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2 Editor-in-Chief of Solvent Extraction and Ion Exchange

3
4 Thank you for sending useful comments.

5 According to your advice, the statement was modified in the revised manuscript.

6 We hope that it will be suitable and acceptable for the publication.

7 Thank you for considering our manuscript.

8 Sincerely yours.

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Recovery of Palladium by Extraction-electrodeposition
Using *N, N, N', N', N'', N''*-Hexaocetyl-nitrilotriacetamide

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1 **ABSTRACT**

2 It is essential to develop solvent extraction (SX), and electrodeposition (ED) processes for
3 palladium to reduce the volume of acid and organic media. In this study, the extraction reaction of
4 Pd(II) in chloride media using of *N, N, N', N', N'', N''*-hexaethyl-nitrilotriacetamide (NTAamide(C8))
5 as a novel extractant has been demonstrated. Three diluents with high dielectric constants
6 (acetophenone (AP), 1,2-dichloroethane (DCE), and 1-octanol (OC)) were used for the solvent
7 extraction reaction. The slope analysis indicated that the anion exchange extraction reaction of Pd(II)
8 was consistent with an approximately 2:1 stoichiometry for the NTAamide(C8)/AP and
9 NTAamide(C8)/DCE systems, and 1:1 for NTAamide(C8)/OC. Moreover, the ED behavior of the
10 extracted Pd(II) complex was investigated using cyclic voltammetry (CV). Palladium reduction was
11 found to be an irreversible process based on analysis of the standard rate constant. A semi-integral
12 analysis of the voltammogram determined the diffusion coefficients of the extracted Pd(II) complex in
13 the AP, DCE, and OC systems to be $3.7 \pm 0.1 \times 10^{-10}$, $2.8 \pm 0.1 \times 10^{-10}$ and $1.5 \pm 0.2 \times 10^{-10}$ m² s⁻¹,
14 respectively. Furthermore, consecutive extraction-electrodeposition processes using the
15 NTAamide(C8)/AP system were carried out for five cycles. High extraction percentage ($E > 91\%$) and
16 current efficiency ($\epsilon > 83.1\%$) were attained in all cycles. The electrodeposits recovered from the
17 extraction-electrodeposition process were identified as Pd metal through X-ray photoelectron
18 spectroscopy (XPS) and X-ray diffraction (XRD) analyses.

19
20 **Keywords:** Chloride media, Extraction-electrodeposition, NTAamide(C8), Palladium

1 1. Introduction

2 Palladium (Pd) is a widely employed three-way catalyst in automobiles and this application makes
3 it one of the vital platinum group metals (PGMs) worldwide. Conventional hydrometallurgical methods
4 such as adsorption [1], electrodeposition (ED) [2,3], ion exchange [4,5], liquid membrane separation [6]
5 precipitation [7,8], and solvent extraction (SX) [9] have been applied in different stages of the
6 hydrometallurgical route to separate PGMs. However, there have been relatively few reports [10-12] on
7 the separation of Pd(II) via SX and the subsequent recovery of Pd metal from the loaded organic phase
8 by ED. The ED and SX procedures have several advantages, such as good selectivity, large capacity,
9 simple equipment, and wide application. Hence, the development of extraction-electrodeposition
10 processes to reduce the volume of secondary waste is very important. We have also demonstrated the
11 recovery of Pd [13], ruthenium (Ru) [14], iridium (Ir) [15], and platinum (Pt) [16] from the loaded organic
12 phase by consecutive extraction-electrodeposition processes in our previous studies.

13 In line with improving the extraction of PGMs, *N, N, N', N'', N'''*-hexaethyl-nitrilotriacetamide
14 (NTAamide(C8)) (**Fig. 1**), a novel triamide extractant with one nitrogen and three oxygen donors
15 included in the central frame has shown exceptional results. It was reported that 0.1 mol dm⁻³
16 NTAamide(C8) in *n*-dodecane was extracted, and the stoichiometry was 1.07 (Ru) and 3.7 (Pd) [17,18].
17 **This** novel extractant is expected to have stronger extractability with PGMs because of its strong
18 affinity for soft acid elements. In this study, we investigated the feasibility of separating Pd(II) using SX
19 and the subsequent ED process from the extraction medium. In addition, we investigated the diffusion
20 coefficient for the extracted Pd(II) complex in three diluents (acetophenone (AP), 1,2-dichloroethane
21 (DCE), and 1-octanol (OC)) with high dielectric constants **because media** with high dielectric constants
22 have high electrical conductivity and are suitable for electrodeposition media. Furthermore, the
23 repeatable use of the NTAamide(C8)/AP system was **investigated** from consecutive extraction-
24 electrodeposition processes for the 5th cycle. This extraction-electrodeposition process could lead to the
25 elimination of several complex processing steps, minimize the generation of secondary wastes, lower
26 the environmental risk of Pd recovery, achieve a considerable reduction in volume, and allow for easy

1 handling of the electrodeposits.

2

3 **2. Experimental**

4 **2.1 Reagents**

5 **The method for synthesis** of NTAamide(C8) is similar to that of amide compounds such as
6 methylimino-*N,N*-dioctylacetamide (MIDOA), methylimino-*N,N'*-diethylacetamide (MIDEA), and
7 NTAamide (C2) [19-21]. The synthesized NTAamide(C8) was a light-yellow liquid, because its melting
8 point was less than the normal temperature. The NTAamide(C8) was identified **by proton nuclear**
9 **magnetic resonance (¹H-NMR) indicating a** triplet at 0.8-0.9 ppm, multiplet at 1.2-1.6 ppm, triplet at
10 3.2-3.3 ppm, and singlet at 3.6-3.7 **ppm**. The **synthesis** yield and purity of NTAamide(C8) were
11 approximately 50 % and 98 %, respectively. The Pd standard solution, hydrochloric acid (HCl),
12 perchloric acid (HClO₄) and three diluents (acetophenone (AP) (purity >98.5%), dichloroethane (DCE)
13 (purity >99.5%), 1-octanol (OC) (purity >97.0%)) were purchased from FUJIFILM Wako Pure
14 Chemical Industries Corp (Japan). All chemicals used were **of analytical** grade.

15

16 **2.2 Solvent **Extraction** (SX)**

17 The aqueous phase was 4.0×10^{-4} mol dm⁻³ [PdCl₄]²⁻ in 1.0 mol dm⁻³ HCl solution using a Pd
18 standard solution. To investigate the concentration dependence of the NTAamide(C8) extractant, the
19 concentration of NTAamide(C8) in the organic phase was varied from 4.0×10^{-4} mol dm⁻³ to 3.0×10^{-1}
20 mol dm⁻³, fixing the other conditions. AP (>98.5%), DCE (>99.5%), and OC (>97.0%) were used as
21 diluents. The equivalent volume ratio of the aqueous (A) and organic (O) phases (A/O=1.0) was kept
22 constant during the SX procedure.

23 To evaluate the activity dependence of the HCl medium, the concentration of HCl solution was
24 varied from 1.0×10^{-1} mol dm⁻³ to 3.0 mol dm⁻³ under the fixed condition of 1.0×10^{-1} mol dm⁻³
25 NTAamide(C8). For this evaluation, the ionic strength *I* in the aqueous phase was maintained at a
26 constant value (*I*=3) using an HClO₄ solution. Moreover, **a fifth** continuous extraction was carried out

1 using a constant volume ratio ($A/O=3.0$) to enrich the extracted Pd(II) complex in the organic phase.
 2 The aqueous phase was $4.0 \times 10^{-4} \text{ mol dm}^{-3}$ $[\text{PdCl}_4]^{2-}$ in 1.0 mol dm^{-3} HCl solution while the
 3 NTAamide(C8) concentration was constant at $1.0 \times 10^{-1} \text{ mol dm}^{-3}$. After **the first** extraction, the organic
 4 phase was separated from the aqueous phase, and the new aqueous phase was **contacted with** the same
 5 organic phase. After **the fifth** continuous extraction, the concentration of Pd(II) in the aqueous phase
 6 was measured by inductively coupled plasma atomic emission spectroscopy (ICP-AES, ICPE-9000,
 7 Shimadzu Co.). The **monitored** wavenumber of Pd(II) in the ICP-AES analysis was 340.458 nm. The
 8 enriched concentration of Pd(II) in each organic phase was **calculated** using the mass balance equation.

9 For the extraction procedure described above, the extraction equilibrium was achieved by stirring
 10 at 298 K with a direct mixer at 2000 rpm for 30 min. The extraction behavior of Pd(II) as a function of
 11 the concentration of NTAamide(C8) was investigated to determine the stoichiometry of the extracted
 12 Pd(II) complex. After the extraction equilibrium, the concentration of Pd(II) in the aqueous phase was
 13 measured by ICP-AES after equilibration. The distribution ratio (D) and extraction percentage (E) were
 14 calculated as follows:

$$16 \quad D = \frac{[M]_{\text{aq}}^{\text{ini}} - [M]_{\text{aq}}^{\text{fin}}}{[M]_{\text{aq}}^{\text{fin}}}, \quad E(\%) = \frac{100D}{D + V_{\text{aq}}/V_{\text{org}}} \quad (1)$$

17 where “aq” is the aqueous phase, “org” is the organic phase, $[M]$ is the concentration of Pd(II), and V is
 18 the extraction volume for each phase. The superscripts “ini” and “fin” imply the initial and final
 19 concentrations, respectively. The dependence of the extraction efficiency was evaluated for each D
 20 value on the NTAamide(C8) concentration to investigate the extraction reaction of Pd(II) in the
 21 NTAamide(C8)/AP, NTAamide(C8)/DCE, and NTAamide(C8)/OC systems.

24 **2.3 Electrochemical analysis**

25 The extracted Pd(II) complexes dissolved in the NTAamide(C8)/AP, NTAamide(C8)/DCE, and

1 NTAamide(C8)/OC systems were prepared and analyzed by cyclic voltammetry (CV) using a three-
2 electrode system. A Pt disk electrode with an inner diameter of 1.6 mm (No. 002422, BAS Inc.) was
3 used as the working electrode. The electrode surface on the working electrode was carefully polished
4 with alumina and diamond paste to prevent IR drop. IR drop is the electrical potential difference
5 between the two ends of a conducting phase, and this voltage drop across any resistance is the product
6 of the current value (I) passing through the resistance value (R). Pt wires with an inner diameter of 0.5
7 mm (No. 002233, BAS Inc.) were used as the counter electrode and quasi-reference electrode (QRE)
8 because the electrode potential was stable and exhibited good reproducibility. The potential was
9 compensated against a ferrocene/ferrocenium (Fc/Fc⁺) redox couple. The cylindrical cell was sealed
10 with a silicone sealant after setting the electrolyte and all the electrodes to prevent the volatility of the
11 organic phase. The cylindrical cell was placed in a glovebox (DBO-1KP-YUM01, MIWA Inc.) under an
12 Ar atmosphere (H₂O, O₂ < 1 ppm). CV measurements were carried out using an electrochemical
13 apparatus (ALS-760E, BAS Inc.), and semi-integral (SI) analysis was applied to the obtained
14 voltammogram.

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16 **2.4 Continuous Extraction-electrodeposition**

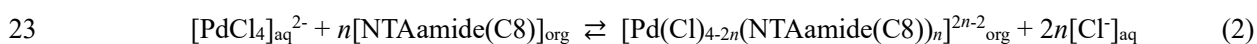
17 To evaluate the repeatable use of the NTAamide(C8)/AP system, a recycling run consisting of
18 extraction-electrodeposition for the 5th cycle was carried out (Fig. 2). For SX, a metal concentration 10-
19 fold higher than that used in the ED evaluation (i.e., $5.0 \times 10^{-2} \text{ mol dm}^{-3} [\text{PdCl}_4]^{2-}$) was employed in the
20 aqueous phase to control the deposition potential related to the increase in the Pd(II) concentration. The
21 volume ratio of the organic phase to the aqueous phase was maintained at 3.0. Thus, a high volume ratio
22 led to the enrichment of the extracted Pd(II) complex in the organic phase. Subsequently,
23 electrodeposition from the extracted Pd(II) complex in the NTAamide(C8)/AP system was carried out
24 using a three-electrode system under an Ar atmosphere. A Ni substrate (99.96%, Nilaco Corp.) was used
25 as the working electrode. A platinum wire with an inner diameter of 0.5 mm was used as the QRE. The

1 counter electrode was separated by a Vycor glass filter at the bottom to prevent diffusion of the
 2 decomposition products from the anode compartment to the electrolyte. A constant overpotential at -2.0
 3 V against QRE was applied to the cathode during ED. After the ED process, all electrodes were
 4 removed from the electrolytic bath and replaced with new electrodes. The organic phase AP was re-used
 5 in the next stage of SX. For the n^{th} ($n = 2-5$) SX, a new aqueous phase containing $5.0 \times 10^{-2} \text{ mol dm}^{-3}$
 6 $[\text{PdCl}_4]^{2-}$ was introduced into the organic phase. After the n^{th} ($n = 2-5$) SX, the same overpotential was
 7 induced for the ED procedure at the n^{th} time. The extraction-electrodeposition process was repeated for
 8 five cycles. After the 5th successive extraction-electrodeposition cycle, the metal concentration of the
 9 organic phase in each cycle was measured by ICP-AES. The current efficiency was calculated from the
 10 weight increase of the Ni substrate during each ED. The oxidation state of the electrodeposits was
 11 evaluated by X-ray photoelectron spectroscopy (XPS) (Quantera SXM, ULVAC-PHI, Inc.) to
 12 investigate the chemical shift due to the valence of palladium. The detection angle from the sample
 13 surface was set to 45 °. The sample on the substrate was analyzed by etching using an Ar ion beam. The
 14 crystalline state of the electrodeposits was identified using XRD (SmartLab Rigaku Corp.).

16 3. Results and Discussion

17 3.1 Solvent Extraction (SX)

18 Preliminary studies indicated that the three diluents (acetophenone (AP), 1,2-dichloroethane
 19 (DCE), and 1-octanol (OC)) could not extract $[\text{PdCl}_4]^{2-}$ without the extractant. Hence, the extraction
 20 reaction of $[\text{PdCl}_4]^{2-}$ was evaluated using the following equilibrium based on a similar extraction
 21 reaction with methylamino-bis-*N, N*-dioctylacetamide (MIDOA) [13].



25 The extraction equilibrium constant (K_{ex}) and distribution ratio ($D_{\text{Pd(II)}}$) are expressed as follows:

26

$$K_{\text{ex}} = \frac{[\text{Pd}(\text{Cl})_{4-2n}(\text{NTAamide}(\text{C8}))_n]_{\text{org}}^{2n-2} [\text{Cl}^-]_{\text{aq}}^{2n}}{[\text{PdCl}_4]_{\text{aq}}^{2-} [\text{NTAamide}(\text{C8})]_{\text{org}}^n} \quad (3)$$

$$D_{\text{Pd(II)}} = \frac{[\text{Pd}(\text{Cl})_{4-2n}(\text{NTAamide}(\text{C8}))_n]_{\text{org}}^{2n-2}}{[\text{PdCl}_4]_{\text{aq}}^{2-}} \quad (4)$$

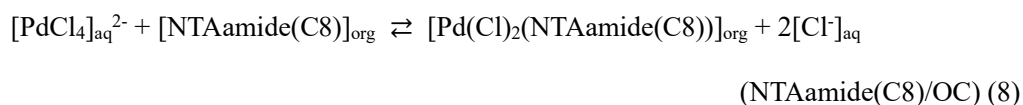
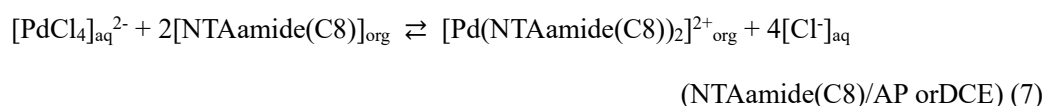
The following relationship is obtained from Eq. (3-4):

$$K_{\text{ex}} = D_{\text{Pd(II)}} \cdot \left(\frac{[\text{Cl}^-]_{\text{aq}}}{[\text{NTAamide}(\text{C8})]_{\text{org}}} \right)^n \quad (5)$$

The logarithm of $D_{\text{Pd(II)}}$ is expressed as follows according to Eq. (5):

$$\log D_{\text{Pd(II)}} = \log K_{\text{ex}} + n \log \left(\frac{[\text{NTAamide}(\text{C8})]_{\text{org}}}{[\text{Cl}^-]_{\text{aq}}} \right) \quad (6)$$

The plot of $\log D_{\text{Pd(II)}}$ versus $\log([\text{NTAamide}(\text{C8})]_{\text{org}}/[\text{Cl}^-]_{\text{aq}}^2)$ shows the stoichiometry of the extracted Pd(II) complex. The variation in $\log D_{\text{Pd(II)}}$ as a function of $\log([\text{NTAamide}(\text{C8})]_{\text{org}}/[\text{Cl}^-]_{\text{aq}}^2)$ in the three types of diluents is shown in **Fig. 3**. The NTAamide(C8)/AP, NTAamide(C8)/DCE, and NTAamide(C8)/OC systems exhibited slopes of 1.76 ± 0.05 , 1.83 ± 0.04 , and 1.24 ± 0.05 , respectively. The slopes of NTAamide(C8)/AP and NTAamide(C8)/DCE indicate a **dominant** 2:1 stoichiometry of NTAamide(C8) to Pd(II), consistent with the **previously reported** extraction behavior of Pd(II) in a MIDOA/AP or MIDOA/DCE system [13]. However, the stoichiometric ratio of NTAamide(C8) to Pd(II) was **primarily** 1:1 for NTAamide(C8)/OC. Based on the above results, the extraction reactions in the NTAamide(C8)/AP, NTAamide(C8)/DCE, and NTAamide(C8)/OC systems are represented as follows:



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2 The equilibrium constants (K_{ex}) obtained from the intercept for NTAamide(C8)/AP,
3 NTAamide(C8)/DCE, and NTAamide(C8)/OC were 5.4 ± 0.2 , 5.2 ± 0.1 , and 2.1 ± 0.2 , respectively. The
4 K_{ex} values of NTAamide(C8)/AP and NTAamide(C8)/DCE were higher than those of
5 NTAamide(C8)/OC. This tendency was observed for the similarly extracted complex of $[Pd(Cl)_4$
6 $_n(MIDO A)_n]^{2n-2}$ ($n=1$ for OC, $n=2$ for AP, DCE) using MIDOA extractant [13]. The viscosity ($\eta_{OC}=7.29$
7 $mPa\cdot s$) [22] of OC is higher than those of AP ($\eta_{AP}=1.68 mPa\cdot s$), and DCE ($\eta_{DCE}=0.84 mPa\cdot s$). The
8 differences in the stoichiometric numbers and the equilibrium constant might be influenced by the
9 rheological properties of each organic phase.

10 The activity dependence of the HCl concentration is shown in **Fig. 3**. The activity was estimated
11 from the activity coefficient of the HCl solution because, in the high concentration region, the activity
12 of the HCl solution was not the same as the HCl concentration. This result indicates that the distribution
13 ratio (D) of Pd(II) did not influence the activity of the HCl solution. This tendency was also observed in
14 a MIDOA/AP system by the protonation of the extractant [17]. The continuous extraction results for the
15 different diluents are listed in **Table 1**. The total concentration of Pd(II) in each electrolytic bath
16 gradually increased with successive extraction procedures. However, the extraction percentage of Pd(II)
17 gradually decreased because of the decrease in the active MIDOA extractant for each extraction.

18

19 3.2 Electrochemical Measurement

20 The voltammogram of the extracted Pd(II) complex in NTAamide(C8)/AP, NTAamide(C8)/DCE,
21 and NTAamide(C8)/OC are shown in **Fig. 4**. One reduction peak around $-2.05 V$ for
22 NTAamide(C8)/AP, $-2.11 V$ for NTAamide(C8)/DCE and $-1.63 V$ for NTAamide(C8)/OC was
23 observed in the voltammogram. This difference in the reduction peaks could be due to the viscosity of
24 the organic solvent and the diffusion coefficient of the electroactive species. Considering the
25 complexation state of Pd(II), this reduction peak corresponds to the following electrodeposition reaction
26 [23,24].

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4 Contrastingly, the oxidation peaks around -0.426 V for NTAamide(C8)/AP, -0.533 V for
5 NTAamide(C8)/DCE, and -0.868 V for NTAamide(C8)/OC were observed in the voltammogram. This
6 oxidation peak was attributed to the anodic decomposition of the organic solvent.

7 The electrodeposition of Pd is thought to be an irreversible reaction because of the relatively wide

8 peak separation between the cathodic and anodic potentials. Assuming that each peak in the

9 voltammogram is based on the cathodic reaction (9), we confirmed that the cathodic peak plot of the

10 current density (j_p) versus the square root of the potential sweep rate ($v^{1/2}$) demonstrated a strong linear

11 relationship. This result indicated that the electrodeposition reaction was diffusion-controlled, that is, it

12 involved mass transport under semi-infinite linear diffusion conditions. In addition, the slope of the j_p

13 versus $v^{1/2}$ plot is different for the three types of electrolytes (NTAamide(C8)/AP, NTAamide(C8)/DCE,

14 and NTAamide(C8)/OC). This outcome indicated that the diffusion coefficients of the extracted Pd(II)

15 complexes are different. Therefore, the diffusion coefficient of the extracted Pd(II) complex was

16 estimated from a semi-integral (SI) analysis of the voltammogram. Concerning the electrodeposition

17 rate, mass transfer related to diffusion is critical. The limiting current in the SI analysis allowed us to

18 evaluate the diffusion coefficient of the extracted Pd(II) complex more precisely in an irreversible

19 process. The SI curves of the extracted Pd(II) complexes in the three types of electrolytes are shown in

20 **Fig. 5.** The value of m^* was conventionally determined by subtracting the background current. The

21 diffusion coefficient of the extracted Pd(II) complex was calculated from the m^* value as follows [25]:

22

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$$m^* = nFAD^{1/2}C^* \quad (10)$$

24

1 where n is the number of electrons involved in the charge transfer reaction, F is the Faraday constant, A
 2 is the electrode surface area, D is the diffusion coefficient, and C^* is the bulk concentration. The
 3 diffusion coefficients of the extracted Pd(II) complex in NTAamide(C8)/AP, NTAamide(C8)/DCE and
 4 NTAamide(C8)/OC was evaluated to be $3.7 \pm 0.1 \times 10^{-10}$, $2.8 \pm 0.1 \times 10^{-10}$ and $1.5 \pm 0.2 \times 10^{-10}$ m² s⁻¹,
 5 respectively. In the case of [PdBr₄]²⁻ in 1-*n*-butyl-1-methylpyrrolidinium bis(trifluoromethylsulfonyl)
 6 amide, [BMP][TFSA] (viscosity: $\eta_{[\text{BMP}][\text{TFSA}]} = 188.9$ mPa·s [26]), the diffusion coefficient was estimated
 7 to be $1-2 \times 10^{-11}$ m² s⁻¹ [23]. As a result, this difference is related to the viscosity of the electrolyte,
 8 although the calculated diffusion coefficient of the extracted Pd(II) complex was larger than that of
 9 [PdBr]²⁻.

10 Furthermore, the standard rate constant k_s can be obtained using the following equation [25]:

$$E = E_s + \frac{RT}{\alpha n F} \ln \left(\frac{k_s}{D^{1/2}} \right) + \frac{RT}{\alpha n F} \ln \left\{ \frac{m^* - m(t)}{i(t)} \right\} \quad (11)$$

11
 12
 13 where E is the electrode potential, E_s is the standard reversible potential of the reaction, R is the gas
 14 constant, T is the thermodynamic temperature, α is the transfer coefficient, m is the current SI, and i is
 15 the Faradaic current. The value of αn was calculated from the slope of the E versus $\log[m^* - m(t)]/i(t)$
 16 plots, and k_s was determined from the intercept of the plots. Matsuda and Ayabe reported the following
 17 equation for irreversible reactions [27]:
 18

$$\frac{k_s}{(D\nu n F / RT)^{1/2}} < 10^{-2(1+\alpha)} \quad (12)$$

19
 20
 21 where ν is the potential scan rate. Therefore, the relation $k_s < 2.3 \times 10^{-5}$ cm s⁻¹ was obtained by
 22 substituting the values in Eq. (12). The k_s value for Eq. (11), as calculated from the intercept of the E
 23 versus $\log[m^* - m(t)]/i(t)$ plot, was 3.6×10^{-3} cm s⁻¹. Accordingly, reducing the extracted Pd(II) complex
 24 in NTAamide(C8)/AP is an irreversible process. This irreversibility of a similar platinum group
 25

1 complex, $[(R_3NH)_2IrCl_6]$ ($R = CH_3(CH_2)_7-/CH_3(CH_2)_9-$), has also been observed in our previous studies
2 [15].

4 3.3 Continuous Extraction-electrodeposition

5 It is necessary to evaluate the consecutive extraction-electrodeposition process as a repeatable
6 performance of the NTAamide(C8) extractant and AP diluent media. The results of the continuous
7 extraction-electrodeposition process are listed in **Table 2**. The volume loss for each sampling was 1.0
8 mL, and the extraction efficiency was evaluated by considering the volume loss. A high extraction
9 percentage of $E > 91\%$ was observed for all cycles. For the ED process, the current efficiency evaluated
10 from the weight of the electrodeposits was 83.1-94.6%. The recovery percentage of the electrodeposited
11 Pd metal was within the range of 86.8-95.6% for all cycles. This result indicates that the extraction-
12 electrodeposition process can be repeated five times without decomposing the NTAamide(C8)
13 extractant and the AP diluent media.

14 Moreover, a major part of the electrodeposited Pd was confirmed to be in the metallic state
15 because only a minimal amount of oxygen was detected on the surface of the electrodeposited Pd metal
16 by XPS. Depth analysis of the electrodeposited Pd was conducted using Al $K\alpha$ radiation and Ar
17 sputtering. The Pd- $3d_{5/2}$ spectrum of the middle layer under 0.5 μm of the electrodeposits is shown in
18 **Fig. 6**. Theoretically, the Pd- $3d_{5/2}$ peaks for the Pd(0) metal, Pd²⁺, and Pd⁴⁺ should be positioned at
19 335.1-335.5, 336.1-336.5, and 337.8-338.2 eV, respectively [28]. As shown in Fig. 6, the Pd- $3d_{5/2}$ peaks
20 of the electrodeposits have a binding energy of 335.1-335.5 eV, which hardly changed before and after
21 Ar etching. In addition, as shown in **Fig. 7**, the peaks of Pd(111) and Pd(200) on the electrodeposits in
22 each ED cycle were detected in the XRD profile. A series of analyses of the Pd electrodeposits enabled
23 us to conclude that most of the metallic Pd could be recovered from the loaded organic phase by SX and
24 ED processes.

1 **Conclusion**

2 Based on a slope analysis of the effect of the NTAamide(C8) concentration on SX, the extraction
3 of Pd(II) with NTAamide(C8) in three diluents, namely AP, DCE, and OC, was found to be preceded by
4 the anion exchange reaction. Moreover, the reduction reaction of the extracted Pd(II) complex is an
5 irreversible process that was investigated by cyclic voltammetry. The diffusion coefficients of the
6 extracted Pd(II) complexes were estimated to range within $1.5 \pm 0.2 - 3.7 \pm 0.1 \times 10^{-10} \text{ m}^2 \text{ s}^{-1}$ for the three
7 diluents.

8 Furthermore, the continuous extraction-electrodeposition over five cycles indicated that the
9 components of the extractant NTAamide(C8) and the AP were continuously available because the
10 extraction percentage of Pd(II) was maintained at $E > 91\%$ over the entire cycle. In addition, the high
11 current efficiency was maintained at 83.1% - 94.6%. Finally, a series of experimental results enabled us
12 to demonstrate that Pd metal can be continuously recovered by applying the extraction-
13 electrodeposition process using the NTAamide(C8)/AP system. The electrodeposits obtained from the
14 loaded organic phase were confirmed to be Pd metal by XPS and XRD analyses.

15

16 **References**

- 17 [1] Godlewska-Żyłkiewicz, B. Biosorption of platinum and palladium for their
18 separation/preconcentration prior to graphite furnace atomic absorption spectrometric determination.
19 Spectrochim. Acta Part B. **2003**, 58(8), 1531-1540. [https://doi.org/10.1016/S0584-8547\(03\)00076-4](https://doi.org/10.1016/S0584-8547(03)00076-4)
- 20 [2] Qian, J.-g.; Yin, Y.; Li, X.; Li, T.-j. Electrodeposition of iridium from composite ionic liquid. Trans.
21 Nonferrous Met. Soc. China. **2015**, 25(5), 1685-1691. [https://doi.org/10.1016/S1003-6326\(15\)63773-6](https://doi.org/10.1016/S1003-6326(15)63773-6)
- 22 [3] Yang, X.; Yang, R.; Shi, D.; Wang, S.; Chen, J.; Guo, H. Hydrophobic ionic liquids as novel
23 extractants for gold(I) recovery from alkaline cyanide solutions. J. Chem. Technol. Biotechnol. **2015**, 90,
24 1102-1109. <https://doi.org/10.1002/jctb.4418>
- 25 [4] Hubicki, Z.; Leszczyńska, M.; Łodyga, B.; Łodyga, A. Recovery of palladium(II) from chloride and
26 chloride–nitrate solutions using ion-exchange resins with S-donor atoms. Desalination. **2007**, 207(1-3),

- 1 80-86. <https://doi.org/10.1016/j.desal.2006.04.068>
- 2 [5] Shams, K.; Goodarzi, F. Improved and selective platinum recovery from spent α -alumina supported
3 catalysts using pretreated anionic ion exchange resin. *J. Hazard. Mater.* **2006**, *131(1-3)*, 229-237.
4 <https://doi.org/10.1016/j.jhazmat.2005.09.044>
- 5 [6] Uheida, A.; Zhang, Y.; Muhammed, M. Transport of palladium(II) through hollow fiber supported
6 liquid membrane facilitated by nonylthiourea. *J. Membr. Sci.* **2004**, *241(2)*, 289-295.
7 <https://doi.org/10.1016/j.memsci.2004.05.020>
- 8 [7] Soylak, M.; Tuzen, M. Coprecipitation of gold(III), palladium-(II) and lead(II) for their flame
9 atomic absorption spectrometric determinations. *J. Hazard. Mater.* **2008**, *152(2)*, 656-661.
10 <https://doi.org/10.1016/j.jhazmat.2007.07.027>
- 11 [8] Ozturk, N.; Bulut, V. N.; Duran, C.; Soylak, M. Coprecipitation of palladium(II) with 1,5-
12 diphenylcarbazite–copper(II) and determination by flame atomic absorption spectrometry. *Desalination.*
13 **2011**, *270(1-3)*, 130-134. <https://doi.org/10.1016/j.desal.2010.11.034>
- 14 [9] Senthil, K.; Akiba, U.; Fujiwara, K.; Hamada, F.; Kondo, Y. New heterocyclic dithioether ligands for
15 highly selective separation and recovery of Pd(II) from acidic leach liquors of spent automobile catalyst.
16 *Ind. Eng. Chem. Res.* **2017**, *56(4)*, 1036-1047. <https://doi.org/10.1021/acs.iecr.6b03874>
- 17 [10] Giridhar P.; Venkatesan K.A.; Srinivasan T.G.; Vasudeva Rao P.R. Extraction of fission palladium
18 by Aliquat 336 and electrochemical studies on direct recovery from ionic liquid phase. *Hydrometallurgy.*
19 **2006**, *81(1)*, 30-39. <https://doi.org/10.1016/j.hydromet.2005.10.001>
- 20 [11] Giridhar P.; Venkatesan K.A.; Reddy B.P.; Srinivasan T.G.; Vasudeva Rao P.R. Recovery of fission
21 palladium by electrodeposition using room temperature ionic liquids. *Radiochim. Acta.* **2006**, *94*, 131-
22 136. <https://doi.org/10.1524/ract.2006.94.3.131>
- 23 [12] Jayakumar M.; Venkatesan K.A.; Srinivasan T.G.; Vasudeva Rao P.R. Extractionelectrodeposition
24 (EX-EL) process for the recovery of palladium from high-level liquid waste. *J. Appl. Electrochem.*
25 **2009**, *39*, 1955-1962.
- 26 [13] Matsumiya M.; Song Y.; Tsuchida Y.; Sasaki Y. Separation of palladium by solvent extraction with
27 methylamino-bis-*N, N*-dioctylacetamide and direct electrodeposition from loaded organic phase. *Sep.*

- 1 Purif. Technol. **2020**, *234*, 115841. <https://doi.org/10.1016/j.seppur.2019.115841>
- 2 [14] Song Y.; Tsuchida Y.; Matsumiya M.; Tsunashima K. Recovery of ruthenium by solvent extraction
3 and electrodeposition using ionic liquid solution. Hydrometallurgy. **2018**, *181*, 164-168.
4 <https://doi.org/10.1016/j.hydromet.2018.09.011>
- 5 [15] Matsumiya M.; Kinoshita R.; Tsuchida Y.; Sasaki Y. Recovery of iridium by solvent extraction and
6 direct electrodeposition using phosphonium-based ionic liquids. J. Electrochem. Soc. **2021**, 168(5),
7 056501. <https://doi.org/10.1149/1945-7111/abfb34>
- 8 [16] Matsumiya M.; Song Y.; Tsuchida Y.; Ota H.; Tsunashima K. Recovery of platinum by solvent
9 extraction and direct electrodeposition using ionic liquid. Sep. Purif. Technol. **2019**, *214*, 162-167.
10 <https://doi.org/10.1016/j.seppur.2018.06.018>
- 11 [17] Sasaki Y.; Morita K.; Shimazaki S.; Tsubata Y.; Ozawa M. Masking effects for Mo, Re, Pd and Ru
12 by S and N-donor reagents through MIDOA and NTAamide extraction. Solvent Extr. Res. Dev. Jpn.
13 **2016**, *23(2)*, 161-174. <https://doi.org/10.15261/serdj.23.161>
- 14 [18] Sasaki Y.; Tsubata Y.; Kitatsuji Y.; Sugo Y.; Shirasu N.; Morita Y.; Kimura T. Extraction behavior
15 of metal ions by TODGA, DOODA, MIDOA, and NTAamide extractants from HNO₃ to *n*-dodecane.
16 Solvent Extr. Ion Exch. **2013**, *31(4)*, 401-415. <https://doi.org/10.1080/07366299.2013.800431>
- 17 [19] Sasaki Y.; Sugo Y.; Suzuki S.; Tachimori S. The novel extractants, diglycolamides, for the
18 extraction of lanthanides and actinides in HNO₃-*n*-dodecane system. Solvent Extr. Ion Exch. **2001**,
19 *19(1)*, 91-103. <https://doi.org/10.1081/SEI-100001376>
- 20 [20] Sasaki Y.; Tachimori S. Extraction of actinides(III), (IV), (V), (VI), and Lanthanides(III) by
21 structurally tailored diamides. Solvent Extr. Ion Exch. **2002**, *20(1)*, 21-34.
22 <https://doi.org/10.1081/SEI-100108822>
- 23 [21] Sasaki Y.; Kitatsuji Y.; Sugo Y.; Tsubata Y.; Kimura T.; Morita Y. Actinides extractability trends for
24 multidentate diamides and phosphine oxides. Solvent Extr. Res. Dev. Jpn. **2012**, *19*, 51-61.
25 <https://doi.org/10.15261/serdj.19.51>

- 1 [22] Handbook of Organic Solvent Properties. Ian M Smallwood. **1996**, 101-103, 149-151, 191-193.
2 <https://doi.org/10.1016/C2009-0-23646-4>
- 3 [23] Bando Y.; Katayama Y.; Miura T. Electrodeposition of palladium in a hydrophobic 1-*n*-butyl-1-
4 methylpyrrolidinium bis(trifluoromethylsulfonyl)imide room-temperature ionic liquid. *Electrochim.*
5 *Acta.* **2007**, *53(1)*, 87-91. <https://doi.org/10.1016/j.electacta.2007.02.074>
- 6 [24] Yoshii K.; Oshino Y.; Tachikawa N.; Toshima K.; Katayama Y. Electrodeposition of palladium
7 from palladium(II) acetylacetonate in an amide-type ionic liquid. *Electrochim. Commun.* **2015**, *52*, 21-
8 24. <https://doi.org/10.1016/j.elecom.2015.01.003>
- 9 [25] Myland J. C.; Oldham K. B.; Zoski C. G. The integration of cyclic voltammograms, *J. Electroanal.*
10 *Chem.* **1985**, *182(2)*, 221-234. [https://doi.org/10.1016/0368-1874\(85\)87001-5](https://doi.org/10.1016/0368-1874(85)87001-5)
- 11 [26] Sánchez-Ramírez N.; Assresahegn B. D.; Bélanger D.; Torresi R. M. A comparison among
12 viscosity, density, conductivity, and electrochemical windows of *N-n*-butyl-*N*-methylpyrrolidinium and
13 triethyl-*n*-pentylphosphonium bis(fluorosulfonylimide) ionic liquids and their analogues containing
14 bis(trifluoromethylsulfonyl) imide anion. *J. Chem. Eng. Data.* **2017**, *62*, 3437-3444.
15 <https://doi.org/10.1021/acs.jced.7b00458>
- 16 [27] Matsuda H.; Ayabe Y. Zur Theorie der Randles-Sevčičsches Kathodenstrahl-Polarographie. *Z.*
17 *Elektrochem.* **1955**, *59(6)*, 494-503. <https://doi.org/10.1002/bbpc.19550590605>
- 18 [28] Moulder J.F.; Stickle W.F.; Sobol P.E.; Bomben K.D. Handbook of X-ray photoelectron
19 spectroscopy. Perkin-Elmer Corp., Eden Prairie, MN, **1992**.
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1 **Caption of Figures**

2 **Fig. 1** Chemical structure of *N, N, N', N', N'', N''*-hexaoctyl-nitrilotriacetamide

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4 **Fig. 2** The schematic illustration of continuous extraction-electrodeposition process.

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6 **Fig. 3** (a) The dependence of [NTAamide(C8)]/[Cl⁻]² concentration and (b) The dependence of the
7 activities of HCl solution for the extraction of Pd(II) using NTAamide(C8).

8 ●: acetophenone, ●: 1,2-dichloroethane and ●: 1-octanol

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10 **Fig. 4** Cyclic voltammogram of the extracted Pd(II) complex with different organic phases.

11 (a) acetophenone, (b) 1,2-dichloroethane and (c) 1-octanol.

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13 **Fig. 5** Semi-integral of the voltammogram for the extracted Pd(II) complex in organic phase.

14 (a) acetophenone, (b) 1,2-dichloroethane and (c) 1-octanol.

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16 **Fig. 6** XPS analysis of the electrodeposits at -0.25 μm thickness on the NTAamide(C8)/AP system.

17 (a) 1st time, (b) 2nd time, (c) 3rd time, (d) 4th time and (e) 5th time

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19 **Fig. 7** XRD profile of the electrodeposits on the NTAamide(C8)/AP system.

20 (a) 1st time, (b) 2nd time, (c) 3rd time, (d) 4th time and (e) 5th time

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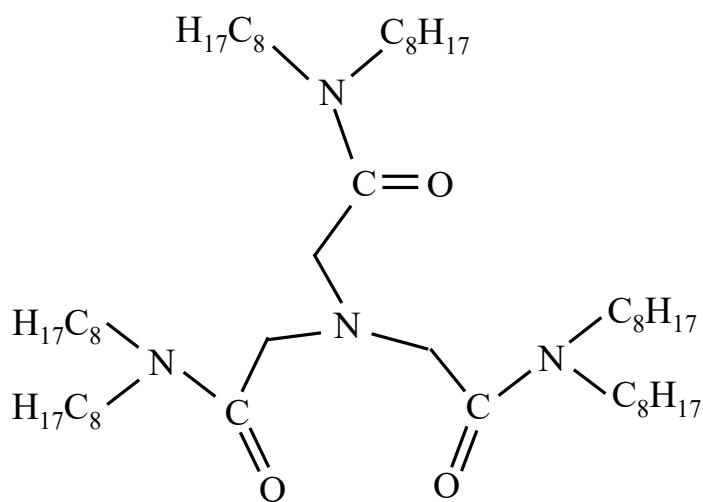
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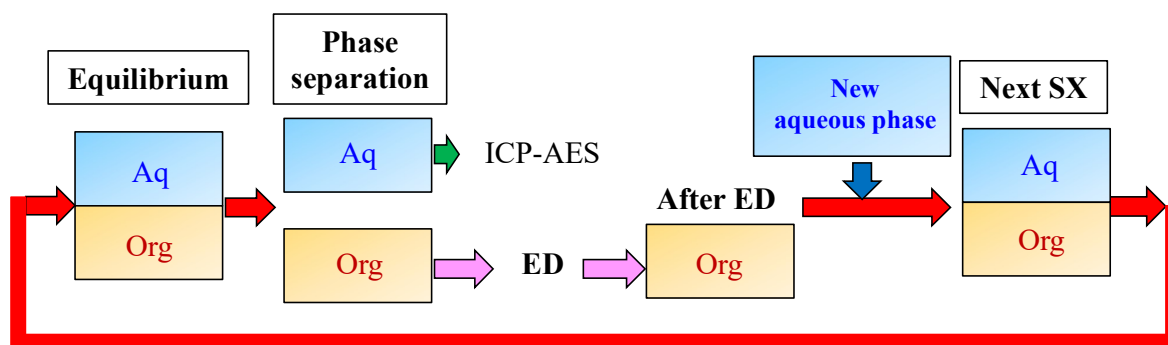
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Fig. 1



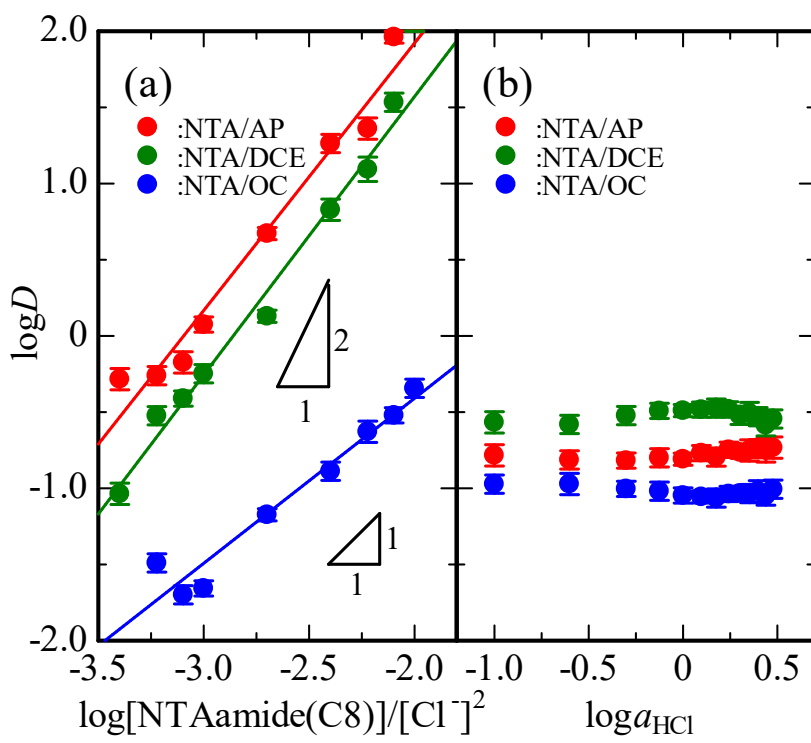
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Fig. 2



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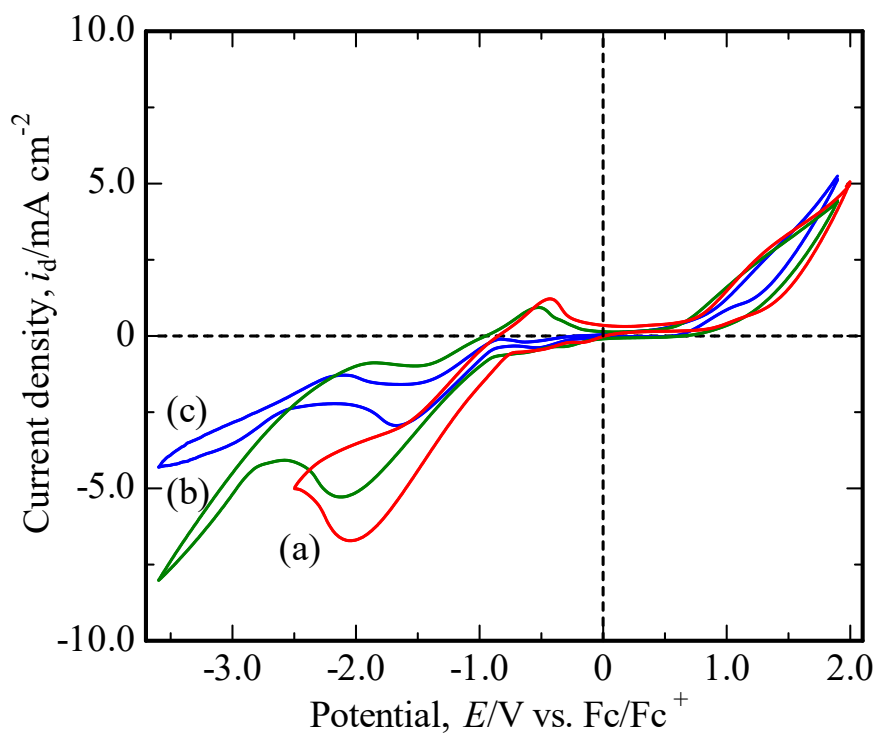
Fig. 3



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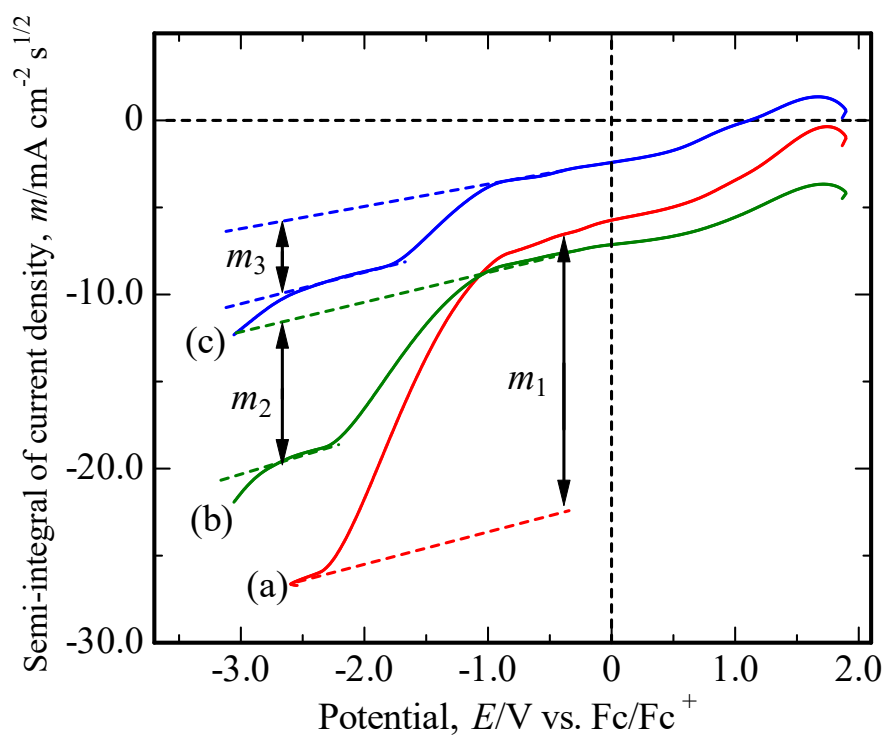
Fig. 4



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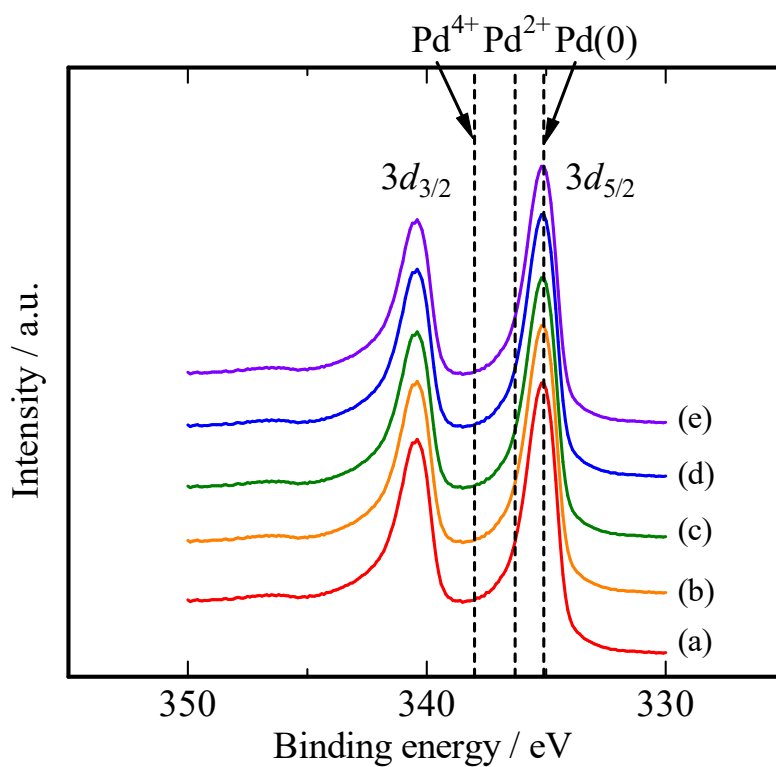
Fig. 5



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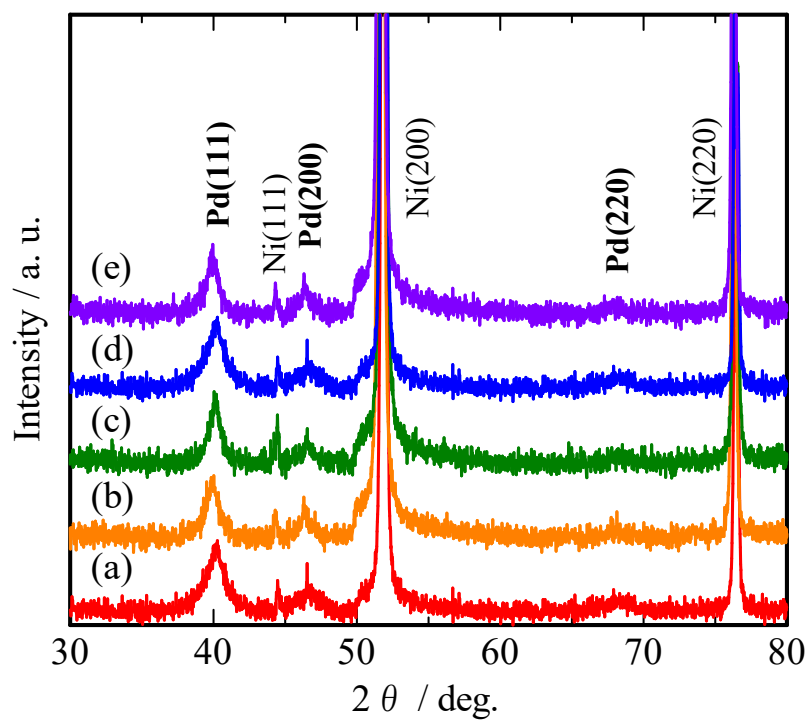
Fig. 6



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Fig. 7



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Table 1 The extraction percentage and the cumulative concentration of Pd(II) in the organic phase for five continuous solvent extraction (SX).

No. of SX	acetophenone		1,2-dichloroethane		1-octanol	
	<i>E</i> /(%)	<i>C</i> _{Pd(II)} /mM	<i>E</i> /(%)	<i>C</i> _{Pd(II)} /mM	<i>E</i> /(%)	<i>C</i> _{Pd(II)} /mM
1 st	100±0.2	28.2	100±0.1	28.2	88±0.5	24.7
2 nd	95±0.3	54.9	89±0.3	53.2	52±0.4	39.2
3 rd	76±0.7	76.4	48±0.5	66.8	33±0.3	48.6
4 th	47±0.6	89.6	41±0.6	78.3	28±0.5	56.4
5 th	31±0.5	98.5	29±0.4	86.4	18±0.2	61.4

E: Extraction percentage on SX, *C*_{Pd(II)}: Concentration of the extracted Pd(II) complex on SX.

Table 2 A series of recovery results of Pd metal for continuous solvent extraction and electrodeposition process for five cycles.

E: Extraction percentage on solvent extraction (SX), w_{SX} : Weight of extracted Pd metal on SX, w_{res} : Weight of residual Pd in electrolyte after electrodeposition, w_{total} : Total weight of Pd metal in electrolyte ($w_{total}=w_{SX}+w_{res}$), w_{dep} : Weight of the electrodeposited Pd metal, Q : Transported charge on electrodeposition, w_{th} : Theoretical weight of Pd metal calculated from transported charge, ε : current efficiency ($\varepsilon=w_{dep}/w_{th}\times 100$), R : recovery yield ($R=w_{dep}/w_{total}\times 100$)

No.	<i>E</i>	w_{SX}	w_{res}	w_{total}	w_{dep}	Q	w_{th}	ε	R
	/%	/mg	/mg	/mg	/mg	/C	/mg	/%	/%
1 st	98±0.3	9.09	0.00	9.09	8.4	16.1	8.85	94.6	92.4
2 nd	91±0.7	7.64	0.63	8.26	7.9	16.6	9.15	86.3	95.6
3 rd	94±0.6	7.07	0.32	7.39	6.6	14.4	7.94	83.1	89.3
4 th	96±0.4	6.33	0.70	7.03	6.1	12.6	6.95	87.8	86.8
5 th	96±0.5	5.48	0.80	6.29	5.8	11.2	6.18	93.9	92.3