

# Supporting information

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

Mathieu Gras<sup>a</sup>, Lucien Duclos<sup>a</sup>, Nicolas Schaeffer,<sup>b</sup> Vijetha Mogilireddy,<sup>a</sup> Lenka Svecova,<sup>a</sup> Eric Chaînet,<sup>a</sup> Isabelle Billard<sup>a</sup> and Nicolas Papaiconomou<sup>a,c\*</sup>

<sup>a</sup> Univ. Grenoble Alpes, Univ. Savoie Mont Blanc, CNRS, Grenoble INP, LEPMI, 1130 rue de la piscine, 38000 Grenoble, France.

<sup>b</sup> CICECO – Aveiro Institute of Materials, Department of Chemistry, University of Aveiro, 3810-193 Aveiro, Portugal.

<sup>c</sup> Institut de Chimie de Nice, 28 avenue Valrose, Université Côte d’Azur, 06108, Nice, France

\* Corresponding author: Nicolas.Papaiconomou@unice.fr

**10 pages, 2 Tables, 4 Figures**

# Methodology

## Chemicals

MQ-grade water (18.2 M $\Omega$ .cm at 25°C) was used to prepare all aqueous solutions. Cobalt chloride (CoCl<sub>2</sub>·6H<sub>2</sub>O, 99.5% purity), and chloroplatinic acid (H<sub>2</sub>PtCl<sub>6</sub>·6H<sub>2</sub>O, 99.9% purity) were purchased from Alfa Aesar. Cyclohexane (C<sub>6</sub>H<sub>12</sub>), pyridine (C<sub>5</sub>H<sub>5</sub>N), dichloromethane (CH<sub>2</sub>Cl<sub>2</sub>), hydrogen peroxide solution (H<sub>2</sub>O<sub>2</sub>, 30% in water), dimethyl sulfoxide (DMSO) and chlorotetradecane (C<sub>14</sub>H<sub>17</sub>Cl) were provided by Sigma Aldrich. Hydrochloric acid (HCl, 37% in water) was obtained from Carl Roth. LiNTf<sub>2</sub> was purchased from Solvionic. Finally, tributyltetradecylphosphonium chloride ([P<sub>44414</sub>]<sup>+</sup>Cl<sup>-</sup>, 95% purity) was provided by Cyttec-Solvay.

## Instruments and measurements

A Mettler Toledo DSC1/500/2412 was used in order to perform differential scanning calorimetry (DSC) measurements. Temperatures were corrected against a cyclohexane standard. DSC curves were recorded between -90 and 110°C at a temperature rate of 10°C/min. A series of two heating and cooling ramps with 2 min stabilization time at -90 and 110 °C was carried out prior to record the DSC curve. For thermodynamic transitions (melting and crystallization), the onset temperatures were used. Thermogravimetric analysis (TGA) was carried out with the help of a Mettler Toledo apparatus, LF1100-XP1. TGA measurements were performed under nitrogen flow in the range 25 to 800°C at a temperature rate of 10°C/min. Temperature was stabilized during 10 min at the beginning and at the end of the analysis at 25°C and 800°C respectively. The onset temperature determined the decomposition temperature of the IL. <sup>1</sup>H-NMR analysis was performed with a spectrometer (Bruker Advance III HD) 400 MHz to check the IL purity after diluting [C<sub>14</sub>pyr][NTf<sub>2</sub>] in DMSO. [P<sub>44414</sub>]<sup>+</sup> concentration in the aqueous phase was analysed by <sup>1</sup>H-NMR with a known concentration of benzene inside a sealed capillary as internal standard. The [NTf<sub>2</sub>]<sup>-</sup> anion was quantified by <sup>19</sup>F-NMR with sodium trifluoroacetate as internal standard according to a previously reported procedure.<sup>1</sup> An 831 KF Coulometer (Metrohm) was used to determine the water content of the IL. A Cary 50 (Varian) UV-vis spectrometer was used in order to record all UV-vis spectra and to determine the solubility of [C<sub>14</sub>pyr][NTf<sub>2</sub>] in aqueous and acidic solutions. The concentrations of metal ions before and after extraction were determined by an atomic absorption spectrophotometer (AAS) using PinAAcle 900F apparatus from Perkin Elmer. Standards were prepared in the range 2.10<sup>-5</sup> to 8.10<sup>-4</sup> mol.L<sup>-1</sup>. Working wavelengths were set to 240.7 and 265.9 nm for cobalt(II) and platinum(IV) respectively. Stirring was performed with a Stuart rotator drive STR4 apparatus.

## Synthesis and characterization of [C<sub>14</sub>pyr][NTf<sub>2</sub>]

The [C<sub>14</sub>pyr][NTf<sub>2</sub>] IL was synthesized according to a previously reported procedure<sup>2,3</sup> and obtained as a white solid with 90.2% reaction yield. KF analysis indicated a water content of 317 ppm. The purity

was verified using the silver nitrate test and  $^1\text{H-NMR}$  (**Figure S1**) with no evidence of impurities observed. The single peak at 3.4 ppm corresponds to water from the DMSO solvent. The thermal properties of  $[\text{C}_{14}\text{pyr}][\text{NTf}_2]$  were determined by TGA and DSC analysis, **Figures S2** and **S3** respectively. TGA analysis confirms the thermal stability of the synthesized IL, with an elevated decomposition temperature of 389 °C. DSC profile exhibits melting and crystallization points at 33 °C and 22 °C respectively. The solubility of the IL in water was also investigated. To that end, 0.2 g of  $[\text{C}_{14}\text{pyr}][\text{NTf}_2]$  was mixed with 10 mL of water or an HCl solution of known molarity (6 or 12 mol.L<sup>-1</sup>). After stirring during 48 to 200 hours at 25°C, two phases were obtained. The IL- saturated aqueous phase was then recovered and analyzed by UV-vis measurements to determine the concentration of IL. A 12 mol.L<sup>-1</sup> H<sub>2</sub>SO<sub>4</sub> solution was used to dilute the aqueous phases containing HCl. All solutions were filled in a 1 cm quartz cell. Ultra-pure water or 12 mol.L<sup>-1</sup> H<sub>2</sub>SO<sub>4</sub> was used as reference based on the experiment.  $[\text{C}_{14}\text{pyr}]\text{Br}$  was used as a standard in the range  $7.10^{-5}$  to  $5.10^{-4}$  mol.L<sup>-1</sup>. The working wavelength was set to 260 nm which corresponds to the maximum absorption of the  $[\text{C}_{14}\text{pyr}]^+$  cation ( $\epsilon = 3975 \text{ L.cm}^{-1}.\text{mol}^{-1}$ ).

#### **Composition of phases in AcABS formed using leachate A, B and C.**

The volume and density of the lower phases obtained upon mixing 1 g  $[\text{P}_{44414}]\text{Cl}$  and 2 mL of leachate A, B and C are reported in Table S1. The composition of lower and upper phases obtained upon mixing 1 g  $[\text{P}_{44414}]\text{Cl}$  and 2 mL of leachate A, B and C are reported in Table S2. Leachate A and B gave the same results due to the fact the initial mixtures are similar (12 M HCl, and same initial amount of ionic liquid). All compositions are given in wt%.

The composition of HCl in the lower phase was obtained according to the density of this phase<sup>4</sup> and neglecting the influence of the ionic liquid in the solution on the density thereof. This approximation is in agreement with the solubility of  $[\text{P}_{44414}]\text{Cl}$  in water obtained in this work and detailed in the manuscript (see Table 3).

The concentration of water in the upper phases were measured using a Karl Fisher titration method. The concentration of HCl in the upper phase was measured by acid titration. The composition of  $[\text{P}_{44414}]\text{Cl}$  could then be calculated by simple mass action law. All results are collected in Table S2.

#### **$^1\text{H}$ NMR and $^{31}\text{P}$ NMR spectra for $[\text{P}_{44414}]\text{Cl}$**

After extraction of Co(II) and Pt(IV) using  $[\text{P}_{44414}]\text{Cl}$ , precipitation of Pt(IV) upon diluting the ionic liquid-rich phase of the AcABS and precipitation of Co(II) using NaOH,  $[\text{P}_{44414}]\text{Cl}$  was separated from

the aqueous solution upon addition of NaCl. The purity of the ionic liquid obtained was analyzed using  $^1\text{H}$  and  $^{31}\text{P}$  NMR.

The spectra are presented here and compared to the original spectra for  $[\text{P}_{44414}]\text{Cl}$  recorded before any extraction was carried out. They confirm the purity of the ionic liquid and the presence of water in the ionic liquid, as shown by the somehow broader peak at 4.8 ppm.

## References

- [1] Mazan, V.; Billard, I.; Papaiconomou, N., Experimental connections between aqueous aqueous and aqueous ionic liquid biphasic systems. *RSC Adv.*, **2014**, 4, 13371– 13384.
- [2] Crosthwaite, J.M., Muldoon, M.J., Dixon, J.K., Anderson, J.L., Brennecke, J.F., Phase transition and decomposition temperatures, heat capacities and viscosities of pyridinium ionic liquids. *J. Chem. Thermodyn.*, **2005**, 37, 559–568.
- [3] Salminen, J., Papaiconomou, N., Kumar, R.A., Lee, J.-K., Kerr, J., Newman, J., Prausnitz, J.M., Physicochemical properties and toxicities of hydrophobic piperidinium and pyrrolidinium ionic liquids. *Fluid Phase Equilib*, **2007**, 261, 421–426.
- [4] Perry, R.H. Perry's chemical engineers' handbook, 8<sup>th</sup> edition. Mc-Graw Hill: New York, 1997.

## Tables

**Table S1.** Density and volume of the lower aqueous phases of the AcABS formed upon adding 1 g [P44414]Cl to 2 mL leachate A, B or C. B.D.L: Below detection limits

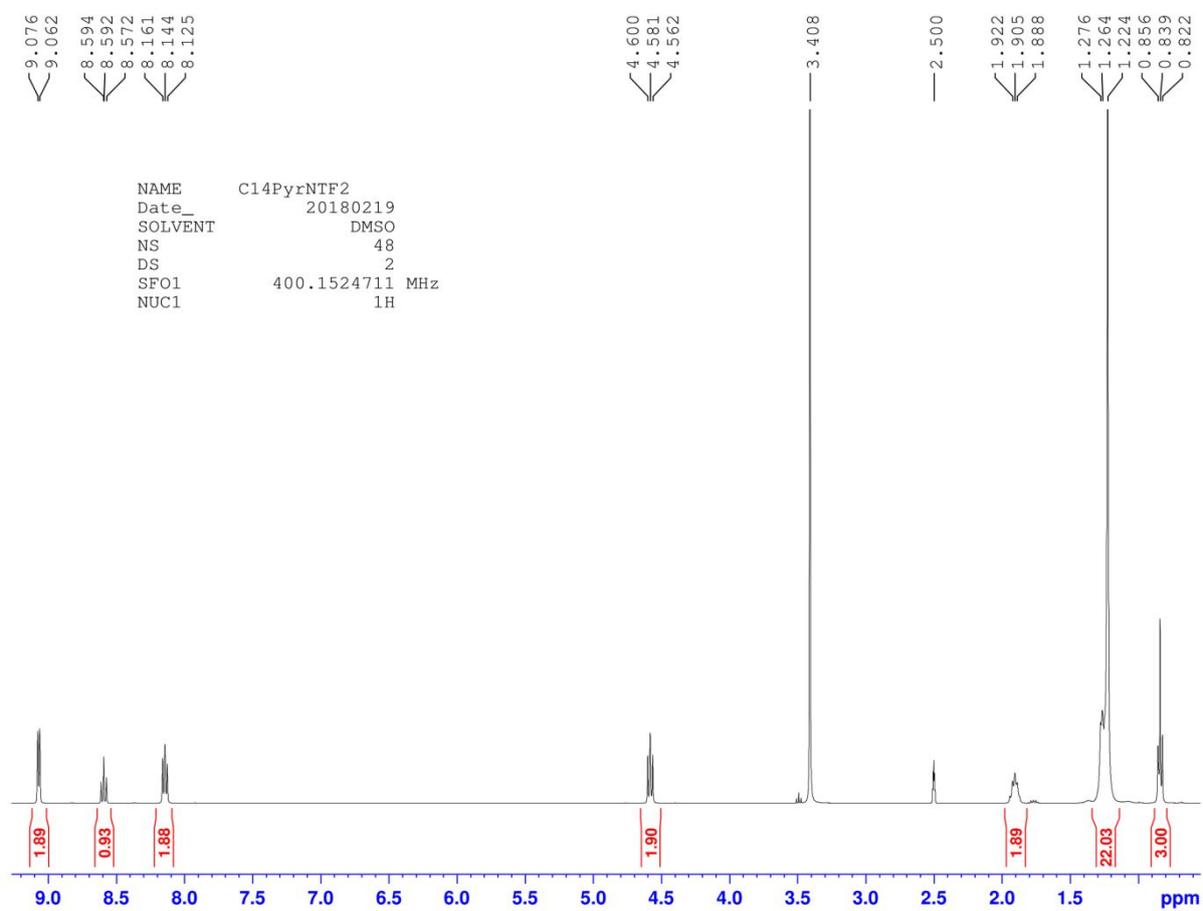
<b>Leachate</b>	<b>Upper phase</b>	<b>Lower phase</b>	
<b>Leachate</b>	<b>Volume(mL)</b>	<b>Volume (mL)</b>	<b>Density (g.mol<sup>-1</sup>)</b>
A / B	1.36 ± 0.1	1.42 ± 0.2	1.15 ± 0.1
C	2.64 ± 0.1	0.32 ± 0.1	1.20 ± 0.1

**Table S2.** Composition of upper and lower phases obtained upon adding 1 g [P44414]Cl with 2 mL leachate A, B or C. B.D.L: Below detection limits

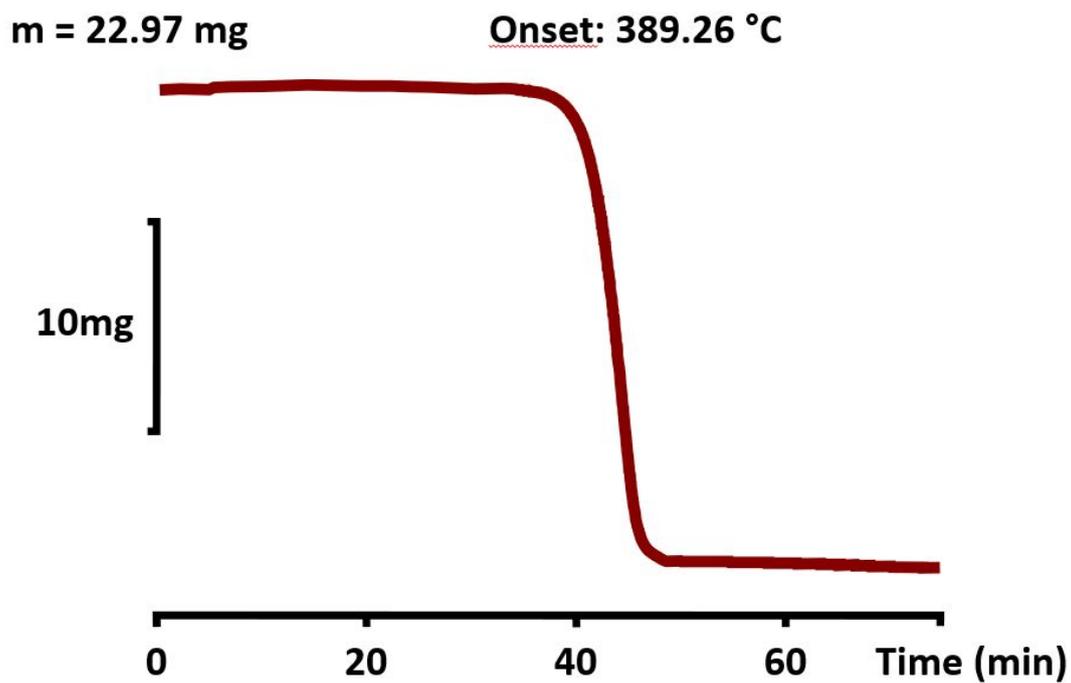
Leachate	Upper phase			Lower phase	
	[P <sub>44414</sub> ]Cl (wt%)	[HCl] (wt%)	H <sub>2</sub> O (wt%)	[P <sub>44414</sub> ]Cl (wt%)	[HCl] (wt%)
A / B	43.2 ± 1.7	14.3 ± 0.7	15.9 ± 1.2	B.D.L	37 <sup>b</sup>
C	69.8 ± 0.4	10.7 ± 0.3	46.1 ± 2.8	0.55 ± 0.07 <sup>a</sup>	30 ± 1 <sup>b</sup>

a: obtained according to the solubility of [P44414 ]Cl as detailed in the article. b: Calculated according to the density of the phase considering it is as a hydrochloric solution °C.

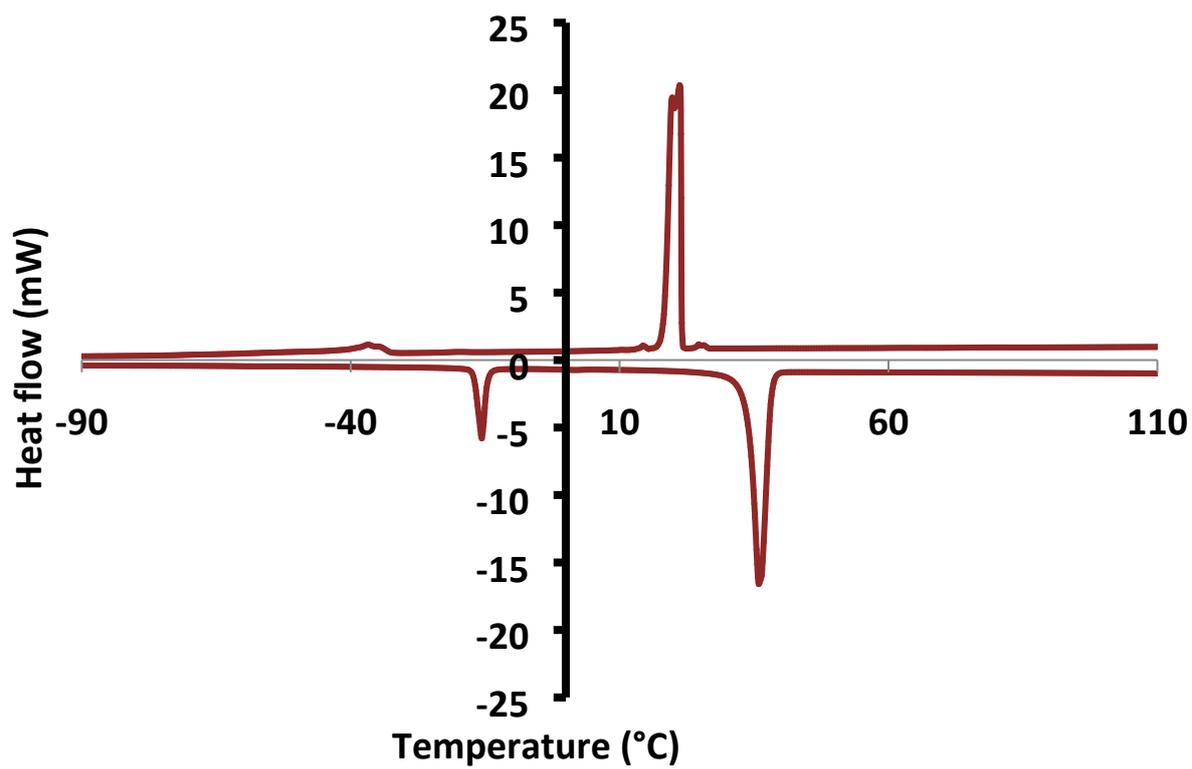
# Figures



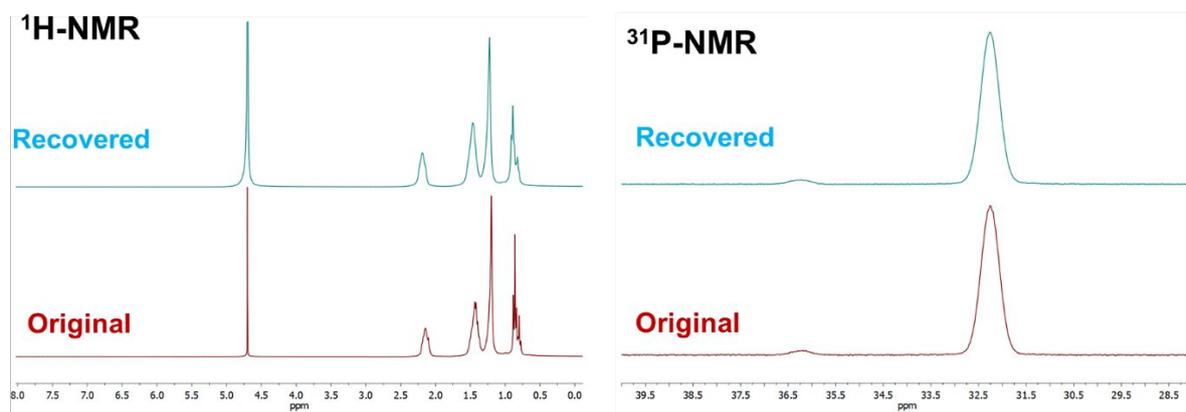
**Figure S1.**  $^1\text{H}$ -NMR spectrum of the synthesised  $[\text{C}_{14}\text{pyr}][\text{NTf}_2]$  in DMSO.



**Figure S2.** Thermogravimetric analysis of  $[\text{C}_{14}\text{pyr}][\text{NTf}_2]$  performed under nitrogen flow in the range 25 to 800 °C (10°C/min)



**Figure S3.** Differential Scanning Calorimetry of  $[C_{14}pyr][NTf_2]$  carried out in the range of -90 to 110°C (10°C/min)



**Figure S4.**  $^1H$  and  $^{31}P$  NMR spectra for  $[P_{44414}]Cl$  before and after the recycling thereof.