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# Halide based ionic liquid mixture for a sustainable electrochemical recovery of precious metals

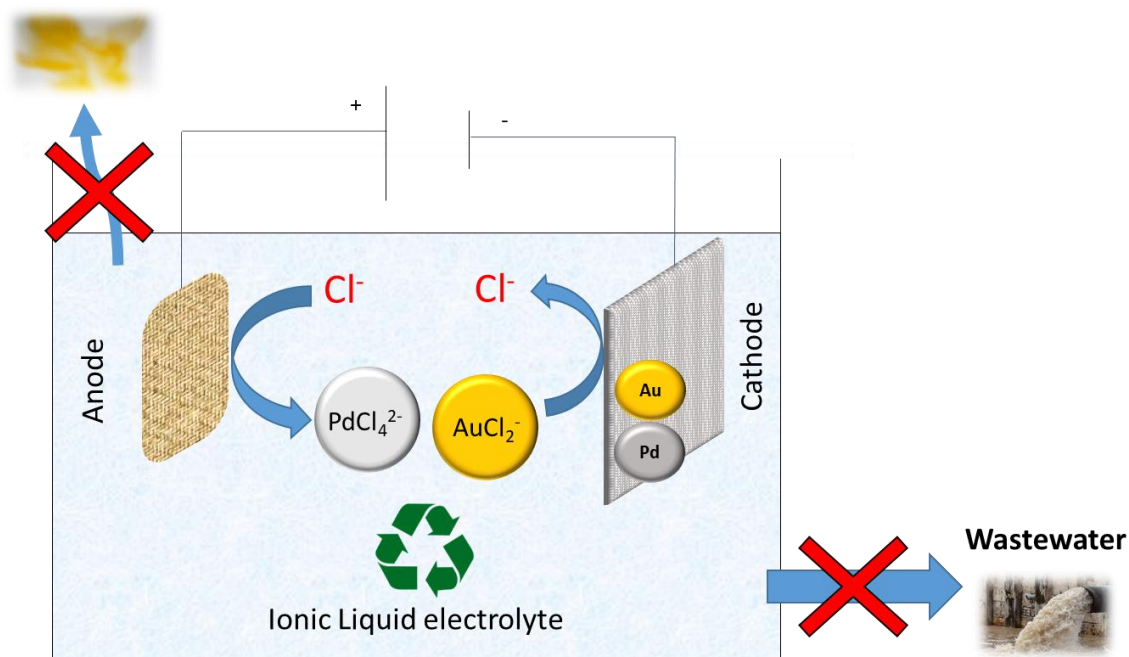
Benoit Villemejeanne <sup>a,b</sup>, Sophie Legeai <sup>b</sup>, Eric Meux <sup>b</sup>, Sandrine Dourdain <sup>c</sup>, Hakima Mendil-Jakani <sup>d</sup> and Emmanuel Billy <sup>a\*</sup>

**ABSTRACT:** Precious metal refining from ore or electronic devices includes hydrometallurgical processes with major concern about toxicity or wastewater production. As an alternative, one-step electroleaching-electrochemical deposition process (EL-ECD) using ionic liquid mixtures was evaluated for palladium and gold recovery. A halide based ionic liquid combined with a diluting ionic liquid was chosen among ten electrolytes after cyclic voltammetry and potentiostatic experiments. These low viscous electrolytes allow complexing Au and Pd, leading to metal leaching at low anodic potential. Moreover, the complexes formed could be simultaneously deposited at the cathode. Metal behaviour is similar for all halide anions tested (chloride, bromide and iodide). Results show that chloride based mixtures are the more suitable electrolyte providing the highest leaching faradic yield. This process appears more sustainable than conventional processes (chlorination, cyanide leaching) thanks to the electrolyte stability limiting solvent losses but also workers exposition.

Keyword : Electrochemistry, Ionic liquids, Precious metals recovery

**GRAPHICAL ABSTRACT:** The EL-ECD process for gold or palladium recovery in ionic liquid mixture allowing a one-step electroleaching-electrochemical deposition of metal without any solvent degradation. This process prevent wastewater production or toxic gases emission.

## Toxic emission



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## 1. Introduction

Nowadays, metallic resource depletion associated with environmental and social burden of primary ore exploitation (Greenhouse Gas emission, water consumption, land-use, non-ethical exploitation ...) are of major concern all over the world. In the same time, the quantity of Waste Electrical and Electronic Equipment (WEEE), which contains close to 40 metals, rises in every continents leading to huge landfills in some developing countries, which exposes soils and humans to pollution. Today, metal production from these "urban mines" appears as an idealistic solution to this issue in order to reduce earth exploitation but also to propose a sustainable e-waste management[1–5]. Especially, precious metals (PM) recovery (including Au, Ag, Pd and Pt) from High Tech end-of-life products like smartphones or tablets is a great 21<sup>st</sup> century challenge. Their concentration is indeed ten to twenty-five times higher in e-waste than in ores[6] leading to softer extraction processes, whereas precious metals production for primary resources leads to massive CO<sub>2</sub> emission and water consumption[7]. Furthermore, Au and Pd represents next to 90 % of rich printed circuit boards (PCBs) value (defined as PCB with Au concentration higher than 400 ppm). Hence, rich PCBs treatment is economically feasible only if gold and palladium are recovered[8,9]. Finally, exploitation of these secondary deposits being not delocalizable and these wastes could be seen as artificial palladium deposits thus reducing criticality (high supply risk in UE)[10–12]. Gold and palladium recycling from WEEE is of high interest for economic, strategic, environmental and social reasons.

Generally, pyrometallurgical and electrochemical treatments[13,14] are used to recover base metals (Cu, Sn, Pb...) from secondary resources. PM sludges produced by this "primary" treatment is then treated using a multi-step complex hydrometallurgical process, composed of a leaching step - cyanide (Mc-Arthur Forest process[15]) or aqua regia leaching [16,17] – and followed by numerous separation steps using volatile solvents - liquid/liquid extraction, fractional distillation – before a final recovery of each PM by electrolysis, cementation or crystallization. These multi-step processes, set up at the end of the 20<sup>th</sup> century, have some important limitations for workers or installation safety and remain far from sustainable development considerations. Notably cyanide leaching step must be carried on at basic pH to avoid HCN formation and wastewaters have to be treated to protect environment from high cyanide concentration by costly processes. Strong acid or aqua regia leaching necessitate specific and expensive anticorrosive installations[18]. To overcome these economic and ecologic limitations, many alternative processes have been proposed during the 20<sup>th</sup> century including thiourea or thiosulfate leaching[19,20]. Nevertheless, these processes are not competitive with old recipes due to high reagent consumption for thiourea leaching or slow kinetics for thiosulfate leaching[18]. Thiourea leaching has also hazardous drawbacks[4,18]

because this compound is harmful for aquatic life and suspected of causing cancer.

For two decades, ionic liquid-based breakthrough processes have been proposed for metal recycling field[21,22]. Most of these low-temperature molten salts have a low vapor pressure that reduces significantly fire hazard and solvent inhalation by workers. They are also less corrosive than mineral acids and avoid solvent losses by evaporation. These resulting properties enable to design new metal recovery processes being more respectful of Green Chemistry principles with less wastewater generation, less reactants used and less hazards associated. This new field of metallurgy using ionic liquids (IL) or deep eutectic solvents (DES) was called "ionometallurgy" by Abbott[23]. First studies of gold chemical leaching in IL systems was reported by Whitehead *et al.* in 2004[21]. Chemical leaching is a process easy to implement but it generally implies the use of a powerful oxidant, leading to subsequent hazards (fire, toxicity...) and to impurities during recovery step. Alternatively, in the case of a conductive waste, electrometallurgy can be performed by combining in a single cell the electrochemical leaching of an anode formed by metallic waste and the electrodeposition of high-grade metals at the cathode[24]. As electrochemical leaching of PM is hindered in aqueous media because of the high yield of side oxygen evolution, it is perfect suitable application for IL because of their broad electrochemical window combined to their chelating properties and relative chemical inertness[25–28]. Recently, Balva *et al.* proposed a one-step electrochemical leaching-electrochemical deposition (EL-ECD) process for platinum recovery from proton exchange membrane fuel cell using an IL electrolyte[29] without any solvent loss by evaporation or degradation[30].

Unfortunately, ionic liquids (IL) present some limits for a metallurgical process including high viscosity, relative low conductivity or toxicity depending on the IL recirculation in the process. Cation or anion substitution and fine-tuning could overcome these limitations. Ionic liquid mixtures are also interesting alternatives to combine useful properties[31,32]. For example, in the field of metallurgy, ionic liquid mixtures, composed of a diluting ionic liquid having a low viscosity, high thermal and chemical stability and a complexing ionic liquid of metals[33] were successfully used. Nevertheless, the main lock to ionic liquid-based process industrialization is the prohibitive price of these solvents. Therefore, ILs may concern high benefit processes like palladium or gold recovery to guarantee economically sustainable processes. Furthermore, ionic liquid recycling is also an important challenge to design competitive processes[34] from economic or environmental point of views. Finally, to avoid high ionic liquid consumption, the waste treated have to be concentrated in precious metals like anode slime obtained after copper production by electrolysis.

Palladium or gold recovery including IL recycling is not straightforward. Indeed, there are many studies about

palladium or gold electrodeposition[35] in ionic liquids, but few concern electroleaching. Anodic leaching of gold in IL was reported in chloroaluminate room temperature molten salt[36], deep eutectic solvents (DES)[37,38] or ionic liquid mixtures [39–41]. Electrocatalytic recovery of gold in Ethaline with iodine as oxidant was also performed on ores and real wastes[38,42]. For palladium, there is an important number of papers concerning nanoparticles electrodeposition[43–45] but to the best of our knowledge, there is no paper concerning bulk palladium electroleaching in ILs.

This work studies the influence of anionic part of various IL mixtures on Au and Pd electrochemical behavior. Linear polarization resistance (LPR) associated to potentiostatic experiments were used to determine the leaching ability of each anion and discriminate the useful mixtures for Au and Pd recycling. Cyclic voltammetry (CV) was then performed to study electrolyte stability and metal behavior in the IL mixtures for electrochemical leaching purposes. Potentiostatic dissolution associated to gravimetric analysis provides information about oxidation state of leached precious metals in the different electrolytes. Finally, EL-ECD experiment was used to study the possibility of designing a one-step electroleaching/electrodeposition process for Au and Pd without any atmosphere control.

## 2. Materials and methods

### 1.1. Chemical reagents

1-Butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide 99 % ( $C_4C_1Im\ NTf_2$ ), 1-Butyl-3-methylimidazolium iodide 99 % ( $C_4C_1Im\ I$ ), 1-Butyl-3-methylimidazolium bromide 99 % ( $C_4C_1Im\ Br$ ), 1-Butyl-3-methylimidazolium trifluoromethanesulfonate 99 % ( $C_4C_1Im\ OTf$ ), 1-Butyl-3-methylimidazolium dimethylphosphate 98 % ( $C_4C_1Im\ DMP$ ), 1-Butyl-3-methylimidazolium dicyanamide 98 % ( $C_4C_1Im\ DCA$ ) were purchased from Iolitec. 1-Butyl-3-methylimidazolium acetate 99 % ( $C_4C_1Im\ OAc$ ), 1-Butyl-3-methylimidazolium chloride 99 % ( $C_4C_1Im\ Cl$ ) were purchased from Solvionic. 1-Butyl-3-methylimidazolium methanesulfonate 95 % ( $C_4C_1Im\ MeSO_3$ ), 1-Butyl-3-methylimidazolium nitrate 95 % ( $C_4C_1Im\ NO_3$ ), silver bis(trifluoromethylsulfonyl)imide 97 % ( $AgNTf_2$ ), silver chloride 99 % ( $AgCl$ ), ferrocene 98 % ( $Fc$ ), and ferrocenium tetrafluoroborate of technical grade ( $FcBF_4$ ) were purchased from Sigma-Aldrich.

### 1.2. Electrolytes

All electrolytes were ionic liquid mixtures combining a diluting ionic liquid with low viscosity and wide electrochemical stability ( $C_4C_1Im\ NTf_2$ ) and an additive ionic liquid ( $C_4C_1Im\ X$ ;  $X = Cl, Br, I, NO_3, MeSO_3, OTf, NTf_2, DMP, DCA, OAc$ ). Additive IL concentration was fixed to 0.1 M, according to previous studies on Pt electrochemical leaching[29]. IL were stored in a glovebox, but electrolytes

were not dried and experiments were conducted without atmosphere control.

$C_4C_1Im\ NTf_2$  was selected as diluting ionic liquid, as it is a well-known and highly described ionic liquid, that has a low viscosity at 25 °C (48.8 cP) compare to similar pyrrolidinium (85 cP) or piperidinium (192 cP) based ILs[46].  $NTf_2^-$  anion guarantees also a great electrochemical stability and hydrophobicity[47]. Furthermore, this anion is poorly coordinating which allows us considering that gold and palladium coordination by  $NTf_2^-$  is negligible compare to coordination with the complexing anion,  $X^-$ . Additive IL anion  $X^-$  was chosen for two major considerations. First, its coordination ability towards metal cations, which is supposed to be enhanced by a greater Lewis basicity has been taken account. Solvatochromic experiments allow classifying ionic liquids according to their polarity thanks to diverse parameters.  $\alpha$  parameter, representing Lewis acidity is highly dependent on the cationic part whereas  $\beta$  parameter, representing Lewis basicity, is anion dependent. In order to influence of  $\beta$  value on the electrochemical leaching ability of an ionic liquid mixture, we choose two highly basic anions ( $DMP^-$ ,  $OAc^-$ ), two poorly basic anions ( $NTf_2^-$ ,  $OTf^-$ ) and two anions of intermediate basicity ( $NO_3^-$ ,  $MeSO_3^-$ ), according to literature data[48–50]. Secondly, usual complexing anions of gold (halides,  $DCA^-$ ) and palladium (halides) in aqueous medium were also selected to observe if the coordination ability of these anions is preserved in ionic liquids.

### 1.3. Instrumentation

All experiments were performed at  $40.0 \pm 0.3$  °C without any atmosphere control. A three-electrode cell containing 1 mL of electrolyte connected to an Ametek Parstat 4000 controlled by Versa Studio software or a Biologic VSP300 controlled by EC-lab software were used.

The working electrode was a 1 mm-diameter gold wire (99.99 %) or a 0.5 mm-diameter palladium wire (99.95 %) provided by Metalor. Glassy carbon (GC) plate (2\*4\*30 mm) was also used as Working Electrode (WE). Immerse surface of electrode was measured after electrochemical experiment. The Counter Electrode (CE) was a platinum grid and references were  $Ag/AgCl$  or  $Ag/Ag^+$  electrodes. References and counter electrodes were separated from the bulk solution by a sintered glass. Two reference electrodes were used. The first one (Ref A) was an  $Ag/AgCl$  electrode.  $AgCl$  was prepared by surface immersion of a silver wire for 15 minutes in a 15 %  $Cl_2$  bleach solution. The resulting  $AgCl$  covered wire was then immersed in an ionic liquid mixture  $C_4C_1Im\ NTf_2 + 0.1M\ C_4C_1Im\ Cl$  containing  $AgCl$  (10 mM). The second one (Ref B) was an  $Ag/Ag^+$  electrode, consisting in a silver wire immersed in  $C_4C_1Im\ NTf_2$  containing  $AgNTf_2$  (10mM). Ref A was used for

highly complexing ionic liquid mixtures containing halides and Ref B for other electrolytes to avoid any reference potential deviation during experiments. References were calibrated against  $\text{Fc}^+/\text{Fc}$  half wave potential and were stable between 40–80 °C during experiments duration. We assume that  $\text{Fc}^+/\text{Fc}$  half-wave potential is the same in all electrolytes and that is equal to 0.63 V against standard hydrogen electrode (SHE) [51]. All potential values measured in this study were referred to SHE that allows comparing results obtained in IL and aqueous media in literature. At 40 °C, Ref A has a potential of 0.15 V vs. SHE whereas Ref B has a potential of 1.01 V vs. SHE.

Linear polarization resistance (LPR) mode ( $0.1667 \text{ mV s}^{-1}$ ) was used to determine  $E_{j=0}$  mixed potential between water/ $\text{O}_2$  reduction and metal oxidation, and study steady-state metal anodic behavior in ionic liquid mixtures. Potentiostatic experiments for metal dissolution kinetics study were performed for 10 000 seconds, three times, and the corresponding amount of leached metal was determined by gravimetric method using a Mettler Toledo XS105 balance with  $\pm 0.01 \text{ mg}$  accuracy.

Cyclic voltammetry curves were performed at  $50 \text{ mV s}^{-1}$  with open circuit voltage (OCV) as initial potential and anodic scanning first.

Before EL-ECD process experiments, synthetic IL solutions containing metallic ions were prepared by running potentiostatic dissolution of Au or Pd under anodic potential control (10 000 s, 600 rpm stirring), the cathode being isolated in a salt bridge containing the same IL. Subsequent cathodic linear scan voltammetry at  $20 \text{ mV s}^{-1}$  was then performed on a platinum substrate in each synthetic solution in order to determine metal deposition peak potential. Finally, potentiostatic EL-ECD process was run in synthetic solutions with cathode as working electrode, without any stirring. The process was performed using a platinum foil ( $0.25 \text{ cm}^2$  immersed) as cathode and a metal (Au or Pd) wire as anode. Faradaic yields of both anodic and cathodic processes were determined by gravimetry, using a microbalance Mettler Toledo XP6 with  $\pm 0.001 \text{ mg}$  accuracy.

No ohmic compensation was applied (ohmic voltage drop as measured lower than 15 mV).

### 3. Results and discussion

#### 3.1. Electrolyte preselection for Au and Pd leaching

##### 3.1.1. Anodic behaviour of gold and palladium:

To know which IL mixtures could be used to perform Au and Pd electroleaching, metal anodic behavior was studied in each electrolyte by LPR experiments. This technique allows us to obtain Tafel representation  $\log(|j|) = f(E)$ , presented in Figure 1. This representation allows to obtain the corrosion potential  $E_{j=0}$  of the metal in the electrolyte but also to determine the limiting step (charge transfer or mass transfer) of the oxidation reaction in this medium. For sake of clarity, only curves corresponding to the characteristic behaviors further described in the text are given in Figure 1. Complete experimental results can be found in supporting information (SI-Figure 1, 2, 3). Whatever the electrolyte, Tafel plots present a cathodic branch for  $E < E_{j=0}$  with a weak current density ( $j < 1 \mu\text{A cm}^{-2}$ ) on gold and palladium which reveals a cathodic reaction due to water reduction (water content available in SI-Table 1). After this branch,  $\log(|j|)$  falls and reaches a minimal value for  $E_{j=0}$ . For  $E > E_{j=0}$ , Tafel plots characteristics depend both on electrolyte anion and considered metal. LPR curves obtained on both electrodes using halide containing electrolytes present a limiting current plateau of significant value (between  $0.08$  and  $0.2 \text{ mA cm}^{-2}$ ), revealing a mass transport-controlled oxidation reaction.  $E_{j=0}$  and potential values corresponding to this limiting current ( $E_{\text{peak}}$ ) follow the order:  $\text{I} < \text{Br} < \text{Cl}$ . Current density plateau follow the same trend. This first typical behavior is represented by the red curve in Figure 1.  $E_{\text{peak}}$  is a potential obtained by tangent method (cf. blue and red curve in Figure 1). It is the intersection between the increasing part of the LPR and the horizontal part. It corresponds to the beginning of the current plateau for complexing electrolytes.

In  $\text{MeSO}_3$ ,  $\text{NO}_3$ , OTf based ionic liquid mixtures, as in pure  $\text{C}_4\text{C}_1\text{Im NTf}_2$ , a low current density plateau ( $j < 0.01 \text{ mA cm}^{-2}$ ) starting at  $E_{\text{peak}}$  is observed using both Pd and Au electrodes, corresponding to side reaction. This second typical behavior,

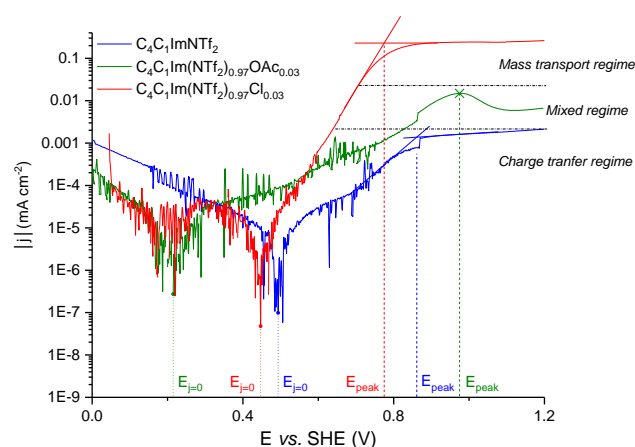


Figure 1 - Tafel plot ( $\log(|j|) = f(E)$ ) on gold electrode for mass transfer control behaviour (represented by  $\text{C}_4\text{C}_1\text{Im NTf}_2 + 0.1 \text{ M C}_4\text{C}_1\text{Im Cl}$  - red curve), charge transfer control (represented by  $\text{C}_4\text{C}_1\text{Im NTf}_2$  - blue curve) and mixed kinetic behaviour (represented by  $\text{C}_4\text{C}_1\text{Im NTf}_2 + 0.1 \text{ M C}_4\text{C}_1\text{Im OAc}$  - green curve)

controlled by charge transfer, is represented by the blue curve in Figure 1. A particular phenomenon is observed in DMP, DCA and OAc-containing electrolytes on each metallic electrode, including an important overpotential (0.6 V) with a low anodic current density ( $0.01 \text{ mA cm}^{-2}$ ) for  $E < E_{j=0}$ , a current rising to reach a maximum for  $E_{\text{peak}}$  close to 1 V vs. SHE and a final current decrease until  $0.01 \text{ mA cm}^{-2}$ . On gold electrode, this behavior is significant when  $\text{DCA}^-$  anion is present in solution (SI-Figure 1). This third typical behavior is a mixed control (charge and mass transfer) represented by the green curve in Figure 1.

In brief, these experiments show three distinct behaviors according to the electrolytes used. The first, named “complexing” behavior, presents a mass transport-controlled behavior. The second shows a small anodic current density for  $E > E_{(E=0)}$  ( $\text{NTf}_2^-$ ,  $\text{OTf}^-$ ,  $\text{NO}_3^-$ ,  $\text{MeSO}_3^-$ ), and can be considered as “non-complexing”, with a reaction limited by charge transfer. The last one exhibits a particular behavior with a significant current rise followed by a current decrease for high

electrode polarization ( $\text{OAc}^-$ ,  $\text{DMP}^-$ , and  $\text{DCA}^-$ ) linked to a mixed behavior controlled by both charge and mass transfer.

### 3.1.2. Potentiostatic experiments:

In order to attribute LPR anodic current to metal leaching or anion oxidation, potentiostatic experiments were conducted at  $E_{\text{Peak}}$ . When metal weight loss was observed, leaching rate  $v_{\text{ox}}$  was calculated in  $\text{mg h}^{-1} \text{ cm}^{-2}$ . Electrolytes ability for Pd and Au electroleaching can be compared by plotting the leaching rate  $v_{\text{ox}}$  versus  $E_{\text{onset}}$  which is defined as the difference between  $E_{\text{peak}}$  and  $E_{j=0}$  (Figure 2). This value corresponds to the minimum overpotential that must be applied to reach maximal anodic current (see inset of Figure 2). It is a qualitative measurement to compare the slope of the curve  $\log |j| = f(E)$  for each electrolyte (*cf.* inset Figure 2). We can see that halide-based electrolytes for both metals have an  $E_{\text{onset}}$  value lower than 0.6 V unlike other electrolytes. Indeed, as we can see in SI-Figure 1 the slope of  $\log |j| = f(E)$  is higher for these electrolytes than for non-complexing one. Furthermore, these electrolytes allow performing metal leaching at  $E_{\text{Peak}}$ . For these

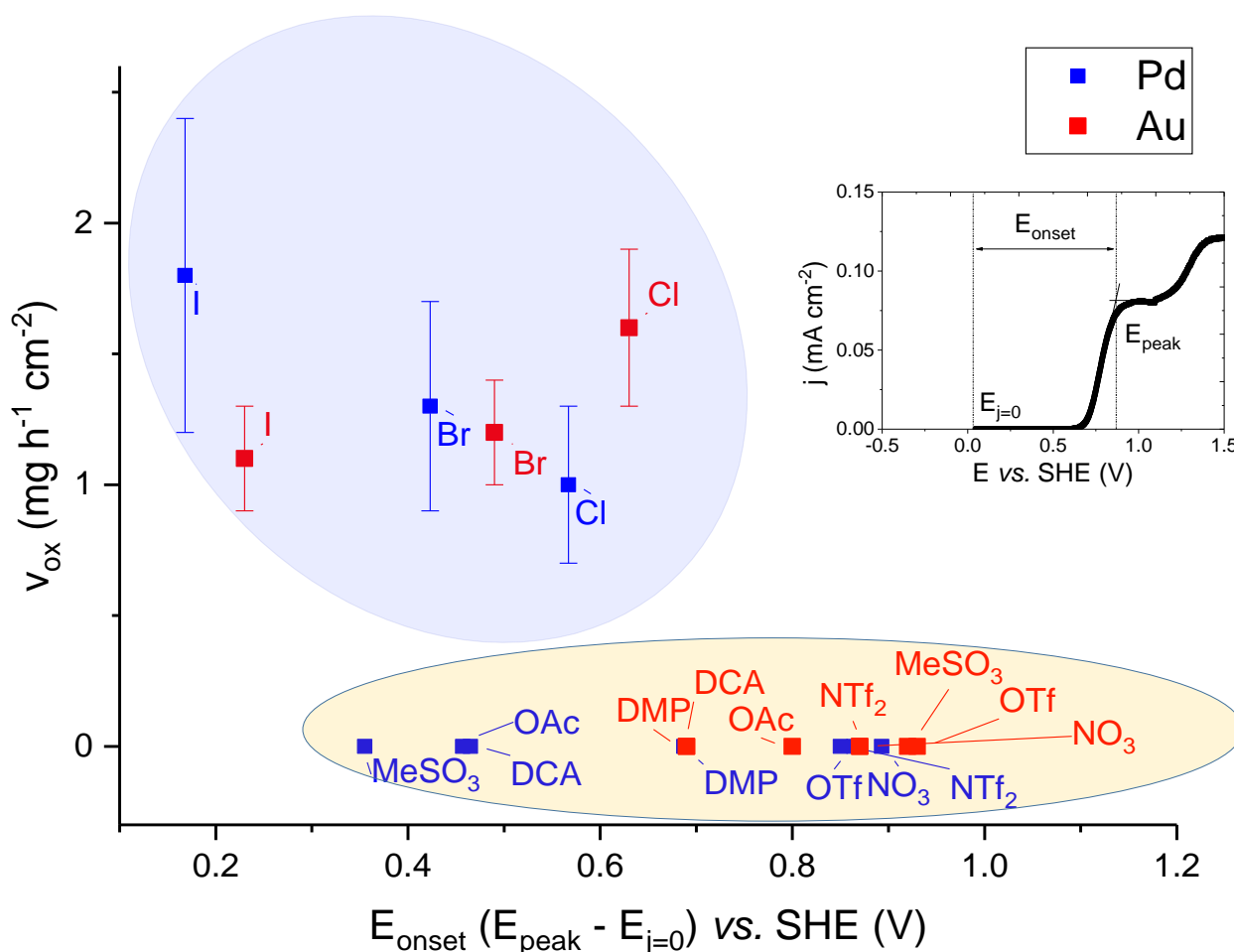
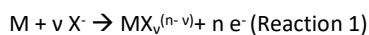


Figure 2. Leaching rate  $v_{\text{ox}}$  ( $\text{mg h}^{-1} \text{ cm}^{-2}$ ) versus  $E_{\text{onset}}$  (V vs. SHE) on gold and palladium electrode for ten ionic liquids mixtures -  $\text{C}_4\text{C}_1\text{Im NTf}_2 + \text{C}_4\text{C}_1\text{Im X}$  ( $\text{X} = \text{Cl}, \text{Br}, \text{I}, \text{DCA}, \text{DMP}, \text{OAc}, \text{MeSO}_3, \text{OTf}, \text{NO}_3, \text{NTf}_2$ ); Inset: Linear polarisation resistance at  $0.1667 \text{ mV s}^{-1}$  for  $\text{C}_4\text{C}_1\text{Im NTf}_2 + 0.1 \text{ M C}_4\text{C}_1\text{Im Cl}$

electrolytes, current density is still higher than  $100 \mu\text{A cm}^{-2}$  after 10 000 s of potentiostatic leaching.

For  $\text{DCA}^-$  anions on gold electrode, a dark compound appears on the metal surface without significant gold dissolution. This compound is assumed to be the dimer  $(\text{CN})_2\text{N}-\text{N}(\text{CN})_2$  previously observed by Mac-Farlane and *al.*[52]. For other IL mixtures, current density is lower than  $50 \mu\text{A cm}^{-2}$  after a few minutes of potentiostatic experiment and no Au or Pd dissolution was observed after 10 000 s. These anions cannot complex Au or Pd. The anodic current observed at  $E_{\text{peak}}$  in LPR experiments corresponds to water or IL anion oxidation, sometimes leading to a film formation on the anode. According to this graph, we can then define two IL categories: complexing (blue area) and non-complexing electrolytes (light yellow area), depending on the metal considered.  $\text{NO}_3^-$ ,  $\text{NTf}_2^-$ ,  $\text{MeSO}_3^-$  and  $\text{OTf}^-$  anions are known to be poor complexing anions. Mixtures including these anions do not show any interesting behavior for precious metals leaching.  $\text{DCA}^-$ ,  $\text{OAc}^-$ ,  $\text{DMP}^-$  based mixtures were not relevant to leach Au and Pd though  $\text{OAc}^-$  and  $\text{DMP}^-$  anion are known to be highly basic[48,49] while  $\text{DCA}^-$  has a great affinity for gold in liquid-liquid extraction[53,54]. It appears therefore that basicity is not a sufficient property to perform PM electroleaching.

Finally, potentiostatic experiments show that only ionic liquids mixtures containing halides can lead to Pd and Au electrochemical leaching. LPR experiments highlight that this leaching step is limited by mass transport. The leaching rate of the electrode  $v_{\text{ox}}$  rises with the current density  $j$ . In our case, metal oxidation can be described by the following reaction 1 where X is a mono-charged anion.



In the case of  $\text{X}^-$  linear diffusion toward a planar electrode, current density  $j$  rises with the diffusing coefficient and the concentration of  $\text{X}^-$  during potentiostatic leaching. Hence, complexing anion  $\text{X}^-$  concentration or transport properties can be increased to improve the leaching current. Results presented in Figure 2 allow then discriminating useful and useless anions to perform gold or palladium electrochemical leaching in the metal recovery field. For the best of our knowledge, no data are available in literature for palladium leaching kinetics. However, the leaching rate in halides electrolytes is in the same order of magnitude than considering the cyanide process for gold leaching ( $1.9 \text{ mg h}^{-1} \text{ cm}^{-2}$ ) reported by Kudryk et Kellogg[55] meaning that leaching kinetics will not be a limiting parameters for these electrolytes. However, cyanide solution is cheaper than an ionic liquid solution. Electrolyte stability during electrochemical leaching has therefore to be high in order to recycle electrolyte and to reduce costs and

environmental impact of such IL process. Moreover, electrodeposition potentials of Au and Pd have to be determine to evaluate if their recovery is practicable in complexing mixtures without any solvent degradation. For this reason, we present in the next part a detailed study of electrochemical behaviors of glassy carbon (GC), Au and Pd electrodes in complexing IL mixtures containing halides.

### 3.2. Electrochemical stability of diluting ionic liquid $\text{C}_4\text{C}_1\text{Im NTf}_2$

Cyclic voltamograms recorded on Au, Pd and GC electrodes in diluting IL,  $\text{C}_4\text{C}_1\text{Im NTf}_2$ , are presented on Figure 3.

On Au and GC electrode,  $\text{C}_4\text{C}_1\text{Im NTf}_2$  anodic degradation determined by tangent method occurs at 2.5 V vs. SHE and cathodic degradation occurs at -1.8 V vs. SHE. Electrochemical stability Window (EW) is then equal to 4.3 V which is consistent with literature[56] and suppliers data (4.6 V). This wide EW is useful to perform electrochemical reactions without any degradation of the IL cation and anion. This window is smaller (4.0 V) with Pd because cathodic and anionic degradations occur at lower polarization. Cathodic signal on GC and Au electrode around -0.5V vs. SHE could be attributed to water impurity reduction/proton adsorption according to Aldous *et al.*[57]. This peak appears at 0.4 V vs. SHE on Pd, which is consistent with cyclic voltamograms of  $\text{C}_4\text{C}_1\text{Im NTf}_2$  on platinum electrode obtained by the same authors. Few peaks are observed on anodic (around 1.5 V vs.

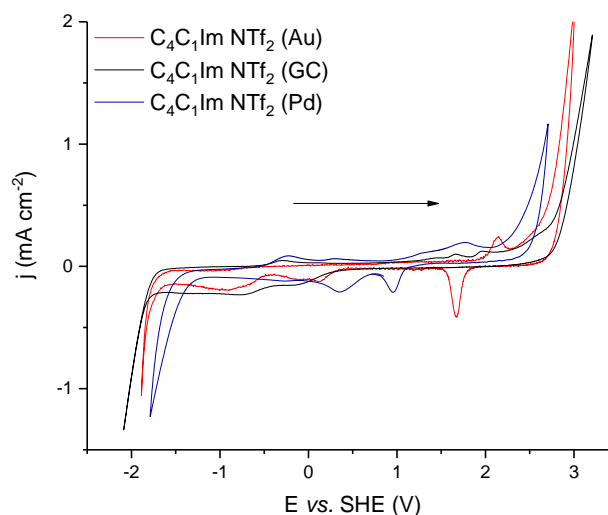


Figure 3. Cyclic voltamograms of  $\text{C}_4\text{C}_1\text{Im NTf}_2$  on Au, Pd and GC electrode at  $50 \text{ mV s}^{-1}$  and  $40 \text{ }^\circ\text{C}$

SHE) and cathodic scan (for  $E < 0 \text{ V vs. SHE}$ ) which can be attributed to impurities (water, halides) or to products formed during cathodic and anionic degradation of IL[30,58]. On Au electrode, an oxidation reaction occurs at 2.1 V vs. SHE associated to a cathodic peak at 1.7 V vs. SHE with a shape

characteristic of a surface reaction. These signals could be attributed to metal oxide formation and reduction. Indeed, this oxide formation/reduction on gold was used to determine water content in ionic liquid because the magnitude of the current peak depends on water content[59,60]. On Pd electrode, a similar oxidation feature occurs between 1 and 1.8 V vs. SHE and cathodic feature at 0.95 V vs. SHE which is comparable to Aldous *et al.* results on platinum[57]. Oxidation peaks could be associated to PdO and PdO<sub>2</sub> formation and cathodic peaks between 0.95 and 0 V vs. SHE to palladium oxide reduction as reported in acidic aqueous solution[61,62]. Finally, oxidation peaks observed before 0 V vs. SHE on Pd and GC electrode are associated to oxidation of products formed after the cathodic limit because they did not occur when scan direction was switched before -1 V vs. SHE.

### 3.3. Gold behavior in complexing electrolytes

Cyclic voltamograms were recorded at 50 mV s<sup>-1</sup> for complexing electrolytes. CV for non-complexing electrolytes are available in supporting information (SI-Figure 4). Within the electrochemical stability window (EW) of diluting IL, CV

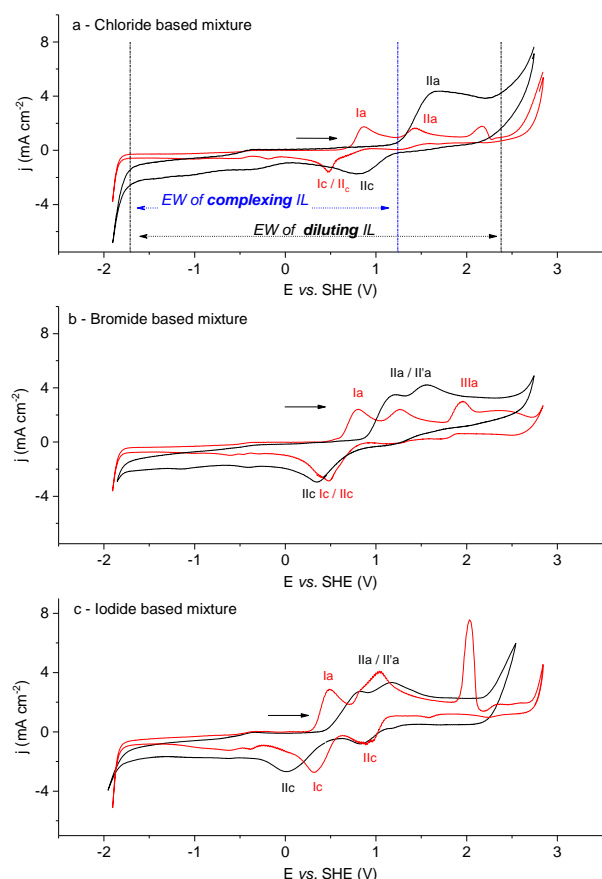


Figure 4. Gold electrochemical behaviour in complexing electrolytes (red curve) and electrolytes behaviour on GC electrode (black curve) at 50 mV s<sup>-1</sup> and 40 °C. C<sub>4</sub>C<sub>1</sub>Im NTf<sub>2</sub> + 0.1 M C<sub>4</sub>C<sub>1</sub>Im Cl (a), C<sub>4</sub>C<sub>1</sub>Im NTf<sub>2</sub> + 0.1 M C<sub>4</sub>C<sub>1</sub>Im Br (b), C<sub>4</sub>C<sub>1</sub>Im NTf<sub>2</sub> + 0.1 M C<sub>4</sub>C<sub>1</sub>Im I (c)

profiles show several anodic and cathodic peaks (Figure 4). CV profiles obtained are very similar to CV reported by previous authors [39–41].

Three main oxidation areas are observed on Au electrode for each electrolyte. I<sub>a</sub> signals are of diffusional shape, corresponding to LPR main feature (red curve on Figure 1) and have a peak potential between 0.3 – 1 V vs. SHE, depending on the anion considered. II<sub>a</sub> peaks have a shape similar to I<sub>a</sub> and appear between 0.8 and 1.3 V vs. SHE. A third peak III<sub>a</sub>, occurs between 1.9 and 2.2 V vs. SHE. These peaks are characterized by an important current rise followed by a sharp drop in current for the iodide-based electrolyte. This can be linked to a gold passivation and was reported in literature as an insoluble gold halide formation[41].

To determine reaction associated to I<sub>a</sub>, previously described potentiostatic experiment was used to determine the number of electrons n<sub>e</sub> exchanged in the involved oxidation reaction thanks to the following equation 1:

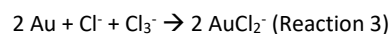
$$ne^- = \frac{Q \cdot M}{\Delta m \cdot F} \text{ (Equation 1)}$$

where Q is the charge in Coulomb (C), M is the molar mass of metal in g mol<sup>-1</sup>, Δm represents the loss in mass of the electrode in grams and F is the Faraday constant in C mol<sup>-1</sup>. For the four mixtures, n<sub>e</sub> is close to one meaning the following electrochemical reaction (2) is involved in the electrochemical leaching of the metal.



This reaction was observed in chloride media by numerous authors who assumed AuCl<sub>2</sub><sup>-</sup> formation in IL [39,40,63]. However, no advanced spectroscopic measurements were performed after bulk electrolysis in order to confirm the presence of this complex.

Aldous *et al.*[41,57] proposed a chloride oxidation into trichloride anions Cl<sub>3</sub><sup>-</sup> at I<sub>a</sub> following by chemical gold dissolution by Cl<sub>3</sub><sup>-</sup> according to the subsequent chemical reaction 3:



In our experiments, I<sub>a</sub> peak is not observed on GC electrode and II<sub>a</sub> peak on GC, corresponding to chloride oxidation, perfectly fits with II<sub>a</sub> peak on Au (Figure 4a). Furthermore, during potentiostatic dissolution, faradic yield obtained with the hypothesis of AuCl<sub>2</sub><sup>-</sup> formation, is respectively 99 %, 98 % and 96 % for chloride, bromide and iodide based electrolytes, which is more suitable with a direct electrochemical leaching than an indirect electrochemical process involving trihalide



formation. Moreover, electrochemical oxidation of chloride was performed at a GC electrode maintained at potential higher than  $II_a$  peak and a gold wire was immersed close to the electrode. After three hours, gold dissolution was not observed meaning that chemical dissolution did not occur during our short experimental time. These considerations allow us to attribute  $I_a$  peak to gold anodic leaching according to reaction (2).

CV experiments on GC exhibit two signals in  $II_a$  area for bromide and iodide containing electrolytes ( $II_a$  and  $II'_a$ ), and a shouldered peak  $II_a$  for  $Cl^-$  containing IL. Cyclic voltamograms performed on GC in a restricted potential range around  $II_a/II'_a$  signals are consistent with halide oxidation in this area, leading to  $X_3^-/X_2^-$  formation, respectively (SI-Figure 5). Moreover, the yellow brown coloration of  $C_4C_1Im NTf_2 + 0.1 M C_4C_1ImI$  after linear anodic scan voltammetry agrees with  $I_2$  or  $I_3^-$  formation. Halide potential oxidation ( $Cl^- > Br^- > I^-$ ) follows the same order as aqueous standard potential  $Cl_2/Cl^-$  (1.3 V vs. SHE)  $> Br_2/Br^-$  (1.1V vs. SHE)  $> I_2/I^-$  (0.9 V vs. SHE). However, we cannot exclude that halide oxidation did not occur at  $I_a$  because faradic yield is not 100%. Figure 5 of SI also highlights that the reduction of halide oxidation products occurs at peak  $II_c$ .

In order to understand cathodic signals recorded on Au electrode, several CV experiments were performed by changing anodic vertex potential. When anodic potential is reversed just after  $I_a$  (Figure 5), CV exhibits on the return scan a cathodic  $I_c$  peak close to  $I_a$ . This peak is well defined for iodide and bromide but less for chloride.  $III_c$  signal can be associated to impurities evolution (as in Figure 3). When potential is switched after  $II_a$  (Figure SI-6), a sharp peak  $II_c$  appears at lower potential than  $I_c$ .  $I_c$  can then be attributed to Au(I) deposition meanwhile  $II_c$  is linked to reduction of products formed at  $II_a$  i.e.  $X_2$ ,  $X_3^-$  or even Au(III). Aldous *et al.* reported the same shouldered peak  $II_c$  (cf. Figure 4) in chloride medium when anodic potential was swiped after  $II_a$ , and attributed these signals to both Au(III) and Au(I) reduction. They also showed an important negative shift for Au(I) reduction potential when a glassy carbon electrode was used instead of gold electrode. In  $C_4C_1Im NTf_2 + 0.01M C_4C_1Im Br + 10mM AuBr_3$ , Katayama *et al.* [64] observed  $I_a/II_a$  peak around 0.3V vs. SHE on a GC electrode but also a cathodic peak around -0.5V vs. SHE attributed to Au(I) reduction.

However, in the case of iodide based IL,  $I_c$  could be a combination of gold electrodeposition and  $I_3^-$  reduction reactions, as observed by Bentley *et al.*[65], using a gold electrode in  $C_4C_1Im NTf_2 + 0.01M C_4C_1Im I$ . Indeed, the

authors associated  $I_a$  mostly to Au(I) formation (88% of charge) but also to  $I_3^-$ .

These experiments confirm previous published results about gold behavior in halide containing ionic liquids[39–41,65] but also highlight the similarity of mixtures features. Halide mixtures allow anodic leaching of gold following a one-electron exchange reaction and gold electrodeposition at  $I_c$  within electrochemical window of complexing ionic liquid. According to potentiostatic results and previous articles,

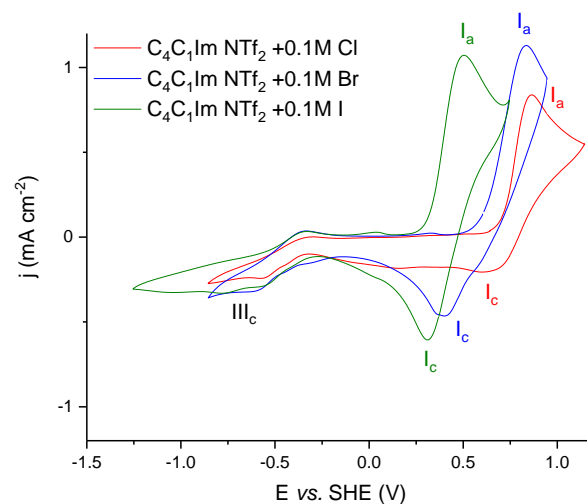


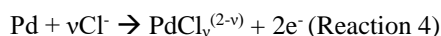
Figure 5. Cyclic voltammetry curves on gold electrode in complexing electrolytes at 50  $mV s^{-1}$  and 40 °C.  $C_4C_1Im NTf_2 + 0.1 M C_4C_1Im Cl$  (red curve),  $C_4C_1Im NTf_2 + 0.1 M C_4C_1Im Br$  (blue curve), and  $C_4C_1Im NTf_2 + 0.1 M C_4C_1Im I$  (green curve).

chloride media allows to obtain the higher faradic yield at  $I_a$ . Gold leaching could be performed without any chloride oxidation, which is of major concern in order to recycle the electrolyte. Furthermore, gold electrodeposition in these media starts at higher potential than in iodide-based IL, which is important to avoid side reactions (like water reduction) during electrodeposition. Meanwhile, Au(I) species are not stable in aqueous media and can undergo a disproportionation reaction leading to the formation of metallic gold and auric ions [66]. This reaction could also be observed in ionic liquids [39,67]. Indeed, previous observations showed that  $Au^I/Au$  potential is still higher than  $Au^{III}/Au$  in  $C_2C_1Im BF_4 + 40mM Cl^-$ [39] like in aqueous media. It is therefore primordial to compare kinetics of  $Au^I$  disproportionation and gold electrodeposition reactions in order to control the recovery process.

#### 3.4. Palladium behavior in complexing electrolytes

Similar CV curves at 50  $mV s^{-1}$  were conducted on palladium. As for gold, two main anodic peaks are observed on the potential range -1 V / 1.5 V (Figure 6) for all electrolytes.  $I_a$  peak potential follows the order  $Cl^- > Br^- > I^-$  like on gold.  $I_a$  is associated to Pd leaching according to GC and Pd CV superposition but also to potentiostatic experiments. Applying

equation 1, palladium loss in mass measured after potentiostatic dissolution at  $I_a$  gives an electron number  $n_e$  close to 2 for all electrolytes. With respect to previous work[68].



Faradic yield of palladium leaching, calculated while assuming a two-electron exchanged reaction, followed the same order than gold one:  $\text{Cl} (100\%) \approx \text{Br} (100\%) > \text{I} (96\%)$ .

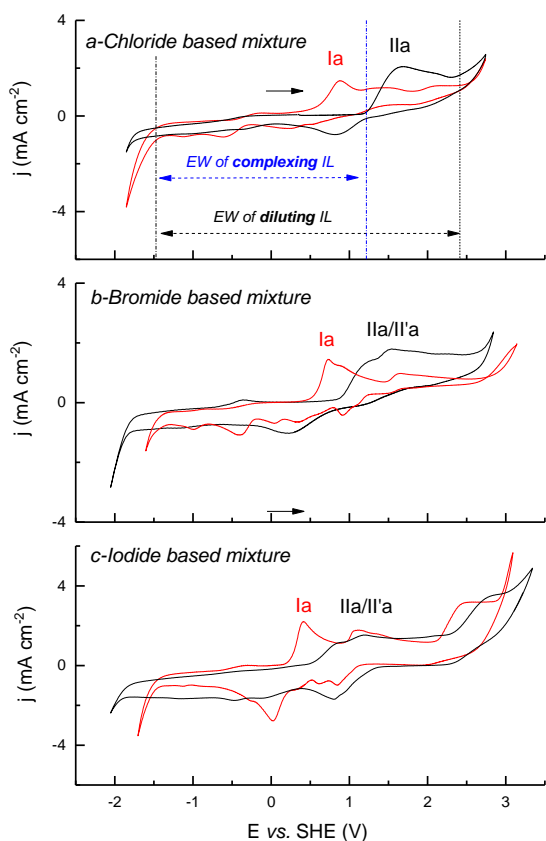


Figure 7. Palladium electrochemical behaviour in complexing electrolytes (red curve) and electrolytes behaviour on GC electrode (black curve) at  $50 \text{ mV s}^{-1}$  and  $40^\circ\text{C}$ .  $\text{C}_4\text{C}_1\text{Im NTf}_2 + 0.1 \text{ M C}_4\text{C}_1\text{Im Cl}$  (a),  $\text{C}_4\text{C}_1\text{Im NTf}_2 + 0.1 \text{ M C}_4\text{C}_1\text{Im Br}$  (b) and  $\text{C}_4\text{C}_1\text{Im NTf}_2 + 0.1 \text{ M C}_4\text{C}_1\text{Im I}$  (c)

As on gold electrode,  $\text{II}_a$  is attributed to anion oxidation according to voltamograms obtained on GC electrodes. Br and I containing IL present two peaks on GC,  $\text{II}_a/\text{II}'_a$ , associated to  $\text{X}_2$  and  $\text{X}_3^-$  formation. Cyclic voltammograms were performed on  $I_a$  area (Figure 7). Contrary to gold, a well-defined  $I_c$  reduction peak occurs using bromide and chloride containing ILs. A particular behavior is observed on iodide based-electrolytes. In this medium,  $I_a$  exhibit a shouldered peak. As on gold electrode, these peaks are associated to metal leaching but also to iodide oxidation which explains the lower faradic yield obtained with iodide based electrolyte. Cathodic

scan exhibits two reduction processes associated respectively to palladium reduction ( $I_c$ ) and iodine reduction ( $\text{II}_c$ ).

As on gold, these experiments are consistent with published results in chloride media[43,68]. Halide mixtures allow anodic leaching of Pd following a two-electron exchange reaction inside the complexing IL electrochemical window without any halide oxidation ( $\text{II}_a$ ) at least for chloride and bromide-based electrolytes. As on gold, faradic yield is lower for iodide-based electrolyte because iodide oxidation occurs during palladium electrochemical leaching. Palladium(II) is assumed to exist mainly as  $\text{PdCl}_4^{2-}$  or  $\text{PdCl}_3^-$  when  $\text{PdCl}_2$  is added in  $\text{C}_4\text{C}_1\text{Im Cl}$ [44]. However, to the best of our knowledge, no speciation analysis was ever published obtained in ionic liquids after an anodic dissolution of palladium electrode in chloride media.

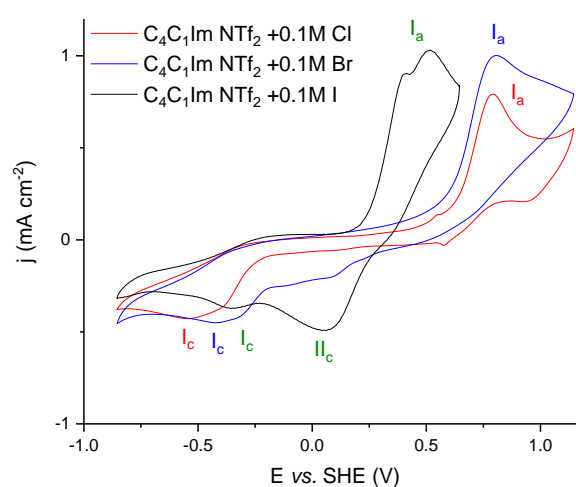


Figure 6. Cyclic voltammograms on palladium electrode in complexing electrolytes at  $50 \text{ mV s}^{-1}$  and  $40^\circ\text{C}$ .  $\text{C}_4\text{C}_1\text{Im NTf}_2 + 0.1 \text{ M C}_4\text{C}_1\text{Im Cl}$  (red curve),  $\text{C}_4\text{C}_1\text{Im NTf}_2 + 0.1 \text{ M C}_4\text{C}_1\text{Im Br}$  (blue curve), and  $\text{C}_4\text{C}_1\text{Im NTf}_2 + 0.1 \text{ M C}_4\text{C}_1\text{Im I}$  (green curve).

### 3.5. Direct electroleaching-electrochemical deposition process

Table 1 presents  $I_a$  (metal leaching),  $\text{II}_a$  (anion oxidation) and  $I_c$  (metal deposition) peak potentials recorded for gold and palladium at  $50 \text{ mV s}^{-1}$  in each complexing electrolyte.

Table 1

Peak potential (V) extracted from Figure 5 and Figure 7

Metal	Complexing anion	$I_a$	$\text{II}_a$	$\Delta E_{I_a-\text{II}_a}$	$I_c$
Au	<i>Cl</i>	0.87	1.42	<b>0.65</b>	<b>0.60</b>
	<i>Br</i>	0.84	1.26	<b>0.42</b>	<b>0.40</b>
	<i>I</i>	0.50	1.04	<b>0.54</b>	<b>0.31</b>
Metal	Complexing anion	$I_a$	$\text{II}_a$	$\Delta E_{I_a-\text{II}_a}$	$I_c$
Pd	<i>Cl</i>	0.79	1.34	<b>0.55</b>	<b>-0.56</b>
	<i>Br</i>	0.81	1.62	<b>0.81</b>	<b>-0.42</b>
	<i>I</i>	0.52	1.08	<b>0.56</b>	<b>-0.37</b>

For each electrolyte, gold and palladium leaching occurs at similar potential  $I_a$ . This highlights the impossibility to leach selectively one metal. However, in the case of chloride,  $\Delta E_{1c}$  (Au-Pd) is equal to 1.16 V meaning that gold deposition occurs at 1.16 V higher than palladium deposition. Selective gold electrodeposition can therefore be performed in this electrolyte. Furthermore, the highest faradic yield faradic yield is obtained in chloride media. In order to validate the one-step electrochemical leaching-electrodeposition concept of gold

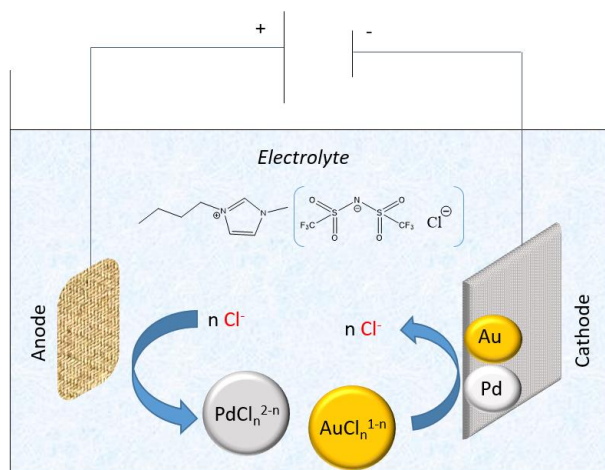


Figure 8. Schematic representation of an EL/ECD process

and palladium in ionic liquid (Figure 8), we chose  $C_4C_1Im$  NTf<sub>2</sub> + 1 M  $C_4C_1Im$  Cl as electrolyte. Chloride content was increased to 1 M in order to improve leaching and deposition kinetics.

To avoid as much as possible the IL degradation by reduction of the IL cation at the early stage of the process, the experiments were conducted in Au and Pd leachates prepared by electroleaching of metallic anode with an isolated CE in a previous step and under cathodic control (cathode = WE). Results are compiled in Table 2. Platinum was chosen as cathode because of his electrochemical stability (cathodic and anodic) in this ionic liquid at 40 °C[29]. We observe first that during the EL-ECD process, leaching faradic yield is close to 100 % although the potential of the anode is not fixed. Indeed, counter electrode potential is recorded at respectively 0.69 V vs. SHE for gold and 0.37 V for Pd meaning that the main anodic reaction is metal leaching according to previous experiments. A yellow deposit is observed on the platinum cathode after EL-ECD process using gold and a black deposit using palladium. These deposits were analysed by Scanning Electron Microscope (SEM) and Energy-Dispersive X-ray spectroscopy (EDX) (Figures SI-8-9-10). Contrarily to gold deposit, palladium deposit did not adhere well to the platinum

substrate and appeared to be cracked whereas gold deposit appears more compact on SEM images. As described in literature, palladium deposition leads to nanoparticles formation[69,70]. SEM images exhibit an inhomogeneous deposit on platinum surface in this case. Thereby, deposition faradic yield calculated is probably underestimated because a part of the deposit fall in solution and then the totality of the deposit cannot be accurately weighted. The lower yield on palladium instead of gold could also be explained because water reduction (present as impurity) is enhanced on palladium and platinum leading to higher hydrogen evolution during metal deposition. Furthermore, deposition was not observed for initial concentration of Pd lower than 10 mM. EL-ECD experiments were also conducted with anodic control *i.e* with metal to be leached as working electrode. In this configuration, leaching yield was maintained close to 100 % but the metal deposition yield was decreased to *ca.* 1 %. This can be explained by the CE potential recorded around -2 V vs. SHE meaning that cationic degradation of the ionic liquids is the predominant reaction. To balance anodic and cathodic process in order to obtain a good recovery efficiency, it is possible to modulate electrode surfaces ratio (larger cathode/smaller anode) or enhance cathodic current by increasing metal concentration or enhancing mass transport in the cell with a higher temperature or higher stirring speed.

Table 2

Potential and faradic yield for working electrode and counter electrode

Metal	C mM	Deposition		
		E-WE (V) vs. SHE	$\Delta m$ - WE (mg)	Faradic yield- WE (%)
Au	15	0.34	0.960	80 ± 1
Pd	23	-0.66	0.135	25 ± 1
Metal	C mM	Leaching		
		E-CE (V) vs. SHE	$\Delta m$ - WE (mg)	Faradic yield- WE (%)
Au	15	0.57	0.943	99 ± 1
Pd	23	0.22	0.547	100 ± 1

These results confirmed that it is possible to recover gold and palladium from a metallic electrode without any solvent oxidation with a careful deposition potential control. Further experiments will be carry out in order to improve faradic yield for palladium recovery to avoid other reduction reaction during EL-ECD and to allow the electrolyte recycling but also to study selective deposition of gold versus palladium.

#### 4. Conclusion:

In this study, electrochemical experiments were performed for several ionic liquid mixtures ( $C_4C_1Im\ NTf_2 + 0.1\ M\ C_4C_1\ X$ ;  $X=Cl, Br, I, NO_3, MeSO_3, OTf, NTf_2, DMP, DCA, OAc$ ) in order to study the influence of anion nature on Pd and Au electrochemical leaching. Electrochemical data allow us to define oxidation/deposition potentials of Au and Pd to perform an electrochemical recovery of these noble metals but also to evaluate solvent stability during the process. Among ten electrolytes studied, gold and palladium electrochemical leaching could be achieved in halide based ionic liquid through a diffusion-controlled reaction.

The results demonstrate a successful recovery of Pd and Au by electrodeposition in the electrochemical window of IL electrolytes containing halides. Finally, we validate the electroleaching/electrochemical deposition coupling (EL-ECD) in chloride-containing electrolyte without any atmosphere control. The approach could be exploited to define a sustainable one-step electrochemical process to recover precious metals from anode slime or other PM concentrated waste. The influence of other parameters on electroleaching or electrodeposition steps as water content but also temperature have to be evaluated to increase faradic yield in order to define a loop process without solvent degradation. This process could avoid large quantities of toxic wastewater generated in current industrial precious metal recovery units if the IL-electrolyte can be reused.

However, we only demonstrate a theoretical stability of halide-based electrolyte during few coulombs electrolysis. In practice, this kind of process will be interesting from the environmental and economical point of view only if we can effectively use the electrolyte during many cycles in order to reduce its price and the environmental impact of its synthesis and elimination. Hence, cyclability experiments will be performed in order to validate the IL stability over time in this process associated with economic and environmental comparison with conventional solutions like HCl, *aqua regia* or cyanide solution. Furthermore, this kind of evaluation has to be done also with deep eutectic solvents. Indeed these solvents are the more and more used for metal recovery and a promising electrocatalytic process (with chemical leaching and oxidant regeneration) associating  $ChCl:EG\ 1:2$  and iodine was reported in 2015 [38] for gold recovery from ore and was recently tested on anode slime[42].

Hence, experiments on multi-metallic anode and real waste are necessary to discuss about electroleaching and electrodeposition selectivity and perform a comparison with existing processes.

#### CRedit authorship contribution statement

Benoit Villemejeanne: Conceptualization, Investigation, Writing - original draft, review & editing;

Eric Meux, Sophie Legeai, Emmanuel Billy, Hakima Mendil-Jakani, Sandrine Dourdain: Conceptualization, Supervision, Project administration, Funding acquisition, Writing - review & editing.

Hakima Mendil-Jakani, Sandrine Dourdain: Supervision, Project administration, Funding acquisition, Writing - review & editing.

#### Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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