



HAL
open science

ElectroLeaching-ElectroChemical Deposition (EL-ECD) of gold and palladium in a deep eutectic solvent (DES)

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.. ElectroLeaching-ElectroChemical Deposition (EL-ECD) of gold and palladium in a deep eutectic solvent (DES). Journal of Environmental Chemical Engineering, 2022, 10 (3), pp.108004. 10.1016/j.jece.2022.108004 . hal-03720676

HAL Id: hal-03720676

<https://hal.univ-lorraine.fr/hal-03720676v1>

Submitted on 29 Sep 2022

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.

ElectroLeaching-ElectroChemical Deposition (EL-ECD) of gold and palladium in a Deep Eutectic Solvent (DES)

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

ABSTRACT:

Keywords: Electrochemistry, Deep eutectic solvents, Precious metals recovery

Precious metals (PM) refining from E-waste recycling are based on hazardous hydrometallurgical processes, including cyanide leaching for gold or aqua regia leaching for palladium, which generates an important wastewater production. In this paper, we present an electrochemical process, based on low viscous deep eutectic solvents ChCl:EG 1:2 and ChCl:EG 1:3. Au and Pd electrochemical leaching and deposition parameters, but also gold and palladium speciation were studied. A one-step electroleaching-electrochemical deposition process (EL-ECD) in a single cell is proposed with high faradic yield of metal recovery. This process avoids electrolyte degradation and is advantageous to limit solvent losses and workers exposition.

1. Introduction

Metals recovery from end-of-life products is one of the most important challenges regarding raw materials depletion and supply but also waste generation. Especially, Waste Electrical and Electronic Equipment (WEEE) are of major concern, as they often contain significant amounts of critical, rare, or precious metals like gold and palladium [1].

Currently, gold and palladium extraction from e-wastes are performed by a multistep process including pyrometallurgical and hydrometallurgical treatments [2,3]. Hydrometallurgical steps have been used for decades but they involve reactants that can be harmful for environment and human health, e.g. cyanide leaching of gold, *aqua regia* or chlorine leaching of palladium [2,4].

Ionometallurgy, namely the use of ionic solvents, is nowadays considered as an alternative to conventional hydrometallurgy, as the low vapor pressure and low flammability of these solvents reduce process hazards [5]. Ionic solvents also have a great electrochemical stability [6,7] and can be considered as complexing agents. These two properties are essential to develop an electrochemical process for precious metals recovery without any solvent degradation and with low effluent generation. Recently, we studied a single step

ElectroLeaching-ElectroChemical Deposition (EL-ECD) process for Au and Pd recovery using ionic liquid (IL) mixtures containing 1-Butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide ($C_4C_1Im\ NTF_2$) as diluting IL and 1-Butyl-3-methylimidazolium chloride ($C_4C_1Im\ Cl$) as complexing IL [8]. This kind of melt was also used successfully for Pt recovery from fuel cell electrodes [9]. High faradic yields (99 %) were obtained for Au EL-ECD using $C_4C_1Im(NTf_2)_{0.78}Cl_{0.22}$ electrolyte. However, yield was limited to 25 % for Pd ECD, and these IL remain quite viscous (60 cP at 40 °C), expensive and not green if their whole life cycle is considered.

In this context, deep eutectic solvents (DES) may be more promising candidates than IL. Described for the first time by Abbott *et al.* in 2003 [10], they have same advantageous properties for EL-ECD (low vapor pressure, good electrochemical stability, complexing properties), while being less expensive and viscous [11,12]. They are moreover considered as greener solvents, as they are often partially bio-sourced and of higher biodegradability (betaine, choline) [13]. DES have already been successfully used for gold electrochemical recovery from electronic waste [14,15]. Palladium electrochemical deposition (ECD) was also achieved in this new solvents family [16,17]. However, no author reported any DES application for direct anodic electroleaching of gold or palladium with their simultaneous recovery by

^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.

electrochemical deposition at the cathode (EL-ECD process). We present here a study of such a process in choline chloride:ethylene glycol (*ChCl:EG*) mixture. Electrochemical stability of *ChCl:EG 1:2* was first determined on different electrode materials, and electrochemical behavior of gold and palladium was studied. The speciation of leached metals was determined by Raman and UV-vis spectroscopies, allowing us to establish electroleaching and electrochemical deposition reactions. The influence of *ChCl:EG* molar composition on DES transport properties was then evaluated, leading to the selection of *ChCl:EG 1:3* as electrolyte for the EL-ECD process. A proof of concept is presented at the end of the paper, with corresponding cathodic/anodic faradic yields, recovery rates and deposit analysis.

2. Experimental

2.1. Chemical reagents

Choline chloride 98% (ChCl), silver chloride 99% (AgCl), ferrocene 98% (Fc), and ferrocenium tetrafluoroborate technical (FcBF₄) were purchased from Sigma-Aldrich. Ethylene Glycol technical (EG) was purchased from Technic.

2.2. Electrolytes

Electrolytes were synthesized by mixing ChCl and EG in different proportions. The solid-liquid mixture was heated around 50 °C overnight until the solution was homogeneous. Electrolytes were prepared without any atmosphere control and stored in airtight bottles. Water content of electrolytes are comprised between 0.2 and 0.8 % weight (Karl-Fischer coulometric titration).

2.3. Instrumentation

All experiments were performed at 40 °C without any atmosphere control. Cyclic voltammetry (CV) was used to study metals electrochemical behavior in *ChCl:EG* mixtures. A three-electrode cell (1 mL of electrolyte) connected to a Biologic VSP300 (EC-lab software) was used. The counter electrode (CE) was a platinum grid and reference electrode (RE) was a Ag⁺/Ag electrode (Ag in *ChCl:EG 1:2* containing 10 mM AgCl). This electrode was calibrated against Fc⁺/Fc half wave potential (equals to 0.63V vs. SHE [18]) and was stable for the duration of the experiments. All potential values measured were referred to standard hydrogen electrode (SHE). At 40°C, RE has a potential of 0.15V vs. SHE. RE and CE were separated from the bulk by a fritted glass. Working electrodes (WE) were 0.5 mm-diameter wires of gold (99.99%), platinum (99.95 %) or palladium (99.95%) supplied

by Metalor. A 1 mm-diameter disk of glassy carbon (GC) was also used.

EL-ECD experiments were performed in two three-electrode cells presented in SI-1 (5-10 mL) and SI-2 (100 mL) under potentiostatic control with a Biologic VSP300. WE was a rectangular GC electrode and CE was a Au or Pd foil. RE was the same electrode as described before. Electrolyte was *ChCl:EG 1:3* containing 25 mM of Au or Pd, dissolved by electroleaching of metals. Electrochemical reaction rate but also faradic yields were determined by gravimetric analysis using a Mettler Toledo XP6 (± 0.001 mg).

UV spectra were obtained on a Varian Cary 5000 spectrometer, using Suprasil® Quartz cells, with a 2 mm-optical length. Raman spectra were performed on a Horiba LabRAM S3000 with a Synapse detector. The laser wavelength was 632.81 nm.

Viscosity analysis were carried out with a rolling ball viscometer Anton Paar LOVIS-DMA. Electrolytes conductivity was evaluated by Potentiostatic Electrochemical Impedance Spectroscopy (PEIS) in the 1 MHz - 1 Hz range, using a calibrated two-platinum plates electrode cell. Scanning Electron Microscopy (SEM) was conducted on a TESCAN Vega 3 SBU and a ZEISS LEO 1530 microscopes.

3. Results and discussion

3.1. Electrochemical behavior of gold and palladium

Electrochemical behavior of Au, Pd, Pt and GC electrodes in *ChCl:EG 1:2* was studied by CV at 50 mV.s⁻¹ (Figure 1), scanning first towards anodic direction.

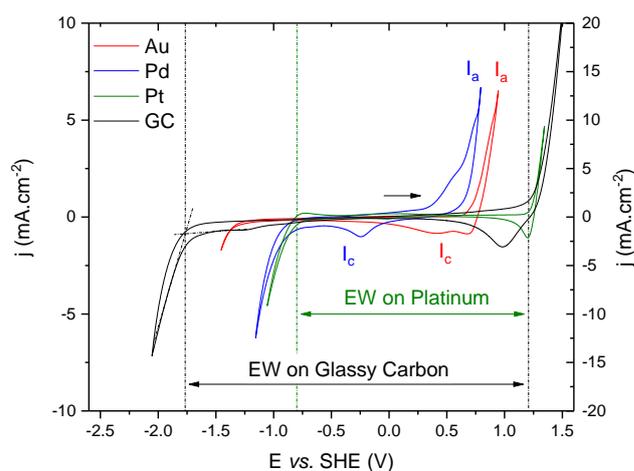


Figure 1 – Cyclic voltammograms obtained on Au (red), Pd (blue), Pt (green) and GC electrodes in *ChCl:EG 1:2*. 50 mV.s⁻¹. Au, Pd, Pt on left scale / GC on right scale

First, no Pt electroleaching was observed at 40 °C. The anodic current around 1.2 V vs. SHE observed on GC and Pt is associated to DES anodic degradation. This oxidation is attributed to EG or chloride oxidation [19].

Interestingly, DES cathodic stability depends on the electrode material, according to the following order:



This reaction is associated to cholinium cation reduction [19].

Au and Pd oxidation arise before DES anodic degradation (I_a) and is associated to cathodic peaks I_c on the reverse scan, corresponding to leached metals reduction. When the electrode potential is fixed at I_a , a quantitative electroleaching of metals occurs. The electrode mass loss Δ_m is linked to the number of electrons n exchanged (Eq. 1).

$$n = \frac{QM}{\Delta_m F} \quad \text{Eq. 1}$$

with M the molecular weight ($\text{g}\cdot\text{mol}^{-1}$), Q the electric charge (C), and F the Faraday's constant ($\text{C}\cdot\text{mol}^{-1}$).

Au and Pd leaching involves one and two electrons, respectively. In aqueous media (except in cyanide media), Au(I) is unstable and Au(III) is formed during Au leaching. The EL-ECD process using DES is then less energy consuming.

Leachates containing Au(I) or Pd(II) were analyzed by Raman spectroscopy (Figure 2). The observed signal at 301 cm^{-1} is associated to the square-planar complex PdCl_4^{2-} [20,21]. This result was confirmed by UV-visible spectroscopy (Fig. 3-SI, absorbance peak at 479 nm) [21]. This complex was already identified in *ChCl:EG* 1:2 by EXAFS [22]. The presence of AuCl_2^-

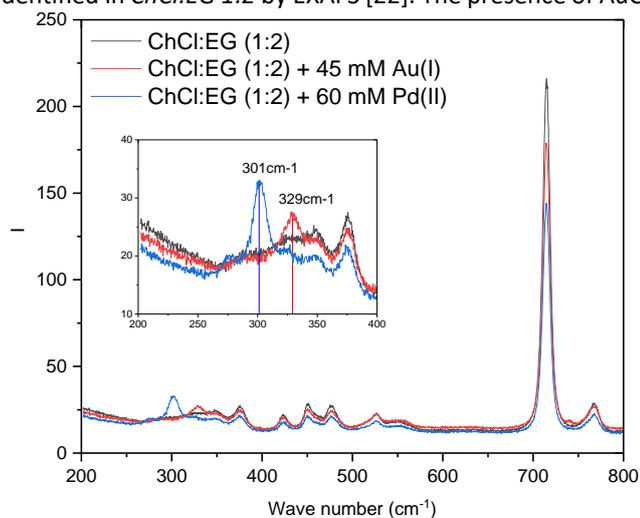
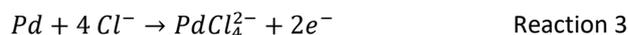
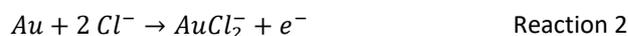
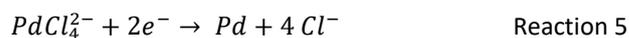
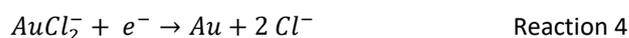


Figure 3 – Raman spectra of *ChCl:EG* 1:2 (black), *ChCl:EG* 1:2 + Au(I) (red) and *ChCl:EG* 1:2 + Pd(II) (blue)

is evidenced by the signal at 329 cm^{-1} on the Raman spectrum [23]. No signal corresponding to Au(I) was clearly identified by UV-visible spectroscopy. In leachates, no Au (III) signal (322 nm [24]) was observed either (Figure SI-3). To the best of our knowledge AuCl_2^- was not clearly identify in DES yet. Hence, we could attribute I_a to Reactions 2 and 3:



CV of 25 mM Au(I) and Pd(II) leachates were recorded on GC electrode (Figure 3). Cathodic peak I_c is observed in both solutions. When working potential is fixed to I_c peak, a yellow deposit is observable on GC in the case of Au. For Pd, a grey deposit appears. Hence, I_c peak could be attributed to Reactions 4 and 5.



In the case of Pd(II), I_c peak potential remains unchanged between the first and the second cycle. For Au(I), I_c peak is shifted towards more positive potential on the second cycle, compared to the first one. This is attributed to an incomplete dissolution of gold during the anodic scan (cycle 1). The second cathodic scan corresponds then to the reduction of Au(I) on Au substrate, which charge transfer kinetics appears to be faster than on GC.

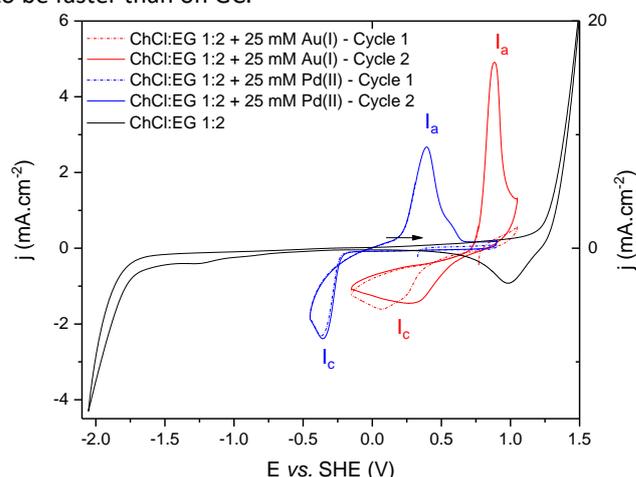


Figure 2 – Cyclic voltammograms obtained on GC electrode in *ChCl:EG* 1:2 (black – right scale), *ChCl:EG* 1:2 + 25 mM Au(I) (red-left scale) and *ChCl:EG* 1:2 + 25 mM Pd(II) (blue-left scale). Dotted lines correspond to cycle 1. Straight lines

These results indicate that Au and Pd electroleaching and electrochemical deposition are possible within the electrochemical stability window of *ChCl:EG* mixtures. Cell voltage ($|E_{WE} - E_{CE}|$ or $|E(I_a) - E(I_c)|$) is around 0.2 V for Au and 1 V for Pd.

3.2. Optimal composition of electrolyte: transport properties

The shape of cathodic peaks I_c on Figure 3 is characteristic of a mass-transport controlled reaction, implying that transport properties of the electrolyte are a major concern.

If mass-transport is ensured by diffusion, the current density j is described as a function of diffusion coefficient D (described by the Stokes-Einstein law in Eq. 3) and bulk concentration C^0 of the diffusing species (Eq. 2). Hence j increases when viscosity η decreases.

$$j = nF \frac{C^0 D}{\delta} \propto \frac{C^0}{\eta} \quad \text{Eq. 2}$$

$$D = \frac{kT}{6\pi r_H \eta} \quad \text{Eq. 3}$$

r_H is the hydrodynamic radius (m) of the diffusing species, k is the Boltzmann's constant ($J.K^{-1}$) and δ is the diffusion layer thickness (m).

These equations show that current density increases as η decreases and C^0 increases. As electrochemical reaction rate generally increases with current density (if the considered reaction is unique), a low electrolyte viscosity is preferable.

Furthermore, a high ionic conductivity σ ($S.m^{-1}$) is desirable for this kind of process, mainly for energetic considerations. Indeed, ohmic drop ΔU within electrolyte during the electrolysis decreases with ionic conductivity (Eq. 4).

$$\Delta U = R_e I = \frac{jL}{\sigma} \quad \text{Eq. 4}$$

with R_e the electrolyte resistance between electrodes (Ω), I the current intensity (A) and L the distance between electrodes (m).

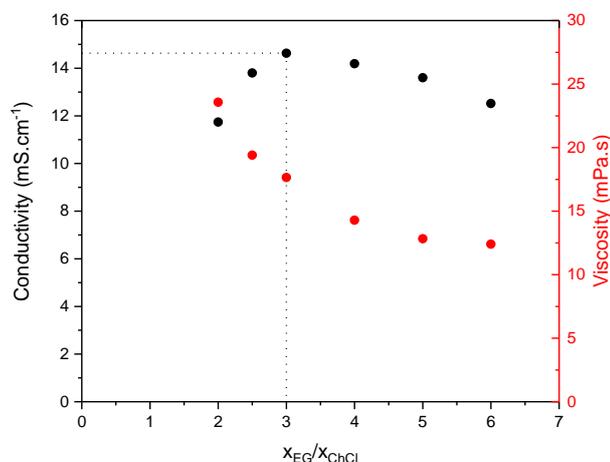


Figure 4 – Ionic conductivity (black) and viscosity (red) of *ChCl:EG (1:x)* electrolytes

Generally, in IL and DES, viscosity and conductivity are strongly linked. It is possible to enhance conductivity or decrease viscosity by electrolyte heating. Another way to decrease viscosity is to increase *EG:ChCl* molar ratio (Figure 4), EG acting like a fluidizing additive. However, as the ionic concentration decreases when EG content increases, ionic conductivity reaches a maximum for a molar ratio equals to 3. This value appears to be the best compromise to get optimal transport properties. *ChCl:EG 1:3* electrolyte was then chosen to implement the EL-ECD process in a single cell.

3.3. EL-ECD of gold and palladium

As the metallic species concentration (0.025 M) is low compared to chloride content (4.2 M), the overall process will be controlled by the diffusion of metallic species. The cathodic current density will then drive the kinetics of the metal recovery (*cf.* Eq. 3 and Figure 1). To avoid solvent degradation and maximize faradic yield, the EL-ECD process must then be conducted under cathodic potential control. In the following study, E_{WE} was fixed at I_c peak potential.

First experiments were carried out using the set-up presented in Fig. SI-2. The anode is a metallic plate (Au/Pd) and the cathode is a GC plate. Immersed surfaces were equal to 1 cm^2 . The solution was unstirred to avoid deposit drop from the cathode. Table 1 summarizes the obtained experimental results. An anodic faradic yield of 100 % is reached for both Au and Pd leaching. In the case of Au, the cathodic faradic yield is also of 100 %, meaning that EL-ECD could be performed without any solvent degradation and with balanced faradic efficiencies. In contrast, the cathodic faradic yield for Pd is only 85 %, meaning that a side reduction reaction occurs simultaneously. As the working potential is fixed below 0 V vs. SHE, this reaction is assumed to be water reduction to H_2 .

Figure 5 presents images of the two deposits. Au deposit (A) appears more homogeneous at macroscopic scale than the Pd one (D) which is poorly adherent. However, SEM images reveal that the gold deposit is dendritic (B,C), with particles that are 1-5 μm large and 20-60 μm long. The Au deposit was easily removed from the GC plate to obtain an Au foil. Palladium nuclei are smaller than 1 μm but the deposit is heterogeneous. It presents nanometric cavities (E) and peels off the substrate (D, F), which agrees with hydrogen evolution side reaction. The thickness of the deposit could reach few hundred of μm . Large particles of Pd could further be recovered by electrode scratching. Only a thin layer of Pd remains attached to the substrate.

Table 1 – Results of EL-ECD experiment

	<i>Au(I)</i> (30 mM)	<i>Pd(II)</i> (25 mM)
Time (h)	18	6
Δm deposit (mg)	15.81	3.34
Applied E_{WE} (V vs. SHE)	0.55	- 0.35
j ($mA.cm^{-2}$)	0.1	0.35
Q_s ($C.cm^{-2}$)	6.4	6.5
v ($mg.h^{-1}.cm^{-2}$)	0.7	0.5
Cathodic yield (%)	100	85
Anodic yield (%)	100	100

In both cases, the electrolysis rate v , is low. Considering a small electrolysis pilot with one cathode ($S \sim 1 \text{ m}^2$), this process would produce 10-20 g of metal per day.

To enhance mass transport of metallic species, another experiment was conducted under stirring in the set-up presented in SI-3. The corresponding results presented in Table 2 show that process rate is increased by 2 to 3 times compared to previous experiments. Au deposit is homogeneous at macroscopic scale (**Erreur ! Source du renvoi introuvable.-B**).

introuvable.-A) and appears brighter than previously. The faradic yield of Pd recovery is improved (close to 100%), but the deposit is still poorly adherent and heterogeneous (**Erreur ! Source du renvoi introuvable.-B**).

Further investigations are in progress to understand parameters influence (applied potential, metal concentration, heating) on Pd deposit morphology. The influence of water content must be studied to confirm that hydrogen evolution is responsible for the poor adherence of the Pd deposit.

Table 2 - Results of EL-ECD experiment in half-circle cell

	<i>Au(I)</i> (40 mM)	<i>Pd(II)</i> (25 mM)
Time (h)	2	3
Δm deposit (mg)	43.0	26.1
Applied E_{WE} (V vs. SHE)	0.55	- 0.35
j ($mA.cm^{-2}$)	0.26	0.5
Q_s ($C.cm^{-2}$)	2.1	5.0
v ($mg.h^{-1}.cm^{-2}$)	2.1	0.9
Cathodic yield (%)	99	96
Anodic yield (%)	98	100

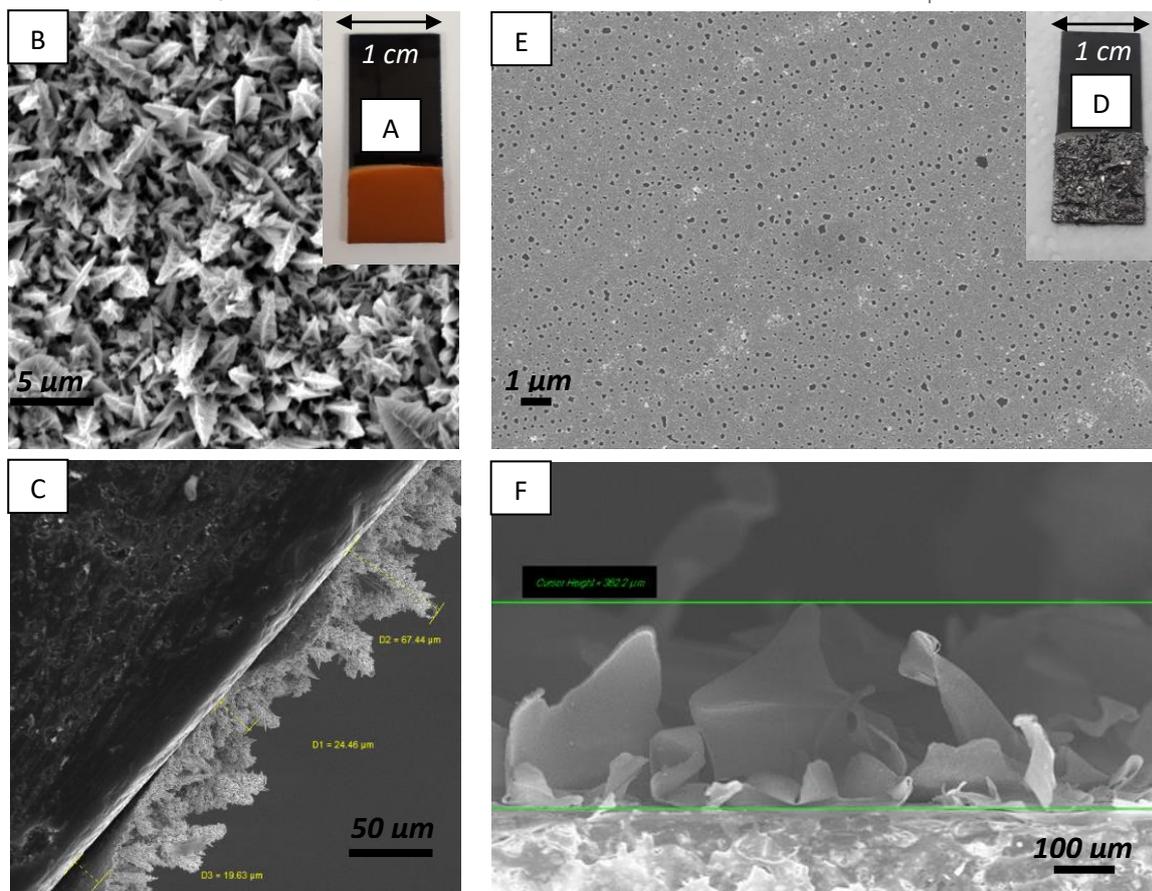


Figure 5 – (A) Au deposit and corresponding SEM images (B) of the surface ($\times 5\,000$) and (C) of the cross-section ($\times 500$) / (D) Pd deposit and corresponding SEM images (E) of the surface ($\times 5\,000$) and (F) of the cross-section ($\times 100$)

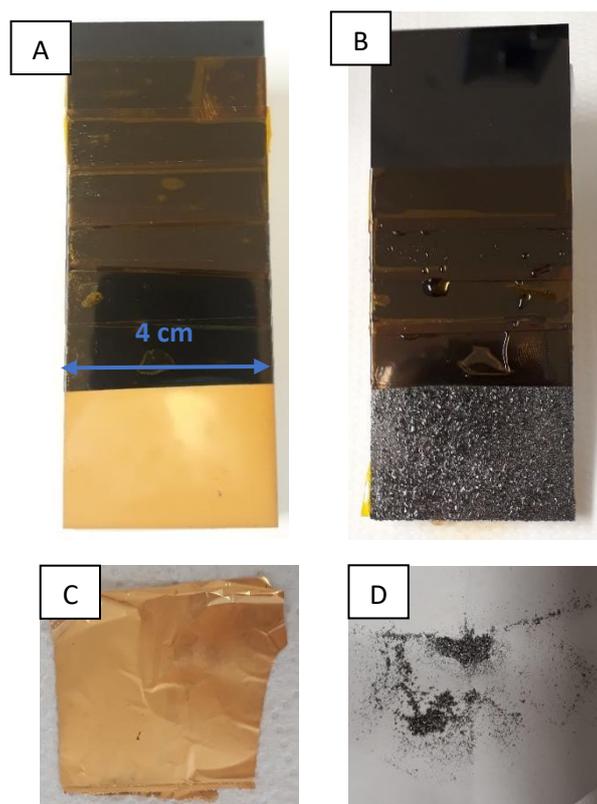


Figure 6 – Au (A-C) and Pd (B-D) deposits obtained after EL-ECD experiment in SI-3 cell

4. Conclusion

Gold and palladium ElectroLeaching-ElectroChemical Deposition (EL-ECD) in a single cell was successfully realized in *ChCl:EG 1:3*. Au and Pd electroleaching could be performed at low potential (< 1 V vs. SHE) with respectively 1 and 2 electrons exchanged. UV-visible and Raman spectroscopy confirmed the presence of chlorocomplexes AuCl_2^- and PdCl_4^{2-} after electroleaching. In metallic leachates and under cathodic control, EL-ECD experiments lead to quantitative anodic faradic yields. For Au, the cathodic faradic yield on glassy carbon is 100 %. For Pd, this yield is between 85 and 96 % meaning that a side reaction occurs during electrolysis, but metal deposition can be favored by stirring. The overall performance of the process using DES is much better than with ionic liquid mixtures in terms of faradic efficiency and recovery rate [8]. This EL-ECD process is therefore of high interest in the recycling field of precious metal rich resources such as waste electrical and electronic equipment (WEEE). It could for example be applied for the refining of anodic sludges issued from pyrometallurgic treatment of printed circuit boards. One can also think about applications in electroplating industry, especially gold electroplating, as alternative to

cyanide baths. The limited solvent degradation allows its recycling, which is primordial to develop a sustainable process from an economical or environmental point of view. Some parameters need however to be optimized: electrolysis rate could for instance be enhanced by decreasing viscosity or increasing metal concentration. Influence of current density and of applied potential on morphology would also need to be studied.

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, 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 LITEN and EE4Precious project, ANR-20-CE08-0035-01.

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] 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>.
- [3] 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>.
- [4] R. Dawson, G. Kelsall, Recovery of platinum group metals from secondary materials. I. Palladium dissolution in iodide solutions, *Journal of Applied Electrochemistry*. 37 (2007) 3–14. <https://doi.org/10.1007/s10800-006-9218-8>.
- [5] M. Galiński, A. Lewandowski, I. Stępnia, Ionic liquids as electrolytes, *Electrochimica Acta*. 51 (2006) 5567–5580. <https://doi.org/10.1016/j.electacta.2006.03.016>.

- [6] Q. Li, J. Jiang, G. Li, W. Zhao, X. Zhao, T. Mu, The electrochemical stability of ionic liquids and deep eutectic solvents, *Science China Chemistry*. 59 (2016) 571–577. <https://doi.org/10.1007/s11426-016-5566-3>.
- [7] P. Gancarz, E. Zorębski, M. Dzida, Influence of experimental conditions on the electrochemical window. Case study on bis(trifluoromethylsulfonyl)imide-based ionic liquids, *Electrochemistry Communications*. 130 (2021). <https://doi.org/10.1016/j.elecom.2021.107107>.
- [8] B. VILLEMEJEANNE, S. Legeai, E. Meux, S. Dourdain, H. Mendil-Jakani, E. Billy, Halide based ionic liquid mixture for a sustainable electrochemical recovery of precious metals, *Journal of Environmental Chemical Engineering*. 10 (2022) 107063. <https://doi.org/10.1016/j.jece.2021.107063>.
- [9] 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>.
- [10] A.P. Abbott, G. Capper, D.L. Davies, R.K. Rasheed, V. Tambyrajah, Novel solvent properties of choline chloride/urea mixtures, *Chem. Commun.* (2003) 70–71. <https://doi.org/10.1039/B210714G>.
- [11] A.P.R. Santana, J.A. Mora-Vargas, T.G.S. Guimarães, C.D.B. Amaral, A. Oliveira, M.H. Gonzalez, Sustainable synthesis of natural deep eutectic solvents (NADES) by different methods, *Journal of Molecular Liquids*. 293 (2019). <https://doi.org/10.1016/j.molliq.2019.111452>.
- [12] Q. Zhang, K. De Oliveira Vigier, S. Royer, F. Jérôme, Deep eutectic solvents: syntheses, properties and applications, *Chemical Society Reviews*. 41 (2012) 7108. <https://doi.org/10.1039/c2cs35178a>.
- [13] J. Płotka-Wasyłka, M. de la Guardia, V. Andrush, M. Vilková, Deep eutectic solvents vs ionic liquids: Similarities and differences, *Microchemical Journal*. 159 (2020). <https://doi.org/10.1016/j.microc.2020.105539>.
- [14] A.P. Abbott, R.C. Harris, F. Holyoak, G. Frisch, J. Hartley, G.R.T. Jenkin, Electrocatalytic recovery of elements from complex mixtures using deep eutectic solvents, *Green Chemistry*. 17 (2015) 2172–2179. <https://doi.org/10.1039/c4gc02246g>.
- [15] 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>.
- [16] F. Soma, Q. Rayée, M. Bougouma, C. Baustert, C. Buess-Herman, T. Doneux, Palladium electrochemistry in the choline chloride-urea deep eutectic solvent at gold and glassy carbon electrodes, *Electrochimica Acta*. 345 (2020) 136165. <https://doi.org/10.1016/j.electacta.2020.136165>.
- [17] M. Manolova, R. Böck, I. Scharf, T. Mehner, T. Lampke, Electrodeposition of Pd alloys from choline chloride/urea deep eutectic solvents, *Journal of Alloys and Compounds*. 855 (2021) 157462. <https://doi.org/10.1016/j.jallcom.2020.157462>.
- [18] 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).
- [19] K. Haerens, E. Matthijs, K. Binnemans, B. Van Der Bruggen, Electrochemical decomposition of choline chloride based ionic liquid analogues, *Green Chemistry*. 11 (2009) 1357–1365. <https://doi.org/10.1039/b906318h>.
- [20] A.N. Pandey, D.K. Sharma, U.P. Verma, V. Kumar, Force constants and bond polarizability derivatives of some XY₄ square-planar type ions, *Journal of Raman Spectroscopy*. 6 (1977) 163–164. <https://doi.org/10.1002/jrs.1250060402>.
- [21] William P. Griffith, Stephen D. Robinson, Kurt Swars, Palladium, 1989.
- [22] J.M. Hartley, C.-M. Ip, G.C.H. Forrest, K. Singh, S.J. Gurman, K.S. Ryder, A.P. Abbott, G. Frisch, EXAFS Study into the Speciation of Metal Salts Dissolved in Ionic Liquids and Deep Eutectic Solvents, *Inorg. Chem*. 53 (2014) 6280–6288. <https://doi.org/10.1021/ic500824r>.
- [23] P. Pan, S.A. Wood, Gold-chloride complexes in very acidic aqueous solutions and at temperatures 25–300 °C: A laser Raman spectroscopic study, *Geochimica et Cosmochimica Acta*. 55 (1991) 2365–2371. [https://doi.org/10.1016/0016-7037\(91\)90112-I](https://doi.org/10.1016/0016-7037(91)90112-I).
- [24] 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>.