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Electrodeposition behavior of extracted platinum complex in phosphonium-based ionic liquids
evaluated by electrochemical quartz crystal microbalance

Masahiko MATSUMIYA^{a*}, Yusuke TSUCHIDA^a, Ryoma KINOSHITA^a and Yuji SASAKI^b

^a Graduate School of Environment and Information Sciences, Yokohama National University,
79-2 Tokiwadai, Hodogaya-ku, Yokohama 240-8501, Japan

^b Nuclear Science and Engineering Directorate, Japan Atomic Energy Agency,
Tokai-mura, Naka-gun, Ibaraki, 319-1195, Japan

* Corresponding author
E-mail address: matsumiya-masahiko-dh@ynu.ac.jp
Tel : +81-45-339-3464

1 **ABSTRACT**

2 It is important to develop solvent extraction and electrodeposition processes for platinum group metals in order
3 to reduce the volume of secondary wastes. In this study, the electrodeposition behavior of the extracted Pt(IV)
4 complex in a phosphonium-based ionic liquid (IL) was investigated by using an electrochemical quartz crystal
5 microbalance (EQCM). The charge transfer reaction $\text{Pt(IV)}+2\text{e}^{-}\rightarrow\text{Pt(II)}$ was observed at -0.53 V. The significant
6 increase in the mass change (Δm) and the apparent molar mass (M_{app}) of 193.7, as evaluated by the EQCM, confirmed
7 that the electrodeposition reaction $\text{Pt(II)}+2\text{e}^{-}\rightarrow\text{Pt(0)}$ proceeded at -1.65 V in this system. Moreover, consecutive
8 solvent extraction and electrodeposition of Pt metal in Alamine336/IL system were performed at 10 cycles. High
9 extraction percentage ($E>95.1\%$) and good current efficiency ($\epsilon>85.8\%$) were maintained in the first to sixth cycles.
10 The XPS Pt-4f_{7/2} spectrum confirmed that all the electrodeposits were in the metallic state.

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12 **Keywords:** Electrodeposition, EQCM, Platinum, Solvent extraction

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1 1. Introduction

2 Pt is widely applied as three-way catalyst in automobiles and is an important member of platinum group metals
3 (PGMs). However, a modern separation process for the purification of Pt has not yet been developed and is an
4 important issue for the future. A hydrometallurgical process for the extraction PGMs from chloride media has
5 reported by many researchers [1-6]. Most of the past studies focused on the extraction behavior and extraction species.
6 Solvent extraction using ionic liquids (ILs) was reported as a promising strategy for nuclear fuel cycles [7]. There
7 have been recent applications aimed at the recovery of Cu[8], Sr[9], Pd[10-12], Cs[9], U[13] by a combination of
8 solvent extraction and direct electrodeposition, which constitutes an advanced strategy. From the standpoint of
9 recovery, this combination method has several advantages such as simple construction, less secondary waste, and
10 easy handling. We demonstrated the recovery of In[14], Fe[15], and Ru[16] by the combination of solvent extraction
11 and direct electrodeposition using phosphonium-based ILs. However, the recovery of Pt metal by the extraction-
12 electrodeposition method has not been reported so far.

13 As a fundamental electrochemical analysis, we previously investigated the electrochemical behavior of the
14 extracted Pt(IV)-tri-*n*-octylamine (TOA) complex in phosphonium-based ILs by using an electrochemical quartz
15 microbalance (EQCM). In this case, the electrodeposition reaction of Pt(II)/Pt(0) was observed in the ILs, but the
16 occurrence of the charge transfer reaction of Pt(IV)/Pt(II) could not be confirmed from the EQCM results. Moreover,
17 there was no clear electrodeposition peak in the voltammogram for the extracted Pd(II)-TOA complex [10-12]. The
18 reduction peak is usually observed based on the appropriate diffusion-controlled process. However, when the
19 electrodeposition of the extracted metal complex is not obeyed on the diffusion-controlled process, the unclear peak
20 shape would be generated in the voltammogram. Otherwise, the reduction peak is also related with the concentration
21 of the electroactive species. In the case of the inappropriate concentration of the extracted metal complex, the peak
22 shape would be involved in the voltammogram.

23 Thus, the electrochemical behavior of the extracted Pt complex in the IL has not been sufficiently clarified till
24 date. In this study, Alamine336 (trioctyl/decyl amine, R₃N, where R = CH₃(CH₂)₇-/CH₃(CH₂)₉-, A336) was selected
25 as the extractant for [PtCl₆²⁻], because of its high extractability of [PtCl₆²⁻]. Then, A336 typically can react with a
26 variety of inorganic and organic acids to form amine salts, which are capable of undergoing ion exchange reactions
27 with a host of other anions. Therefore, the extracted Pt(IV)-Alamine336 complex was investigated by EQCM analysis
28 at an elevated temperature. The feasibility of the extractant and IL bath was evaluated based on continuous solvent

1 extraction and electrodeposition of Pt metal on the A336/IL system. Furthermore, the extraction percentage on solvent
2 extraction process, the current efficient on electrodeposition process and the total recovery yield on the combined
3 processes were estimated in this study.

4 5 **2. Experimental**

6 **2.1 Sample preparation**

7 Triethylpentylphosphonium bis(trifluoromethyl)sulfonylamide; [P₂₂₂₅][NTf₂] was synthesized by the metathesis
8 reaction of [P₂₂₂₅][Br] (Nippon Chemical Industry Co., Ltd., >99.5%) and [Li][NTf₂] (Kanto Chemical Co., Ltd.,
9 99.7%) [17]. [P₂₂₂₅][Br] was reacted with [Li][NTf₂] in distilled water, which was heated up to 373 K. The phase-
10 separated [P₂₂₂₅][NTf₂] against the aqueous phase was washed with distilled water at least five times to remove the
11 halogen component. A small amount of dichloromethane was added to the IL phase for reducing the viscosity and
12 improving the stirring efficiency. The removal of halogens after washing was confirmed by the dropwise addition of
13 silver nitrate. A white precipitate of the Ag halide salt would be detected if there are residual halogens in the system.
14 The synthesized [P₂₂₂₅][NTf₂] was heated up to 423 K on a hot plate to remove water and dichloromethane, and the
15 residual water was removed by vacuum drying with stirring at 383 K for more than 12 h.

16 17 **2.2 Solvent extraction**

18 Alamine336 (trioctyl/decyl amine, R₃N, where R = CH₃(CH₂)₇-/CH₃(CH₂)₉-, A336) is a C8–C10 saturated
19 straight-chain tertiary amine mixture, and the pale yellow extractant is insoluble in water (<5 mg L⁻¹). A336 had an
20 average molecular weight of 392 g mol⁻¹, density of 0.81 g cm⁻³, and viscosity of 11 mPa·s at 303 K. The aqueous
21 phase of the [PtCl₆²⁻] sample was prepared from the platinum standard solution (FUJIFILM Wako Pure Chemical
22 Corp.). The aqueous phase was a 0.5, 1.0, or 1.5 M HCl solution containing 5.0 × 10⁻³ M of [PtCl₆²⁻]_{aq}. The
23 concentration of A336 in the IL phase was varied from 4.0 × 10⁻³ to 3.0 × 10⁻² M while fixing the aqueous phase. The
24 IL phase contained [P₂₂₂₅][NTf₂] as a diluent, and the extraction experiments were carried out at 298 K. The volume
25 ratio of the IL to the aqueous phase was 1.0. Stirring during the extraction procedure was effected by a direct mixer
26 at 2000 rpm for 5 min. The extraction behavior of Pt(IV) as a function of the A336 concentration was studied to
27 determine the stoichiometry of the extracted metal complex. After equilibration, the concentrations of the four
28 metallic species in the aqueous phase were measured by inductively coupled plasma-atomic emission spectroscopy

1 (ICP-AES, ICPE-9000, Shimadzu Co.). The distribution ratio (D) and extraction efficiency (E) were calculated from
2 the ICP-AES quantitative data, as follows.

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

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6 where “aq” is the aqueous phase, “IL” is the IL phase, $[M]$ is the concentration of each metal ion, and V is the
7 volume. The superscripts “ini” and “fin” represent the initial and final concentrations, respectively. The dependence
8 of the extraction efficiency on the A336 concentration was evaluated for each D value to investigate the mechanism
9 of extraction of Pt(IV) in the A336/[P₂₂₂₅][NTf₂] system.

11 2.3 Electrochemical measurement

12 The resonance frequency and resistance of an AT-cut Pt-coated quartz oscillator [9MHz, $\phi = 5.0$ mm, Seiko
13 EG&G, QA-A9M-PT(P)] were measured using an EQCM system (Seiko EG&G, QCA922) with a well-type cell.
14 The temperature of the EQCM system was elevated using a heating mantle (P10-2, Tokyo Glass Instruments Co.,
15 Ltd.,) controlled by a thermostat with a PID controller. In order to reduce the thermal gradient, a thick layer of
16 insulator was placed between the EQCM cell and the heating mantle. The applicability of the EQCM technique at
17 elevated temperatures was demonstrated in our previous study [18]. Normally, the adapter cable (QCA922-10,
18 SEIKO EG&G) is connected directly to the EQCM cell. An extension cord (QCA922-10-EX10, SEIKO EG&G) was
19 used to connect the heating mantle in this measurement system. Voltammetric measurements were carried out using
20 an electrochemical analyzer (ALS-440A, BAS Inc.) with a Pt-coated quartz oscillator in the EQCM system as a
21 working electrode. The surface area of the QCM crystal was 1.96×10^{-5} m². Two Pt wires (No. 002233, BAS Inc.)
22 with an inside diameter of 0.5 mm were used as the counter electrode and quasi-reference electrode (QRE). The
23 counter electrode was surrounded by a Vycor glass filter at the bottom to prevent diffusion of the decomposition
24 components from the anode into electrolyte. The Pt QRE showed high stability and good reproducibility of the
25 potential at elevated temperatures. All potentials are referenced for the IL standard using a ferrocene (Fc)/ferrocenium
26 (Fc⁺) redox couple. The electrochemical behavior of the extracted Pt(IV) complex, [R₃NH]₂[PtCl₆], R = CH₃(CH₂)₇-
27 /CH₃(CH₂)₉- was investigated at 373 K under Ar flow at a sweep rate of 10 mV s⁻¹. All the media to be used were

1 vacuum-treated under reduced pressure and controlled so that the moisture content was less than 50 ppm in the case
2 of a liquid, as measured using a Karl Fischer moisture titrator (MKC-610-NT/ADP-611, Kyoto Electronics
3 Manufacturing Co., Ltd.). The resonance frequency change: Δf , the weight change of the surface of the electrode: Δm
4 and the resonance resistance: ΔR can be evaluated in situ conditions during CV/EQCM. Preliminary, the Δf and ΔR
5 values for $[P_{2225}][NTf_2]$, A336/ $[P_{2225}][NTf_2]$, and $[R_3NH]_2[PtCl_6]_{IL}$ in A336/ $[P_{2225}][NTf_2]$ were measured. The
6 electromechanical coupling constant k was observed to be 2.2 ± 0.4 for the single-IL system and the A336/IL media
7 including the extractant, indicating that this type of IL media can be treated as a Newton's fluid. Then, the
8 electrodeposition behavior of the extracted Pt(IV) complex was evaluated from the expression $M_{app}=(\Delta m/\Delta Q)\times F$.
9 The theoretical value of M_{app} based on the reaction $Pt(II)+2e^- \rightarrow Pt(0)$ was 195.8.

11 2.4 Consecutive solvent extraction and electrodeposition

12 A336/ $[P_{2225}][NTf_2]$ was selected as a continuous electrodeposition medium for the solvent extraction and
13 electrodeposition process in order to evaluate the repeatability of the extractant and IL bath. For solvent extraction, a
14 metal concentration 10-fold higher than that used in the EQCM evaluation, i.e., 5.0×10^{-2} M $[PtCl_6^{2-}]$, was employed
15 in the aqueous phase to increase the metal concentration in the IL bath. The volume ratio of the IL to the aqueous
16 phase was maintained at 3.0. Thus, the high volume ratio led to enrich the extracted Pt complex in the IL phase. Then,
17 the electrodeposition of Pt metal from the Pt(IV) complexes extracted in the A336/ $[P_{2225}][NTf_2]$ system was carried
18 out using a three-electrode system in a cylinder cell under an Ar atmosphere. A Cu substrate (99.96%, Nilaco Corp.)
19 was used as the working electrode. A platinum wire with an inner diameter of 0.5 mm was used as the QRE. The
20 counter electrode was separated by a soda lime tube with a Vycor glass filter at the bottom to prevent diffusion of the
21 decomposition products from the anode to the electrolyte. In the case of electrodeposition at a constant overpotential,
22 the overpotential applied to the cathode was -2.0 V vs. Fc/Fc⁺. After electrodeposition, all the electrodes were
23 removed from the electrodeposition bath and replaced with new electrodes. The IL bath was repeatedly used for the
24 next stage of solvent extraction. For the n^{th} ($n = 2-10$) solvent extraction, a new aqueous phase containing 5.0×10^{-2}
25 M $[PtCl_6^{2-}]$ was introduced into the IL phase. After the n^{th} ($n = 2-10$) solvent extraction, the same overpotential was
26 induced for the electrodeposition at n -th time. The solvent extraction and electrodeposition processes were repeated
27 for 10 cycles. After the 10th successive extraction-and-electrodeposition procedure, the metal concentration of the IL
28 phase in each cycle was determined by ICP-AES. The current efficiency was calculated from the weight increase of

1 the Cu substrate during each electrodeposition. The metallic state of Pt in the electrodeposits was evaluated by XPS
 2 (Quantera SXM, ULVAC-PHI, Inc.) to investigate the chemical bonding state and the ratio of each element. The
 3 detection angle from the sample surface was set to 45°. The sample on the substrate was analyzed with etching by
 4 using an Ar ion beam. The crystalline state of the metallic Pt was investigated by XRD (SmartLab Rigaku Corp.).

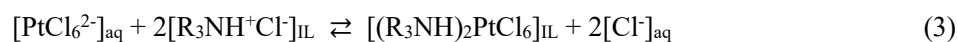
6 3 Results and discussion

7 3.1 Solvent extraction

8 This type of extractant is first protonated in the acidic medium, and the protonated extractant undergoes an
 9 anion-exchange reaction with the Pt(IV) metal anion. Thus, the extraction mechanism for Pt(IV) with A336 can be
 10 expressed as follows. At first, the Alamine336 extractant is protonated with HCl.



14 The extraction of Pt(IV) by A336 from HCl medium is represented by the anion exchange reaction, as follows.



18 The extraction equilibrium constant ($K_{Pt(IV)}$) and distribution ratio ($D_{Pt(IV)}$) are expressed as follows.

$$20 \quad K_{Pt(IV)} = \frac{[(R_3NH)_2PtCl_6]_{IL} [Cl^-]_{aq}^2}{[PtCl_6^{2-}]_{aq} [R_3NH^+Cl^-]_{IL}^2}, \quad D_{Pt(IV)} = \frac{[(R_3NH)_2PtCl_6]_{IL}}{[PtCl_6^{2-}]_{aq}} \quad (4)$$

22 The following relationship is obtained from Eq. (4).

$$24 \quad K_{Pt(IV)} = \frac{D_{Pt(IV)}}{([R_3NH^+Cl^-]_{IL} / [Cl^-]_{aq})} \quad (5)$$

26 The logarithm of $D_{Pt(IV)}$ is expressed as follows, according to the relation in Eq. (5):

$$\log D_{\text{Pt(IV)}} = \log K_{\text{Pt(IV)}} + 2\log\left(\frac{[\text{R}_3\text{NH}^+\text{Cl}^-]_{\text{IL}}}{[\text{Cl}^-]_{\text{aq}}}\right) \quad (6)$$

The plot of $\log D_{\text{Pt(IV)}}$ against $\log\left(\frac{[\text{R}_3\text{NH}^+\text{Cl}^-]_{\text{IL}}}{[\text{Cl}^-]_{\text{aq}}}\right)$ showed a linear relationship with a slope of about 2. This trend indicated that the stoichiometry of the extractant and $[\text{PtCl}_6^{2-}]_{\text{aq}}$ was 2:1, which was consistent with the extracted Pt-TOA complex [19]. Then, the intercept of the plot of $\log D_{\text{Pt(IV)}}$ vs. $\log\left(\frac{[\text{R}_3\text{NH}^+\text{Cl}^-]_{\text{IL}}}{[\text{Cl}^-]_{\text{aq}}}\right)$ can be used to calculate the equilibrium constant ($\log K_{\text{ex}}$). Thus, the equilibrium constant for A336/[P2225][NTf₂] extraction was estimated as $\log K_{\text{Pt(IV)}}=5.26$ in 0.5–1.5 M HCl solutions. The value of $\log K_{\text{ex}}$ for ternary amines is high (3.08–6.78) [20], and it is consistent with this experimental result. The high dielectric constant of ILs ($\epsilon_r = 10\text{--}12$) [21] allows for the easy extraction of acidified A336 complexes from the aqueous phase.

3.2 Electrochemical measurements

A frequency shift (Δf) in the EQCM analysis includes effects related to the mass change (Δm) in the quartz crystal electrode as well as the viscosity (η) and density (ρ) of the liquid adjacent to the quartz. The relationship among these factors were expressed as follows [22].

$$\Delta f = \Delta f_m + \Delta f_{\eta\rho} \quad (7)$$

$$\Delta f_m = -\frac{2f_0^2 \Delta m}{A(\mu_q \rho_q)^{1/2}}, \quad \Delta f_{\eta\rho} = -f_0^{3/2} \sqrt{\frac{\Delta\eta\rho}{\pi\mu_q \rho_q}} \quad (8)$$

Here, f_0 is the fundamental resonance frequency, A is the surface area of the electrode (0.196 cm²), μ_q is the shear modulus of quartz (2.95×10^{10} kg m⁻¹ s⁻²) and ρ_q is the density of quartz (2.65×10^3 kg m⁻³). The value of $(\eta\rho)^{1/2}$ was also estimated from the resonance resistance (R) [23].

$$\Delta R = \frac{A(2\pi f_0 \Delta\eta\rho)^{1/2}}{k^2} \quad (9)$$

Δf_m can be determined from the measured frequency shift (Δf) using Eq. (8). The electromechanical coupling factor (k) was estimated from the shift in the resonance according to the above equations.

1 The CV/EQCM results for A336/[P₂₂₂₅][NTf₂] without the Pt(IV) complex are shown in **Fig. 1**. The anodic and
2 cathodic limits were observed in the voltammogram. Then, from the almost constant value of Δm under the potential
3 from -3.1 V to +2.2 V, there was essentially unchanged in weight on the electrode interface. Since $\Delta\eta\rho$ was almost
4 unchanged, there was no change in the density or viscosity of locally IL near the electrode interface. This result
5 indicated that the extractant Alamine336 was not involved in the electrochemical degradation in both the cathodic
6 and anodic regions. On the other hand, the electrochemical behavior in [P₂₂₂₅][NTf₂] containing the extracted Pt(IV)
7 complex was different. The CV/EQCM results for A336/[P₂₂₂₅][NTf₂] including the extracted Pt(IV) complex are
8 shown in **Fig. 2**. For the Pt(IV) extracted complex, a small peak was observed at -0.53 V in voltammogram. The
9 current value of the extracted Pt(IV) complex was almost equal to Δm , indicating that the reaction was a Pt(IV)/Pt(II)
10 charge transfer reaction. The most significant peak was clearly observed at -1.65 V, where a drastic increase in Δm
11 and the apparent molar mass ($M_{app} = 193.7$) were observed in **Fig. 2(b)**. These results indicated that the
12 electrodeposition reaction of the Pt(II)/Pt(0) couple occurred on the electrode surface. **The similar electrodeposition**
13 **behaviors were observed on the electrolyte after 3rd and 5th electrodeposition as shown in the dotted and the chain**
14 **lines in Fig. 2(b)**. A similar behavior of Δm during electrodeposition was observed in the EQCM analysis of
15 Ag(I)/Ag(0) [24]. The decrease in $\Delta\eta\rho$ over the potential region 0 to -1.65 V might be related to a local decrease in
16 the concentration of Pt(II) in the A336/[P₂₂₂₅][NTf₂] system near the electrode interface. **The similar decrease in $\Delta\eta\rho$**
17 **were observed on the electrolyte after 3rd and 5th electrodeposition considering from the dotted and the chain lines in**
18 **Fig. 2(c)**. On the other hand, two peaks at -0.95 V and -0.19 V were also observed in the anodic region. The change
19 in Δm from -0.95 V to -0.19 V corresponded to $M_{app} = 185.8$, suggesting the dissolution reaction of Pt(0)/Pt(II). In a
20 previous study, the electrochemical behavior of the extracted [R₃NH]₂[PtCl₆], R = (CH₂)₇CH₃ species using tri-*n*-
21 octylamine (TOA) [19] was investigated by the EQCM method. In this case, the reduction behavior of Pt(II)/Pt(0)
22 was not clearly observed during the EQCM analysis. This anodic behavior might be due to the lower extraction
23 capacity of TOA. In this case, a higher extracted metal complex loading on the IL phase using Alamine336 might be
24 necessary for detecting clearer peaks in the voltammogram.

25

26 3.3 Continuous solvent extraction and electrodeposition

27 It is necessary to evaluate the consecutive solvent extraction and electrodeposition process as repeatable
28 performance of Alamine336 extractant and [P₂₂₂₅][NTf₂] diluent media. The results of the continuous solvent

1 extraction and electrodeposition process is summarized in **Table 1**. The volume loss for each sampling was 1.0 mL,
2 and the extraction efficiency was evaluated by considering the volume loss. A high extraction percentage of $E >$
3 88.0% was exhibited on the whole cycles, and the extracted Pt concentration reached 13.5–15.3 mM on each
4 extraction process. This result indicated that the extraction and subsequent electrodeposition process can be repeated
5 at least 10 times without decomposition of the Alamine336 extractant and the $[P_{2225}][NTf_2]$ diluent media. In addition,
6 the current efficiency evaluated from the weight of electrodeposits was 85.8-91.9% in the 1st to 6th cycles of the
7 electrodeposition process. Then, the recovery percentage of the electrodeposited Pt metal was within the range of
8 75.1-90.4% on 1st-6th cycles. This result indicates that the electrodeposition reaction of the extracted Pt(IV) species
9 was smoothly occurred in the $[P_{2225}][NTf_2]$ electrolyte. The trend in the amount of Pt metal recovered from the solvent
10 extraction and electrodeposition in each cycle is shown in **Fig. 3**. The amount of Pt metal extracted on solvent
11 extraction was similar amount of the recovered Pt metal on electrodeposition and residual Pt metal after
12 electrodeposition. This result indicates that the mass balance between the solvent extraction and electrodeposition
13 procedures is approximately consistent.

14 Moreover, a major part of the electrodeposited Pt was confirmed to be in the metallic state, because only a very
15 small amount of oxygen was detected on the surface of the electrodeposited Pt metal by EDX mapping. The results
16 of EDX analysis also showed that high-purity Pt element was electrodeposited at 94%, although a small amount of
17 anionic component (S) was detected. Depth analysis of the electrodeposited Pt was conducted by XPS with Al-K α
18 radiation. XPS analysis of the inner part of the electrodeposits was performed by Ar sputtering. The Pt-4f_{7/2} spectrum
19 of the middle layer (under 0.5 μ m) of the electrodeposits is shown in **Fig. 4**. Theoretically, the Pt-4f_{7/2} peaks for the
20 Pt(0) metal, Pt²⁺, and Pt⁴⁺ should be positioned at 71.2, 73.5, and 75.5 eV, respectively [25]. As shown in Fig. 4, the
21 Pt-4f_{7/2} peaks of the electrodeposits have a binding energy of 71.0–71.2 eV, which hardly changed before and after
22 Ar etching. In addition, the peak due to Pt(200) on the electrodeposits in each electrodeposition cycle was detected
23 in the XRD profile, as shown in **Fig. 5**. The abovementioned series of analyses of the Pt electrodeposits enabled us
24 to conclude that most of the metallic Pt can be recovered from a phosphonium-based IL by our extraction-and-
25 electrodeposition process.

26 27 **4. Conclusion**

28 In the present study, the extracted Pt(IV); $[R_3NH]_2[PtCl_6]$, R=CH₃(CH₂)₇-/CH₃(CH₂)₉- was recovered from

1 phosphonium-based ILs, [P₂₂₂₅][NTf₂], by solvent extraction. Slopes analysis during the solvent extraction revealed
2 that the extracted Pt(IV) complex formed a 1:2 complex with amine hydrochloride in the Alamine336/[P₂₂₂₅][NTf₂]
3 system as follows, indicating that it proceeded in the extraction equilibrium by the anion extraction mechanism;
4 $[\text{PtCl}_6^{2-}]_{\text{aq}} + 2[\text{R}_3\text{NH}^+\text{Cl}^-]_{\text{IL}} \rightleftharpoons [\text{R}_3\text{NH}]_2[\text{PtCl}_6]_{\text{IL}} + 2[\text{Cl}^-]_{\text{aq}}$.

5 CV/EQCM analysis of Alamine336/[P₂₂₂₅][NTf₂] without the extracted Pt(IV) complex indicated that
6 Alamine336 did not participate in the electrochemical degradation. CV/EQCM analysis of the extracted Pt(IV)
7 complex showed that the reduction behavior of the extracted Pt(IV) complex proceeded in two steps: Pt(II)
8 [Pt(IV)+2e⁻→Pt(II), Pt(II)+2e⁻→Pt(0)]. The objective electrodeposition Pt(II)/Pt(0) was confirmed at -1.65 V,
9 because a clear cathodic peak was observed and the apparent molar mass (*M*_{app}) was calculated to be 193.7.
10 Furthermore, the continuous extraction-electrodeposition in 10 cycles indicated that the components of the extractant
11 Alamine336 and the [P₂₂₂₅][NTf₂] IL were continuously available, because the extraction percentage of Pt(IV) was
12 maintained at E > 88.0% in the 1st to 10th cycles. In addition, the current efficiency was maintained at a high level
13 (85.8% to 91.9%) in the 1st to 6th cycles of the electrodeposition process. It was effective to continuously applied on
14 extraction-cum-electrodeposition process, because the recovery yield of Pt metal can lead to a good performance
15 (75.1% to 90.4%) on 1st-6th cycles. The experimental results led us to conclude that Pt metal can be continuously
16 recovered by applying the combined solvent extraction and electrodeposition process using the Alamine336/
17 [P₂₂₂₅][NTf₂] system.

18 **Acknowledgments**

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Table 1 A series of results of Pt for solvent extraction and electrodeposition at ten cycles.

No.	<i>E</i>	<i>w_{SX}</i>	<i>w_{res}</i>	<i>w_{total}</i>	<i>w_{dep}</i>	<i>Q</i>	<i>w_{th}</i>	ε	<i>R</i>
	/%	/mg	/mg	/mg	/mg	/C	/mg	/%	/%
1st	99.2	8.63	0.00	8.63	7.8	16.8	8.49	91.9	90.4
2nd	97.1	7.57	0.79	8.36	7.2	15.9	8.04	89.6	86.1
3rd	97.1	6.41	0.98	7.39	6.1	13.4	6.77	90.1	82.5
4th	97.8	6.16	1.24	7.40	5.7	12.6	6.37	89.5	77.0
5th	95.1	5.70	1.62	7.32	5.5	12.2	6.17	89.2	75.1
6th	96.0	4.89	1.55	6.44	4.9	11.3	5.71	85.8	76.1
7th	94.0	3.95	1.27	5.22	3.8	10.2	5.16	73.7	72.8
8th	91.0	3.27	1.26	4.53	3.3	8.3	4.20	78.7	72.8
9th	89.1	2.67	1.03	3.70	2.7	7.2	3.64	74.2	73.0
10th	88.0	2.37	0.95	3.32	2.4	6.5	3.29	73.0	72.3

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

1 **Captions of Figures**

2 **Fig. 1** CV/EQCM results of A336/[P₂₂₂₅][NTf₂] without Pt(IV) complex at 373 K. The initial potential was 0 V vs.
3 Pt Q.R.E., and the initial scan direction is cathodic. (a) voltammogram, (b) Δm and (c) $\Delta\eta\rho$

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5 **Fig. 2** CV/EQCM results for A336/[P₂₂₂₅][NTf₂] at 373K containing the extracted Pt(IV) complexes. The initial
6 potential was 0 V vs. Pt Q.R.E. (a) voltammogram, (b) Δm and (c) $\Delta\eta\rho$

7 **Solid line: 1st electrodeposition, dotted line: 3rd electrodeposition, chain line: 5th electrodeposition**

8

9 **Fig. 3** The recovered weight of Pt metal by extraction-sum-electrodeposition process.

10 SX: The recovered weight of Pt metal by solvent extraction,

11 Dep: The recovered weight of Pt metal by electrodeposition,

12 Res: The weight of residual Pt metal in the electrolyte after electrodeposition.

13

14 **Fig. 4** Pt-4f_{5/2} and 4f_{7/2} spectra of 10th electrodeposits by XPS,

15 (a) 2nd (b) 4th, (c) 6th, (d) 8th and (e) 10th cycles.

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17 **Fig. 5** XRD profile of the electrodeposits after electrodeposition on each cycle.

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Fig. 1

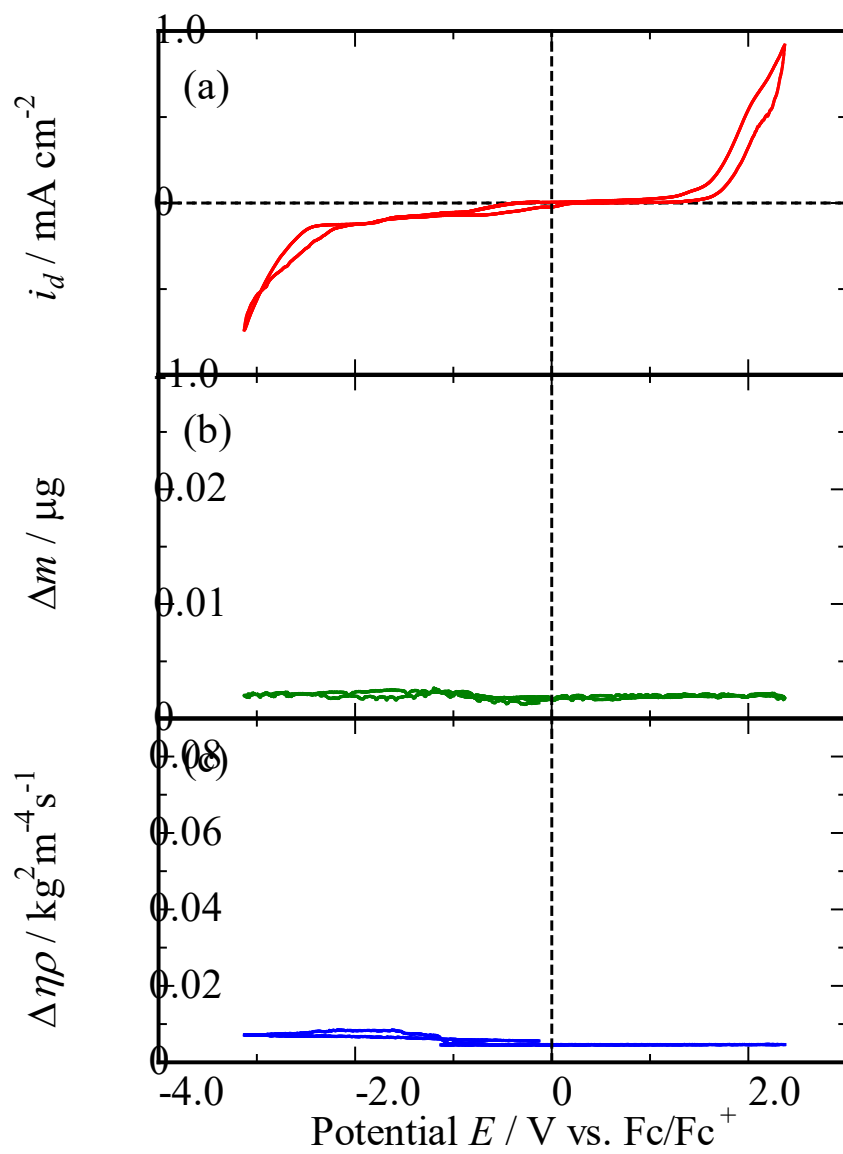


Fig. 2

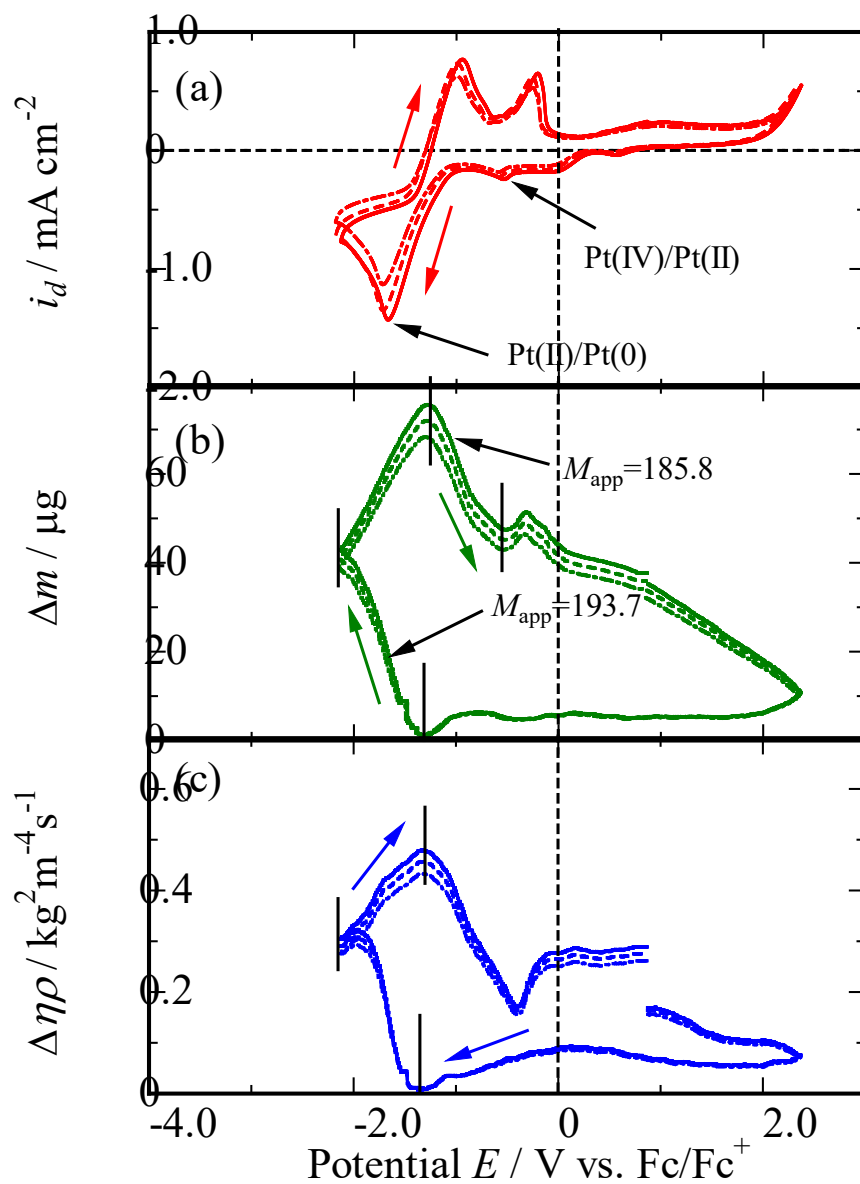


Fig. 3

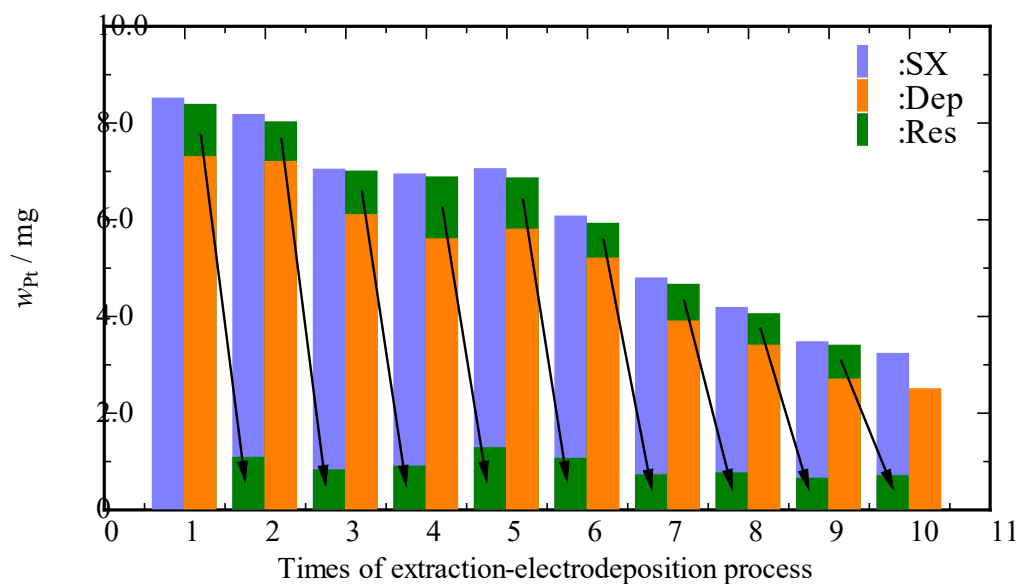


Fig. 4

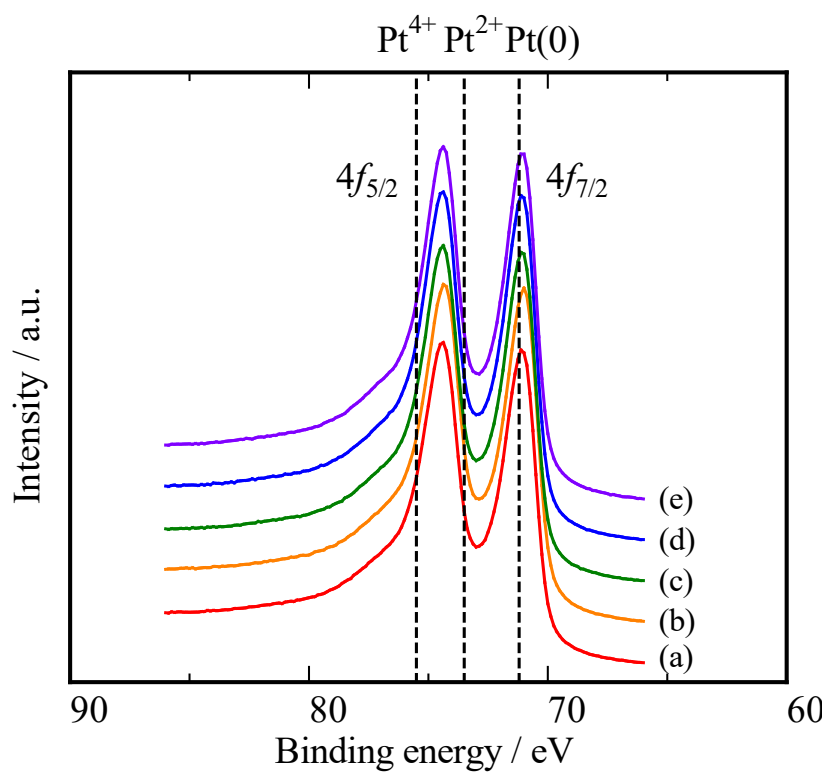


Fig. 5

