



HAL
open science

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

Benoit Villemejeanne, Sophie Legeai, Eric Meux, Sandrine Dourdain, Hakima Mendil-jakani, Emmanuel Billy

► **To cite this version:**

Benoit Villemejeanne, Sophie Legeai, Eric Meux, Sandrine Dourdain, Hakima Mendil-jakani, et al.. Halide based ionic liquid mixture for a sustainable electrochemical recovery of precious metals. *Journal of Environmental Chemical Engineering*, 2022, 10 (1), pp.107063. 10.1016/j.jece.2021.107063. hal-03932714

HAL Id: hal-03932714

<https://hal.univ-lorraine.fr/hal-03932714>

Submitted on 10 Jan 2023

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.



Distributed under a Creative Commons Attribution - NonCommercial - NoDerivatives 4.0 International License

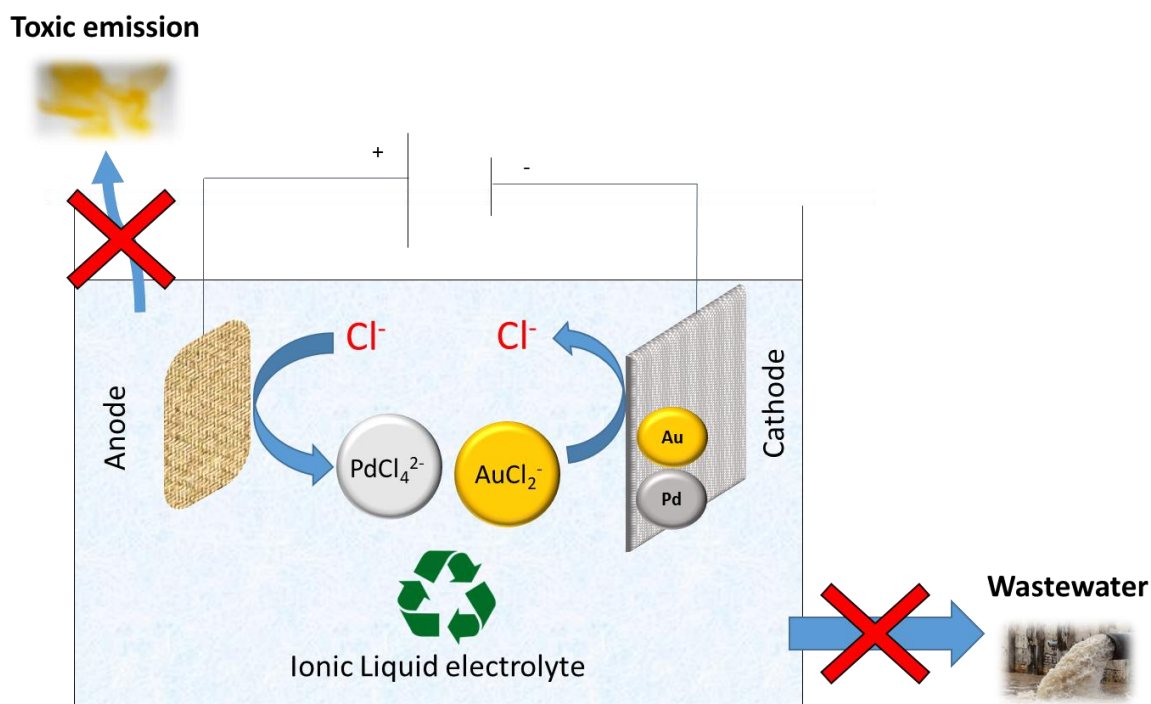
Halide based ionic liquid mixture for a sustainable electrochemical recovery of precious metals

Benoit Villemejeanne ^{a,b}, Sophie Legeai ^b, Eric Meux ^b, Sandrine Dourdain ^c, Hakima Mendil-Jakani ^d and Emmanuel Billy ^{a*}

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.



^a Univ. Grenoble Alpes, CEA Liten, 38000 Grenoble, France. emmanuel.billy@cea.fr

^b Institut Jean Lamour, UMR CNRS 7198, Université de Lorraine – 1 bd Arago BP 95823, 57078 Metz Cedex 3, France

^c Institut de Chimie Séparative de Marcoule (ICSM/LTSM) Site de Marcoule – Bât. 426 – BP 17171 30207 Bagnols sur Cèze Cedex

^d Univ. Grenoble Alpes, CEA, CNRS, IRIG-SyMMES, 38000 Grenoble, France.

Electronic Supplementary Information (ESI) available: [details of any supplementary information available should be included here]. See DOI: 10.1039/x0xx00000x Received ...

Accepted 00th January 20xx

DOI: 10.1039/x0xx00000x

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 21st 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 CO₂ 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 20th 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 20th 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. α parameter, representing Lewis acidity is highly dependent on the cationic part whereas β parameter, representing Lewis basicity, is anion dependent. In order to influence of β 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 ± 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 Fc^+/Fc half wave potential and were stable between 40–80 °C during experiments duration. We assume that Fc^+/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 mV s^{-1}) was used to determine $E_{j=0}$ mixed potential between water/ 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 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 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 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 mA cm^{-2}), revealing a mass transport-controlled oxidation reaction. $E_{j=0}$ and potential values corresponding to this limiting current (E_{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_{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 MeSO_3 , 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_{peak} is observed using both Pd and Au electrodes, corresponding to side reaction. This second typical behavior,

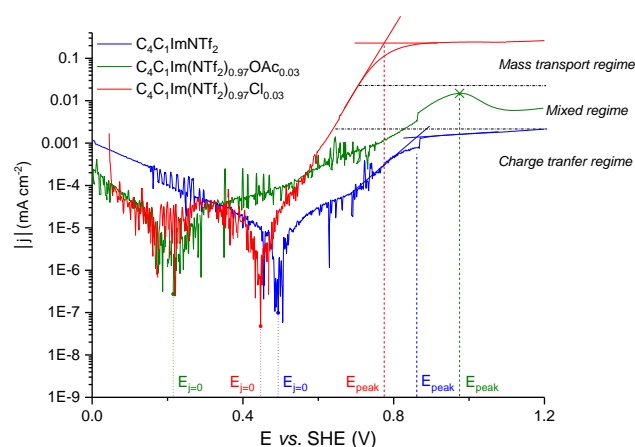


Figure 1 - Tafel plot ($\log(|j|) = f(E)$) on gold electrode for mass transfer control behaviour (represented by $\text{C}_4\text{C}_1\text{Im NTf}_2 + 0.1 \text{ M C}_4\text{C}_1\text{Im Cl}$ -red curve), charge transfer control (represented by $\text{C}_4\text{C}_1\text{Im NTf}_2$ -blue curve) and 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 mA cm^{-2}) for $E < E_{j=0}$, a current rising to reach a maximum for E_{peak} close to 1 V vs. SHE and a final current decrease until 0.01 mA cm^{-2} . On gold electrode, this behavior is significant when 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 $E > E_{(E=0)}$ (NTf_2^- , OTf^- , NO_3^- , 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 (OAc^- , DMP^- , and 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_{Peak} . When metal weight loss was observed, leaching rate v_{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_{ox} versus E_{onset} which is defined as the difference between E_{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_{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_{Peak} . For these

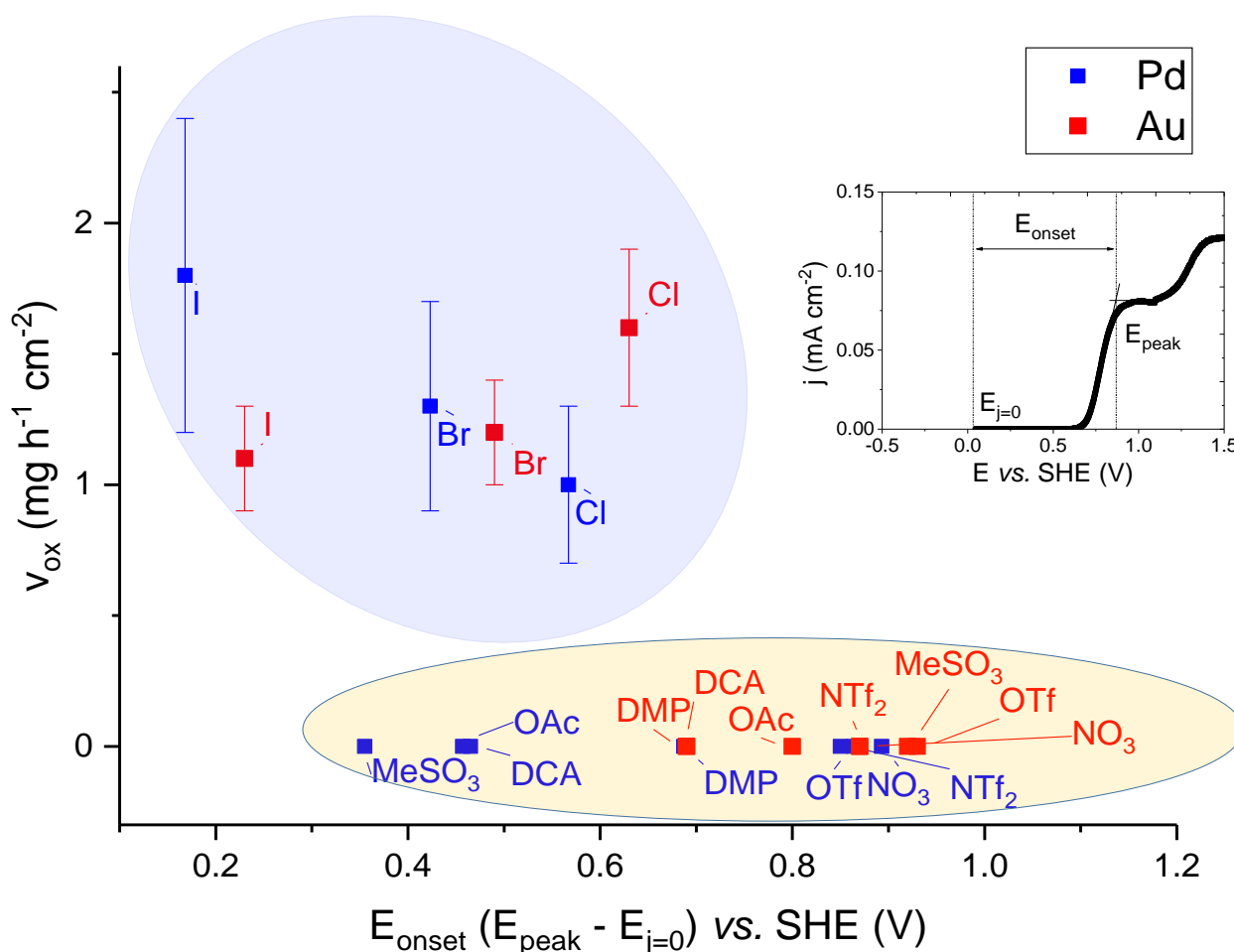
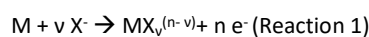


Figure 2. Leaching rate v_{ox} ($\text{mg h}^{-1} \text{ cm}^{-2}$) versus E_{onset} (V vs. SHE) on gold and palladium electrode for ten ionic liquids mixtures - $\text{C}_4\text{C}_1\text{Im NTf}_2 + \text{C}_4\text{C}_1\text{Im X}$ ($\text{X} = \text{Cl}, \text{Br}, \text{I}, \text{DCA}, \text{DMP}, \text{OAc}, \text{MeSO}_3, \text{OTf}, \text{NO}_3, \text{NTf}_2$); Inset: Linear polarisation resistance at 0.1667 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 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_{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. NO_3^- , NTf_2^- , MeSO_3^- and OTf^- anions are known to be poor complexing anions. Mixtures including these anions do not show any interesting behavior for precious metals leaching. DCA^- , OAc^- , DMP^- based mixtures were not relevant to leach Au and Pd though OAc^- and DMP^- anion are known to be highly basic[48,49] while 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_{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 X^- linear diffusion toward a planar electrode, current density j rises with the diffusing coefficient and the concentration of X^- during potentiostatic leaching. Hence, complexing anion 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.

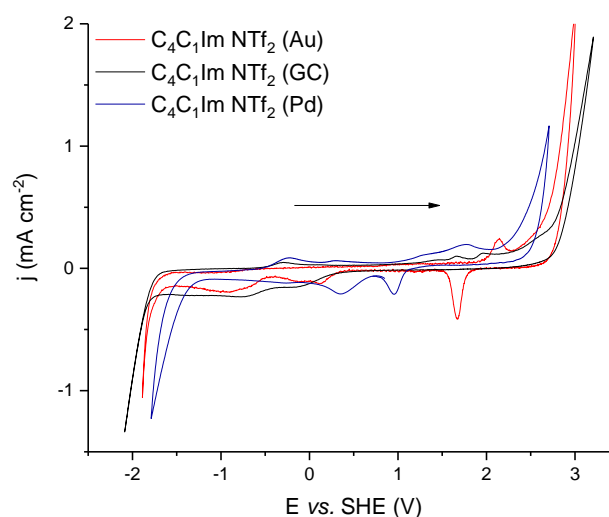


Figure 3. Cyclic voltamograms of $\text{C}_4\text{C}_1\text{Im NTf}_2$ on Au, Pd and GC electrode at 50 mV s^{-1} and $40 \text{ }^\circ\text{C}$

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 PdO₂ 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⁻¹ 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

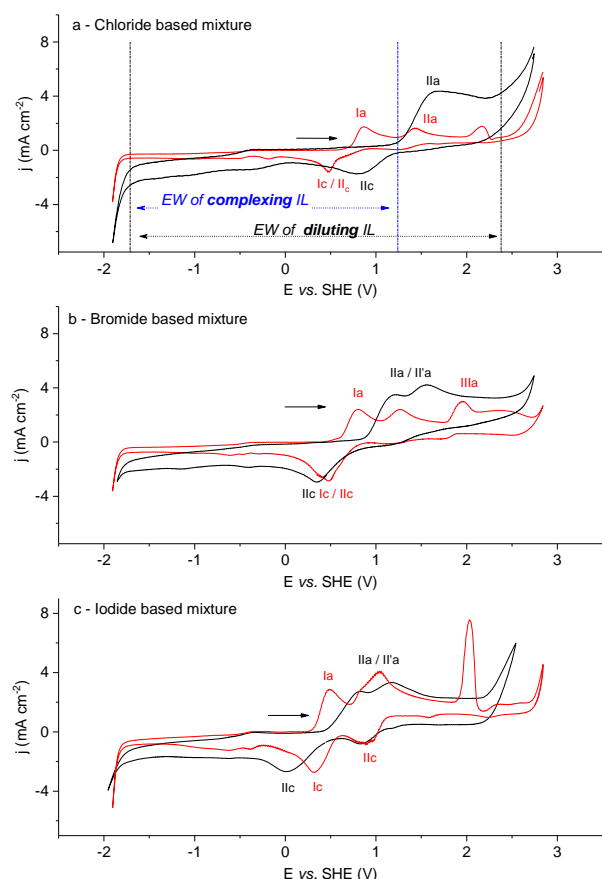


Figure 4. Gold electrochemical behaviour in complexing electrolytes (red curve) and electrolytes behaviour on GC electrode (black curve) at 50 mV s⁻¹ and 40 °C. C₄C₁Im NTf₂ + 0.1 M C₄C₁Im Cl (a), C₄C₁Im NTf₂ + 0.1 M C₄C₁Im Br (b), C₄C₁Im NTf₂ + 0.1 M C₄C₁Im I (c)

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_a 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_a peaks have a shape similar to I_a and appear between 0.8 and 1.3 V vs. SHE. A third peak III_a, 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_a, previously described potentiostatic experiment was used to determine the number of electrons n_e exchanged in the involved oxidation reaction thanks to the following equation 1:

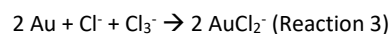
$$ne^- = \frac{Q \cdot M}{\Delta m \cdot F} \text{ (Equation 1)}$$

where Q is the charge in Coulomb (C), M is the molar mass of metal in g mol⁻¹, Δm represents the loss in mass of the electrode in grams and F is the Faraday constant in C mol⁻¹. For the four mixtures, n_e 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 AuCl₂⁻ 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 Cl₃⁻ at I_a following by chemical gold dissolution by Cl₃⁻ according to the subsequent chemical reaction 3:



In our experiments, I_a peak is not observed on GC electrode and II_a peak on GC, corresponding to chloride oxidation, perfectly fits with II_a peak on Au (Figure 4a). Furthermore, during potentiostatic dissolution, faradic yield obtained with the hypothesis of AuCl₂⁻ 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 $\text{C}_4\text{C}_1\text{Im NTf}_2 + 0.1 \text{ M C}_4\text{C}_1\text{ImI}$ after linear anodic scan voltammetry agrees with I_2 or I_3^- formation. Halide potential oxidation ($\text{Cl}^- > \text{Br}^- > \text{I}^-$) follows the same order as aqueous standard potential Cl_2/Cl^- (1.3 V vs. SHE) $> \text{Br}_2/\text{Br}^-$ (1.1V vs. SHE) $> \text{I}_2/\text{I}^-$ (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 $\text{C}_4\text{C}_1\text{Im NTf}_2 + 0.01\text{M C}_4\text{C}_1\text{Im Br} + 10\text{mM AuBr}_3$, 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 $\text{C}_4\text{C}_1\text{Im NTf}_2 + 0.01\text{M C}_4\text{C}_1\text{Im I}$. 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,

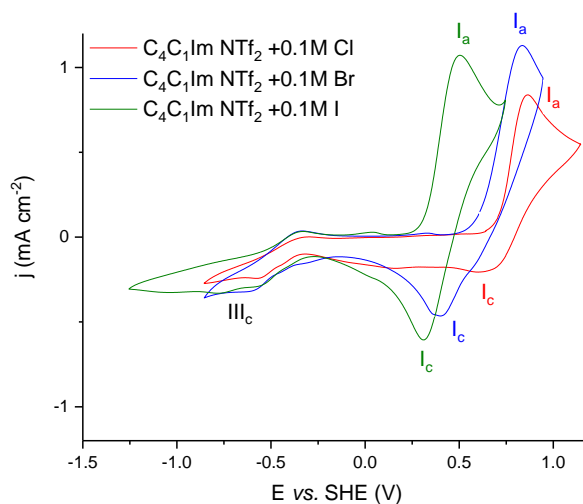


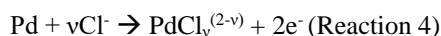
Figure 5. Cyclic voltammetry curves on gold electrode in complexing electrolytes at 50 mV s^{-1} and 40°C . $\text{C}_4\text{C}_1\text{Im NTf}_2 + 0.1 \text{ M C}_4\text{C}_1\text{Im Cl}$ (red curve), $\text{C}_4\text{C}_1\text{Im NTf}_2 + 0.1 \text{ M C}_4\text{C}_1\text{Im Br}$ (blue curve), and $\text{C}_4\text{C}_1\text{Im NTf}_2 + 0.1 \text{ M C}_4\text{C}_1\text{Im I}$ (green curve).

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 $\text{Au}^{\text{I}}/\text{Au}$ potential is still higher than $\text{Au}^{\text{III}}/\text{Au}$ in $\text{C}_2\text{C}_1\text{Im BF}_4 + 40\text{mM Cl}^-$ [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 $\text{Cl}^- > \text{Br}^- > \text{I}^-$ 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: $\text{Cl} (100\%) \approx \text{Br} (100\%) > \text{I} (96\%)$.

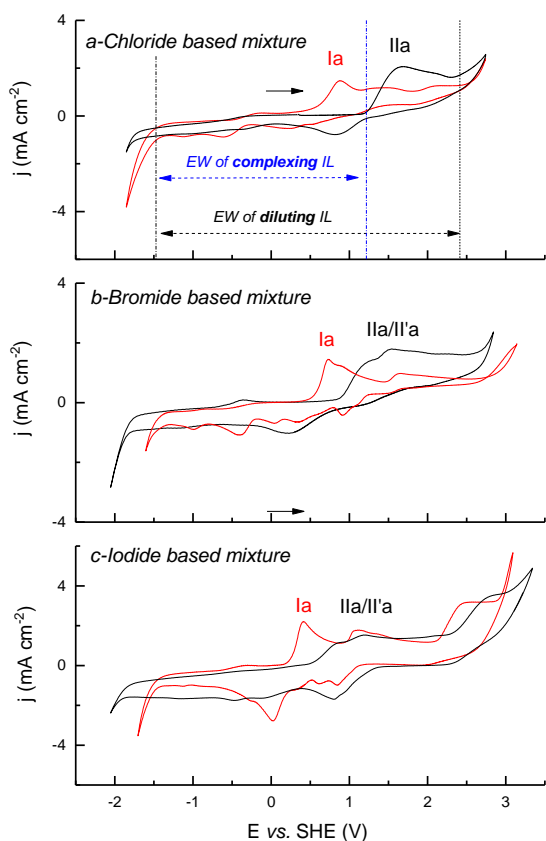


Figure 7. Palladium electrochemical behaviour in complexing electrolytes (red curve) and electrolytes behaviour on GC electrode (black curve) at 50 mV s^{-1} and 40°C . $\text{C}_4\text{C}_1\text{Im NTf}_2 + 0.1 \text{ M C}_4\text{C}_1\text{Im Cl}$ (a), $\text{C}_4\text{C}_1\text{Im NTf}_2 + 0.1 \text{ M C}_4\text{C}_1\text{Im Br}$ (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, II_a is attributed to anion oxidation according to voltamograms obtained on GC electrodes. Br and I containing IL present two peaks on GC, II_a/II'_a , associated to X_2 and 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 (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 (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 PdCl_4^{2-} or PdCl_3^- when 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.

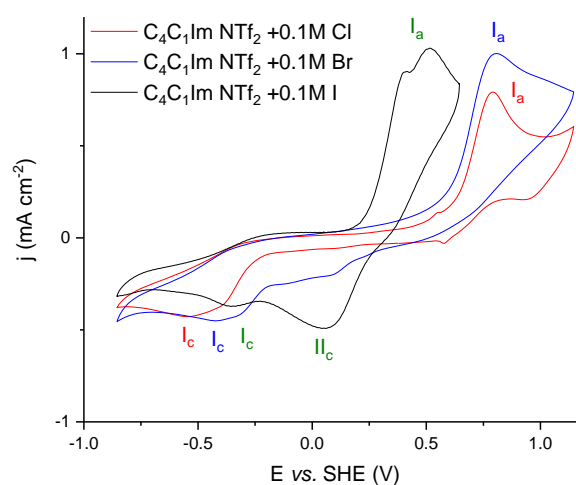


Figure 6. Cyclic voltammograms on palladium electrode in complexing electrolytes at 50 mV s^{-1} and 40°C . $\text{C}_4\text{C}_1\text{Im NTf}_2 + 0.1 \text{ M C}_4\text{C}_1\text{Im Cl}$ (red curve), $\text{C}_4\text{C}_1\text{Im NTf}_2 + 0.1 \text{ M C}_4\text{C}_1\text{Im Br}$ (blue curve), and $\text{C}_4\text{C}_1\text{Im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

3.5. Direct electroleaching-electrochemical deposition process

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

Table 1

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

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

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, ΔE_{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

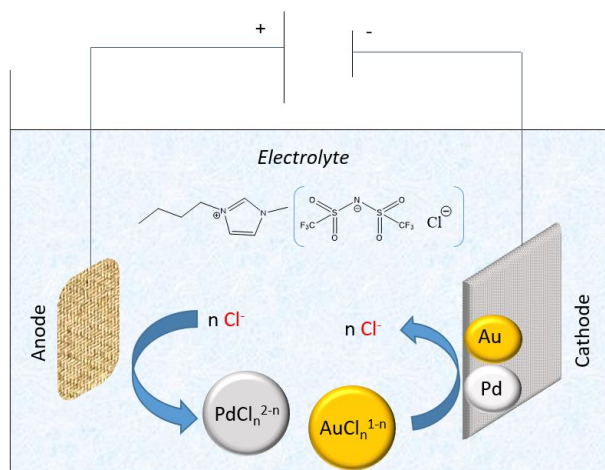


Figure 8. Schematic representation of an EL/ECD process

and palladium in ionic liquid (Figure 8), we chose C_4C_1Im NTf₂ + 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	Δm - 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	Δm - 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.

Funding sources :

This research was supported by the CEA DRT-LITEN-DTNM.

Notes and references

- [1] M. Kaya, *Electronic Waste and Printed Circuit Board Recycling Technologies*, Springer International Publishing, Cham, 2019. <https://doi.org/10.1007/978-3-030-26593-9>.
- [2] A. Marra, A. Cesaro, V. Belgiorno, The recovery of metals from WEEE: State of the art and future perspectives, *Global Nest Journal*. 20 (2018) 679–694. <https://doi.org/10.30955/GNJ.002626>.
- [3] F.O. Ongondo, I.D. Williams, T.J. Cherrett, How are WEEE doing? A global review of the management of electrical and electronic wastes, *Waste Management*. 31 (2011) 714–730. <https://doi.org/10.1016/j.wasman.2010.10.023>.
- [4] J. Cui, L. Zhang, Metallurgical recovery of metals from electronic waste: A review, *Journal of Hazardous Materials*. 158 (2008) 228–256. <https://doi.org/10.1016/j.jhazmat.2008.02.001>.
- [5] H. Li, J. Eksteen, E. Oraby, Hydrometallurgical recovery of metals from waste printed circuit boards (WPCBs): Current status and perspectives – A review, *Resources, Conservation and Recycling*. 139 (2018) 122–139. <https://doi.org/10.1016/j.resconrec.2018.08.007>.

- [6] P. Chancerel, C.E.M. Meskers, C. Hagelüken, V.S. Rotter, Assessment of Precious Metal Flows During Preprocessing of Waste Electrical and Electronic Equipment, *Journal of Industrial Ecology*. 13 (2009) 791–810. <https://doi.org/10.1111/j.1530-9290.2009.00171.x>.
- [7] C. Hagelüken, C.W. Corti, Recycling of gold from electronics: Cost-effective use through 'Design for Recycling,' *Gold Bull.* 43 (2010) 209–220. <https://doi.org/10.1007/BF03214988>.
- [8] I. D'Adamo, F. Ferella, M. Gastaldi, F. Maggiore, P. Rosa, S. Terzi, Towards sustainable recycling processes: Wasted printed circuit boards as a source of economic opportunities, *Resources, Conservation and Recycling*. 149 (2019) 455–467. <https://doi.org/10.1016/j.resconrec.2019.06.012>.
- [9] F. Cucchiella, I. D'Adamo, S.C. Lenny Koh, P. Rosa, Recycling of WEEEs: An economic assessment of present and future e-waste streams, *Renewable and Sustainable Energy Reviews*. 51 (2015) 263–272. <https://doi.org/10.1016/j.rser.2015.06.010>.
- [10] R.H. Arduin, F. Mathieux, J. Huisman, G.A. Blengini, C. Charbuillet, M. Wagner, C.P. Balde, N. Perry, Novel indicators to better monitor the collection and recovery of (critical) raw materials in WEEE: Focus on screens, *Resour. Conserv. Recycl.* 157 (2020) 104772. <https://doi.org/10.1016/j.resconrec.2020.104772>.
- [11] A. Marra, A. Cesaro, V. Belgiorno, Recovery opportunities of valuable and critical elements from WEEE treatment residues by hydrometallurgical processes, *Environmental Science and Pollution Research*. (2019). <https://doi.org/10.1007/s11356-019-05406-5>.
- [12] M. Gislev, M. Grohol, Report on critical raw material and the circular economy, Commission européenne, 2018.
- [13] S.A. Shuey, P. Taylor, Review of Pyrometallurgical Treatment of Electronic Scrap, *Mining Engineering*. 57 (2005) 67–70.
- [14] C. Hagelüken, Recycling of Electronic Scrap at Umicore's Integrated Metals Smelter and Refinery, *World of Metallurgy - ERZMETALL*. 59 (2006) 152–161.
- [15] J.C. Yannopoulos, Cyanidation of Gold Ores, in: J.C. Yannopoulos (Ed.), *The Extractive Metallurgy of Gold*, Springer US, Boston, MA, 1991: pp. 141–170. https://doi.org/10.1007/978-1-4684-8425-0_8.
- [16] A. Akcil, C. Erust, C.S. Gahan, M. Ozgun, M. Sahin, A. Tuncuk, Precious metal recovery from waste printed circuit boards using cyanide and non-cyanide lixivants – A review, *Waste Management*. 45 (2015) 258–271. <https://doi.org/10.1016/j.wasman.2015.01.017>.
- [17] C. Hagelüken, Recycling of Electronic Scrap at Umicore. *Precious Metals Refining*, 12 (2006) 111–120.
- [18] Y. Zhang, S. Liu, H. Xie, X. Zeng, J. Li, Current Status on Leaching Precious Metals from Waste Printed Circuit Boards, *Procedia Environmental Sciences*. 16 (2012) 560–568. <https://doi.org/10.1016/j.proenv.2012.10.077>.
- [19] H.A. White, The solubility of gold in thiosulphates and thiocyanates, *South African Journal of Science*. 1 (1905) 211–215.
- [20] J. Li, J.D. Miller, A Review of Gold Leaching in Acid Thiourea Solutions, *Mineral Processing and Extractive Metallurgy Review*. 27 (2006) 177–214. <https://doi.org/10.1080/08827500500339315>.
- [21] J.A. Whitehead, G.A. Lawrance, A. McCluskey, 'Green' leaching: recyclable and selective leaching of gold-bearing ore in an ionic liquid, *Green Chem.* 6 (2004) 313–315. <https://doi.org/10.1039/B406148A>.
- [22] J. Park, Y. Jung, P. Kusumah, J. Lee, K. Kwon, C.K. Lee, Application of ionic liquids in hydrometallurgy, *International Journal of Molecular Sciences*. 15 (2014) 15320–15343. <https://doi.org/10.3390/ijms150915320>.
- [23] A.P. Abbott, G. Frisch, S.J. Gurman, A.R. Hillman, J. Hartley, F. Holyoak, K.S. Ryder, Ionometallurgy: Designer redox properties for metal processing, *Chemical Communications*. 47 (2011) 10031–10033. <https://doi.org/10.1039/c1cc13616j>.
- [24] N. Leclerc, S. Legeai, M. Balva, C. Hazotte, J. Comel, F. Lapique, E. Billy, E. Meux, Recovery of Metals from Secondary Raw Materials by Coupled Electroleaching and Electrodeposition in Aqueous or Ionic Liquid Media, *Metals*. 8 (2018) 556. <https://doi.org/10.3390/met8070556>.
- [25] A.P. Abbott, G. Frisch, K.S. Ryder, Metal complexation in ionic liquids, *Annu. Rep. Prog. Chem., Sect. A: Inorg. Chem.* 104 (2008) 21–45. <https://doi.org/10.1039/B716593P>.
- [26] E.L. Smith, A.P. Abbott, K.S. Ryder, Deep Eutectic Solvents (DESs) and Their Applications, *Chemical*

- Reviews. 114 (2014) 11060–11082.
<https://doi.org/10.1021/cr300162p>.
- [27] A.P. Abbott, K.S. Ryder, U. König, Electrofinishing of metals using eutectic based ionic liquids, *Transactions of the IMF*. 86 (2008) 196–204.
<https://doi.org/10.1179/174591908X327590>.
- [28] Z. Xue, L. Qin, J. Jiang, T. Mu, G. Gao, Thermal, electrochemical and radiolytic stabilities of ionic liquids, *Physical Chemistry Chemical Physics*. 20 (2018) 8382–8402.
<https://doi.org/10.1039/C7CP07483B>.
- [29] M. Balva, S. Legeai, N. Leclerc, E. Billy, E. Meux, Environmentally Friendly Recycling of Fuel-Cell Membrane Electrode Assemblies by Using Ionic Liquids, *ChemSusChem*. 10 (2017) 2922–2935.
<https://doi.org/10.1002/cssc.201700456>.
- [30] N. DeVos, C. Maton, C.V. Stevens, Electrochemical Stability of Ionic Liquids: General Influences and Degradation Mechanisms, *ChemElectroChem*. 1 (2014) 1258–1270.
<https://doi.org/10.1002/celec.201402086>.
- [31] F. D’Anna, S. Marullo, P. Vitale, R. Noto, Binary Mixtures of Ionic Liquids: A Joint Approach to Investigate their Properties and Catalytic Ability, *ChemPhysChem*. 13 (2012) 1877–1884.
<https://doi.org/10.1002/cphc.201100878>.
- [32] H. Niedermeyer, J.P. Hallett, I.J. Villar-Garcia, P.A. Hunt, T. Welton, Mixtures of ionic liquids, *Chem. Soc. Rev.* 41 (2012) 7780–7802.
<https://doi.org/10.1039/C2CS35177C>.
- [33] E. Billy, Application des liquides ioniques à la valorisation des métaux précieux par une voie de chimie verte, PhD Thesis, Grenoble, 2012.
- [34] N.V. Plechkova, K.R. Seddon, Applications of ionic liquids in the chemical industry, *Chem. Soc. Rev.* 37 (2008) 123–150.
<https://doi.org/10.1039/B006677J>.
- [35] Q. Zhang, Q. Wang, S. Zhang, X. Lu, X. Zhang, Electrodeposition in Ionic Liquids, *ChemPhysChem*. 17 (2016) 335–351.
<https://doi.org/10.1002/cphc.201500713>.
- [36] X.-H. Xu, C.L. Hussey, Electrodeposition of Metals from Room-Temperature Chloroaluminate Molten Salts, *Proc. Vol.* 1992–16 (1992) 445.
<https://doi.org/10.1149/199216.0445PV>.
- [37] A.P. Abbott, G. Frisch, J. Hartley, W.O. Karim, K.S. Ryder, Anodic dissolution of metals in ionic liquids, *Progress in Natural Science: Materials International*. 25 (2015) 595–602.
<https://doi.org/10.1016/j.pnsc.2015.11.005>.
- [38] A.P. Abbott, R.C. Harris, F. Holyoak, G. Frisch, J. Hartley, G.R.T. Jenkin, Electrochemical recovery of elements from complex mixtures using deep eutectic solvents, *Green Chemistry*. 17 (2015) 2172–2179. <https://doi.org/10.1039/c4gc02246g>.
- [39] T. Oyama, T. Okajima, T. Ohsaka, Electrodeposition of Gold at Glassy Carbon Electrodes in Room-Temperature Ionic Liquids, *Journal of The Electrochemical Society*. 154 (2007) D322. <https://doi.org/10.1149/1.2724706>.
- [40] E. Billy, E. Chainet, F. Tedjar, Anodic behavior of gold in 1-butyl-3-methylimidazolium methanesulfonate ionic liquid with chloride anion, *Electrochimica Acta*. 56 (2011) 10340–10346.
<https://doi.org/10.1016/j.electacta.2011.04.055>.
- [41] L. Aldous, D.S. Silvester, C. Villagrán, W.R. Pitner, R.G. Compton, M. Cristina Lagunas, C. Hardacre, Electrochemical studies of gold and chloride in ionic liquids, *New J. Chem.* 30 (2006) 1576–1583.
<https://doi.org/10.1039/B609261F>.
- [42] A.M. Popescu, V. Soare, O. Demidenko, J.M. Calderon Moreno, E.I. Neacșu, C. Donath, M. Burada, I. Constantin, V. Constantin, Recovery of silver and gold from electronic waste by electrodeposition in ethaline ionic liquid, *Revista de Chimie*. 71 (2020) 122–132.
<https://doi.org/10.37358/RC.20.1.7822>.
- [43] Y. Bando, Y. Katayama, T. Miura, Electrodeposition of palladium in a hydrophobic 1-n-butyl-1-methylpyrrolidinium bis(trifluoromethylsulfonyl)imide room-temperature ionic liquid, *Electrochimica Acta*. 53 (2007) 87–91.
<https://doi.org/10.1016/j.electacta.2007.02.074>.
- [44] P. Giridhar, K.A. Venkatesan, B.P. Reddy, T.G. Srinivasan, P.R. Vasudeva Rao, Recovery of fission palladium by electrodeposition using room temperature ionic liquids, *Radiochimica Acta*. 94 (2006) 131–136.
<https://doi.org/10.1524/ract.2006.94.3.131>.
- [45] X. Xi, S. Song, Z. Nie, L. Ma, Electrodeposition and behavior of palladium in a room-temperature ionic liquid, *International Journal of Electrochemical Science*. 12 (2017) 1130–1145.
<https://doi.org/10.20964/2017.02.16>.
- [46] S. Jiang, Y. Hu, Y. Wang, X. Wang, Viscosity of Typical Room-Temperature Ionic Liquids: A Critical Review, *Journal of Physical and Chemical*

- Reference Data. 48 (2019).
<https://doi.org/10.1063/1.5090486>.
- [47] P. Bonhote, A.-P. Dias, N. Papageorgiou, K. Kalyanasundaram, M. Grätzel, Hydrophobic, highly conductive ambient-temperature molten salts, *Inorganic Chemistry*. 35 (1996) 1168–1178.
- [48] M.A. Ab Rani, A. Brant, L. Crowhurst, A. Dolan, M. Lui, N.H. Hassan, J.P. Hallett, P.A. Hunt, H. Niedermeyer, J.M. Perez-Arlandis, M. Schrems, T. Welton, R. Wilding, Understanding the polarity of ionic liquids, *Physical Chemistry Chemical Physics*. 13 (2011) 16831.
<https://doi.org/10.1039/c1cp21262a>.
- [49] P.G. Jessop, D.A. Jessop, D. Fu, L. Phan, Solvatochromic parameters for solvents of interest in green chemistry, *Green Chemistry*. 14 (2012) 1245.
<https://doi.org/10.1039/c2gc16670d>.
- [50] J.M. Padró, M. Reta, Solvatochromic parameters of imidazolium-, hydroxyammonium-, pyridinium- and phosphonium-based room temperature ionic liquids, *Journal of Molecular Liquids*. 213 (2016) 107–114.
<https://doi.org/10.1016/j.molliq.2015.10.055>.
- [51] V.V. Pavlishchuk, A.W. Addison, Conversion constants for redox potentials measured versus different reference electrodes in acetonitrile solutions at 25°C, *Inorganica Chimica Acta*. (2000). [https://doi.org/10.1016/S0020-1693\(99\)00407-7](https://doi.org/10.1016/S0020-1693(99)00407-7).
- [52] D.R. MacFarlane, S.A. Forsyth, J. Golding, G.B. Deacon, Ionic liquids based on imidazolium, ammonium and pyrrolidinium salts of the dicyanamide anion, *Green Chem*. 4 (2002) 444–448. <https://doi.org/10.1039/B205641K>.
- [53] S. Boudesocque, A. Mohamadou, L. Dupont, Efficient extraction of gold from water by liquid-liquid extraction or precipitation using hydrophobic ionic liquids, *New Journal of Chemistry*. 38 (2014) 5573–5581.
<https://doi.org/10.1039/c4nj01115e>.
- [54] P. Diabate, L. Dupont, S. Boudesocque, A. Mohamadou, Novel Task Specific Ionic Liquids to Remove Heavy Metals from Aqueous Effluents, *Metals*. 8 (2018) 412.
<https://doi.org/10.3390/met8060412>.
- [55] V. Kudryk, H.H. Kellogg, Mechanism and rate-controlling factors in the dissolution of gold in cyanide solution, *JOM*. 6 (1954) 541–548.
<https://doi.org/10.1007/BF03398872>.
- [56] A.M. O’Mahony, D.S. Silvester, L. Aldous, C. Hardacre, R.G. Compton, Effect of Water on the Electrochemical Window and Potential Limits of Room-Temperature Ionic Liquids, *Journal of Chemical & Engineering Data*. 53 (2008) 2884–2891. <https://doi.org/10.1021/je800678e>.
- [57] L. Aldous, D.S. Silvester, W.R. Pitner, R.G. Compton, M.C. Lagunas, C. Hardacre, Voltammetric Studies of Gold, Protons, and [HCl₂]⁻ in Ionic Liquids, *Journal of Physical Chemistry C*. 111 (2007) 8496–8503.
- [58] M.C. Kroon, W. Buijs, C.J. Peters, G.-J. Witkamp, Decomposition of ionic liquids in electrochemical processing, *Green Chem*. 8 (2006) 241–245.
<https://doi.org/10.1039/B512724F>.
- [59] C. Zhao, A.M. Bond, X. Lu, Determination of Water in Room Temperature Ionic Liquids by Cathodic Stripping Voltammetry at a Gold Electrode, *Anal. Chem*. 84 (2012) 2784–2791.
<https://doi.org/10.1021/ac2031173>.
- [60] A. Garcia-Mendoza, J.C. Aguilar, Analysis of water in room temperature ionic liquids by linear sweep, differential pulse and square wave cathodic stripping voltammetries, *Electrochim. Acta*. 182 (2015) 238–246.
<https://doi.org/10.1016/j.electacta.2015.09.045>.
- [61] L.H. Dall’Antonia, G. Tremiliosi-Filho, G. Jerkiewicz, Influence of temperature on the growth of surface oxides on palladium electrodes, *Journal of Electroanalytical Chemistry*. 502 (2001) 72–81. [https://doi.org/10.1016/S0022-0728\(00\)00505-2](https://doi.org/10.1016/S0022-0728(00)00505-2).
- [62] M. Grdeń, M. Łukaszewski, G. Jerkiewicz, A. Czerwiński, Electrochemical behaviour of palladium electrode: Oxidation, electrodisolution and ionic adsorption, *Electrochimica Acta*. 53 (2008) 7583–7598.
<https://doi.org/10.1016/j.electacta.2008.05.046>.
- [63] T. Oyama, T. Okajima, T. Ohsaka, S. Yamaguchi, N. Oyama, In Situ Electrochemical Quartz Crystal Microbalance Measurement of Au Deposition and Dissolution in Room-Temperature Ionic Liquid Containing Chloride Ion, *BCSJ*. 81 (2008) 726–732.
<https://doi.org/10.1246/bcsj.81.726>.
- [64] Y. Katayama, T. Endo, T. Miura, K. Toshima, Electrodeposition of gold in an amide-type ionic liquid, *Journal of The Electrochemical Society*. 161 (2014) D87–D91.
- [65] C.L. Bentley, A.M. Bond, A.F. Hollenkamp, P.J. Mahon, J. Zhang, Unexpected Complexity in the

- Electro-Oxidation of Iodide on Gold in the Ionic Liquid 1-Ethyl-3-methylimidazolium bis(trifluoromethanesulfonyl)imide, *Anal. Chem.* 85 (2013) 11319–11325.
<https://doi.org/10.1021/ac402150y>.
- [66] A.D. Goolsby, D.T. Sawyer, Electrochemistry of gold(I) and its complexes in acetonitrile, *Anal. Chem.* 40 (1968) 1978–1983.
<https://doi.org/10.1021/ac60269a020>.
- [67] X.-H. Xu, C.L. Hussey, The Electrochemistry of Gold at Glassy Carbon in the Basic Aluminum Chloride-1-Methyl-3-ethylimidazolium Chloride Molten Salt, *J. Electrochem. Soc.* 139 (1992) 3103–3108. <https://doi.org/10.1149/1.2069039>.
- [68] M. Jayakumar, K.A. Venkatesan, T.G. Srinivasan, Electrochemical behavior of fission palladium in 1-butyl-3-methylimidazolium chloride, *Electrochimica Acta.* 52 (2007) 7121–7127.
<https://doi.org/10.1016/j.electacta.2007.05.049>.
- [69] Y. Katayama, Y. Oshino, N. Ichihashi, N. Tachikawa, K. Yoshii, K. Toshima, Electrochemical preparation of palladium nanoparticles in bis(trifluoromethylsulfonyl)amide ionic liquids consisting of pyrrolidinium cations with different alkyl chain lengths, *Electrochimica Acta.* 183 (2015) 37–41.
<https://doi.org/10.1016/j.electacta.2015.02.211>.
- [70] Y. Katayama, Y. Bando, T. Miura, Electrodeposition of nanoscaled palladium from hydrophobic ionic liquid, *Transactions of The Institute of Metal Finishing - TRANS INST MET FINISH.* 86 (2008) 205–210.
<https://doi.org/10.1179/174591908X327563>.