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Preparation and Electrochemical Behavior of Palladium in Ionic Liquid

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The preparation of palladium (Pd) from a water- and air-stable room-temperature ionic liquid, 1-ethyl-3-methylimidazolium trifluoromethanesulfonate ([emim]OTf), was investigated. Cyclic voltammetry was applied in examining the electrochemical behavior of Pd (II) chloride and in identifying the current density for the electrodeposition of Pd. The optimum parameters of Pd electrodeposition were obtained through single-factor experiments. Surface morphology and elemental composition of final products were probed by scanning electron microscopy and energy- disperse spectrometer analyses. The deposition of crystalline Pd metals was confirmed by X-ray diffraction (XRD). Results demonstrated that 1-ethyl-3-methylimidazolium trifluoromethanesulfonate was a potential electrolytic medium for electrodepositing high-purity Pd at room temperature.

Keywords: palladium; electrodeposition; electrochemical behavior; ionic liquid;

1. INTRODUCTION

Palladium (Pd) is an essential platinum group metal that exhibits excellent properties, such as electrical conductivity, wear and corrosion resistance, catalytic activity, and thermal stability, which makes this metal useful for catalysis and producing electrical devices and jewelry [1]. However, statistical date reveal that the proportion of Pd in the earth's crust is very limited (around 0.1 ppm) [2] even though the global demand for this metal is increasing each year. For example, the demand for Pd in automotive and industrial applications, jewelry production, and investment increased to 299.5 tons from 2011 to 2013, but the amount of available Pd in the world was only 200 tons [3]. Therefore, the recovery of Pd from E-waste or spent catalyst and other secondary resources is very important.

Compared to ion exchange [4,5], adsorption [6], precipitation [7], and solvent extraction [8,9], the electrochemical method is considered one of the easiest and promising Pd recovery techniques because of its simplicity, cost effectiveness, accessibility, and need for no external reagents [10,11].

Traditional electrolysis systems comprise an aqueous solution and high-temperature melt salts. In an aqueous solution, Pd has a high catalytic activity against hydrogen evolution as well as absorbs a great amount of hydrogen to produce hydrogen embrittlement that can influence the quality of production [1]. High-temperature melt salts are inconvenient because of their high melting points. Room temperature ionic liquids (RTILs) comprise ions and are molten at temperatures that are lower than 373k. These liquids generally comprise a bulky, unsymmetrical organic cation and an organic or inorganic anion [12]. Recently, ionic liquids have been used in many applications as emerging green solvents. Given their unique ionic structure, these liquids have many attractive properties, such as their favorable conductivity, wide electrochemical window, and tunability by changing the combination of cations and anions [13]. The wide electrochemical window makes these liquids serve as electrolytic mediums of many metals that cannot be deposited in aqueous solutions at near-ambient temperature. Given their non-aqueous solutions, these liquids have a negligible amount of hydrogen to be released during electrodeposition, which ensures the superior quality and purity of the products [14].

Electrodepositing Pd from AlX_3 (X=Cl or Br)-based ionic liquid has been investigated previously [15]. The advantages of this haloaluminate-based ionic liquid include its tunable composition and property as well as its relatively cheaper cost than other hydrophobic ionic liquids. However, the moisture-sensitive and strict operating conditions of this liquid limit its applications [12]. Therefore, the search for a water- and air-stable, high-performance, and relatively inexpensive ionic liquid as an electrolytic medium presents a new research topic in electrochemistry. A novel extraction-electrodeposition process for the quantitative recovery of Pd from nitric acid medium and fast rector-simulated high-level liquid waste (FR-S-HLLW) has been reported [16,17]. Tri-n-octylmethylammonium nitrate (TOMAN) was used as extractant and electrolytic medium. More than 60% of Pd was extracted in a single process, where ~98% of Pd was recovered from nitric acid after 20h electrolysis and ~96% of Pd was recovered from FR-S-HLLW after 30 h. However, TOMAN has a relatively high viscosity and exists in a semi-solid state at room temperature (298K), hence requiring an additional dilution process. M. Jayakumar et al. [18-21] reported the electrodeposition of platinum group metals from 1-butyl-3-methylimidazolium chloride (bmimCl) ionic liquid as well as studied the influence of electrodeposition on the surface morphology and electrochemical behavior of the metal ions. However, the melting point of bmimCl was reported at 341 K [20,21], and electrodeposition was required at such high temperature. Y. Katayama [1,22] investigated the electrodeposition of Pd in BMPTFSI. Although those RTILs that comprise $TFSI^-$ anion exhibit excellent hydrophobicity and electrochemical stability, these ionic liquids have a very high market price according to a market survey. Therefore, the properties, cost, and potential of 1-ethyl-3-methylimidazolium trifluoromethanesulfonate ([emim]OTf) with a melting point of -25.7℃ [23] must be investigated in future research.

2. EXPERIMENTAL

2.1 Materials

All chemicals used were analytical grade. 1-ethyl-3-methylimidazolium trifluoromethanesulfonate ([emim]OTf) with a purity of greater than 99% was procured from Dibo

Chemical Technology Co., Ltd, Shanghai, China. Palladium Chloride ($PdCl_2$) with a purity of greater than 99% was procured from Sinopharm Chemical Reagent Co., Ltd, Beijing, China.

2.2 Cyclic Voltammetry

Cyclic voltammetry was recorded at three-electrode system. Pt wire (Φ0.5 mm) was used as working and counter electrodes, while Pd wire (Φ1 mm) was used as the reference electrode. A homemade three-electrode cell was used for the electrochemical measurements and electrodeposition experiments.

2.3 Electrodeposition of Pd from [emim]OTf

Galvanostatic electrodeposition was conducted by using a DC power equipment (Agilent Technologies E361×A) after performing the electrochemical measurements. Ti plates (1.5 cm×0.5 cm) were used as substrates and counter electrodes, while Pd wire was used as the reference electrode. Given that the DC power equipment provides a two-electrode system, the counter electrode and the Pd wire reference electrode were connected together as an anode. Ti plates were mirror-polished, were treated in diluted hydrochloric acid, and were rinsed with deionized water and acetone. After electrodeposition, the products were separated from the ionic liquid through centrifuge, were washed extensively with alcohol, dilute hydrochloric acid, and deionized water, and were dried before the surface morphology and phase analysis. All the electrochemical measurements, including the electrodeposition experiments, were conducted in the Ar-filled globe box.

2.4 Instrumentation

Cyclic voltammograms of the solutions were measured using an electrochemical workstation (ZAHNER IM6e), A SU-8020 field effect SEM with an energy-disperse spectrometer (EDS) working at 15.0 K V was used to examine the surface morphology and elemental composition of the deposit. The phase constitution of the deposit was characterized by XRD-7000.

3. RESULTS AND DISCUSSION

3.1 Electrodeposition of palladium from [emim]OTf

Figs. 1(a) and 1(b) show the electrochemical window of ionic liquid 1-ethyl-3-methylimidazolium trifluoromethanesulfonate [emim]OTf and the cyclic voltammogram of Pd (II) chloride in [emim]OTf that is recorded at 298 K. The inset is a larger version of Fig. 1(b).

In our operation condition, the ionic liquid 1-ethyl-3-methylimidazolium trifluoromethanesulfonate exhibited an electrochemical window at almost 3.0V (vs. Pd), which was wider than the reported ionic liquid bmimCl (2.5V at 373K) [19]. When scanning in the negative direction, a prominent reduction wave was observed at about -0.8V. When the scan was reversed at -2.0V, an anodic current wave was observed at -0.6V, but the current of the anodic wave was smaller than that of the cathodic wave.

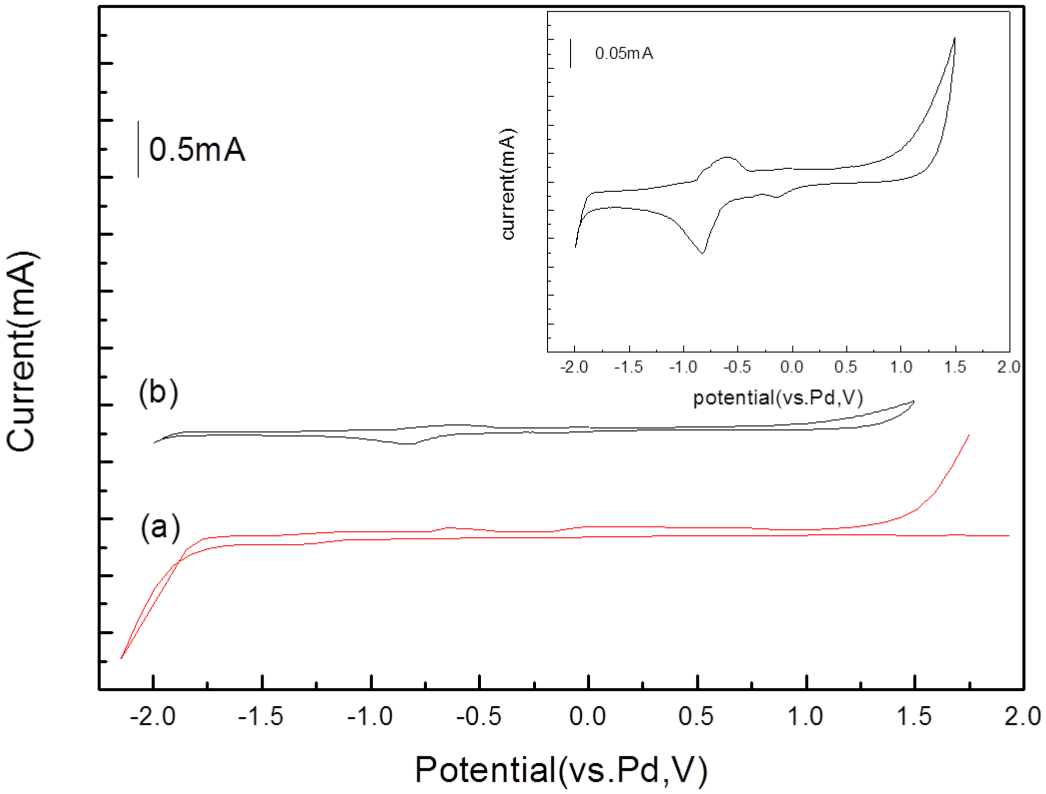


Figure 1. Electrochemical window of [emim]OTf (a) and cyclic voltammograms of Pd (II) chloride in [emim]OTf (b). T=298K; Scan rate: 50mV/s; Working and counter electrodes: Pt wire; Reference electrode: Pd wire; Mole ratio of [emim]OTf and $PdCl_2$: 45:1.

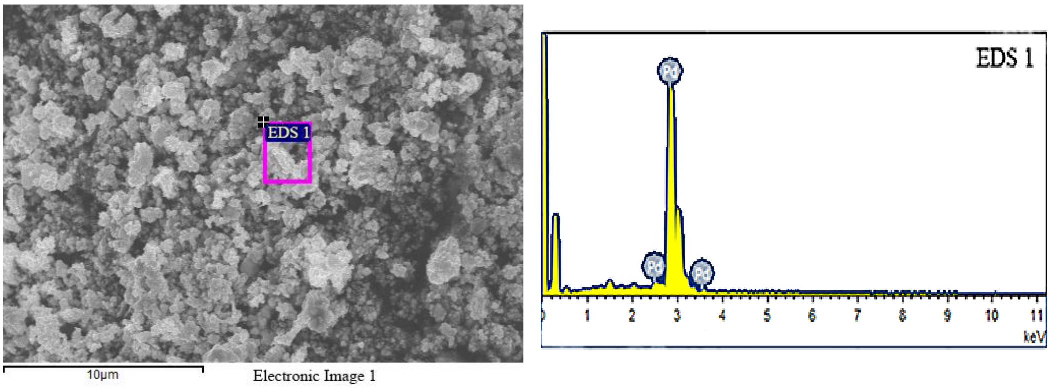


Figure 2. Surface morphology and EDS pattern of the Pd deposits from [emim]OTf taken by galvanostatic electrodeposition.

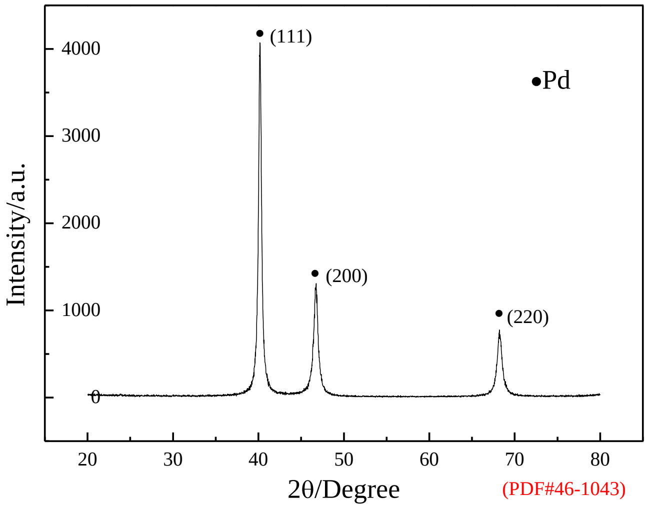


Figure 3. XRD pattern of the depositions obtained by electrolysis of [emim]OTf-$PdCl_2$.

The current density is then calculated based on the cathodic wave current at -0.8V and the surface area of Pt wire that was immersed into the electrolyte. Electrolysis was then performed by using DC power at an average current of 4.56 mA at 298 K. The mole ratio of [emim]OTf and $PdCl_2$ was 45:1, the electrolysis time was 22h, and the electrode distance was 23mm. The electrodeposits were characterized by SEM and EDS as shown in Fig.2. The XRD pattern of the deposits as shown in Fig.3.

The depositions were confirmed as metal Pd. The single anodic current wave at -0.6V could be attributed to the anodic dissolution of Pd that was deposited in the preceding cathodic potential sweep. The smaller anodic current wave could be attributed to the irreversible electrode reaction or to the dropping of some deposited Pd from the electrode during the preceding cathodic scan [1].

3.2 Influence of scan rate

Cyclic voltammetry as a basic and important electrochemical diagnostic technique, has been widely used for many fields, such as analyze the electrochemical behavior of metal ions, biological electroactive species [24,25], et al. Through the approach of CV, reversibility of electrochemical reaction, control step, diffusion coefficient and the energy of activation can be determined.

The cyclic voltammograms of saturated Pd (II) chloride in [emim]OTf (about 12mM) at various scan rates are compared in Fig.4. Two prominent reduction waves were observed at about -0.39V (E_p^{c1}) and -0.9V (E_p^{c2}) when scan rate was 60mV/s, and two weak oxidation waves were observed at about -0.58V (E_p^{a2}) and 0.26V (E_p^{a1}), which are corresponding to the reduction waves in previous cathodic scan when the scan is reserved at -1.5V. The cathodic peak current increased and the cathodic peak potential slightly shifted in the negative direction when the scan rate was increased, and the range of cathodic peaks were wide, moreover the difference in the value of (E_p^{a2}-E_p^{c2}) (320mV) was considerably larger than a reversible process ($E_p^{a}-E_p^{c} \approx 2.3RT/(nF) \approx 30mV$, at 303K), which indicated that the reduction on the Pt working electrode was irreversible [26]. The data of E_p^{c1} that are obtained at different scan rates are shown in Table 1. As for the irreversible electrode processes, the value of charge transfer coefficient α can be determined as follows:

$$|E_p - E_{p/2}| = 1.857RT/(\alpha n_\alpha F) \qquad (3\text{-}1)$$

Where $E_{p/2}$ is the half-peak potential, n_α is the number of electrons in control step, F is the Faraday constant, and T is the absolute temperature in K. The average value of αn_α was 0.27 for the measurements at 303K.

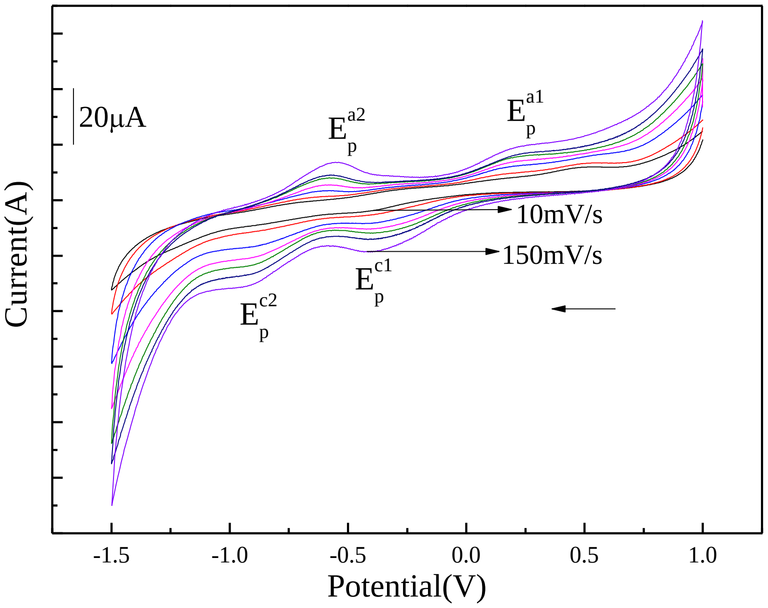


Figure 4. Cyclic voltammograms of a solution of 12mM $PdCl_2$ in [emim]OTf at various sweeping rates at 303K. Working and counter electrodes: Pt wire; Reference electrode: Pd wire. Sweeping rates (mV s^{-1}): (a) 10, (b) 20, (c) 40, (d) 60, (e) 80, (f) 100, and (g) 150.

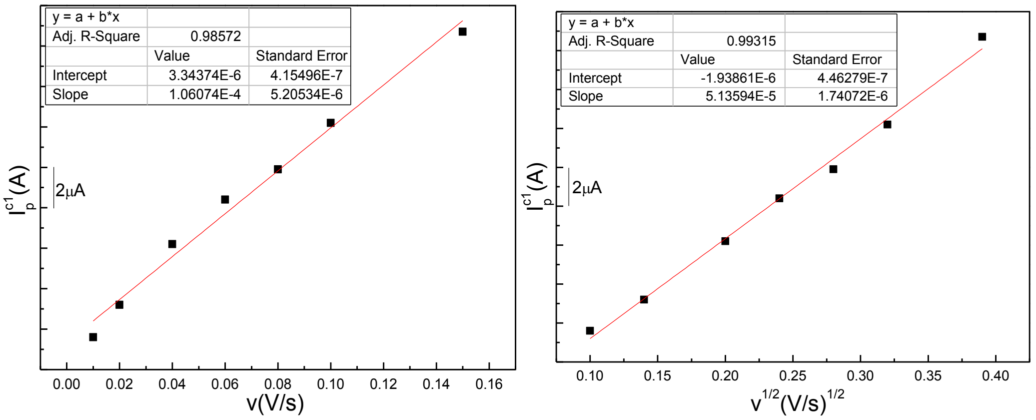
Table 1. Parameters of cyclic voltammogram with various sweeping rates at 303K

v ($mV \cdot s^{-1}$)	$v^{1/2}$ $(V \cdot s^{-1})^{1/2}$	E_p^{c1} (V)	$E_{p/2}$ (V)	$\lvert E_p - E_{p/2} \rvert$ (V)	I_p^{c1} (mA)	αn_α
10	0.1	-0.381	-0.287	0.094	0.0036	0.52
20	0.14	-0.384	-0.242	0.142	0.0052	0.34
40	0.2	-0.387	-0.188	0.199	0.0082	0.24
60	0.24	-0.394	-0.164	0.23	0.0104	0.21
80	0.28	-0.395	-0.143	0.252	0.0119	0.19
100	0.32	-0.403	-0.143	0.26	0.0142	0.19
150	0.39	-0.405	-0.142	0.263	0.0187	0.18
average						0.27

The plot of the cathodic peak current (I_p^{c1}) against the scan rate (v) and the square root of scan rate ($v^{1/2}$) are shown in Fig. 5. Comparing the R-Square and the Standard Error of slope respectively, a linear relationship was found between I_p^{c1} and $v^{1/2}$, which indicated that the electrodeposition of Pd was determined by diffusion [27]. A relation between I_p^{c1} and $v^{1/2}$ for an irreversible process is given as follows [19]:

$$I_p^c = 0.4958 nFC_0^* AD^{1/2} \left(\frac{(\alpha n_\alpha)Fv}{RT}\right)^{1/2} \qquad (3\text{-}2)$$

Where C_0^* is the Pd (II) concentration in mol/cm^3, A is the electrode area in cm^2, n is the number of exchanged electrons, D is the diffusion coefficient in cm^2/s, and v is the scan rate in V/s. From the slop of the straight line in Fig. 5(b), the diffusion coefficient of Pd (II) was estimated at 8.05×10^{-8}cm^2/s. By the same analysis method, the diffusion coefficients at different temperatures were tabulated in Table 2.



(a) (b)

Figure 5. Relationship between cathodic peak current I_p^{c1} and v (a) or $v^{1/2}$ (b) for the reduction of Pd (II) at 303K.

Table 2. Diffusion coefficient of Pd (II) in [emim]OTf-PdCl$_2$ at different temperatures

T (K)	D ($\times10^{-7}$)
303	0.81
308	0.98
313	1.42
318	1.43
323	1.81

It was shown that the diffusion coefficient increase with increasing temperatures and the relationship between them conform to Arrhenius equation that is shown as follow [19]:

$$D = Ae^{\left(-\frac{E_a}{RT}\right)} \qquad (3\text{-}3)$$

Where A is the pre-exponential factor, and E_a is the energy of activation. The plot of lnD against 1/T is shown in Fig. 6, from the slope of the straight line, the energy of activation for diffusion of Pd (II) can be estimated to 33.05KJ/mol. The value is considerably lower than the activation energy of Pd (II) (63KJ/mol) in bmimCl [19].

To determine the optimum technological parameter, a series of optimization experiments were performed. The results are shown in Fig.7 (a) to 7(d).

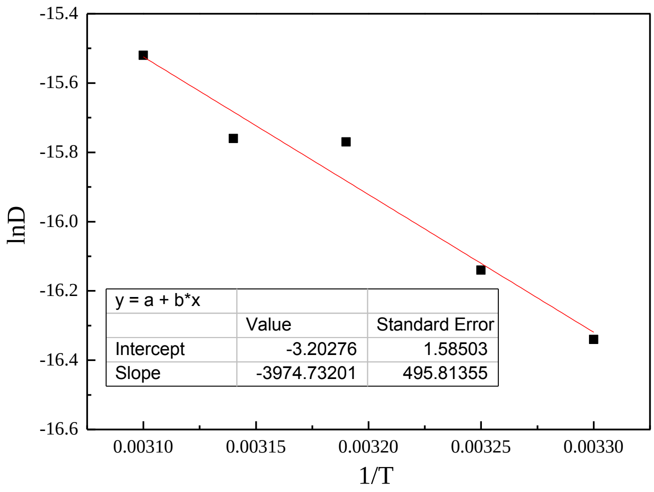


Figure 6. The plot of lnD against 1/T of [emim]OTf-$PdCl_2$

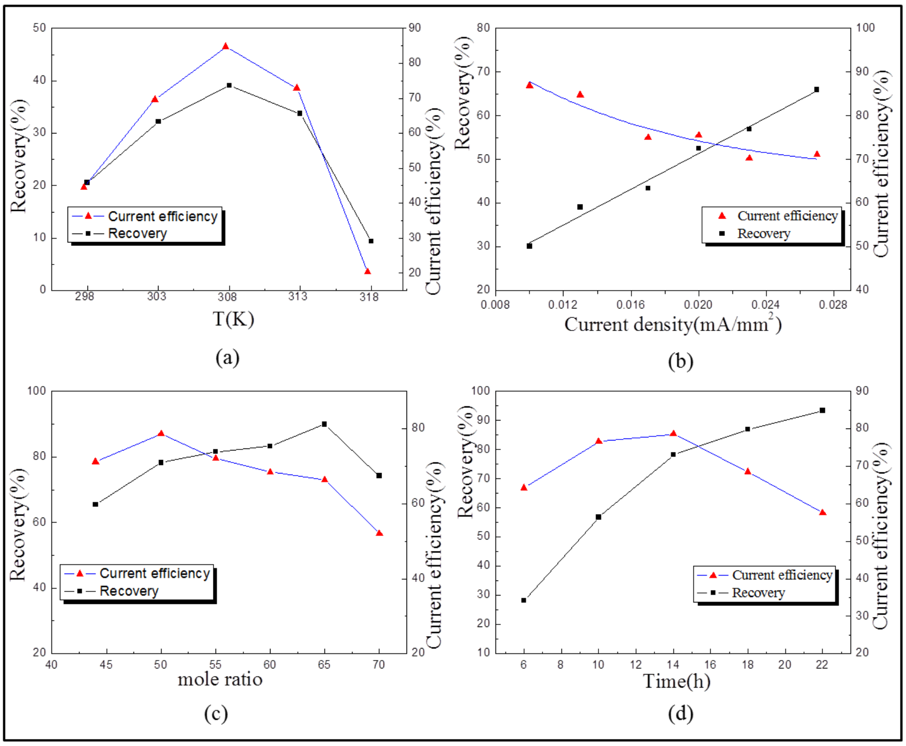


Figure 7. Effect of temperature (a), current density (b), mole ratio (c), and electrolysis time (d) on current efficiency and recovery of electrodeposited Pd.

3.3 Temperature

The temperature of electrodeposition Pd in ionic liquid [emim]OTf was set from 298 K to 318 K and was controlled by thermostatic oil bath. The current density was 0.013 mA/mm^2, the mole ratio of [emim]OTf and $PdCl_2$ was 45:1, the electrolysis time was 14 h, and the electrode distance was 23 mm. Current efficiency is computed as follows :

$$\eta = m'/(cIt) \times 100\% \qquad (3\text{-}4)$$

Where η is the current efficiency, m' is the actual amount of cathode depositions (g), I is the current (A), t is the electrolysis time (h), c is the electrochemical equivalent ($g \cdot A^{-1} \cdot h^{-1}$). The effect of temperature on current efficiency and recovery is shown in Fig. 7(a). The curve reveals that current efficiency increases and reaches the maximum (84.74%) at 308 K, and then decreases as the temperature continues to increase. When the temperature rises to 318 K, the current efficiency obviously decreases. At the beginning, the viscosity of ionic liquid was reduced along with the increasing temperature to promote the diffusion rate of ions, which in turn increased the amount of Pd ions discharged at the cathode. As a result, the current efficiency was increased. The cathode depositions that were anti-dissolved into electrolyte at a higher temperature rapidly decreased the amount of collectable depositions within a temperature range of 313 K to 318 K. After the depositions were collected by centrifuge, many ultrafine black particles could still be observed in the electrolyte.

The recovery of Pd was calculated as follows:

$$\eta_{Recovery} = \frac{m_{Recovery}}{m_{PdCl_2} \times \frac{M_{Pd}}{M_{PdCl_2}}} \times 100\% \qquad (3\text{-}5)$$

Where $m_{Recovery}$ is the actual amount of cathode depositions (g), m_{PdCl2} is the mass of $PdCl_2$ added into [emim]OTf, M_{Pd} and M_{PdCl2} are the relative molecular masses of Pd (106.42) and $PdCl_2$ (177.31), respectively.

Equation 3-5 shows that when the mass of $PdCl_2$ is certain, the recovery is proportional to the mass of cathode depositions. Given the existence of the anti-dissolved phenomenon, the curve presents a similarity with current efficiency. A peak (39.09%) at 308 K is also observed. In conclusion, 308 K is confirmed as the optimum parameter. The temperature finally choice is far lower than the electrowinning of PGMs in bmimCl at 373K [19-21], and without any additives like diluents compare to electrolysis of palladium from quaternary ammonium ionic liquid TOMAN, even though it perform at 298K [16].

3.4 Current density

The electrodepositions of Pd from [emim]OTf in different current densities ranging from 0.010 mA/mm^2 to 0.027 mA/mm^2 were taken at 308 K. The electrolysis time was 14 h, the mole ratio of [emim]OTf and $PdCl_2$ was 45:1, and the electrode distance was 23 mm. The cathode current efficiency and recovery of Pd were calculated using equations 3-4 and 3-5, and the result is shown in Fig. 7(b).

The cathode current efficiency decreased from 86.84% to 71.16% along with the increasing current density, whereas the recovery increased from 30.14% to 65.95% under similar conditions. According to Faraday’s Law, the mass of the depositions is directly proportional to the quantity of electrical charges that pass through the electrolyte. Therefore, the mass of Pd ions on the cathode is proportional to the current density. Given that the decrease in current efficiency (15.68%) is lower than the increase in recovery (35.81%), the optimum current density was determined as 0.027 mA/mm^2.

In previous studies, control potential electrolysis was always adopted on electroseposition metal, and the results always indicate the deposition potential has a significant effect on the surface morphology and grains size of electrodeposits. For example, electrodeposition of Sn from EMI-DCA on Cu substrate, the morphologies of hollow tubes, entangled wires, and dendrites were discovered at various deposition potential [28]. The experiment of electrodeposition of Ni in EMI-DCA indicates the roughness of the Ni-deposited surface and the grains size is dependent on the deposition potential [29]. Electrodeposition of palladium from bmimCl indicates the deposited palladium with dendrite morphology, and the density of dendrites increased with increase of applied potential [18]. But the investigations about the effect of current density on cathodic deposits are limited, so we focus on the current density at present.

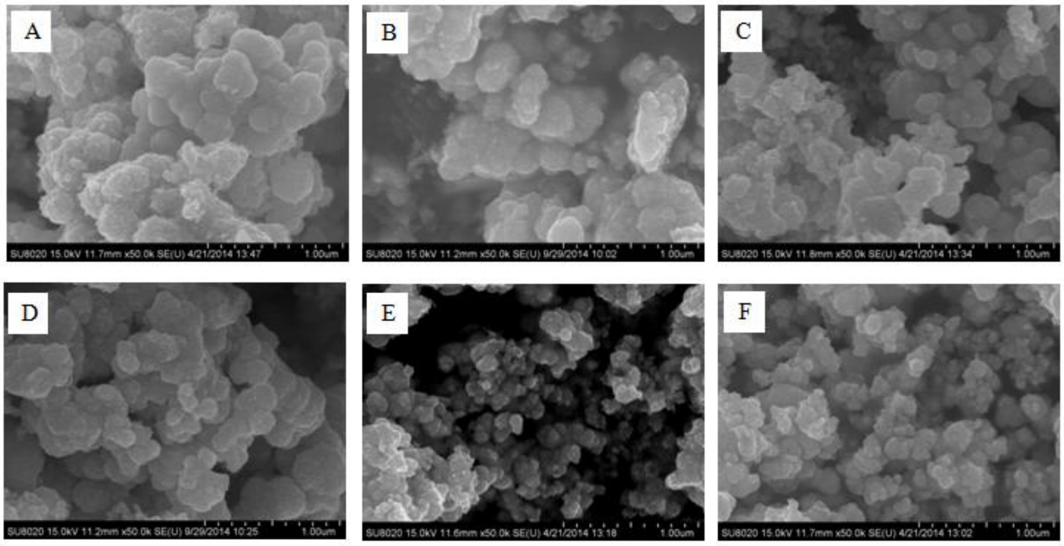


Figure 8. Surface morphology of electrodeposited Pd from [emim]OTf at the current densities of 0.010 mA/mm^2 (A), 0.013 mA/mm^2 (B), 0.017 mA/mm^2 (C), 0.020 mA/mm^2 (D), 0.023 mA/mm^2 (E), and 0.027 mA/mm^2 (F).

The surface morphology of the depositions at different current densities is shown in Fig. 8. The SEM images indicate that the depositions on the cathode are mainly spherical and that the particle size becomes finer when the current density ranges from 0.010 mA/mm^2 to 0.027 mA/mm^2. The particle size reaches the nanoscale when the current density exceeds 0.023 mA/mm^2.

3.5 Mole ratio of [emim]OTf and $PdCl_2$

The mole ratio of [emim]OTf and $PdCl_2$ ranged from 45 to 70, the temperature was 308 K, the current density was 0.027 mA/mm^2, the electrolysis time was 14h, and the electrode distance was 23mm. Fig. 7(c) shows the effect of mole ratio on current efficiency and recovery.

As the mole ratio of [emim]OTf and $PdCl_2$ increases, the proportion of Pd (II) in the electrolyte is decreasing. At the beginning, when the amount of Pd ions in the solution gradually decreased, the collision between ions might be weakened. Therefore, the Pd ions participate in discharging on the cathode increasing. As the added Pd (II) continued to decrease, the concentration of Pd ions in the solution would decrease, which would lower the conductivity of the whole electrolyte. The concentration gradient of Pd ions would also decrease and affect the diffusion rate, which would subsequently decrease the mass of reduction products. Equation 3-4 shows that the calculated current efficiency increases to a maximum of 78.63% at 50 mole ratio and then decreases to 52.09% at 70 mole ratio.

Equation 3-5 shows that the recovery of Pd in this experiment is related to the mass of $PdCl_2$ that is added into electrolyte. The recovery reaches a maximum of 89.93% at 65 mole ratio (the current efficiency is 66.39%) and then decreases as the amount of $PdCl_2$ continues to decrease. By comparing the data that are obtained at 50 and 65 mole ratio, the current efficiency is observed to decrease from 78.63% to 66.39%, the recovery increases from 78.22% to 89.93%, and the decrease of the former (12.24%) is larger than the increase of the latter (11.71%). Therefore, the optimum parameter was confirmed at 50 mole ratio.

3.6 Electrolysis time

The time of electrolysis was set from 6 h to 22 h, the electrolysis temperature was 308 K, the current density was 0.027 mA/mm^2, the mole ratio of [emim]OTf and $PdCl_2$ was 50, and the electrode distance was 23 mm. The influence of electrolysis time on the current efficiency and recovery of Pd is shown in Fig. 7(d).

The increasing and then decreasing trend of current efficiency followed the extension of electrolysis time. The maximum current efficiency reached 78.63% when the electrolysis time was set to 14 h. However, the recovery of Pd increased all the time. When the electrolysis time was extended, more Pd ions were dissolved into the solution and participated in the discharge on the cathode. Therefore, a longer electrolysis time would lead to a fuller reaction. However, if the time of electrolysis was too long, the loss of electric charges in the connection of each part on the circuit would also increase. The affection of concentration polarization would also become apparent, the nucleation rate would decrease, and the current efficiency would subsequently decreased [30]. After comprehensive consideration, the ultimate electrolysis time was set to 14h.

3.7 Electrode distance

The temperature was 308 K, the current density was 0.027 mA/mm^2, the mole ratio was 50, and the time of electrolysis was 14 h. Given the actual volume of the electrolytic cell, the electrode distance was selected at 19 mm, 23 mm, and 27 mm. The results are shown in Table 3. Given that the space volume of the electrolytic cell is relatively small, the affection of electrode distance is not apparent.

Table 3. Effect of electrode distance on current efficiency and recovery.

No.	T/K	Current density mA/mm^2	Mole ratio ($IL:PdCl_2$)	t/h	Electrode distance /mm	Current efficiency /%	Recovery /%
1	308	0.027	50	14	19	77.36	80.88
2	308	0.027	50	14	23	78.63	78.22
3	308	0.027	50	14	27	76.11	79.36

4. CONCLUSIONS

[emim]OTf has a lower melting point and viscosity as well as a better electrochemical stability at room temperature. The ionic liquid can also act as an electrolytic medium for electrodeposition of Pd. Research on the electrochemical behavior of Pd (II) chloride in [emim]OTf reveals two prominent reduction waves in cyclic voltammograms, two weak oxidation waves are observed when the sweeping is reversed. Given that the cathodic wave potential shifts negatively as the scan rate is increased, and the difference in the value of (E_p^a-E_p^c) is considerably larger than a reversible process demonstrate the reduction on the Pt working electrode is irreversible. The linear relationship between I_p^{c1} and $v^{1/2}$ indicates the reduction of Pd (II) is determined by diffusion. The diffusion coefficient is 8.05×10^{-8} cm^2/s at 303 K The relationship between diffusion coefficient and temperature conform to Arrhenius equation, and the energy of activation for diffusion of Pd(II) in [emim]OTf is 33.05 KJ/mol. The optimum conditions for the electrodeposition of Pd in [emim]OTf include a temperature of 308 K, a current density of 0.027 mA/mm^2, a mole ratio ([emim]OTf:$PdCl_2$) of 50, and an electrolysis time of 14h. The affection of electrode distance can be ignored.

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