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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.<sup>1-4</sup> 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.<sup>5</sup> 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.<sup>6</sup> Due to this  
44 design versatility, ILs are often referred to as “designer solvents”.<sup>1</sup> 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.<sup>7</sup> 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 metals<sup>8-11</sup> as well as gold<sup>12-14</sup> and  
54 platinum group metals<sup>12,14-16</sup> 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.<sup>3,17</sup> 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.<sup>3,18-20</sup> 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.<sup>21</sup> 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,<sup>22</sup> 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.<sup>23,24</sup> Despite their use limited to highly  
76 specific applications,<sup>25</sup> PEMFC remain an important area of research activity due to their potential.<sup>24-29</sup>  
77 Most notably, the electrode material forming the membrane electrode assembly (MEA) is composed of  
78 highly valuable  $Pt_3Co$  nanoparticles deposited onto a carbon substrate.<sup>30-31</sup> Since both platinum and  
79 cobalt were identified as critical metals by the European Commission,<sup>32</sup> 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  $27900 \text{ \$.kg}^{-1}$  in 2019 whilst the price of cobalt has wildly fluctuated over the last three  
83 years, peaking in 2018 at over  $94 \text{ \$.kg}^{-1}$  before falling to an average of  $37.4 \text{ \$.kg}^{-1}$  in 2019.<sup>33</sup>

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,<sup>31</sup> 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 [C<sub>14</sub>pyr][NTf<sub>2</sub>] was carried out  
 104 between 1 and 12 mol.L<sup>-1</sup> HCl and the results are presented in **Figure 1A**. The extraction yield (%E)  
 105 using [C<sub>14</sub>pyr][NTf<sub>2</sub>], distribution coefficient (D<sub>M</sub>) and the platinum/cobalt separation factor (α<sub>Pt/Co</sub>)  
 106 were calculated according to the following equations:

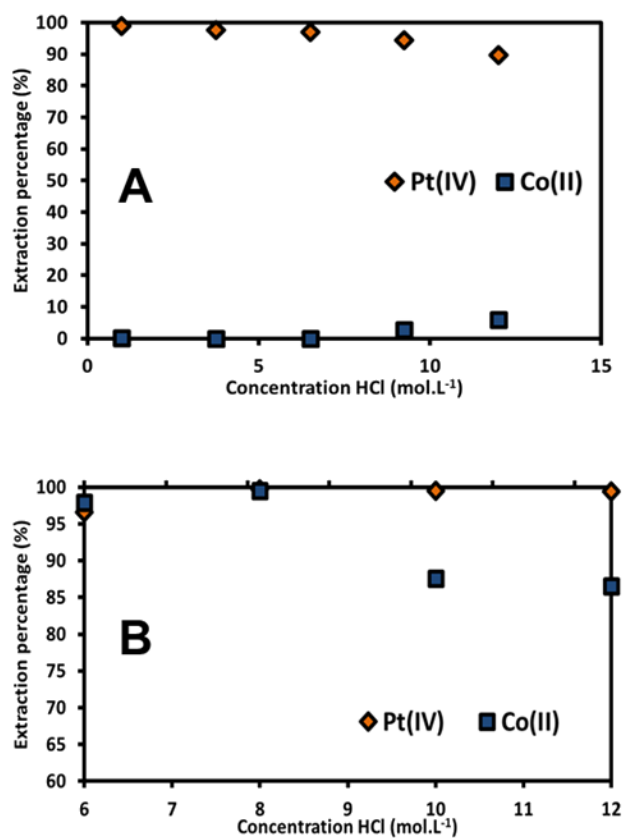
$$107 \quad \%E1 = \frac{([M]_{aq,0} - [M]_{aq,f})}{[M]_{aq,0}} \times 100 \quad (1)$$

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

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

110 Where the subscript *aq* and *IL* denote the respective phase and [M]<sub>0</sub> and [M]<sub>f</sub> the metal concentrations  
 111 in mol.L<sup>-1</sup> 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<sup>-2</sup> mol.L<sup>-1</sup>) using (A) [C<sub>14</sub>pyr][NTf<sub>2</sub>] and (B) [P<sub>44414</sub>]Cl-HCl-

116 H<sub>2</sub>O 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<sup>-1</sup>  
 118 <sup>1</sup> HCl, orange diamond is hidden by blue dot. Extraction yields for Pt(IV) and Co(II) are not reported  
 119 below 6 mol.L<sup>-1</sup> HCl because [P<sub>44414</sub>]Cl is miscible in aqueous solutions under such conditions.

120

121 Results indicate that Pt(IV) is extracted by [C<sub>14</sub>pyr][NTf<sub>2</sub>] 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<sup>-1</sup> 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.<sup>16</sup> In contrast, Co(II) was not extracted using [C<sub>14</sub>pyr][NTf<sub>2</sub>] at HCl concentrations below  
 126 6.5 mol.L<sup>-1</sup> (%E<sub>Co</sub> < 0.1 %). Under these conditions, Pt(IV) is effectively separated from Co(II) with  
 127  $\alpha_{Pt/Co} > 1000$ . At higher concentrations of HCl, namely 9.25 and 12 mol.L<sup>-1</sup>, 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 ([C<sub>14</sub>pyr][NTf<sub>2</sub>] and [P<sub>44414</sub>]Cl) on the  
 131 extraction efficiency of platinum(IV) and cobalt(II) and their separation from single element solutions.

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

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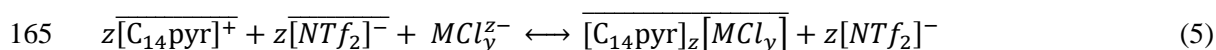
133 Compared to SX, the study of metal extraction with HCl concentration in AcABS is restricted by the  
 134 extent of the biphasic region at a given temperature. All extractions were performed at 50 °C due to the  
 135 greater HCl composition range available ( $\geq 6$  mol.L<sup>-1</sup> HCl) with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

136 the presence of lower critical solution temperature (LCST).<sup>34</sup> The selected mixture points for the  
 137  $[P_{44414}]Cl-HCl-H_2O$  AcABS are based on previously reported phase diagrams,<sup>34</sup> 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).<sup>21</sup>

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

143 where  $[M]_{low}$  represents the concentration in mol.L<sup>-1</sup> 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.<sup>21</sup> In contrast to the  $[C_{14}pyr][NTf_2]$   
 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<sup>-1</sup> HCl and decreases  
 150 thereafter to 86.5% for 12 mol.L<sup>-1</sup> 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  $\alpha_{Pt/Co} \leq 25$ .

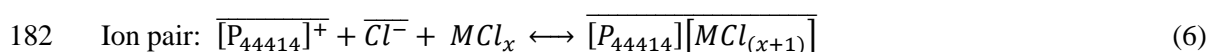
152 Both Pt(IV) and Co(II) are known to form various chlorometallate complexes as a function of chloride  
 153 concentration. In the HCl concentration range 1 to 12 mol.L<sup>-1</sup> HCl, Pt(IV) is present as the anionic  
 154  $PtCl_6^{2-}$  complex.<sup>16,35</sup> In contrast, Co(II) is predominantly under the form of a positively charged or  
 155 neutral cobalt(II) complex containing H<sub>2</sub>O and 1 or 2 Cl<sup>-</sup> anions for HCl concentrations below 6 mol.L<sup>-1</sup>.  
 156 At HCl concentrations 8 mol.L<sup>-1</sup> and above, Co(II) can form anionic chlorocobaltate(II) complexes  
 157 such as  $CoCl_3^-$  and  $CoCl_4^{2-}$  when the  $[Co]/[H_2O]$  ratio is low.<sup>36-38</sup> The transition from cationic to anionic  
 158 cobalt complexes can be visually observed as the solution color gradually shifts from red for  
 159  $[Co.6H_2O]^{2+}$  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  $[C_{14}pyr][NTf_2]$  but is slightly extracted as the tetrachlorocobaltate(II) complex. Extraction of negatively  
 162 charged complexes ( $MCl_y^{z-}$ ), such as  $PtCl_6^{2-}$  or  $CoCl_4^{2-}$ , in hydrophobic IL with fluorinated anions  
 163 occurs via anion exchange and the formation of a hydrophobic ion-pair<sup>16</sup> 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 [C<sub>14</sub>pyr][NTf<sub>2</sub>] to extract metals when in their highly solvated cationic form due to an  
 171 extremely unfavourable cation exchange mechanism. Conversely, the hydrophobic [NTf<sub>2</sub>]<sup>-</sup> 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 CoCl<sub>4</sub><sup>2-</sup> is low whilst the more charge diffused PtCl<sub>6</sub><sup>2-</sup> is  
 175 quantitatively extracted from 1 mol.L<sup>-1</sup> HCl.<sup>36-40</sup> According to equation (5), one expects the more  
 176 hydrophobic the cation, the lower the solubility of the resulting [C<sub>14</sub>pyr]<sub>2</sub>[PtCl<sub>6</sub>] complex in water and  
 177 the higher the extraction yield. In fact, the extraction efficiencies reported using [C<sub>14</sub>pyr][NTf<sub>2</sub>] 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.<sup>12,14,16</sup>

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 PtCl<sub>6</sub><sup>2-</sup> in the studied HCl concentration range, Pt(IV) extraction  
 185 proceeds exclusively by anion exchange according to equation (7) to form the complex [P<sub>44414</sub>]<sub>2</sub>[PtCl<sub>6</sub><sup>2-</sup>  
 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<sup>-1</sup> HCl before decreasing for [HCl] ≥ 10 mol.L<sup>-1</sup>. At 8 mol.L<sup>-1</sup>  
 190 <sup>1</sup> HCl, CoCl<sub>3</sub><sup>-</sup> as the predominant cobalt species in solution is then gradually replaced by the more  
 191 charge dense CoCl<sub>4</sub><sup>2-</sup> at higher concentrations of HCl.<sup>8,21,22,36-40</sup> 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 CoCl<sub>2</sub> species  
 195 to the IL phase in accordance with that found for Co(II) partition from chloride media with other basic  
 196 extractants.<sup>38</sup> The drop in Co(II) extraction for [HCl] ≥ 10 mol.L<sup>-1</sup> 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).<sup>8,21,22,38</sup> Even for 12 mol.L<sup>-1</sup> HCl, the  
 200 selectivity of the Pt(IV)/Co(II) separation is far inferior to that obtained in the [C<sub>14</sub>pyr][NTf<sub>2</sub>] system.

201

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



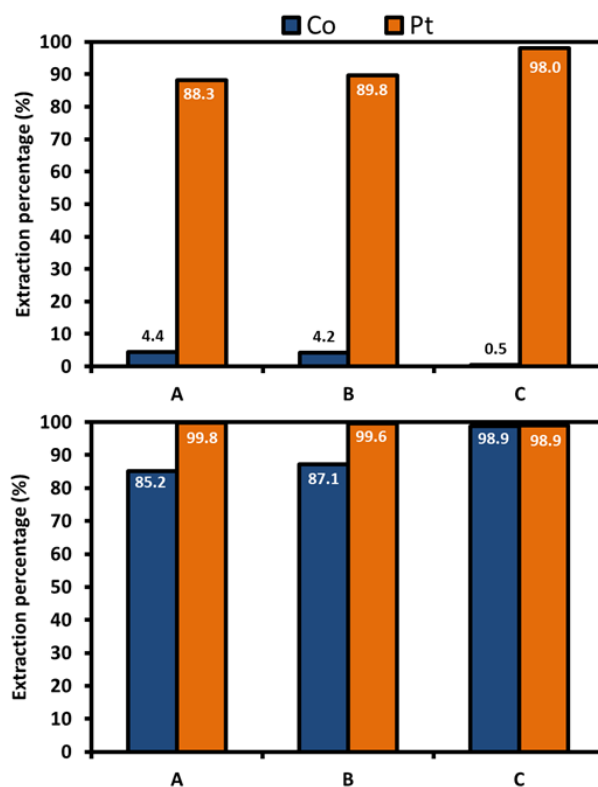
203 Based on the extraction results from synthetic solution, IL-based SX and AcABS separation were  
 204 applied to the separation and recovery of the critical metals Co(II) and Pt(IV) from the MEA materials  
 205 of a real PEMFC. We previously showed that 12 mol.L<sup>-1</sup> HCl with 3 vol.% H<sub>2</sub>O<sub>2</sub> 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.<sup>30-31</sup> 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<sup>-1</sup> HCl or H<sub>2</sub>O. Extraction results  
 211 for all three leachates using [C<sub>14</sub>pyr][NTf<sub>2</sub>] and [P<sub>44414</sub>]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 <sup>-1</sup> )	[Co(II)] (mol.L <sup>-1</sup> )	[Pt(IV)] (mol.L <sup>-1</sup> )
A	12.0	1.2x10 <sup>-2</sup>	4.8x10 <sup>-3</sup>
B	12.0	6.0x10 <sup>-3</sup>	2.4x10 <sup>-3</sup>
C	6.0	6.0x10 <sup>-3</sup>	2.4x10 <sup>-3</sup>

216



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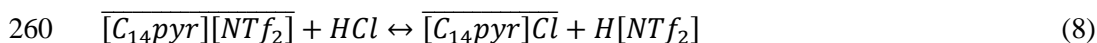
218 **Figure 2.** Extraction efficiency of metals from a PEMFC leachate using [C<sub>14</sub>pyr][NTf<sub>2</sub>] (top) and  
219 [P<sub>44414</sub>]Cl (bottom). Initial aqueous phase composition corresponds those listed in **Table 2**. Color code  
220 - platinum(IV) in orange and cobalt(II) in blue.

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.<sup>31</sup> 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<sup>-1</sup>). 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 [C<sub>14</sub>pyr][NTf<sub>2</sub>] and [P<sub>44414</sub>]Cl systems respectively. In  
233 the [C<sub>14</sub>pyr][NTf<sub>2</sub>] 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 [C<sub>14</sub>pyr]<sup>+</sup>,  
240 [NTf<sub>2</sub>]<sup>-</sup> and [P<sub>44414</sub>]<sup>+</sup> 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 [C<sub>14</sub>pyr]<sup>+</sup>  
242 was measured in solutions containing no metals due to the overlap of the [C<sub>14</sub>pyr]<sup>+</sup> and PtCl<sub>6</sub><sup>2-</sup> UV-vis  
243 peaks. Solubility kinetics of the [C<sub>14</sub>pyr][NTf<sub>2</sub>] performed in pure water is presented in **Figure 3**.  
244 [C<sub>14</sub>pyr][NTf<sub>2</sub>] is continuously solubilizing in water until a plateau observed after 150 hours stirring  
245 reaching a value of 0.19 mmol.L<sup>-1</sup>. 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.<sup>19,41,42</sup> 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<sup>-1</sup> and 2.5 mmol.L<sup>-1</sup> respectively.<sup>19,42</sup> 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.<sup>18-20,42</sup> A similar  
251 salting-in behavior is reported here, with the solubility of [C<sub>14</sub>pyr]<sup>+</sup> increasing by almost two orders of  
252 magnitudes to 9.7 mmol.L<sup>-1</sup> in 12 mol.L<sup>-1</sup> HCl solution (leachate B). The ion-pair extraction mechanism

253 for  $\text{PtCl}_6^{2-}$  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  $\text{PtCl}_6^{2-}$  from  
 255 synthetic leachates B and C ( $[\text{Pt(IV)}] = 2.4 \text{ mmol.L}^{-1}$ ), this would entail the release of  $4.8 \text{ mmol.L}^{-1}$  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  $\text{Cl}^-$   
 258 to  $[\text{NTf}_2]^-$  ratio as described in equation (8),<sup>18-20,42</sup> 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  $12 \text{ mol.L}^{-1}$  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.<sup>34,43</sup>

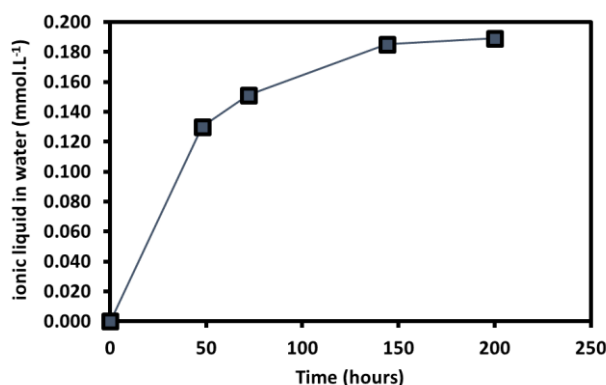
265

266 **Table 3.** Aqueous solubility of the IL component studied after contacting for 150 h and  $50^\circ\text{C}$  with  
 267 synthetic leachate B and C (BDL – Below detection limit). The experimental detection limit for  
 268 quantitative NMR is 5 mol%.

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

269 <sup>a</sup> Measured at  $25^\circ\text{C}$ ; <sup>b</sup> 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  $25^\circ\text{C}$ .

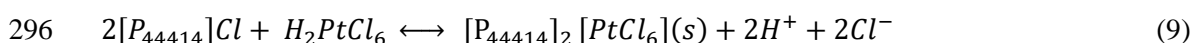
273

## 274 **Selective precipitation of platinum from cobalt in AcABS**

275 The difference in Co(II) extraction and Pt(IV) separation selectivity between the [C<sub>14</sub>pyr][NTf<sub>2</sub>] and  
276 [P<sub>44414</sub>]Cl based systems (**Figures 1-2**) entails the development of two separate methodologies. In the  
277 case of SX using [C<sub>14</sub>pyr][NTf<sub>2</sub>], 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,<sup>44,45</sup> or through its reductive precipitation by hydrazine  
280 addition<sup>46</sup> as was previously detailed for IL-based SX.

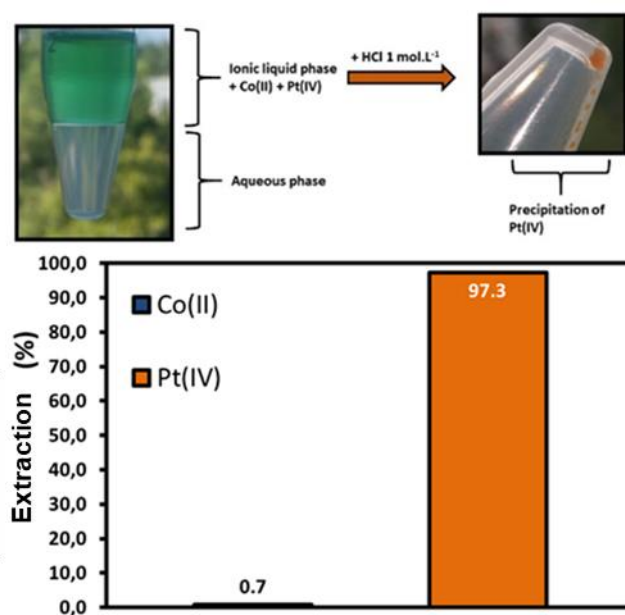
281 In the AcABS, the quantitative extraction of both Co(II) and Pt(IV) implies the need for an additional  
282 selective stripping step compared to the SX separation. Following extraction of Co(II) and Pt(IV) from  
283 real leachate C using AcABS, the phases were separated and the [P<sub>44414</sub>]Cl-rich phase carefully isolated.  
284 The isolated [P<sub>44414</sub>]Cl-rich phase was subsequently diluted with 0.3g of 1 mol.L<sup>-1</sup> 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 [PtCl<sub>4</sub>]<sup>2-</sup> anion, [P<sub>44414</sub>]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 AuCl<sub>4</sub><sup>-</sup>, PtCl<sub>6</sub><sup>2-</sup> or PdCl<sub>4</sub><sup>2-</sup>.<sup>13-14</sup> 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 PtCl<sub>6</sub><sup>2-</sup> and the cation of the IL. The precipitation can thus be represented according  
295 to equation (9):<sup>14</sup>



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).<sup>40</sup> 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 [NTf<sub>2</sub>]-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.<sup>44-48</sup> 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.<sup>47</sup> As a proof of concept,  
 326 a similar method for recycling [P<sub>44414</sub>]Cl is presented here.

327 At the end of the separation process, [P<sub>44414</sub>]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 from 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 [P<sub>44414</sub>]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 [P<sub>44414</sub>]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,<sup>49</sup> a biphasic system was then  
 337 obtained. The upper phase was found to contain [P<sub>44414</sub>]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 <sup>1</sup>H and <sup>31</sup>P 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 [P<sub>44414</sub>]Cl  
 343 can be elaborated.

344

345 **Table 4.** Stripping of Co(II) at the end of extraction cycle 1, recovery of [P<sub>44414</sub>]Cl and extraction of  
 346 metal ions from leachate C in extraction cycle 2.

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

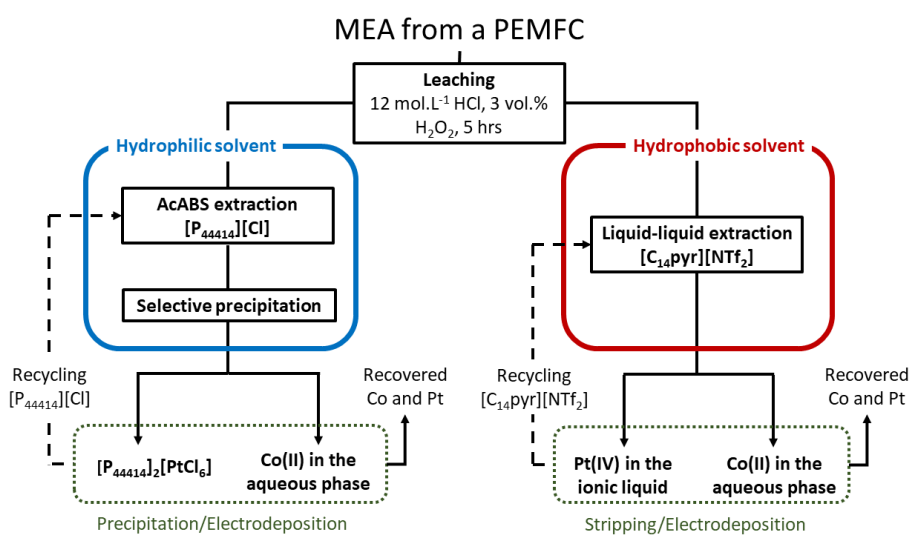
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348

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 [C<sub>14</sub>pyr][NTf<sub>2</sub>] and a hydrophilic [P<sub>44414</sub>][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 Na<sub>2</sub>CO<sub>3</sub>.<sup>47</sup> Co(II) can  
356 also be reduced by electrodeposition to a metallic form both in aqueous solution as well as from the  
357 [P<sub>44414</sub>][Cl]-rich phase.<sup>48→49</sup> 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 [C<sub>14</sub>pyr][NTf<sub>2</sub>]  
370 to selectively extract Pt(IV) directly from the leach solution across a broad range of HCl concentrations  
371 (1 to 12 mol.L<sup>-1</sup> 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 temperature<sup>34</sup> or addition of NaCl,<sup>48→49</sup> 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 [C<sub>14</sub>pyr][NTf<sub>2</sub>] and a [P<sub>44414</sub>]Cl respectively.

Criteria	[C <sub>14</sub> pyr][NTf <sub>2</sub> ] (SX)	[P <sub>44414</sub> ]Cl (AcABS)
Operational limit	Independent of HCl concentration	Temperature and HCl concentration dependent
Process simplicity	Simple	Simple
Process flexibility	Inflexible	Flexible
<b>Selectivity</b>	<b>Selective for Pt(IV)</b>	<b>Non-selective</b>
<b>Extraction mechanism</b>	<b>Ion-pair/anion-exchange</b>	<b>Ion-pair/anion-exchange</b>
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 [P<sub>44414</sub>]Cl system under experimental conditions below  
 383 50 cP.<sup>34</sup> The viscosity of the [P<sub>44414</sub>]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 [P<sub>44414</sub>][CoCl<sub>3</sub>] and [P<sub>44414</sub>]<sub>2</sub>[CoCl<sub>4</sub>]  
 385 complexes.<sup>49</sup> Even after extraction, viscosity in AcABS are still lower than that of the water-saturated  
 386 trihexyltetradecyl phosphonium chloride before extraction ([P<sub>66614</sub>]Cl, around 830 cP),<sup>8</sup> the hydrophobic  
 387 counterpart to [P<sub>44414</sub>]Cl. Finally, the water-soluble nature of AcABS allows for the direct precipitation  
 388 of PtCl<sub>6</sub><sup>2-</sup> 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.<sup>49</sup> However, the usability of the precipitated [P<sub>44414</sub>]<sub>2</sub>[PtCl<sub>6</sub>] 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 [NTf<sub>2</sub>]<sup>-</sup> 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  $[\text{P}_{44414}]\text{Cl}-\text{HCl}-\text{H}_2\text{O}$  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.<sup>21,49</sup> 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  $\text{PtCl}_6^{2-}$   
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.<sup>17,50</sup> 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.<sup>17</sup> 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.<sup>50-52</sup> 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,<sup>52</sup> 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. [P<sub>44414</sub>]Cl AcABS appears better  
431 suited to concentrated HCl solutions whilst [C<sub>14</sub>pyr][NTf<sub>2</sub>] excels under more dilute conditions. The  
432 lower energy of solvation of [NTf<sub>2</sub>]<sup>-</sup> from [C<sub>14</sub>pyr][NTf<sub>2</sub>] compared to the Cl<sup>-</sup> from [P<sub>44414</sub>]Cl suppresses  
433 the exchange of anionic metal complexes with higher energies of solvation, thereby conferring a greater  
434 selectivity to [C<sub>14</sub>pyr][NTf<sub>2</sub>]. However, loss of the [NTf<sub>2</sub>]<sup>-</sup> 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 [C<sub>14</sub>pyr][NTf<sub>2</sub>]  
442 synthesis protocol and the characterization by <sup>1</sup>H-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 [C<sub>14</sub>pyr][NTf<sub>2</sub>] and [P<sub>44414</sub>]Cl-HCl-H<sub>2</sub>O systems respectively.  
447 [P<sub>44414</sub>]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<sup>-2</sup> mol.L<sup>-1</sup>. Typically, 2 g of [C<sub>14</sub>pyr][NTf<sub>2</sub>] or 1 g  
450 of [P<sub>44414</sub>]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.<sup>21</sup> 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.<sup>30-31</sup>  
464 Briefly, 16 cm<sup>2</sup> of MEA was treated with 200 mL of aqueous solution containing 3 vol.% H<sub>2</sub>O<sub>2</sub> in HCl  
465 12 mol.L<sup>-1</sup>. 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<sup>-2</sup> and 4.8x10<sup>-</sup>  
467 <sup>3</sup> mol.L<sup>-1</sup> for platinum(IV) and cobalt(II) were respectively measured in agreement with the reference  
468 study.<sup>30,31</sup> The extraction of metallic ions from solutions A, B and C (composition given in **Table 2**)  
469 using [P<sub>44414</sub>]Cl or [C<sub>14</sub>pyr][NTf<sub>2</sub>] 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 [P<sub>44414</sub>]Cl-HCl-H<sub>2</sub>O AcABS. The precipitation of Pt(IV) from  
472 the loaded IL-rich phase in AcABS was adapted from a previous work.<sup>25</sup> Briefly, following extraction  
473 of metals from leachate C using the [P<sub>44414</sub>]Cl-HCl-H<sub>2</sub>O 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<sup>-1</sup> 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 [C<sub>14</sub>pyr][NTf<sub>2</sub>],**  
490 **composition of phases in AcABS formed using leachate A, B and C, <sup>1</sup>H NMR and <sup>31</sup>P NMR spectra for**  
491 **[P<sub>44414</sub>]Cl**

492

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