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Abstract

It is important to recover Ru metal from spent target materials including Pt, Co and Cr. The extraction behavior using Di-(2-ethylhexyl)phosphoric acid (HDEHP) and ionic liquid (IL), triethyl-n-pentyl phosphonium bis(trifluoromethyl-sulfonyl)amide ; [P2225][TFSA] diluent was investigated with pH dependence. Co(II) and Cr(II) were selectively extracted into the organic phase because the extraction of Co(II) and Cr(II) proceeded by cation exchange. As a result, Pt(IV) and Ru(III) can be separated from Co(II) and Cr(II) by controlling the pH. Moreover, the extraction mechanism of Ru(III) with the Alamine336 (A336)/[P2225][TFSA] system was based on the following anion exchange reaction; [R3NH+Cl-]org + [RuCl4(H2O)2-]aq ⇔ [R3NH+RuCl4(H2O)2-]org + [Cl-]aq, (R = CH3(CH2)7-/CH3(CH2)9-). The electrochemical behavior for Ru(III) in the [P2225][TFSA] was investigated by cyclic voltammetry at 373 K. It was revealed that two step cathodic reactions: Ru(III) + e- → Ru(II) and Ru(II) + 2e- → Ru(0) were proceeded in the [P2225][TFSA] system. Moreover, the potentiostatic electrodeposition allowed us to recover the blackish electrodeposits, which were identified as most of Ru metal by EDX analysis. Finally, we investigated the reuse of the Ru(III) in A336/IL solvent for continuous extraction and electrodeposition. The extraction percentage of Ru(III) using A336/IL remained relatively high (81.5−96.1%) for the 1st−5th cycles. This series of experimental results enabled us to demonstrate that Ru metal can be obtained from direct electrodeposition of the extracted [R3NH+RuCl4(H2O)2-] in the A336/[P2225][TFSA] system.

Keywords	Direct electrodeposition, Ionic liquid, Ruthenium, Solvent extraction

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Thank you for sending many useful comments.

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The abstract is too long. Suggest revise based on the following points:

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Highlights

・Co(II) and Cr(II) were selectively extracted into the organic phase by cation exchange.

・Ru(III) was extracted by anion exchange reaction with Alamine336 in ionic liquids.

・The electrochemical behavior of the extracted Ru complex was investigated in ionic liquids.

・Ru metal was recovered by potentiostatic electrodeposition of the loaded organic phase.

Recovery of ruthenium by solvent extraction and direct electrodeposition using ionic liquid solution

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ABSTRACT

It is important to recover Ru metal from spent target materials including Pt, Co and Cr. The extraction behavior using Di-(2-ethylhexyl)phosphoric acid (HDEHP) and ionic liquid (IL), triethyl-*n*-pentyl phosphonium bis(trifluoromethyl-sulfonyl)amide ; $[P_{2225}]$[TFSA] diluent was investigated with pH dependence. Co(II) and Cr(II) were selectively extracted into the organic phase because the extraction of Co(II) and Cr(II) proceeded by cation exchange. As a result, Pt(IV) and Ru(III) can be separated from Co(II) and Cr(II) by controlling the pH. Moreover, the extraction mechanism of Ru(III) with the Alamine336 (A336)/$[P_{2225}]$[TFSA] system was based on the following anion exchange reaction; $[R_3NH^+Cl^-]_{org} + [RuCl_4(H_2O)_2^-]_{aq} \Leftrightarrow [R_3NH^+RuCl_4(H_2O)_2^-]_{org} + [Cl^-]_{aq}$, ($R = CH_3(CH_2)_7$-/$CH_3(CH_2)_9$-).

The electrochemical behavior for Ru(III) in the $[P_{2225}]$[TFSA] was investigated by cyclic voltammetry at 373 K. It was revealed that two step cathodic reactions: Ru(III) + $e^- \rightarrow$ Ru(II) and Ru(II) + $2e^- \rightarrow$ Ru(0) were proceeded in the $[P_{2225}]$[TFSA] system. Moreover, the potentiostatic electrodeposition allowed us to recover the blackish electrodeposits, which were identified as most of Ru metal by EDX analysis. Finally, we investigated the reuse of the Ru(III) in A336/IL solvent for continuous extraction and electrodeposition. The extraction percentage of Ru(III) using A336/IL remained relatively high (81.5−96.1%) for the 1st−5th cycles. This series of experimental results enabled us to demonstrate that Ru metal can be obtained from direct electrodeposition of the extracted $[R_3NH^+RuCl_4(H_2O)_2^-]$ in the A336/$[P_{2225}]$[TFSA] system.

Key words: Direct electrodeposition, Ionic liquid, Ruthenium, Solvent extraction

1. Introduction

Platinum group metals (PGMs) are conventionally recovered by a series of pyrometallurgical methods, where the solvent extraction process is considered as one useful option (Lo T.C. et al., 1983) for separating PGMs from secondary resources. Studies on the separation of PGMs by solvent extraction using conventional organic solvents have been investigated (Lokhande, T.N. et al., 2000, Mhaske, P.D. et al., 2002, Kedari, C.S. et al., 2005). The application of platinum and ruthenium, as PGMs, in industrial products has increased due to the catalytic properties of these PGMs. Ru metal is resistant to corrosion and stable under various operating conditions. Because the abundance of these elements in the earth's crust is less than 1.0×10^{-3} ppm, it is important to recover Ru metal from spent target materials, which may also contain Pt, Co and Cr.

Thus, developing solvent extraction and direct electrodeposition processes for the volume reduction of secondary wastes is an important task. Direct electrodeposition by employing ionic liquids (ILs) in a solvent based on the aqueous solution-IL distribution equilibrium is important for the extraction process. Thus far, ILs have been evaluated for possible application in various stages of the recovery of metallic species. The wide electrochemical window, in conjunction with the hydrophobicity of ILs, has been exploited in the recovery of Cu (Hsu, C.N.S. et al., 2009), Sr (Chen, P.-Y., 2007), Pd (Giridhar, P. et al., 2006, Giridhar P. et al., 2006, Jayakumar, M. et al., 2009), and U (Giridhar, P. et al., 2008) by solvent extraction and direct electrodeposition. Recently, we also demonstrated the recovery of Fe (Matsumiya, M. et al., 2016) and Nd (Matsumiya, M. et al., 2014) from a loaded organic phase using phosphonium-based ILs by solvent extraction and direct electrodeposition. Thus far, there are no reports on the recovery of Ru metal by extraction and direct electrodeposition.

In this study, we investigate the feasibility of using ILs for the recovery of Ru metal from spent target materials. The solvent extraction process uses Alamine 336 (tri-octyl/decyl amine, R_3N, where R = $CH_3(CH_2)_7$-/$CH_3(CH_2)_9$-, A336) as an adequate extractant in IL as a diluent based on the high solubility of A336 in the organic phase and its high hydrophobicity. In addition, triethyl-*n*-pentyl phosphonium bis(trifluoromethyl-sulfonyl)amide ([P_{2225}][TFSA]) is applied as the main organic phase in the extraction process. This novel solvent extraction-electrodeposition process using an IL has several advantages, which lead to the elimination of

several complex processing steps, minimize the generation of secondary wastes, lower the environmental risk, achieve large volume reduction, and provide easy handling of the electrodeposits.

2. Experimental

2.1 Solvent extraction

A 7.0 mL aliquot of the aqueous phase containing 43.2 mg L^{-1} Co(II), 3.03 mg L^{-1} Cr(II), 35.3 mg L^{-1} Pt(IV), and 3.8 mg L^{-1} Ru(III) was prepared in 1.0 M HCl aqueous solution. The metal composition of the spent target materials was determined. Aqueous solutions with pH values from 3.0 to 5.5 were prepared by adding a small amount of NaOH solution, and the pH after extraction was measured with a digital high-precision pH meter (MM-60R, DKK-TOA Corp.). Di-(2-ethylhexyl)phosphoric acid (HDEHP) was used as the acidic extractant to separate Co(II) and Cr(II) selectively. Alamine 336 (tri-octyl/decyl amine, R_3N, where R = $CH_3(CH_2)_7$-/$CH_3(CH_2)_9$-, A336) was selected as the extractant for [$RuCl_6^{3-}$] because of its high solubility in the IL and its high hydrophobicity. A336 is a C8−C10 saturated straight-chain tertiary amine mixture, and the pale yellow extractant is insoluble in water (<5 mg L^{-1}). A336 has an average molecular weight of 392 g mol^{-1}, a density of 0.81 g cm^{-3}, and viscosity of 11 mPa·s at 303 K. [P_{2225}][TFSA] was used as the diluent, and 10 vol.% of 1-decanol was used as the phase modifier to prevent the formation of emulsions or third phases during the extraction process. Solvent extraction with the IL system was performed, where all of the extraction studies were carried out at 298 K with a 1:1 organic to aqueous phase ratio. Stirring during the extraction process was performed at 2000 rpm for 5 min. The extraction behavior of [$RuCl_6^{3-}$] as a function of variation of the A336 was studied in order to determine the stoichiometry of the extracted metal complex. After equilibration, the concentration of the four metallic species in the aqueous phase was measured by inductively coupled plasma atomic emission spectroscopy (ICP-AES, ICPE-9000, Shimadzu Co.). The distribution ratio (*D*) and the extraction efficiency (*E*) were calculated from the ICP-AES quantitative data according to Eqs. (1) and (2).

$$D = \frac{[\mathrm{M}]_{\mathrm{aq}}^{\mathrm{ini}} - [\mathrm{M}]_{\mathrm{aq}}^{\mathrm{fin}}}{[\mathrm{M}]_{\mathrm{aq}}^{\mathrm{fin}}} \tag{1}$$

$$E(\%) = \frac{100D}{D + V_{\mathrm{aq}} / V_{\mathrm{org}}} \tag{2}$$

Here, [*M*] and *V* represent the concentration of each metal ion and the volume, respectively. The subscripts '*aq*' and '*org*' represent the aqueous and organic phases, respectively. The superscripts '*ini*' and '*fin*' represent the initial and final concentrations, respectively.

In order to investigate the mechanism of extraction of Ru(III) in the A336/[P_{2225}][TFSA] extraction system, the dependence of the extraction efficiency on the concentration of the A336 extractant was evaluated for each *D* value. The concentration of A336 in the organic phase was varied from 4.0×10^{-4} to 3.0×10^{-2} M while fixing the aqueous phase.

2.2 Electrochemical analysis

Cyclic voltammetry (CV) was carried out using a three-electrode system with a cylindrical cell. A Pt disk electrode with an inner diameter of 1.6 mm was employed as the working electrode, and the electrode surface was polished with an alumina and a diamond paste before use. Pt wires with an inner diameter of 0.5 mm were used as the counter and quasi-reference electrode (QRE), because the potential using the Pt QRE was stable and exhibited good reproducibility at mid-range temperatures. The potential was compensated for the IL standard using the Fc/Fc^{+} redox couple. The CV measurement was carried out 373 K with an electrochemical analyzer (ALS-760E, BAS, Inc.). The extracted Ru(III) dissolved in A336/[P_{2225}][TFSA] was used as the electrolyte for the CV analysis, and was dried under vacuum at 373 K for 48 h. The water content of the extracted and dried IL was less than 100 ppm, as measured with a Karl-Fischer moisture titrator (MKC-610-NT, Kyoto Electronics Manufacturing Co., Ltd.). The electrochemical analysis was conducted under dry Ar atmosphere (H_2O < 1.0 ppm) in a glovebox (DBO-1KP-YUM01, MIWA, Inc.).

The electrodeposition of Ru metal from the extracted Ru(III) complex in the A336/[P_{2225}][TFSA] system was carried out using a three-electrode system inside a cylindrical cell at 373 K under Ar atmosphere in a glovebox. In this study, a Pt wire and a Cu substrate were employed as the anode and cathode, respectively. The anode was

surrounded by a soda lime tube with a Vycor glass filter at the bottom in order to prevent diffusion of the decomposition products from the anode into the electrolyte. The surface of each electrode was polished with suitable fine-grade waterproof abrasive papers. The QRE was composed of a Pt wire with an inner diameter of 0.5 mm. For potentiostatic electrodeposition, the overpotential applied to the cathode was -2.5 V, -2.7 V, and -2.9 V for Ru versus the extracted media at 373 K. The metallic states of Ru in the electrodeposits were evaluated by scanning electron microscopy/energy dispersive X-ray spectrometry (SEM/EDX, JSM-6510LA, JEOL).

2.3 Reuse of organic solvent for extraction-electrodeposition

In order to evaluate the reuse of A336/[P_{2225}][TFSA] organic solvent system, a recycling run consisting of solvent extraction and electrodeposition for 10 cycles was performed. For solvent extraction, 1.0×10^3 mg L^{-1} [$RuCl_6^{3-}$] was used as the aqueous phase because the continuous solvent extraction-electrodeposition process was needed to enrich the metal concentration in the organic phase. The volume ratio (A/O) of the aqueous and organic phase was maintained at A/O = 3.0. After solvent extraction, electrodeposition was performed under potentiostatic electrolytic conditions. The electrodeposition of Ru metal from the extracted Ru(III) complex in the A336/[P_{2225}][TFSA] system was carried out using a three-electrode system inside a cylindrical cell at 298 K under Ar atmosphere. A Pt wire and a Cu substrate were employed as the anode and cathode, respectively. The anode was surrounded by a soda lime tube with a Vycor glass filter at the bottom in order to prevent diffusion of the decomposition products from the anode into the electrolyte. The QRE was composed of a Pt wire with an inner diameter of 0.5 mm. For the potentiostatic electrodeposition, the overpotential applied to the cathode was -2.7 V for Ru relative to the extracted media. After electrodeposition, all the electrodes from the electrolytic bath were replaced and the electrolytic bath was reused for the next stage of the solvent extraction. In the second solvent extraction, the new aqueous phase containing 1.0×10^3 mg L^{-1} [$RuCl_6^{3-}$] was introduced into the organic phase with A/O = 3.0. After the second solvent extraction, the second electrodeposition was performed with the same overpotential. Thus, the procedure for solvent extraction and electrodeposition was repeatedly carried out for 10 cycles. After the tenth continuous extraction-electrodeposition cycle, the metal concentration in the

organic phase for each cycle was determined by ICP-AES. The current efficiency was calculated from the weight increase of the cathode at each electrodeposition. The metallic state of Ru in the electrodeposits was evaluated by scanning electron microscopy/energy dispersive X-ray spectrometry (SEM/EDX, JSM-6510LA, JEOL). The material balance was evaluated via back-extraction of the organic phase and ICP-AES analysis. 0.1 M thiourea (TU = H_2NCSNH_2) and 2.0 M NH_3 + 3.0 M NH_4Cl solution with high extraction performance were respectively selected as the complexing agents for back-extraction of Ru(III).

3. Results and discussion

3.1 Extraction behavior

The pH-dependent extraction behavior of Co(II), Cr(II), Pt(IV), and Ru(III) using HDEHP as the extractant is shown in **Fig. 1(a)**. Co(II) and Cr(II) were selectively extracted into the organic phase because the extraction of Co(II) and Cr(II) proceeded by cation exchange. From analysis of the slope **Fig. 1(b)**, the stoichiometry of HDEHP relative to the metal was confirmed to be 2, indicating that the mechanism of extraction of Co(II) and Cr(II) can be expressed as: $[M^{2+}]_{aq} + 2[HDEHP]_{org} \Leftrightarrow [M(DEHP)_2]_{org} + 2[H^+]_{aq}$ (M = Co and Cr). On the other hand, relatively low extraction of Pt(IV) and Ru(III) into the organic phase was achieved because Pt(IV) and Ru(III) are stable as anionic species, i.e., $[PtCl_6^{2-}]$ and $[RuCl_6^{3-}]$, in this pH range. As a result, Pt(IV) and Ru(III) can be separated from Co(II) and Cr(II) by controlling the pH.

It is important to understand the state of the complex in the aqueous phase. Ru(III) chloride and aqua complexes, $[RuCl_{6-n}(H_2O)_n^{n-3}]$ (n = 0−5), are six kinds of octahedral species, i.e., $[RuCl(H_2O)_5^{2+}]$, $[RuCl_2(H_2O)_4^+]$, $[RuCl_3(H_2O)_3]$, $[RuCl_4(H_2O)_2^-]$, $[RuCl_5(H_2O)^{2-}]$, and $[RuCl_6^{3-}]$ in the chloride solution. The equilibrium constants from $\log K_1$ to $\log K_5$ for $[RuCl_{6-n}(H_2O)_n^{n-3}]$ were reported as follows (Connick, R.E., 1961):

$$[RuCl(H_2O)_5^{2+}] + Cl^- \Leftrightarrow [RuCl_2(H_2O)_4^+] + H_2O,\ \log K_1 = 1.477 \quad (3)$$

$$[RuCl_2(H_2O)_4^+] + Cl^- \Leftrightarrow [RuCl_3(H_2O)_3] + H_2O,\ \log K_2 = 0.431 \quad (4)$$

$$[RuCl_3(H_2O)_3] + Cl^- \Leftrightarrow [RuCl_4(H_2O)_2^-] + H_2O,\ \log K_3 = -0.097 \quad (5)$$

$$[RuCl_4(H_2O)_2^-] + Cl^- \Leftrightarrow [RuCl_5(H_2O)^{2-}] + H_2O,\ \log K_4 = -0.854 \quad (6)$$

$$[RuCl_5(H_2O)^{2-}] + Cl^- \Leftrightarrow [RuCl_6^{3-}] + H_2O, \log K_5 = -1.000 \quad (7)$$

According to the above equilibrium constants, the distribution of $[RuCl_{6-n}(H_2O)_n^{n-3}]$ (n = 0−5) was calculated in this study and the relationship between the concentration of HCl and the distribution ratio is shown in **Fig. 2**. As shown in Fig. 2, $[RuCl_2(H_2O)_4^+]$, $[RuCl_3(H_2O)_3]$, $[RuCl_4(H_2O)_2^-]$, $[RuCl_5(H_2O)^{2-}]$, and $[RuCl_6^{3-}]$ were the predominant anionic species in the range of 0<[HCl]<0.38, 0.38<[HCl]<1.27, 1.27<[HCl]<7.14, 7.14<[HCl]<10.05, and 10.05<[HCl], respectively. Considering the experimental extraction conditions, the predominant species related to the extraction mechanism were $[RuCl_4(H_2O)_2^-]$.

It is important to understand the stoichiometry of the extracted metal species because the overpotential during electrodeposition of the organic phase depends on the extracted species. The effect of the extractant concentration on Ru(III) extraction from the aqueous solution bearing 1.0×10^2 mg L^{-1} Ru(III) in 1.0 M HCl was studied with variation of the concentration of A336 within the range of 4.0×10^{-4} to 3.0×10^{-2} M at an A:O ratio of 1:1. The results indicate that the extraction of Ru(III) increased from 19.6 to 96.4% with a change in the A336 concentration from 4.0×10^{-4} to 3.0×10^{-2} M. The plot of log$D$ vs. $\log([R_3N\cdot HCl]_{org}/[Cl^-]_{aq})$ is shown in **Fig. 3**. The respective slope of 1.09 indicates the association of one mole of the extractant with one mole of Ru(III) during extraction.

As a result, A336 is an anion-exchange extractant for the extraction of Ru(III) from chloride media in the form of anions. This type of extractant is firstly protonated in the acidic medium, and the protonated extractant undergoes an anion-exchange reaction with Ru(III) metal anion. Thus, the extraction mechanism for Ru(III) with A336 can be expressed as follows: first, the A336 extractant is protonated with HCl.

$$[R_3N]_{org} + [HCl]_{aq} \Leftrightarrow [R_3NH^+Cl^-]_{org} \quad (8)$$

$[RuCl_4(H_2O)_2^-]_{aq}$ undergoes anion exchange with the protonated A336 and the reaction is expressed as follows:

$$[RuCl_4(H_2O)_2^-]_{aq} + [R_3N \cdot HCl]_{org} \Leftrightarrow [R_3NH^+RuCl_4(H_2O)_2^-]_{org} + [Cl^-]_{aq} \quad (9)$$

The extraction equilibrium constant and the distribution ratio are expressed as follows.

$$K_{Ru(III)} = \frac{[R_3NH^+RuCl_4(H_2O)_2^-]_{org}[Cl^-]_{aq}}{[RuCl_4(H_2O)_2^-]_{aq}[R_3N \cdot HCl]_{org}} \quad (10)$$

$$D_{Ru(III)} = \frac{[R_3NH^+RuCl_4(H_2O)_2^-]_{org}}{[RuCl_4(H_2O)_2^-]_{aq}} \quad (11)$$

The following relationship is obtained from Eqs. (10) and (11).

$$K_{Ru(III)} = \frac{D_{Ru(III)}}{([R_3N \cdot HCl]_{org} / [Cl^-]_{aq})} \quad (12)$$

The logarithm of D is expressed as follows, according to the relation in Eq. (12):

$$\log D_{Ru(III)} = \log K_{Ru(III)} + \log([R_3N \cdot HCl]_{org}/[Cl^-]_{aq}) \quad (13)$$

The slope of the plot for $\log D_{Ru(III)}$ vs. $\log[R_3N \cdot HCl]/[Cl^-]$ is shown in Fig. 3. This result is consistent with the above extraction mechanism. Thus, for the extraction of Ru(III) using conventional organic solvents with a tertiary amine (Goralska, E. et al., 2007, Panigrahi, S. et al., 2014), the extraction mechanism is in good agreement with Eq. (9). The extraction result indicates that Ru(III) was easily extracted by the anion exchange reaction in the A336/[P_{2225}][TFSA] system, as well as in the conventional organic solvents.

3.2 Electrochemical analysis of Ru(III)

The cyclic voltammogram of the extracted [$R_3NH^+RuCl_4(H_2O)_2^-$] complex (i.e., Ru(III) in [P_{2225}][TFSA]) at 373 K is shown in **Fig. 4**. As seen from Fig. 4, there were two cathodic peaks around -0.26 V and -1.16 V in the voltammogram. These cathodic peaks, c_1 and c_2, can be assigned to the following reactions:

$$Ru(III) + e^- \rightarrow Ru(II) \text{ (peak } c_1) \quad (14)$$

$$Ru(II) + 2e^- \rightarrow Ru(0) \text{ (peak } c_2) \quad (15)$$

For each peak based on the cathodic reactions (14) and (15), it was confirmed that the plot of the cathodic peak of the current density (j_p) vs. the square root of the scan rate ($v^{1/2}$) showed a good linear relation ($j_p \propto v^{1/2}$). This result indicated that both reduction reactions were controlled by the diffusion process, i.e., mass transport under semi-infinite linear diffusion conditions. Moreover, this result indicated that the extracted [$R_3NH^+RuCl_4(H_2O)_2^-$] present in the IL phase can also be electrochemically reduced and deposited as Ru metal, provided that the IL phase is a good electrical conductor and has a wide electrochemical window.

Based on the above fundamental electrochemical analysis, the electrodeposition of Ru metal was conducted against the extracted sample in A336/[P_{2225}][TFSA] using a cathodic Cu substrate, an anodic Pt wire, and a Pt QRE. The applied overpotentials on the cathode for the potentiostatic electrolysis were set at -2.5 V, -2.7 V, and -2.9 V for Ru vs. Pt QRE; the electrolyte was stirred at 250 rpm to increase the current density during electrodeposition by continuously supplying electroactive species to the electrode surface. The average current density and the total charge transported during electrodeposition were -13.6 mA cm^{-2} and 18.4 C, respectively. After electrodeposition, in order to evaluate the material balance of the metal deposited from the loaded organic phase, the organic phase containing Ru(III) was subjected to back-extraction with 0.1 M thiourea or 2.0 M NH_3 + 3.0 M NH_4Cl solution. For the back-extraction, the extracted Ru(III) species in the organic phase were stripped as the [$Ru(NH_3)_6^{3+}$] complex. The extraction percentage for back extraction was 97.0−100.0 (%) for Ru, where this result was consistent with the reference (Kedari, S., 2005). Thus, the material balance of the metal deposited from the loaded organic

phase was demonstrated in this study. It was confirmed that the blackish electrodeposits were strongly adhered to the Cu substrate of the cathode. The surface morphology investigated by SEM is shown in **Fig. 5**. An island structure and agglomeration of the small metallic particles were observed from the SEM image. Most of the Ru and some light elements were detected from EDX analysis. The weight percentage of the electrodeposited Ru is listed in and **Tables 1**. The purity of electrodeposited Ru metal was relatively high when a negative overpotential was applied. This electrodeposition behavior may be related to nucleation of the metal complex species.

Finally, we investigated the reuse of the Ru(III) in A336/IL solvent for continuous extraction and electrodeposition. The result for solvent extraction of Ru(III) and electrodeposition over ten cycles was summarized in **Table 2**. The extraction percentage of Ru(III) in A336/IL gradually decreased and reached to 56.7%. This may be due to the high enrichment of the extracted Ru(III) species. In the 1st−6th cycles of Ru electrodeposition using A336/IL, the current efficiency was maintained relatively high (87.6−96.3%). This series of experimental results enabled us to conclude that Ru metal can be obtained from direct electrodeposition of the extracted $[R_3NH^+RuCl_4(H_2O)_2^-]$ in the A336/$[P_{2225}]$[TFSA] system. f The multistage extraction-electrodeposition process for mutual separation of Pt(IV) and Ru(III) would be developed in near future.

4. Conclusions

The recovery of Ru from spent target materials including Pt, Co and Cr was investigated in this study. According to the extraction behavior using Di-(2-ethylhexyl)phosphoric acid (HDEHP) and ionic liquid (IL), triethyl-*n*-pentyl phosphonium bis(trifluoromethyl-sulfonyl)amide ; $[P_{2225}]$[TFSA] diluent, Co(II) and Cr(II) were selectively extracted into the organic phase, because the extraction of Co(II) and Cr(II) proceeded by cation exchange. From the slope analysis, the mechanism of extraction of Co(II) and Cr(II) can be implied as: $[M^{2+}]_{aq} + 2[HDEHP]_{org} \Leftrightarrow [M(DEHP)_2]_{org} + 2[H^+]_{aq}$ (M = Co, Cr). Therefore, Pt(IV) and Ru(III) can be selectively separated from Co(II) and Cr(II) by controlling the pH. In addition, the extraction mechanism of Ru(III) with the Alamine336 (A336)/$[P_{2225}]$[TFSA] system was based on the anion exchange reaction; $[R_3NH^+Cl^-]_{org}$ +

$[RuCl_4(H_2O)_2^-]_{aq} \Leftrightarrow [R_3NH^+RuCl_4(H_2O)_2^-]_{org} + [Cl^-]_{aq}$, (R = $CH_3(CH_2)_7$-/$CH_3(CH_2)_9$-).

The electrochemical behavior for Ru(III) in the $[P_{2225}]$[TFSA] was investigated by cyclic voltammetry at 373 K. It was revealed that two step cathodic reactions: Ru(III) + e^- → Ru(II) and Ru(II) + $2e^-$ → Ru(0) were proceeded in the $[P_{2225}]$[TFSA] system. Moreover, the potentiostatic electrodeposition allowed us to recover the blackish electrodeposits, which were identified as most of Ru metal by EDX analysis. Finally, the reuse availability of the Ru(III) in A336/IL solvent was investigated by continuous extraction and electrodeposition. The extraction percentage of Ru(III) using A336/IL remained relatively high (81.5−96.1%) for the 1st−5th cycles. This series of experimental results allowed us to conclude that Ru metal can be obtained from direct electrodeposition of the extracted $[R_3NH^+RuCl_4(H_2O)_2^-]$ using the A336/$[P_{2225}]$[TFSA] system.

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Caption of Figures

Fig. 1 (a) Extraction behavior of Co(II), Cr(II), Pt(IV) and Ru(III) using HDEHP in $[P_{2225}]$[TFSA] extraction system, ■: Co, □:Cr, ●:Pt and ○:Ru

(b) Slope analysis of Co(II) and Cr(II), ■: Co, □:Cr

Fig. 2 Distribution diagram for $[RuCl_{6-n}(H_2O)_n]^{n-3}$ (n=0-5) calculated from the equilibrium constants. orange line: $[RuCl(H_2O)_5^{2+}]$, red line: $[RuCl_2(H_2O)_4^{+}]$, yellow green line: $[RuCl_3(H_2O)_3]$, green line: $[RuCl_4(H_2O)_2^{-}]$, blue line: $[RuCl_5(H_2O)^{2-}]$, purple line: $[RuCl_6^{3-}]$

Fig. 3 Slope analysis of Ru(III) using Alamine 336 in $[P_{2225}]$[TFSA] extraction system.

Fig. 4 Cyclic voltammogram of $[R_3NH^{+}RuCl_4(H_2O)_2^{-}]$ in $[P_{2225}]$[TFSA] at 373 K.

Fig. 5 The surface morphology of Ru electrodeposits under potentiostatic condition at -2.7 V vs. Pt QRE by SEM.

Fig. 1

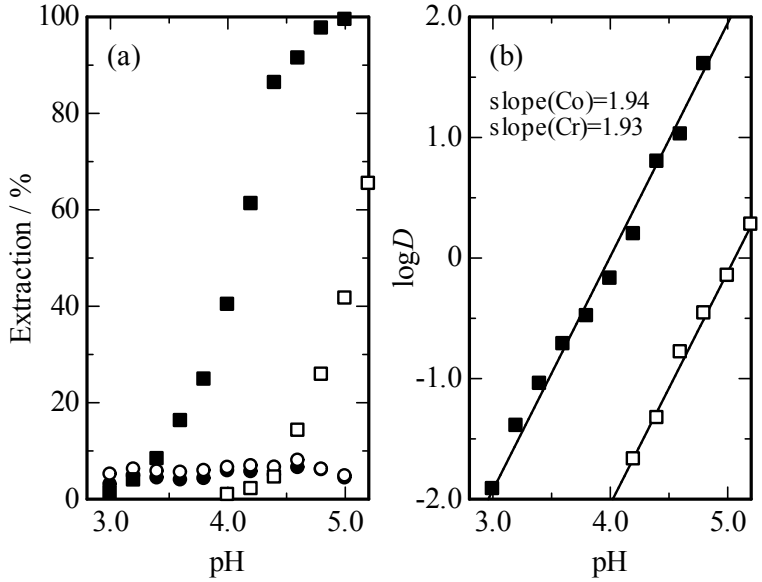

(a)
Extraction / %
100
80
60
40
20
0
3.0
4.0
5.0
pH
(b)
slope(Co)=1.94
slope(Cr)=1.93
log*D*
2.0
1.0
0
-1.0
-2.0
3.0
4.0
5.0
pH

Fig. 2

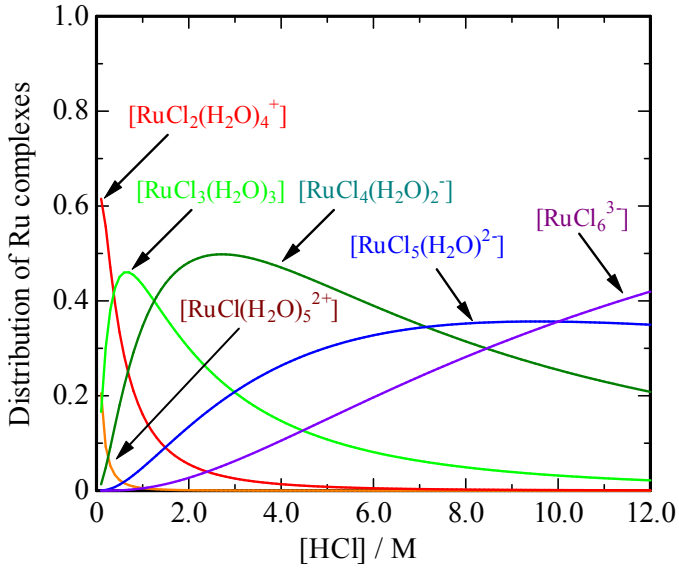

1.0
0.8
0.6
0.4
0.2
0
0
2.0
4.0
6.0
8.0
10.0
12.0
Distribution of Ru complexes
[HCl] / M
[RuCl2(H2O)4+]
[RuCl3(H2O)3]
[RuCl4(H2O)2-]
[RuCl5(H2O)2-]
[RuCl6 3-]
[RuCl(H2O)5 2+]

Fig. 3

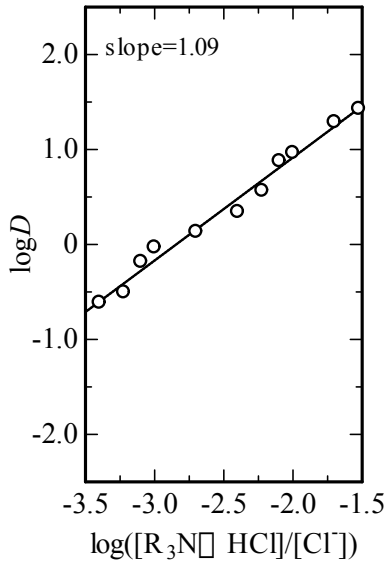
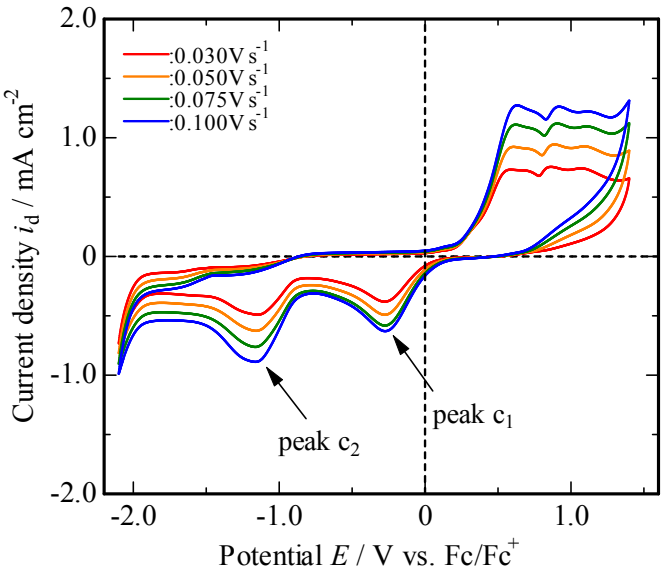


Fig. 4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1.0
0
-1.0
-2.0
-2.0
-1.0
0
1.0
Current density id / mA cm-2
Potential E / V vs. Fc/Fc+
peak c2
peak c1

Fig. 5

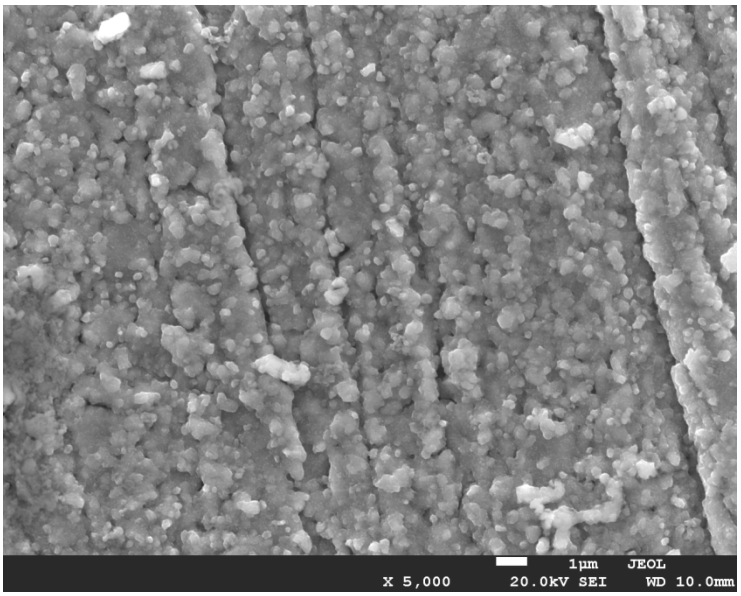

Table 1 Composition of Ru electrodeposits on the potentiostatic conditions by EDX analysis.

Overpotential	Composition (wt.%)						
E/V vs. Pt QRE	C	N	O	F	P	S	Ru
-2.5	1.97	0.64	4.38	3.32	1.83	1.64	86.22
-2.7	1.78	0.82	3.83	2.28	1.76	1.32	88.21
-2.9	1.92	0.78	4.64	2.16	1.58	1.49	87.43

Table 2 A series of results of Ru for solvent extraction and electrodeposition at tenth cycles.

No.	Solvent extraction Alamine336/[P_{2225}][TFSA]			Electrodeposition Alamine336/[P_{2225}][TFSA] including extracted Ru(III)					
	E /(%)	$C_{Ru(III)\_sx}$ /10^{-2} mol L^{-1}	$w_{Ru(III)\_sx}$ /mg	$w_{Ru\_residue}$ /mg	w_{Ru_total} /mg	Q /C	$w_{Ru\_deposit}$ /mg	ε /(%)	R /(%)
1st	96.1	2.854	8.36	0.00	8.36	23.2	7.8	96.3	93.3
2nd	91.1	2.703	7.10	0.51	7.61	22.6	7.2	91.2	94.6
3rd	90.7	2.691	5.98	0.35	6.33	19.7	6.1	88.7	96.4
4th	82.6	2.452	5.20	0.22	5.42	15.9	4.9	88.3	90.3
5th	81.5	2.419	4.89	0.50	5.39	14.8	4.8	92.9	89.1
6th	73.8	2.191	3.76	0.50	4.26	12.1	3.7	87.6	86.8
7th	71.4	2.119	3.00	0.46	3.46	10.8	3.1	82.2	89.5
8th	64.6	1.917	2.33	0.31	2.64	7.9	2.2	79.8	83.4
9th	59.5	1.766	1.79	0.36	2.15	6.4	1.8	80.5	83.7
10th	56.7	1.513	1.53	0.31	1.84	6.1	1.6	75.1	86.8

E: Extraction percentage on SX, $C_{Ru(III)\_sx}$: Concentration of extracted Ru(III) on SX, $w_{Ru(III)\_sx}$: Weight of extracted Ru(III) on SX

$W_{Ru\_residue}$: Weight of residual Ru in electrolyte after electrodeposition, w_{Ru_total}: Total weight of Ru in electrolyte (w_{Ru_total}=$w_{Ru(III)\_sx}$ + $w_{Ru\_residue}$)

Q: Transported charge on electrodeposition, $w_{Ru\_deposit}$: Weight of Ru on electrodeposition, ε: Current efficiency,

R: Recovery yield (R=$w_{Ru\_deposit}$ / w_{Ru_total} ×100)