Recovery of Pd(II) from Hydrochloric Acid Medium by Solvent Extraction–Direct Electrodeposition Using Hydrophilic/Hydrophobic ILs

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ABSTRACT: Mixed [C8bett]Br/[C4mim][NTf2] ionic liquids were used as a new extraction system to extract Pd(II) from multimetal-ion solutions. The separation factors K_{Pd/M} (M: Cu, Fe, Ni, Zn, Co) are greater than 10^3. Thiourea was found to be an effective stripping agent. After three cycles, the recovery efficiency was higher than 91.0%. Direct electrodeposition of palladium from the mixed ionic liquid phase was also studied. The Pd(II) complex in [C8bett]Br/[C4mim][NTf2] system was studied by cyclic voltammetry at 348 K. The results indicate the existence of three types of Pd(II) complex in the [C8bett]Br/[C4mim][NTf2] system, leading to three reductive waves. The reduction of Pd(II) to Pd(0) in this system is irreversible. A uniform black coating was obtained by constant-potential deposition at −1.7 V on a nickel foil, confirmed to be palladium metal by energy-dispersive spectrometry, X-ray photoelectron spectroscopy, and high-resolution transmission electron microscopy analyses. After three cycles of continuous extraction–electrodeposition, over 90.0% of palladium was recovered.

1. INTRODUCTION

Palladium is an important element in platinum group metals (PGMs). Palladium is widely used in electronic devices, aerospace, nuclear energy, and other high-tech fields owing to its wide range of conductivity, catalysis, ductility, high-temperature resistance, and corrosion resistance.1,2 However, the application of palladium is limited because it is scarcely available in nature, and its consumption is increasing. Therefore, it is particularly essential to recover palladium from secondary resources.

In the last few decades, the methods used to recover palladium include precipitation,3,4 adsorption,5 solvent extraction,6 electrodeposition,7,8 solvent extraction,9 liquid membrane separation,10 and ion exchange.11 Among these processes, the solvent extraction method has the advantages of simple equipment, simple process, low cost, large extraction capacity, good selectivity, and wide application, making it more suitable for large-scale industrial use.12–14 As a new generation of extractant, ionic liquids (ILs) have been widely used in the extraction and separation of palladium.15–18 Quaternary phosphonium salts ILs, that is, CYPHOSIL 101, CYPHOSIL 102, and CYPHOSIL 104, can effectively extract and separate Pd(II) from a four-component mixture solution of PGMs. The extraction efficiency of Pd(II) is all higher than 99% in an acidic chlorination medium.18 The pyridinium and ammonium ILs were also widely used for Pd(II) extraction.19 However, green extraction was not achieved using an IL dissolved in toluene or chloroform for solvent extraction; these solvents are very environmentally unfriendly. In recent years, the mixed hydrophilic/hydrophobic IL systems have been used to extract platinum,20,21 where volatile organic solvents are not required. Compared with a single hydrophobic IL, the extraction efficiency is also significantly improved. However, until now, hydrophilic/hydrophobic IL systems have not been reported for the extraction and separation of palladium.

In the last decade, electrodeposition has been widely used for the purification and separation of metal ions. Many studies have reported the recovery of metals such as Cu,22 Sr,23 U,24 Pt,25 and Ru26 through solvent extraction–direct electrodeposition. Compared with the conventional organic phase back-extraction method, direct electrodeposition can reduce the use of volatile organic solvents. The combination of solvent extraction and electrodeposition is a promising and simplest method.
new process for effective recovery of palladium. A variety of extractants such as Aliquat 336, tri-n-octylmethylammonium nitrate, and methyliminobis-N,N-diocetylacetamide were used to extract Pd(II) from an acidic medium. After extraction, the electrochemical characteristics of Pd(II) ions present in the organic phase were evaluated by cyclic voltammetry (CV). However, the solvent extraction–direct electrodeposition of palladium from HCl media in a hydrophilic/hydrophobic IL system has not been reported.

In this study, the precipitation of Pd(II) in HCl medium by [C8bet]Br was investigated. Based on low aqueous solubility and low viscosity (69 mPa s), hydrophobic [C4mim][NTf2] acts as the main ingredient of the organic phase. A mixed hydrophilic/hydrophobic IL extraction system was obtained by adding hydrophilic [C8bet]Br to [C4mim][NTf2]. The mixed [C8bet]Br/[C4mim][NTf2] ILs achieved significantly better extraction efficiency for Pd(II) than single IL. The extraction parameters were optimized, and the precipitation mechanism of [C8bet]Br and Pd(II) was elucidated. Direct electrodeposition of palladium from the mixed IL system was also studied. Pd(II) was recovered from acidic media by electrodeposition from the extraction system using hydrophobic IL [C4mim][NTf2] with a wide electrochemical window, high electrical conductivity, and high boiling point as a diluent.

2. RESULTS AND DISCUSSION

2.1. Mechanism Analysis between [C8bet]Br and Pd(II) 2.1.1. UV–Vis Spectrum. [C8bet]Br has no characteristic UV–Vis absorption peak (Figure 1a). The characteristic UV–Vis absorption peaks of Pd(II) aqueous solution appeared at 222 and 280 nm (Figure 1b). The peaks can be attributed to the [PdCl4]2− complex, similar to the characteristic UV–Vis absorption spectrum of the [C8bet]-Pd(II) complex in a methanol solution (Figure 1c). The characteristic absorption peaks shifted slightly (222 → 238 nm, 280 → 278 nm) in methanol solution. This indicates that the precipitation species is [C8bet]2−[PdCl4]2−.

2.1.2. [C8bet]-Pd(II) Complex Analysis. The molar ratio of [C8bet]Br and Pd(II) was calculated using Job’s method. The total amount of [C8bet]Br and aqueous Pd(II) was maintained as 6 × 10−3 mmol, and the concentration of HCl was kept constant at 0.1 M. By measuring the concentration of Pd(II) in the aqueous phase after the reaction is completed, the amount of Pd(II) needed for the reaction to generate the precipitate was calculated by conducting a mass balance, and a continuous variation of [C8bet]Br combined with Pd(II) was obtained. The results are shown in Figure 2. The maximum equilibrium precipitation molar ratio of [C8bet]Br/Pd(II) is 2:1, and the highest precipitation amount formed in the extraction experiment is the molar ratio closest to the theoretical molar ratio of the [C8bet]-Pd(II) complex. Using the Job’s method, a chemical equation for the [C8bet]Br precipitation of Pd(II) can be written as follows

\[2[C8bet]Br + [PdCl4]^{2−} \leftrightarrow [C8bet]_{2−}[PdCl4] + 2Br^{−}\] (1)

2.1.3. Fourier transform infrared and 1H NMR Analyses. To confirm the interaction between Pd(II) and [C8bet]Br, [C8bet]Br and [C8bet]-Pd(II) complexes were analyzed by Fourier transform infrared (FTIR) and 1H NMR spectroscopy. Compared with the [C8bet]-Pd(II) complex, the FTIR spectra (Figure 3a) of [C8bet]Br is the same. Only the peaks shifted slightly: 2959 → 2957, 2917 → 2925, 1750 → 1748, 1475 → 1469, and 1206 → 1208. The experimental results show that the exchange between [C8bet]Br and [PdCl4]2− is mainly affected by electrostatic attraction.

Figure 3b shows the 1H NMR spectra of [C8bet]Br and [C8bet]-Pd(II) complexes. A chemical shift was observed for [C8bet]-Pd(II) complexes. A chemical shift was observed for [C8bet]-Pd(II) complexes. A chemical shift was observed for [C8bet]-Pd(II) complexes.
Precipitation reaction mechanism is anion-exchange,$^{32}$ consistent with Job’s method and UV–Vis analyses.

### 2.2. Precipitation and Extraction Behavior

#### 2.2.1. Effect of [C₈bet]Br Concentration

To evaluate the effect of concentration of [C₈bet]Br on precipitation efficiency, the effect of different contents of [C₈bet]Br on the precipitation percentage of Pd(II) and the effect of its addition to hydrophobic phase [C₄mim][NTf₂] on the extraction efficiency were evaluated. Figure 4b shows that when the amount of [C₈bet]Br is 20 times that of [PdCl₄]²⁻, the precipitation percentage reached 100%. Based on the excellent precipitation efficiency of [C₈bet]Br, hydrophobic IL [C₄mim][NTf₂] and a quantitative amount of [C₈bet]Br were added to form the extracted organic phase. Figure 4a shows that the extraction efficiency of [C₈bet]Br/[C₄mim][NTf₂] system for Pd(II) reached 98.3% with an aqueous-oil volume ratio (Rᴬ/O) of 5, while the extraction efficiency of [C₄mim][NTf₂] for Pd(II) is only 30.1%. Even if the content of [C₄mim][NTf₂] is 1000 times that of Pd(II), the extraction efficiency is still low. Therefore, a hydrophilic/hydrophobic IL [C₈bet]Br/[C₄mim][NTf₂] system was developed to extract Pd(II). The amount of [C₈bet]Br in the organic phase was selected to be 20 times that of [PdCl₄]²⁻ for subsequent experiments.

#### 2.2.2. Effect of Vibration Time

Vibration time is one of the factors that affect the extraction efficiency. To evaluate the effect of vibration time on extraction efficiency and optimize the experimental parameters, Rᴬ/O was set as 5, and 2 mM Pd(II) solution containing 0.1 M acid chloride media was added. The vibration time was set as 1–40 min (Figure 5).

The extraction efficiency shows a stable trend after 20 min. Thus, all the experiments were conducted at a vibration time of 30 min, following centrifugation at 9000 rpm for 5 min.

#### 2.2.3. Effect of HCl Concentration

Figure 6 shows the extraction efficiency of Pd(II) when the concentration of hydrochloric acid varied from 0.01 to 5 M. When the concentration of HCl in the aqueous phase is higher than 0.2 M, both [PdCl₄]²⁻ and Cl⁻ act as anions in a competitive system and combine with [C₈bet]+ cations, consistent with other studies of similar palladium extraction systems in hydrochloric acid media.$^{34,35}$ When the concentration of HCl in the aqueous phase is lower than 0.1 M, the morphology of Pd(II) under low acidity was dominated by [PdCl₃(H₂O)]⁻ and [PdCl₂(H₂O)₂].$^{36}$ Thus, when C₄HCl = 0.1 M, the highest extraction efficiency was obtained.

#### 2.2.4. Effect of NaCl and NaBr Concentration

The concentration of Cl⁻ or Br⁻ ions can significantly affect the

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**Figure 3.** (a) FTIR spectra and (b) ¹H NMR [in dimethyl sulfoxide (DMSO)] spectra of [C₈bet]Br and [C₈bet]-Pd(II).

**Figure 4.** Precipitation and extraction efficiency of Pd(II) by using (a) [C₈bet]Br or (b) [C₈bet]Br/[C₄mim][NTf₂] system. Aqueous phase: 2 mM Pd(II) solution, C₄HCl = 0.1 M, Rᴬ/O = 5. The mixed IL phase: n[C₈bet]Br/n[C₄mim][NTf₂]: 0–5.85 × 10⁻⁵.

**Figure 5.** Effect of vibration time on the extraction efficiency. Aqueous phase: 2 mM Pd(II) solution, C₄HCl = 0.1 M, Rᴬ/O = 5. The mixed IL phase: 0.5 mL [C₄mim][NTf₂], C₄[C₈bet]Br = 0.04 mol L⁻¹.

**Figure 6.** Effect of vibration time on the extraction efficiency. Aqueous phase: 2 mM Pd(II) solution, C₄HCl = 0.1 M, Rᴬ/O = 5. The mixed IL phase: 0.5 mL [C₄mim][NTf₂], C₄[C₈bet]Br = 0.04 mol L⁻¹.
extraction of Pd(II). With increasing concentration of NaCl or NaBr from 0.25 to 5 M, the extraction efficiency of Pd(II) decreased (Figure 7). This experiment further confirmed that the extraction involves the anion-exchange mechanism.

2.3. Selective Extraction of Pd(II) from Multimetal Mixture Solution. Natural palladium ores are usually obtained from basic volcanic rocks, usually accompanied by sulfide ores of copper, nickel, iron, and other metals. If palladium is enriched or refined by extraction, these multimetal components might affect the extraction of palladium. The selectivity of Pd(II) extraction in the [C8bet]Br/[C4mim][NTf2] system was evaluated. First, a variety of chloride salts of metals were added to 0.1 M HCl solution to obtain a multimetal system. The concentration of each metal ion is 2 mM. As shown in Figure 8, the extraction efficiency of [C8bet]Br/[C4mim][NTf2] for Pd(II) is as high as 98.1%, and the distribution ratio is as high as 261. The extraction efficiencies, distribution ratios, and separation factors of other metal ions are as follows: Cu(II): 3.1%, 0.16, 1.6 × 10³; Fe(III): 5.2%, 0.27, 1.0 × 10³; Ni(II): 4.7%, 0.25, 1.0 × 10³; Zn(II): 1.8%, 0.094, 2.8 × 10³; Co(II): 4.2%, 0.22, 1.2 × 10³. The separation factors K_{Pd/M} (M: Cu, Fe, Ni, Zn, Co) are greater than 1.0 × 10³. The experiment results show that the mixed [C8bet]Br/[C4mim][NTf2] ILs can selectively extract Pd(II) from multimetal-ion solutions in hydrochloric acid media.

2.4. Stripping of Pd(II) and Regeneration of ILs. After Pd(II) was extracted using the [C8bet]Br/[C4mim][NTf2] system, thiourea was selected as the stripping agent for Pd(II). The concentration of thiourea was 1.2 M in 0.5 M HCl; the vibration time was 30 min. When the R_{A/O} was 5, the stripping efficiency was higher than 99.0%.

Table 1 shows the reuse performance of the [C8bet]Br/[C4mim][NTf2] system. After the stripping experiment, the upper aqueous phase was separated by centrifuging for 5 min. The regenerated organic phase was obtained by mixing with saturated KBr solutions. The extraction—stripping process was repeated three times; the recovery was always more than 91.0%.

2.5. Electrochemical Analysis. Figure 9a shows that [C4mim][NTf2] IL is relatively stable in the range from 1.8 to −2.5 V. The electrochemical window exceeds 4.3 V (the blue line). At −2.6 V, [C4mim]^+ begins to decompose. Figure 9b shows the CV of Pd(II) complex in the [C8bet]Br/[C4mim][NTf2] system at 348 K (the red line). Three peaks (e.g., −0.05, −1.04, and −1.58 V) were observed at the cathode; the peaks at −0.05, −1.04, and −1.58 V can be attributed to Pd(0), indicating that Pd(II) was reduced

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Pd(II) + 2e^- = Pd(0)
\]

Three types of Pd complex ions ([C8bet].Pd(II), [C4mim].Pd(II), and [PdCl4]^−) were assumed to be present in the mixed IL system, exhibiting three reductive waves. Three oxidation peaks were also observed in the anode at 0.045, 0.18, and 0.95 V; they can be attributed to Pd(II), indicating
that a small amount of electrodeposited Pd was reoxidized on the electrode surface during cathode scanning.\textsuperscript{37,39}

Figure 10 shows the CV curves of the Pd(II) complex in the [C\textsubscript{8}bet]Br/[C\textsubscript{4}mim][NTf\textsubscript{2}] system for different scanning rates. With the increase in scanning speed, the reduction peak current density \(J_P\) increased gradually, while the peak potential \(\phi_P\) shifted negatively (Figure 10). The electrode reaction of Pd(II) reduction to Pd(0) is irreversible. Figure 11 shows the change in potential \(\phi_P\) from Pd(II) to Pd(0) with the scanning rate. The results show a good linear relationship between \(\phi_P\) and the natural logarithm of \(\ln \nu\), indicating that it is feasible to promote palladium separation by controlling potential deposition.

To obtain the palladium metal, a constant-potential deposition was carried out on nickel foil at \(-1.6\) and \(-1.7\) V. After 16 h, a black coating was obtained at \(-1.6\) V; it was uneven and easily fell off. At \(-1.7\) V, a uniform black solid was observed on the coating surface. Then, the samples at \(-1.7\) V were analyzed by scanning electron microscopy (SEM) and HRTEM. The SEM images show nanoparticles with a spherical structure and even distribution (Figure 12a). Figure 12b shows that the size of nanoparticles is not uniform, probably because of different current densities during deposition.\textsuperscript{38} According to the HRTEM atomic lattice fringe analysis (Figure 12c), the lattice spacing is 0.23 nm, conforming to the crystal surface size of Pd(111). It is very close to the crystal surface of Pd(111) reported in the literature.\textsuperscript{41,42} Other crystal faces of Pd(0) can be obtained from the electron diffraction pattern of the selected region (Figure 12d). HRTEM analysis did not show other crystal phases except Pd(0). It was verified that the electrodeposited nanoparticles are palladium metal. After 16 h electrolysis, 92.8% of palladium metal was obtained.

Figure 13 shows a composition analysis. Energy-dispersive spectrometry (EDS) (Figure 13a) analysis shows that the peaks of Pd particles also include some small signals from ILs (O, S), nickel foil (Ni), and other elements on the deposition layer. Figure 13b shows the XPS spectrum. The double peaks at 335.7 and 341.0 eV belong to Pd 3d\textsubscript{5/2} and Pd 3d\textsubscript{3/2}, respectively, consistent with the energy spectrum of Pd(0).\textsuperscript{43} Any valence of Pd other than Pd(0) was not observed in XPS analysis.
Finally, continuous extraction-electrodeposition of Pd(II) in the [C8bet]Br/[C4mim][NTf2] system was evaluated to determine the reusability of the [C8bet]Br/[C4mim][NTf2] IL system. After each electrodeposition, the mixed ILs of palladium were mixed with a saturated KBr solution and regenerated after washing. Figure 14 shows the corresponding extraction efficiency and recovery efficiency for three extraction-electrodeposition cycles. After three cycles, the recovery is still over 90.0%. The mixed [C8bet]Br/[C4mim][NTf2] system is very stable and provides a basis for solvent extraction-electrodeposition of Pd(II) in future industrial applications.

3. CONCLUSIONS

Hydrophilic betaine-based IL ([C8bet]Br) forms a precipitate with Pd(II) in acidic chloride media. The [C8bet]-Pd(II) precipitate was identified by UV−Vis, FTIR, 1H NMR spectroscopy, and Job’s method as a form of ion pair ([C8bet]2+PdCl4−). The mixed hydrophilic/hydrophobic IL ([C8bet]Br/[C4mim][NTf2]) system shows a higher extraction efficiency for Pd(II) than single hydrophobic IL ([C4mim][NTf2]). At a low hydrochloric acid concentration, the [C8bet]Br/[C4mim][NTf2] system shows excellent selectivity for Pd(II) over mixed metal-ion solutions. Moreover, the recovery of palladium from the organic phase can be achieved by thiourea stripping or direct electrodeposition.

4. EXPERIMENTAL SECTION

4.1. Instruments and Reagents. Palladium powder (>99.99%) was purchased from the Institute of Precious Metals (Kunming, China). Betaine, 1-bromooctane, and [C4mim][NTf2] were purchased from Alfa Aesar company (Beijing, China). Other reagents were purchased from Shanghai Titan Technology Co., Ltd. (Shanghai, China). All the reagents were of commercially available AR grade unless specified otherwise.

The chemical composition of betaine-based functionalized IL was analyzed by HR-MS (Agilent 1100 HPLC/TOF, Agilent Technologies Inc, Beijing, China). The concentration of single palladium ions in the solution was determined using an atomic absorption spectroscopy (AAS) (HITACHI Z-2000, Hitachi, Tokyo, Japanese). The concentrations of multimetal-ion mixture solutions were determined by ICP-AES (Thermo Fisher ICAP 6300 USA). The form of the Pd(II) complex was analyzed by UV−Vis spectroscopy (Lambda 365, PerkinElmer, Waltham, USA). The change in characteristic structural groups of [C8bet]Br before and after precipitation was determined by 1H NMR (Ascend Aeon 400, Bruker, Germany) and FTIR (NicoletiS10, Waltham, MA, USA) analyses. The melting point of compound [C8bet]Br was determined using a microscopic melting point meter (Beijing Taike Instrument Co., Ltd., Beijing, China). The Pd(II) complex in the mixed IL system was electrochemically analyzed and electrodeposited using an electrochemical workstation (CHI760E, Shanghai Chenhua Instrument Co., Ltd., Shanghai, China). The morphology and EDS analyses of palladium after deposition were carried out by SEM (Nova NanoSEM, Thermo Scientific, Waltham, USA), and the valence of palladium on the surface of coating was analyzed by XPS (K-Alpha+, Thermo USA) and HRTEM (JEM-210, JEOL, Tokyo, Japan).
The value of $\text{HCl}$ was 0.1 M. Concentration of working of palladium solution can be obtained by diluting the standard stock solution.

The precipitation experiment was conducted by mixing different contents of $[C_{8}\text{bet}]\text{Br}$ with 2 mM solution of Pd(II) (HCl: 0.1 M) in a constant-temperature oscillator. The amount of $[C_{8}\text{bet}]\text{Br}$ was 1.5−20 times that of Pd(II), and the vibration time was 30 min. Precipitation was obtained by centrifuging the mixture for 5 min. The aqueous phase was analyzed with AAS, and the precipitate was analyzed by UV−Vis, FTIR, and $^1$H NMR spectroscopies.

In the extraction study, an organic phase was obtained by adding a specified amount of $[C_{8}\text{bet}]\text{Br}$ required for the experiment to the hydrophobic IL $[C_{8}\text{mim}][\text{NTf}_2]$, and an extraction system was obtained using Pd(II) or aqueous solutions of mixed metal ions. The concentration of metal ions in the aqueous phase was 2 mM, and that of HCl was 0.1 M. The value of $R_{A/O}$ was 5. The mixture was vibrated for 30 min to achieve equilibrium. After separating at 9,000 rpm for 5 min, the metal concentration of aqueous phase was analyzed. All the extraction experiments were performed three times with a standard deviation of less than ±3%.

The precipitation percentage ($P\%$) or extraction efficiency ($E\%$), distribution ratio ($D$), separation factor ($K$), stripping efficiency ($S\%$), and recovery efficiency ($R\%$) were calculated as follows:

$$P\% = \frac{[C_{\text{in}}] - [C_{\text{eq}}]}{[C_{\text{in}}]} \times 100$$

$$D = \frac{[C_{\text{eq}}]}{[C_{\text{in}}]} \times R_{A/O}$$

$$K = D_{Pd}/D_M$$

$$S\% = \frac{[C_{\text{eq}}]}{[C_{\text{in}}]} \times 100$$

$$R\% = E\% \times S\%$$

where $[C_{\text{in}}]$ and $[C_{\text{eq}}]$ are the concentrations of Pd(II) in the aqueous phase before and after precipitation or extraction; $[C_{\text{eq}}]$ is the concentrations of Pd(II) in the mixed IL phase.

4.2.2. Synthesis of $[C_{8}\text{bet}]\text{Br}$. Scheme 1 shows the synthesis of target hydrophilic IL $[C_{8}\text{bet}]\text{Br}$. First, 1-bromooctane (0.06 mol, 11.52 g) was slowly added to acetonitrile (100 mL), and the mixture was stirred for 10 min. A certain amount of betaine (0.05 mol, 5.86 g) was added to the mixture and stirred at 90 °C and refluxed for 24 h. The solvent was removed by rotary evaporation in vacuum at 50 °C. Thus, a solid white product $[C_{8}\text{bet}]\text{Br}$ was obtained. Yield: 14.27 g (92%); melting point: 57.5 ± 0.5 °C.

$[C_{8}\text{bet}]\text{Br}$ was characterized by HR-MS and $^1$H NMR analyses. $^1$H NMR (400 MHz, DMSO) δ 4.47 (s, 2H), 4.18 (t, $J = 8.0$ Hz, 2H), 3.24 (s, 9H), 1.61 (m, 2H), 1.45−1.23 (m, 10H), 0.88−0.85 (m, 3H). HR-MS (ESI$^+$): [M − Br]$^+$ calcd: (C$_{13}$H$_{28}$NO$_2$) 230.2114; found, 230.2115.

4.2.3. Electrochemical Test. Constant-potential deposition and electrochemical analysis were carried out using an electrochemical workstation. A three-electrode system was prepared as follows: a platinum wire with an inner diameter of 0.5 mm was used as the reference electrode. A platinum plate (1.2 mm × 1.2 mm) was used as the counter electrode. A glassy carbon (GC) electrode was used as the working electrode. Before measurement, the GC electrode was polished with alumina, successively washed with acetone and distilled water, and dried. CV was conducted using an electrochemical workstation at 348 K. For CV analysis, an electrolyte containing 2250 mg L$^{-1}$ Pd(II) dissolved in the $[C_{8}\text{bet}]\text{Br}/[C_{8}\text{mim}][\text{NTf}_2]$ system was used. The scanning rate was 50 mV/s. All ILs were vacuum-dried at 385 K for 12 h.

To separate Pd(0) from the Pd(II) complex, a three-electrode system with a platinum wire as the reference electrode, a platinum sheet as the counter electrode, and a nickel foil (1 cm$^2$) as the working electrode was used. Pd(II) (C = 2250 mg L$^{-1}$) was extracted by electrodepositing with controlled potentiostatic deposition (deposition temperature: 348 K, potential: −1.7 V, deposition time: 16 h). The amount of Pd(II) in the mixed IL system after electrodeposition was determined following the literature method.

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Notes
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