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Research Article

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Platinum Recovery from Industrial Process Solutions by Electrodeposition-Redox Replacement

Petteri Halli,[†] Joonas J. Heikkinen,[‡] Heini Elomaa,[†] Benjamin P. Wilson,[†] Ville Jokinen,[‡] Kirsi Yliniemi,[§] Sami Franssila,[‡] and Mari Lundström*,[†]

[†]Hydrometallurgy and Corrosion, Department of Chemical and Metallurgical Engineering (CMET), School of Chemical Engineering, Aalto University, Otakaari 3 J, P.O. Box 12200, FI-00076 Aalto, Finland

^{*}Microfabrication, Department of Chemistry and Materials Science (CMAT), School of Chemical Engineering, Aalto University, Micronova, Tietotie 3, P.O. Box 13500, Fi-00076 Aalto, Finland

[§]Department of Chemistry and Materials Science (CMAT), Aalto University, School of Chemical Engineering, Kemistintie 1, P.O. Box 16100, FI-00076 Aalto, Finland

ABSTRACT: In the current study, platinum-present as a negligible component (below 1 ppb, the detection limit of the HR-ICP-MS at the dilutions used) in real industrial hydrometallurgical process solutions-was recovered by an electrodeposition-redox replacement (EDRR) method on pyrolyzed carbon (PyC) electrode, a method not earlier applied to metal recovery. The recovery parameters of the EDRR process were initially investigated using a synthetic nickel electrolyte solution ([Ni] = 60 g/L, [Ag] = 10 ppm, [Pt] = 20 ppm, $[H_2SO_4] = 10 \text{ g/L}$, and the results demonstrated an extraordinary increase of 3×10^5 in the [Pt]/[Ni] on the electrode surface cf. synthetic solution. EDRR recovery of platinum on PyC was also tested with two real industrial process solutions that contained a complex multimetal solution matrix: Ni as the major component (>140 g/L) and very low contents of Pt, Pd, and Ag (i.e., <1 ppb, 117 and 4 ppb,



respectively). The selectivity of Pt recovery by EDRR on the PyC electrode was found to be significant-nanoparticles deposited on the electrode surface comprised on average of 90 wt % platinum and a [Pt]/[Ni] enrichment ratio of 10¹¹ compared to the industrial hydrometallurgical solution. Furthermore, other precious metallic elements like Pd and Ag could also be enriched on the PyC electrode surface using the same methodology. This paper demonstrates a remarkable advancement in the recovery of trace amounts of platinum from real industrial solutions that are not currently considered as a source of Pt metal. KEYWORDS: Circular economy, Critical precious metals, Electrochemistry, Green chemistry, Electrochemically assisted cementation

INTRODUCTION

In hydrometallurgical industries, significant amounts of impurities¹⁻⁵ and some additives⁶⁻⁸ are present in the base metal (Cu, Ni, Zn)-rich process solutions. The presence of such contaminants can be either detrimental to the process/ base metal product or beneficial as they help improve process operation and feasibility. Typically, most impurities are other base metals,^{9,10} which subsequently end up in the process bleed solution or leach residue, and the recovery can be a challenge as processing consumes additional chemicals and energy.^{11,12} In addition, noble metals like Pt, Pd, and Ag¹¹ can also be present in these types of solutions, albeit at much lower concentrations. It is widely known¹³ that minor amounts of noble elements can be found in the final products of hydrometallurgical processing like copper, nickel, or zinc cathodes; i.e., the noble metals are "diluted" within the bulk metal. Nevertheless, according to circular economic principles, and more importantly due to the ever-increasing need for

critical precious metals, it is essential that the loss of even minor amounts of noble elements into bulk metals be avoided.

The basic idea of electrodeposition-redox replacement (EDRR)—and related methods like surface-limited redox replacement (SLRR)¹⁴—is to deposit a more noble metallic element via the spontaneous redox replacement reaction of a more reactive metal as a result of reduction potential difference between the metals.^{15–25} Although SLRR and related methods have been previously utilized on the laboratory scale for the formation of smooth monolayers, mostly relying on underpotential deposition, or nanoparticles, so far only very few studies have made use of the EDRR method specifically for metal recovery-all of them using synthetic solutions: Ag retrieval from synthetic Zn process solutions,^{26,27} Au recovery from simulated cyanide-free cupric chloride leaching sol-

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Solution #1								
	Al	As	Cu	Fe	Ni	Pb	Zn	
	ppm	ppm	ppm	ppm	ppm	ppm	ppm	
	24.8	767	5850	15,900	141,000	40	236	
Sn	Ga	Ge	In	Cd	Ag	Au	Pd	Pt
ppb	ppb	ppb	ppb	ppb	ppb	ppb	ppb	ppb
220	155.4	3339	919	280	4.1	<lod< td=""><td>117</td><td>$<$LOD (1.3^{b})</td></lod<>	117	$<$ LOD (1.3^{b})
Solution #2								
	Al	As	Cu	Fe	Ni	Pb	Zn	
	ppm	ppm	ppm	ppm	ppm	ppm	ppm	
	<lod< td=""><td><lod< td=""><td><lod< td=""><td>4.2</td><td>144,000</td><td>28.5</td><td>21.8</td><td></td></lod<></td></lod<></td></lod<>	<lod< td=""><td><lod< td=""><td>4.2</td><td>144,000</td><td>28.5</td><td>21.8</td><td></td></lod<></td></lod<>	<lod< td=""><td>4.2</td><td>144,000</td><td>28.5</td><td>21.8</td><td></td></lod<>	4.2	144,000	28.5	21.8	
Sn	Ga	Ge	In	Cd	Ag	Au	Pd	Pt
ppb	ppb	ppb	ppb	ppb	ppb	ppb	ppb	ppb
<lod< td=""><td>10.6</td><td>1344</td><td><lod< td=""><td>353</td><td><LOD $(1.3b)$</td><td><lod< td=""><td><LOD (2.17^b)</td><td><LOD (1.3^b)</td></lod<></td></lod<></td></lod<>	10.6	1344	<lod< td=""><td>353</td><td><LOD $(1.3b)$</td><td><lod< td=""><td><LOD (2.17^b)</td><td><LOD (1.3^b)</td></lod<></td></lod<>	353	<LOD $(1.3b)$	<lod< td=""><td><LOD (2.17^b)</td><td><LOD (1.3^b)</td></lod<>	<LOD (2.17 ^b)	<LOD (1.3 ^b)
"All results were analyzed by ICP-OES (ppm) or HR-ICP-MS (ppb). LOD = Limit of detection. ^b value below detection limit.								

Table 1. Compositions of	Two Investigated	Solutions from an	Industrial Hydrometa	llurgical Plant"
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utions,²⁸ and formation of Pt/Ni nanoparticles from hydrometallurgy-type solutions.²⁹ In contrast to the earlier studies, in this paper, EDRR is employed as part of a comprehensive investigation of the recovery of Pt from real industrial hydrometallurgical process solutions—including at least 16 elements—an undertaking that has not been previously reported. This is despite the fact that the global annual production of Ni (2.1 Mt), Cu (19.7 Mt), and Zn (13.2 Mt) is based primarily on hydrometallurgical refining operations, all of which have base metal- rich electrolytes with very low concentrations (<ppm or even <ppb) of critical metals such as Pt, Pd, and Ag.³⁰

Furthermore, the current study also makes use of a novel porous pyrolytic carbon electrode (PyC) for metal recovery, as the associated high surface area and larger potential window offers advantageous properties for the selective metal recovery by EDRR.³¹ As EDRR allows direct metal recovery from complex multimetal process solutions without additional chemicals, unlike, e.g., precipitation or solvent extraction methods, both chemical and energy consumption levels can be decreased while simultaneously enhancing the circular economy of metals.

During optimized EDRR operation, only a very thin (porous) layer of a sacrificial metal is deposited during an ED step, and this is then spontaneously replaced by a nobler metal during redox replacement step (and RR step is performed without the use of any externally applied potential or current). In hydrometallurgy, this process is known as cementation,³² and thus, the EDRR methodology can also be considered as an electrochemically assisted cementation. Repetition of this procedure multiple times results in a high quality noble metal deposit that enables the selective recovery of, e.g., platinum from complex industrial solutions where it is present at very low concentrations.

EXPERIMENTAL PROCEDURE

Materials. Chemicals used in this work included NiSO₄· $6H_2O$, Pt AAS standard, Ag AAS standard (Alfa Aesar, Germany), and H_2SO_4 (VWR Chemicals, Belgium). All chemicals were of high purity grade except for the technical grade NiSO₄· $6H_2O$, which contained the following impurities in the range of 0.001% to 0.01%: Na, Mg, Ca, K, Co, Cu, Mn, Zn, Pb, and Fe. All synthetic solutions were made using distilled water. The measurements were conducted in a three-electrode cell with a saturated calomel electrode (BS21, SI Analytics) as a reference electrode (RE), a 25 mm \times 25 mm \times 3 mm type 1

glassy carbon plate (Alfa Aesar) as counter electrode (CE), and PyC (pyrolyzed carbon) as a working electrode (WE). An IviumStat 24-bit CompactStat (Ivium, NL) was employed for the electrochemical measurements, and scanning electron microscope-energy dispersion spectroscopy, SEM-EDS (Leo 1450 VP, Zeiss, Germany, INCAsoftware, Oxford Instruments, UK) was used for the chemical analysis of the electrodes after each EDRR experiment, whereas a Mira³ Tescan GM (Czech Republic) was used for higher magnification imaging. In addition, the components within the two industrial solution samples investigated were determined using either inductively couple plasma-optical emission spectroscopy or high resolution mass spectroscopy, ICP-OES/HR-MS (OES: Iris intrepid, Thermo Fisher Scientific, USA, and HR-MS: Nu AttoM, Nu Instruments Ltd., UK, housed at GTK, Espoo). Prior to analysis, the two sulfate-based industrial process solutions were diluted with 2 vol % HNO3 in order to prevent any precipitation of the investigated elements during the analysis and to put them in the working range of the ICP-OES/HR-MS. The resulting clear solutions were run on the ICP (OES or MS) along with appropriate blanks and multielement standards prepared from ultrapure 1000 ppm standard solutions. With OES, the linear calibration lines with known concentrations were drawn from blanks and standard solutions before analyzing the samples. The analyses with MS were performed by using a standard liquid sample introduction system involving a 50 μ L Meinhart nebulizer, a cyclonic spray chamber and a single-collector ICP-MS at low mass resolution ($\Delta m/m = 300$). The trace element measurements were performed in Escan mode using peak jumping, 5 blocks with 800 sweeps per block. The peak dwell time of 5 ms.

The composition of industrial solutions #1 and #2 are presented in Table 1, which shows that both solutions had extremely low Pt and Ag content, for example, solution #1 [Ag] = 5.9 ppb and [Pt] < LOD (limit of detection), whereas in solution #2 both Pt and Ag were below the detection limit. While Ni content was high in both solutions (from 141 to 144 g/L), the iron and copper content was determined to be higher in solution #1 than in solution #2 (Fe 16 g/ L, Cu 6 g/L vs Fe 4.2 ppm, Cu < LOD). In contrast, the composition of the synthetic solution was 60 g/L Ni, 10 ppm Ag, 20 ppm Pt, and 10 g/L H_2SO_4 , with copper present as an impurity (~1 ppm) that originated from the purity of the technical grade NiSO4.6H2O used in preparation. The selected concentrations of the synthetic solution ([Ni] = 60 g/L, [Ag] = 10 ppm, [Pt] = 20 ppm) were selected to be representative of the nickel levels in industrial hydrometallurgical base metal solutions, whereas Ag and Pt concentrations were high enough to get a clear response for the EDRR parameter optimization; it is worth noting that according to the literature, $^{33-36}$ the composition of nickel-rich process solutions can vary considerably.

The PyC electrodes used were made via a pyrolysis process that involved the fabrication of a thin epoxy film on a silicon wafer surface. The wafer was first cleaned with 10:1 DIW:HF (deionized water:hydrofluoric acid) in order to make the surface more hydrophobic and at the same time to remove excess silicon dioxide from the wafer surface. This freshly cleaned surface was then spin coated with a negative photoactive epoxy SU-8 50 using a BLE spinner (Georgia Tech) at 9000 rpm for 45 s with standard baking and exposure steps to generate an approximately 13 μ m thick layer on top of the wafer. Pyrolysis was performed at 900 °C for 60 min in an inert nitrogen atmosphere with a horizontal tube furnace (Nabertherm RS 170/1000/13). This pyrolysis procedure results in an approximately 2.4 μ m thick film on top of the silicon wafer and more details of the fabrication process can be found elsewhere.³¹

EDRR Parameters. Prior to the commencement of the EDRR experiments, cyclic voltammetry (CV) measurements in the synthetic solution were undertaken in order to determine the deposition and stripping peaks of the metals under investigation. CVs were performed over the potential ranges typical for Pt, Ag, and Cu deposition (0.0 mV \rightarrow 1100 mV \rightarrow -250 mV \rightarrow 0.0 mV vs SCE) and Ni deposition (0.0 mV \rightarrow 400 mV \rightarrow -1000 mV \rightarrow 0.0 mV vs SCE) with a sweep rate of 20 mV/s. During the EDRR experiments, three deposition potentials (E_1) were investigated, -750, -500, and -175, mV vs SCE, and the deposition time was t_1 varied between 2 and 10 s. Cutoff potential E_2 was = 350 mV vs SCE, and the associated cutoff time was t_2 = 1000 s; i.e., the next ED step started when the cutoff potential E_2 or cutoff time t_2 was reached, whichever occurred first. In addition, the number of EDRR cycles, *n*, was selected to be within the range of 10-400 cycles.

RESULTS AND DISCUSSION

Optimizing EDRR Potentials. The cyclic voltammograms using PyC electrode were determined before the EDRR measurements in order to study the characteristic oxidation and reduction peaks of Pt, Ag, and Cu as well as to determine the optimum deposition (E_1) and cutoff (E_2) potentials for Pt enrichment (Figures 1 and 2). Figure 1 displays a CV with a



Figure 1. Cyclic voltammetry measurements (0.0 mV \rightarrow + 1100 mV \rightarrow -250 mV \rightarrow 0.0 mV vs SCE) of a solution containing 60 g/L Ni, 20 ppm Pt, 10 ppm Ag, ~1 ppm of Cu, and 10 g/L H₂SO₄ performed with a pyrolyzed carbon (PyC) WE at a scan rate of 20 mV/s (10 cycles at room temperature).

potential range where the oxidation/reduction peaks of Pt, Ag, and Cu are expected, as indicated. Figure 2A shows a magnification of the Ni reduction area with competing H_2 evolution reaction, whereas Figure 2B presents the Ni oxidation occurring during the reverse scan. The equilibrium potential—or OCP (open circuit potential)—of the synthetic solution was measured to be +370 mV vs SCE, and therefore, the cutoff potential (E_2) in EDRR was defined to be just below at +350 mV vs SCE.

Figure 3 presents an example of the EDRR data obtained ($E_1 = -175 \text{ mV}$ and $E_2 = +350 \text{ mV}$ vs SCE, $t_1 = 10 \text{ s}$, $t_2 = 1000 \text{ s}$ and n = 10), and all EDRR data recorded showed similar profiles, independent of deposition time or number of cycles.

In the first instance, the EDRR parameters in synthetic solutions were optimized for Pt recovery, primarily E_1 , t_1 , and n. More information about the definition of the parameters have been outlined previously,^{26,28} and they are also denoted in Figure 3. Three deposition potentials (E_1) at a deposition time $t_1 = 10$ s were investigated to ascertain the role of different sacrificial metals. Two of these potential (-750 and -500 mV and vs SCE) were chosen to be within the nickel deposition region (Figure 2), while the third and most positive deposition potential (-175 mV vs SCE) was selected such that minor elements like Cu and Ag would be deposited in preference to Ni. This is due to the fact that the sacrificial metal, which deposits at the most positive potential,³² is beneficial in terms of energy efficiency.

Table 2 outlines the metal compositions of the resultant particles as analyzed by SEM-EDS. The amount of platinum in the deposited particles was high (over 90 wt %), and this was found to remain relatively constant irrespective of the applied deposition potential. Nevertheless, the more negative deposition potential of $E_1 = -750$ mV resulted in higher Ni contents—more than eight times—when compared to $E_1 =$ -175 mV vs SCE. The same amount of process time (16 h) was used for all three samples (Table 2), although due to cutoff time limitation, this resulted in a different number of cycles (*n*): For $E_1 = -750$ mV vs SCE only 79 EDRR cycles were completed, whereas $E_1 = -500$ mV finished 303 cycles and E_1 = -175 mV resulted in a total of 723 cycles. The average times required to complete one EDRR cycle using $E_1 = -750, -500,$ and -175 mV vs SCE were 729, 190, and 80 s, respectively, and this behavior indicates that more base metal was deposited at $E_1 = -750$ mV vs SCE, resulting in slower redox replacement step.

Figure 4 shows SEM BSE micrographs of PyC electrodes after 16 h of the EDRR operation and shows that the deposited particles cannot be separately resolved. In addition, these micrographs (Figure 4B and C) also highlight the fact that competitive hydrogen evolution reaction has taken place at the surface—observed as metal-deficient circles in the images during the electrodeposition step at $E_1 = -750$ and -500 mV. In contrast, the deposition potential of -175 mV vs SCE (Figure 4A) shows no circular patterns, indicating that no significant H₂ evolution has occurred, and the deposited material on the surface is primarily smooth with the exception of only a few deposit clusters. Additionally, Figure 5 presents the average current densities (mA/cm²) obtained during the first 50 ED cycles (n = 50) when deposition (E_1) potentials of -175, -500, and -750 mV vs SCE were applied. As can be seen, there is a significant difference in the current density obtained when more cathodic deposition potentials are applied, and consequently, a deposition potential of -175mV vs SCE was selected for the following experiments in order to avoid excess current consumption due to H₂ evolution.

Effect of EDRR Cycles and Deposition Time. Figure 6A shows the effect of cycles (n) and the deposition time (t_1) on the metal content deposited at the PyC electrode with a potential of -175 mV vs SCE. In addition, Figure 6D displays the [Pt/sacrificial elements] ratio, which is a critical factor for determining the recovery in the terms of the product quality obtained. The chemical analyses of the deposits were



Figure 2. (A) Ni deposition and (B) stripping peak 0.0 mV \rightarrow 400 mV \rightarrow -1000 mV \rightarrow 0.0 mV vs SCE) obtained in a solution containing 60 g/L Ni, 20 ppm Pt, 10 ppm Ag, ~1 ppm of Cu, and 10 g/L H₂SO₄ performed with a pyrolyzed carbon (PyC) WE at a scan rate of 20 mV/s (10 cycles at room temperature).



Figure 3. Example of EDRR data (A, potential; B, current density) recorded during measurements in a solution containing 60 g/L Ni, 20 ppm Pt, 10 ppm Ag, ~1 ppm of Cu, and 10 g/L H₂SO₄. EDRR parameters were $E_1 = -175$ mV and $E_2 = +350$ mV vs SCE, $t_1 = 10$ s, $t_2 = 1000$ s, and n = 10. N.B. Examples of E_1 , E_2 , t_1 , and n are included in the figure for clarity.

Table 2. SEM-EDS Results of Metal Particles on PyC Electrodes at $E_1 = -175$, -500, and -750 mV vs SCE (60 g/ L Ni, 20 ppm Pt, 10 ppm Ag, ~ 1 ppm of Cu, and 10 g/L H₂SO₄), Deposition Time $t_1 = 10$ s^a

E_1 vs SCE	-175 mV	-500 mV	-750 mV			
Pt [wt %]	97.68	95.95	94.95			
Ag [wt %]	1.52	2.00	1.49			
Cu [wt %]	0.67	0.63	0.99			
Ni [wt %]	0.12	1.42	2.56			
^{a} N.B. Base material of the PyC electrode (Si, O and C) is excluded from the results						

conducted with SEM-EDS and the response of PyC electrode itself (i.e., Si, O, and C) was excluded from the data. As can be observed from Figure 6A, both the Pt and Ag content in the deposits is similar (42 wt % cf. 45 wt %) after only 10 EDRR cycles and short deposition time $(t_1 = 2 \text{ s})$. Nevertheless, when the deposition time is increased—to $t_1 = 5$ and 10 s, respectively—the proportion of Pt increases with a corresponding decrease in Ag content (Figure 6B and C). This is believed to be due to the fact that at longer deposition times, more sacrificial metal (like Ni or Cu) is deposited, resulting in the longer redox replacement time. Longer redox replacement time seems to favor Pt as it also provides time for the Ag to be first deposited (via RR reaction) and then start to act as sacrificial metal for Pt. From the results, it can also be determined that silver, nickel, and copper contents in the deposited material all reduce with a higher number of cycles. For example, Ni and Cu contents were in the region of 5–15 wt % with n = 10, and these decreased to 1–3 wt % with an increase in the number of cycles. This finding suggests that all three can act as the sacrificial metal when the number of EDRR cycles increases beyond n = 10. Further analysis of the Pt to sacrificial element (Ni, Cu, and Ag) ratios clearly demonstrates the effect of deposition time; when $t_1 = 10$ s, the highest level of Pt enrichment (Pt/(Ni + Cu + Ag) ≈ 35) after 400 cycles was recorded (Figure 6D), indicating that longer durations between deposition steps favors the redox replacement.

The results clearly verify the effectiveness of the EDRR method for the recovery and enrichment of Pt metal. When the optimal parameters were used, the Pt/(Ni + Cu+ Ag) ratio increased from 3×10^{-4} (solution) to 33.6 (metal deposit), which is equivalent to an enrichment ratio of ~10⁵ for Pt. It is also worth noting that Ag can be enriched when a lower number of deposition cycles are used, for example, [Ag]/[Ni] = 2×10^{-4} (in solution) to 4.4 (at the electrode)—an ~2.6 × 10^{4} enrichment for Ag—after 10 cycles.

Investigation of the surfaces using a SEM backscatter imaging (Figure 7) also shows that as the number of EDRR cycles (at $E_1 = -175$ mV) was increased from 10 to 400, and



Figure 4. SEM BSE micrographs of PyC electrodes with deposition time t_1 = 10s and applied potentials E_1 = -175 mV (A), -500 mV (B), and -750 mV (C) vs SCE. Solution contains 60 g/L Ni, 20 ppm Pt, 10 ppm Ag, ~1 ppm of Cu, and 10 g/L H₂SO₄. The black spots on the electrode surface are indicative of hydrogen evolution.



Figure 5. Average current density of electrodes during the first 50 EDRR cycles at $E_1 = -175$, -500, and -750 mV vs SCE and $t_1 = 10$ s (60 g/L Ni, 20 ppm Pt, 10 ppm Ag, \sim 1 ppm of Cu and 10 g/L H₂SO₄).

there is an analogous enhancement in the density of particles that can be observed on the PyC electrode surface.

The average size of the deposited platinum particles on the PvC surface ranged from tens to several hundreds of nanometers as can be observed in Figure 8. This micrograph of the PyC electrode shows that the surface is covered with small clusters deposited platinum, which most likely nucleate preferentially on areas of surface inhomogeneity.^{26,37} Formation of Pt nanoparticles on the surface of the PyC electrode followed the same pattern in every experiment; initially, a small Pt particle forms on the electrode surface during one cycle, from which new particles grow during the subsequent cycles. This clustering nature is only observable at higher magnifications, as can be seen by comparison between Figure 4 (×100 magnification) and Figures 7 and 8 (×3500 and ×20000 magnification, respectively). Such a growth mechanism correlates with that previously reported in literature for platinum electrodeposition experiments.38-43

Comparison of EDRR and EW. In order to compare the efficiency of EDRR to the more traditional electrochemical recovery method electrowinning (EW), i.e., electrodeposition without a redox replacement step, six EW experiments were performed with synthetic solutions at two EW potentials: (i) -175 mV (equivalent to the E_1 potential) and (ii) + 350 mV vs SCE (= E_2). The latter potential also favors selective Ag deposition without pulsing (Figure 1), and the time used for EW was equal to the duration of 100 cycles of EDRR deposition. Quality of the deposition produced by EW was compared to the those produced by EDRR at -175 mV vs

SCE (for $t_1 = 2$, 5, or 10 s, n = 100) by SEM-EDS analysis of 5 to 10 distinct areas $-30 \pm 10 \times 15 \pm 5 \ \mu\text{m}$ —on the each electrode. N.B. This is in contrast to the analysis presented in Table 2 and Figure 6, where the metal particles were sufficiently large to perform point analysis. The contents of Pt, Ag, and Cu determined from the surface analysis are presented in Figure 9. The area analysis shows that the content of platinum was highest (24.4 wt %, Figure 9) when EDRR was performed at $t_1 = 10$ s and n = 100, while with the equivalent EW experiment the corresponding Pt content was only 9.7 wt %. Further results from deposition times of 2 and 5 s also show a 2-10 fold increase in platinum content for EDRR vs EW. Overall these differences, determined between the Pt enrichment with EDRR when compared to EW, clearly demonstrate how critical the redox replacement step is for the recovery of Pt from \leq ppm-level solution concentrations.

Recovery of Pt, Ag, and Pd from Industrial Process Solutions. The applicability of the EDRR method for Pt recovery from complex multimetal solutions was verified with real industrial hydrometallurgical solutions (Table 1). Solution #2 comprised solution #1 that had been purified via an industrial precipitation process that resulted in a lower concentration of both impurities and precious metals.⁴⁴

Industrial Process Solution #1. On the basis of the results from the EDRR optimization experiments with synthetic solution, the following parameters were used with solution #1 for Pt recovery: n = 10-400, $t_1 = 2-10$ s, $t_2 = 1000$ s, $E_1 =$ -175 mV, and $E_2 = +350$ mV vs SCE. N.B. Industrial solution #1 contained almost double the level of nickel as the synthetic solution investigated (140 g/L vs 60 g/L) and a significantly lower level of Pt (<LOD) and Ag (4.4 ppb). Moreover, the copper content of the solution was also much higher in industrial solution #1 (5850 ppm) and contained relatively high levels of Pd (~100 ppb) in contrast to the synthetic solution. Figure 10A outlines the content of Pt on the surface of PyC as a function of deposition time (n = 10), whereas Figure 10B displays the respective Pd and Ag contents. As can be seen, the level of Pt increases almost linearly with longer deposition times (from $t_1 = 2$ to 10 s), and as the most noble metal, it is major replacement metal (up to 80 wt %). However, deposited Pd and Ag is clearly lower, and behavior is more transient (Figure 10B). The results suggest that Ag dominates over Pd at short t_1 (2 s) and long t_1 times (10 s), whereas in the interim periods $(t_1 = 4, 6, 8 \text{ s})$ Ag and Pd are present at a similar level in the Pt-rich deposits. One possible reason could be that especially at short deposition times—which lead also to short redox replacement times (Figure 10C)-Ag predominates over Pd. Currently, the reason for this is unknown, but



Figure 6. Content of investigated metals on the surface of the electrode as a function of EDRR cycles (*n*) with three different deposition times (t_1) 2 s (A), 5 s (B), and 10 s (C) and the Pt/(Ni + Cu + Ag) ratio (D). EDRR potentials ($E_1 = -175$ mV and $E_2 = +350$ mV vs SCE) were the same for each experiment. The solution contained 60 g/L Ni, 20 ppm Pt, 10 ppm Ag, ~1 ppm of Cu, and 10 g/L H₂SO₄. N.B. Base material of the PyC electrode (Si, O and C) is excluded from the results.

results from the literature related to electroless plating⁴⁵ indicate that the activation energy (E_a) for Ag can be lower (~50 kJ/mol) than that for Pd (~62 kJ/mol). It is also possible that the complex chemistry of such industrial solutions will have an effect on redox replacement behavior, especially when compared to simpler standardized solutions. Nevertheless, such hypotheses remain highly speculative, and the exact nature of the Ag and Pd redox replacement behavior in the complex industrial solution is to be studied further. The levels of enrichment achieved is remarkable given that the contents of Pt, Pd, and Ag in the industrial hydrometallurgical solution were only <LOD, 117, and 4.4 ppb, respectively (Table 1).

Figure 10C outlines the Pt/Ni ratio obtained after the first 10 cycles and the time needed to complete all these n = 10 cycles. N.B. The time spent for the deposition, $t_1 = 2-10$ s, is excluded from the results in order to better correlate the actual redox replacement times. As can be observed, the total time needed for redox replacement increased linearly with the increasing deposition time, while in contrast the [Pt]/[Ni] ratio obtained increased exponentially. This clearly demonstrates that longer deposition times result in the presence of more sacrificial base metal deposition, and as a result, the

subsequent Pt replacement reaction duration needed to achieve the cutoff potential (+350 mV vs SCE) is also prolonged. When the deposition time was changed to 10 s (from $t_1 = 2$ s), the [Pt]/[Ni] ratio on the electrode underwent a 100-fold increase from 9 to ~900. Figure 10D shows the effect of current density during the deposition (ED step) on the average time needed for one RR cycle. As expected, when the average cathodic current density was at the lowest level, the time required to complete the RR cycle was also the shortest; i.e., as less base metal is deposited during the ED step, the cutoff potential resulting from the replacement between sacrificial and more noble metals is reached faster.

In order to further understand the effect of the number of EDRR cycles on the enrichment behavior from industrial solutions, experiments were performed with 100, 200, and 400 cycles for $t_1 = 8$ and 10 s. Figure 11 shows that the platinum content in the measured deposits varied between 65 and 90 wt % depending on the parameters utilized. At the same time, the [Pt]/[Ni] ratio of the deposits displays a similar behavior as the Pt content becomes more significant cf. other elements with a maximum Pt enrichment ratio of 7.6 × 10¹⁰ achieved at $t_1 = 10$ s and 100 cycles. Figure 11B shows that the concentration of Pd (<1 wt %) and Ag (<4 wt %) is relatively



Figure 7. BSE micrographs of the employed electrodes when applying deposition potential of -175 mV vs SCE for 10 s and varying the EDRR cycles: n = 10 (A), n = 100 (B), n = 200 (C), and n = 400 (D). The solution contained 60 g/L Ni, 20 ppm Pt, 10 ppm Ag, ~ 1 ppm of Cu, and 10 g/L H₂SO₄.



Figure 8. Secondary electron micrograph of the PyC electrode after EDRR at $E_1 = -175$ mV vs SCE for 10 s with n = 400.



Figure 9. Comparison between EDRR (-175 mV, 100 cycles) and EW (-175 and +350 mV vs SCE) on the platinum contents on the surface of the PyC. Solution contained 60 g/L Ni, 20 ppm Pt, 10 ppm Ag, \sim 1 ppm of Cu, and 10 g/L H₂SO₄.

low when compared to the Pt content (60-90 wt %); nevertheless, the enrichment of these elements is also significant. Industrial Process Solution #2. In order to confirm the ability of EDRR to recover precious metals, another industrial solution (solution #2)—an industrially purified version of #1 with precious metal contents below the detection limit of HR-ICP-MS—was also investigated. In these experiments, the cutoff time (t_2) was reached before cutoff potential (E_2), in contrast to the previous investigations performed at higher concentrations. Figure 12 shows that the valuable metal recovery was successful even at these ultralow (\leq ppb) concentrations. The actual enrichment ratios could not be calculated due to limit of detection in the original industrial solution analysis, but when taking threshold value for Pt detection by HR-ICP-MS (LOD = 1.3 ppb), a truly outstanding enrichment ratio for platinum was achieved of at least 7.2×10^{10} .

Summary of Enrichment Ratio. Enrichment ratios of Pt, Pd, and Ag were determined from their original ratios to nickel in the industrial solution and from the deposits on the PyC electrode. Table 3 summarizes the calculated enrichment ratios using the element specific LOD values (Pt = 1.3 ppb, Pd = 2.17 ppb, Ag = 1.3 ppb) where necessary. The results shown in Table 3 are remarkable and clearly demonstrate the power of the EDRR method for recovering valuable and critical elements from industrial complex multimetal solutions where concentrations are at the ppb level. Moreover, with the indicative contents of Pt, Pd, and Ag in the solution (measured values below LOD), the calculated enrichment ratios for Pt, Pd, and Ag were several times higher.

In addition, the platinum concentration on the surface of the PyC electrodes was measured to be around 90 wt % with a Pt/ Ni ratio ca. 900. When the number of EDRR cycles (*n*) was increased, the platinum concentration was also found to be enhanced. The EDRR method was able to recover Pt, Pd, and Ag from industrial process solutions with \leq ppb level concentrations. The highest metal contents analyzed on PyC were 90 wt % (Pt), 2.1 wt % (Pd), and 5.5 wt % (Ag) from



Figure 10. Recovery of valuable metals from industrial solution #1: (A) Pt, (B) Pd, and Ag. (C) Pt/Ni ratio and time needed to complete 10 RR cycles, and (D) applied current density during ED step and average time needed to complete one RR cycle. The EDRR parameters were: $t_1 = 2-10$ s, $E_1 = -175$ mV, and $E_2 = +350$ mV vs SCE. The base material of PyC is excluded from the results.



Figure 11. Effect of EDRR cycles, *n*, on the valuable metal content and the product quality from industrial solution #1: (A) Pt/Ni ratio and Pt content and (B) (Ag+Pd)/Ni and the Ag and Pd contents. The EDRR parameters were $E_1 = -175$ mV and $E_2 = +350$ mV vs SCE, $t_1 = 8$ or 10 s, $t_2 = 1000$ s, and n = 100, 200 or 400.

solution #1 and 85 wt % (Pt), 0.2 wt % (Pd), and 3.0 wt % (Ag) from solution #2.

In conclusion, this paper clearly demonstrates the outstanding performance of EDRR combined with the PyC electrode in the recovery of precious metals from solutions where they are present below the detection limits of HR-ICP-MS. Moreover, it is worth noting that this methodology is selective for platinum—a critical catalysis element—without the need for any chemical additions, which makes this methodology competitive with respect to traditional cementation processes. This was enabled by the use of a novel high surface area pyrolyzed 3D carbon (PyC) electrode material. The deposition potential (-175 mV vs SCE) was found to be very effective in terms of recovering Pt from a concentrated synthetic NiSO₄ solutions, and it was also observed that Pt also



Figure 12. Effect of EDRR cycles, *n*, on the valuable metal content and the product quality from industrial solution #2: (A) content of platinum and the product quality and (B) contents of Ag and Pd and the product quality.

Table 3. Calculated Enrichment Ratios of Pt, Pd, and Ag from Industrial Solutions

Solution	Pt	Pd	Ag
#1	7.6×10^{10}	1.4×10^{6}	1.0×10^{9}
#2	7.2×10^{10}	4.3×10^{7}	2.5×10^{9}

replaced the deposited Cu and Ag via the redox replacement process, resulting in a product quality of Pt > 95 wt %.

Overall, this paper shows that EDRR in industrial hydrometallurgical solutions provides new opportunities for the circular economy of critical metals and can effectively recover Pt from very complex industrial Ni solutions even when present at concentrations \leq ppb.

AUTHOR INFORMATION

Corresponding Author

*E-mail: mari.lundstrom@aalto.fi.

ORCID [©]

Petteri Halli: 0000-0002-1803-7632 Kirsi Yliniemi: 0000-0003-2536-388X

Author Contributions

All authors have given approval to the final version of the manuscript.

Notes

The authors declare no competing financial interest.

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ABBREVIATIONS

EDRR,electrodeposition-redox replacement; SEM,scanning electron microscope; EDS,energy dispersion spectroscopy; HR-ICP-MS,high resolution-inductively couple plasmamass spectroscopy; ICP-OES,inductively couple plasmaoptical emission spectroscopy; SCE,saturated calomel electrode; WE,working electrode; CE,counter electrode; PyC,pyrolyzed carbon; LOD,limit of detection; EW,electrowinning

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