ The viscosity of the [P₄₄₄₁₄]Cl-rich phase was shown to increase to 629 cP following extraction
 384 of a concentrated Co(II) solution due to the formation of the [P₄₄₄₁₄][CoCl₃] and [P₄₄₄₁₄]₂[CoCl₄]
 385 complexes.⁴⁹ Even after extraction, viscosity in AcABS are still lower than that of the water-saturated
 386 trihexyltetradecyl phosphonium chloride before extraction ([P₆₆₆₁₄]Cl, around 830 cP),⁸ the hydrophobic
 387 counterpart to [P₄₄₄₁₄]Cl. Finally, the water-soluble nature of AcABS allows for the direct precipitation
 388 of PtCl₆²⁻ without the need of an additional stripping stage as in conventional SX. Alternatively, AcABS
 389 can provide a tailored electrodeposition environment by variation in the ionic strength, acidity and water
 390 content of the media suitable for metals with reduction potentials within the limit imposed by hydrogen
 391 evolution.⁴⁹ However, the usability of the precipitated [P₄₄₄₁₄]₂[PtCl₆] complex remains to be seen, an
 392 additional purification step is most likely required to separate and recover the IL cation and Pt(IV).

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

395 to poorly hydrated anionic complexes of low charge densities, such as $[\text{PtCl}_6]^{2-}$. In contrast, the extent
396 of separation in $[\text{P}_{44414}]\text{Cl-HCl-H}_2\text{O}$ AcABS solely depends on the metal cation – chloride complexation
397 constant of differing metals: metals with high to medium complexation constants such as Pt(IV), Fe(III),
398 Co(II) or Mn(II) were reported as extracted whilst Ni(II) was not.^{21,49} This suggests that the
399 $[\text{C}_{14}\text{pyr}][\text{NTf}_2]$ -based process could be more robust to the presence of common metallic impurities like
400 Fe(III). A non-negligible impediment to extraction using $[\text{C}_{14}\text{pyr}][\text{NTf}_2]$ is the partial loss of the $[\text{NTf}_2]^-$
401 anion (Eq(5) and **Table 3**) to the aqueous phase during extraction to charge balance the incoming PtCl_6^{2-}
402 anion. Loss of the $[\text{NTf}_2]^-$ anion is both costly and not sustainable. $[\text{NTf}_2]^-$ is consistently identified as
403 a clear (eco)toxicological hazard across a range of trophic levels whilst its complex synthesis process
404 is reflected in the high cost of the precursor salt.^{17,50} Loss of the IL cationic moiety to the aqueous phase
405 also presents a significant toxicity hazard potential due to the lipophilicity conferred by the cation
406 tetradecyl alkyl chain.¹⁷ As the $[\text{C}_{14}\text{pyr}]^+$ and $[\text{P}_{44414}]^+$ cations present opposite solubility trends with
407 acid concentration, the $[\text{C}_{14}\text{pyr}][\text{NTf}_2]$ system appears best suited in dilute HCl solutions whilst AcABS
408 excels in concentrated HCl solution.

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

420

421 **Conclusions**

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

430 determined by the effluent acidity due to the increased loss of the IL. [P₄₄₄₁₄]Cl AcABS appears better
431 suited to concentrated HCl solutions whilst [C₁₄pyr][NTf₂] excels under more dilute conditions. The
432 lower energy of solvation of [NTf₂]⁻ from [C₁₄pyr][NTf₂] compared to the Cl⁻ from [P₄₄₄₁₄]Cl suppresses
433 the exchange of anionic metal complexes with higher energies of solvation, thereby conferring a greater
434 selectivity to [C₁₄pyr][NTf₂]. However, loss of the [NTf₂]⁻ anion during extraction negatively impacts
435 the extraction process, something that is avoided in the more tunable AcABS process. Ultimately, the
436 feasibility of IL processes is dependent on the market price of the target metals and their recovered
437 purity.

438

439 **Experimental**

440 A detailed description of the chemicals and instruments used in this work as well as the experimental
441 protocol followed can be found in the Supplementary Information. This includes the [C₁₄pyr][NTf₂]
442 synthesis protocol and the characterization by ¹H-NMR (Figure S1), thermogravimetric analysis (Figure
443 S2) and by differential scanning calorimetry (Figure S3) of the obtained IL.

444 **Metal extraction from ideal solutions**

445 In a first instance, the extraction of Co(II) and Pt(IV) from model leach solution containing variable
446 concentration of HCl was studied in the [C₁₄pyr][NTf₂] and [P₄₄₄₁₄]Cl-HCl-H₂O systems respectively.
447 [P₄₄₄₁₄]Cl has the form of a white waxy solid and is fully water soluble for all compositions but forms
448 a reversible biphasic system in the presence of HCl. For all extraction experiments from model
449 solutions, the concentration of metals was of 1.0x10⁻² mol.L⁻¹. Typically, 2 g of [C₁₄pyr][NTf₂] or 1 g
450 of [P₄₄₄₁₄]Cl was mixed with 2 mL of an aqueous solution. The tubes were placed in a rotator installed
451 in a heat chamber in order to control the temperature. All extraction experiments were performed at 50
452 °C. After 3 hours of agitation, the aqueous phases were carefully separated from the hydrophobic ionic
453 liquid and were analyzed by AAS. In the case of AcABS, both the IL- and acid-rich phase were analyzed
454 by atomic absorption spectrophotometry (AAS) as all components are water soluble. Quantification of
455 the water content in the IL-rich phase at 25 and 50 °C under the tested conditions was reported in a
456 previous work.²¹ All extraction percentages (equations (1) and (4)) were given with an error of +/- 1
457 and 5 % for %E1 and %E2 respectively. The loss in accuracy for AcABS extractions is due to the
458 experimental uncertainty associated with the accurate measurement of phase volume.

459 **Leaching, separation and precipitation of metals from PEM fuel cell**

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

463 Leaching of the MEA was performed according to an optimized procedure previously published.³⁰⁻³¹
464 Briefly, 16 cm² of MEA was treated with 200 mL of aqueous solution containing 3 vol.% H₂O₂ in HCl
465 12 mol.L⁻¹. The leaching step was carried out at 25°C for 5 hours. After that, the obtained leachate
466 solution was filtered in a Büchner funnel and analyzed by AAS; concentrations of 1.2x10⁻² and 4.8x10⁻
467 ³ mol.L⁻¹ for platinum(IV) and cobalt(II) were respectively measured in agreement with the reference
468 study.^{30,31} The extraction of metallic ions from solutions A, B and C (composition given in **Table 2**)
469 using [P₄₄₄₁₄]Cl or [C₁₄pyr][NTf₂] was carried out following the same procedure as that detailed in the
470 preceding subsection using model solutions. The inherent acid concentrations in all leachates was
471 sufficient to yield a biphasic system in the [P₄₄₄₁₄]Cl-HCl-H₂O AcABS. The precipitation of Pt(IV) from
472 the loaded IL-rich phase in AcABS was adapted from a previous work.²⁵ Briefly, following extraction
473 of metals from leachate C using the [P₄₄₄₁₄]Cl-HCl-H₂O AcABS, the IL-rich phase (corresponding to
474 the upper phase) was carefully separated and cooled down to 25°C. To this, 0.3 g of HCl 1 mol.L⁻¹ was
475 added to induce the selective precipitation of Pt(IV). The metal content of the IL-rich phase before and
476 after precipitation was analyzed by AAS to determine the extent of precipitation.

477

478 **Conflicts of interest**

479 Authors declare no conflicts of interest.

480

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487

488 **Supporting information**

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

492

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