Study on Electrochemical Properties of Palladium in Nitric Acid Medium

Shengchu Liu\textsuperscript{a}, Ruiqin Liu\textsuperscript{a}, Yan Wu\textsuperscript{a}, Yuezhou Wei\textsuperscript{a,}\textsuperscript{*}, Baizeng Fang\textsuperscript{b}

\textsuperscript{a} School of Nuclear Science and Engineering, Shanghai Jiao Tong University, Shanghai 200240, People’s Republic of China
\textsuperscript{b} Department of Chemical & Biological Engineering, University of British Columbia, 2360 East Mall, Vancouver, B.C., Canada V6T 1Z3

Abstract

The electrochemical behavior of palladium (II) in nitric acid was studied using various electrochemical techniques. The cyclic voltammogram of palladium (II) recorded at Pt electrode presented a series of electrochemical reactions corresponding to the redox behavior of palladium. SEM images of palladium obtained by electrolysis revealed the dendrite growth, which was uniform all over the entire surface of Pt electrode. The recovery ratios of palladium at different nitric acid concentrations were high, and the Faradic efficiency decreased as the nitric acid concentration was increased, which might be due to the reduction of nitric or H\textsuperscript{+} ions. The reduction of palladium (II) was irreversible and stirring during electrolysis could improve the electrodeposition rate.

Keywords: Palladium; Fission product; Electrochemical techniques; Electrodeposition

* Corresponding author. Tel.:+86-21-34205684; fax: +86-21-34205182.
E-mail address: yzwei@sjtu.edu.cn.
1. Introduction

Palladium is a noble metal. Owing to its irreplaceable physical and chemical properties, such as high ductility, strong hydrogen adsorption capability [1] and excellent catalytic properties [2], there is a huge demand for palladium and its compounds in various industrial fields [3]. The natural abundance of palladium in the earth’s crust is very low (1×10^{-6} %) and only occurs in a few countries. All the mines are likely to be consumed in another few decades at its current rate of use [4]. The price of palladium is rising steadily every year on the world market, and predictably, will keep rising in the long run due to the growing mining costs.

Palladium and other platinum group metals (PGMs) namely, ruthenium, rhodium are produced as man-made precious metal after nuclear fissions [5]. At a burn up of 33 GWD/t (gigawatt days per metric ton), one metric ton of spent fuel contained more than 1 kg palladium. It’s estimated that by 2030 spent nuclear fuel could provide as much as 1000t palladium. This would be a considerable addition to the yield from natural sources [6]. Fission palladium is comprised of isotopes 104 (17 wt.%), 105 (29 wt.%), 106 (21 wt.%), 107 (17 wt.%), 108 (12 wt.%), and 110 (4 wt.%). Among them, Pd-107 is the only radioactive isotope with a half-life of 6.5×10^5 years. Since the maximum energy of β-ray emitted by Pd-107 is 35 KeV [5] and the radiation intensity at the surface of fission palladium is only merely 520 Bq•cm^{-2}. Thus, if recovered, its weak radioactivity can be tolerated for many industrial applications [7]. On the other hand, in the process of vitreous solidification for HLLW, short for nuclear high level liquid waste, PGMs are harmful, and so far, Rokasho reprocessing plant in Japan has been compelled to stop running because they formed separate phases, causing deterioration in the stability of the glass, which is very adverse to the storage of vitreous solidification [8].

Based on these facts, to separate and recover PGMs, especially palladium, from HLLW has been one of the focused research topics in the field of radiochemistry in the past few decades [7]. Solvent extraction and ion exchange are the most studied methods for the recovery of palladium from nitric acid solutions worldwide [3], which have been described by many documents [9-11]. In comparison with solvent extraction, electrochemical approaches are reported as the most promising methods because of their simplicity, cost effectiveness, accessibility to recover palladium from acid solution and no need of external reagents [12]. The rate of cathodic deposition of palladium from nitrate solutions and the current efficiency of the process were studied by Kirshin et al [13]. However, very little work was reported about the detailed electrochemical behavior and kinetic parameters of palladium (II) in nitric acid medium. In this study, we intend to clarify the electrochemical behavior of palladium (II) in nitric acid by using various electrochemical techniques. Electrowinning of palladium under different voltages and effect of nitric acid concentration were also investigated.

2. Experimental

All the chemical agents used in the study are of analytical grade and used without any further purification. Pd(NO_3)_2•2H_2O was procured from ACROS, Belgium. The Pd(II) in nitric acid media was made by dissolving a required quantity of Pd(NO_3)_2•2H_2O in appropriate concentration of nitric acid.

A UV-Vis spectrometer (UV-3600, Shimadzu, Japan) was used to record the absorption spectrum of palladium (II) in various concentrations of nitric acid. Electrodeposition studies were carried out in a single-chamber electrolysis cell in which the temperature was controlled by an electric-heated thermostatic water bath with built-in magnetic stirrer which could provide stirring during electrolysis. In all the electrochemical measurements, platinum plate (surface area= 8 cm^2), platinum wire and Ag/AgCl electrode acted as working, counter and reference electrodes, respectively. All the electrochemical studies were controlled with a potentiostat (CHI 660D, Shanghai Chenhua Electric Co, China). The
concentrations of palladium present in aqueous phase before and after electrolysis at different time points were determined by an inductively coupled plasma atomic emission spectrometry (ICP-AES) instrument (ICP-7510, Shimadzu, Japan). After the electrodeposition, the platinum plate was washed extensively with deionized water and dried in a vacuum drying oven for surface characterization. A scanning electron microscope (SU-1510, Hitachi, Japan) working at 10kV was used to examine the surface morphology.

3. Results and Discussion

3.1. The UV-vis absorption patterns

![Fig. 1. UV-vis absorption patterns of palladium (II) in various concentrations of nitric acid. [Pd]=0.5mM](image)

Figure 1 shows the absorption spectra of palladium (II) in various concentration nitric acid (ranging from 0.1M to 9M), the absorption peaks exhibit a red-shift and the peak value increases as the concentration of nitric acid increases. This is caused by the formation of different nitrato-complexes. This is caused by the formation of different nitrato-complexes. Tarapcik et al[14] reported that [Pd(H$_2$O)$_4$]$^{2+}$, [Pd(NO$_3$)(H$_2$O)$_3$]$^+$, [Pd(NO$_3$)(H$_2$O)$_2$] and [Pd(NO$_3$)(H$_2$O)]$^-$ are the four main species in HNO$_3$ solution, their stability constants are 3.28, 2.13, 0.223 and 0.004, respectively. However, by using UV/Vis absorption spectrophotometry, Toshiyuki Fujii et al[15] found that the major palladium species were Pd$^{2+}$,[Pd(NO$_3$)]$^+$ and Pd(NO$_3$)$_2$, and the stability constants of [PdNO$_3$]$^+$ was calculated to be $\beta_1=1.32$(HNO$_3$=1M), 1.49(HNO$_3$=3M), or1.47(HNO$_3$=5M), and that of Pd(NO$_3$)$_2$ to be $\beta_2=0.45$ (HNO$_3$=3M) or 0.14(HNO$_3$=5M). On the whole, the proportion of palladium anion species rises with the increase of nitric acid concentration.

3.2. The cyclic voltammogram

The cyclic voltammogram of palladium (II) in 3M nitric acid recorded at 298 K is shown in Fig.2, the sweeping rate of which is 20 mV/s.
Within the scanning potential range of \(-0.175 \sim 1.2\) V (vs. Ag/AgCl), there are two sharp oxidation peaks and three sharp reduction peaks, all of which associate with palladium. On the negative-going forward scan, the first peak located at ca.0.3 V (1) is due to the reduction of palladium (II) into palladium (0), shown as Eq. (1). A weak reduction wave starting from ca. 0 V and a strong reduction peak observed at ca. \(-0.125\) V (2) correspond to weak and strong adsorption of H respectively on metallic palladium formed, as described in Eq. (2). Hydrogen evolution reaction (3), shown as Eq. (3), begins at \(-0.17\) V, where a large amount of tiny bubbles occurs. On the positive-going reverse scan, a large oxidation peak occurs at \(-0.08\) V (4) and a weak oxidation wave starting at ca. \(-0.062\) V suggest the desorption of H from palladium, as described in Eq. (4). A surge in anodic current occurring at a potential of 0.4 V, which culminates in a peak at ca. 0.71 V, confirms the oxidation of palladium (0) into palladium (II) as expressed by Eq.(5). Evidently, the cyclic voltammogram of palladium (II) provides us with a series of electrochemical reactions corresponding to redox behavior of palladium and the possibility to recover palladium in metallic form by direct electrolysis from nitric acid.

\[
\begin{align*}
\text{Pd}^{2+} & \rightarrow \text{Pd}^0 \\
Pd + x\text{H}^+ + xe^- & \rightarrow \text{PdH}_x \\
2\text{H}^+ & \rightarrow \text{H}_2 \\
\text{PdH}_x & \rightarrow \text{Pd} + x\text{H}^+ + xe^- \\
\text{Pd}^0 & \rightarrow \text{Pd}^{2+}
\end{align*}
\]

In order to investigate the influence of HNO\(_3\) concentration, cyclic voltammogram measurements of 5mM Pd (II) in 0.1M, 1M and 3M HNO\(_3\) were conducted at 298 K.

Within the scanning potential range of \(-0.1 \sim 1\) V (vs. Ag/AgCl), in all three cases, one reduction peak (Eq. (1)) and one reduction peak (Eq. (5)) could be get on the negative-going and positive-going forward scan, respectively. From Fig.3, the redox peak currents reduced as HNO\(_3\) concentration increases, this may be caused by the decrease of diffusion coefficients of Pd complexes which change with the HNO\(_3\) concentration as we discussed. Moreover, when HNO\(_3\) concentration increases from 0.1 to 3 M, the reduction peaks shifted negatively and the peak potentials separation for the redox reactions increased from 295mv to 461mv. Obviously, low HNO\(_3\) concentration is electrochemically favourable for the
reduction of palladium (II) for the reason that we can get a higher reduction current and the reduction reaction could proceed in a relatively high potential.

![Cyclic voltammogram of 5mM palladium (II) in 0.1M, 1M and 3M HNO₃ at 298 K; Scan rate: 20 mV/s. (Unit: Potential, V vs Ag/AgCl)](image)

**3.3. Sampled-current voltammetry of palladium (II)**

![Sampled-current voltammetry curve of palladium (II) in 3M HNO₃ solution at 298K (Unit: Potential, V vs Ag/AgCl).](image)

Potential step method was employed to get sampled-current voltammetry. A representative sampled-current voltammetry curve is shown in Fig.4 for palladium (II) in 3M HNO₃ solution, the initial potential of which was 1.2 V, the sampling time was 0.2 s. According to Tomes criterion [16], the value of $|E_{3/4}$ -
$E_{1/2}$ is much larger than the value required for a reversible process, which means that the reduction of palladium (II) in nitric acid at Pt electrode is irreversible and the process is not only controlled by diffusion but also charge transfer kinetics.

3.4. Electrowinning of palladium

Figure 5 shows the comparison of recovery ratio for the electrodeposition of palladium during electrolysis in 3M HNO$_3$ medium at three different potentials. Controlled potential electrolysis of a solution of palladium (II) (5mM) in 3M HNO$_3$ were performed at three different potentials (−0.3 V, −0.2 V, −0.1V vs. Ag/AgCl) on Pt plate (8 cm$^2$) as cathode with a 4h electrolytic time in all cases. The selections of voltage were based on the information provided by cyclic voltammogram (Fig. 2). As shown in Fig. 8, the curves obtained at −0.2 V and −0.1 V are close to each other while a much higher recovery ratio was observed when −0.3 V was applied in electrolysis. In the later case, many small bubbles were clearly observed in the beginning of electrolysis, which stirred the bulk solution and accelerated the electrodeposition rate of palladium and gradually decreased over time. After 4h electrolysis, the recovery of palladium was quantitative, and the recovery ratio of which at −0.3 V, −0.2 V and −0.1V are 100%, 50% and 47%, respectively.

![Graph showing recovery ratio for electrodeposition of palladium from 3M HNO$_3$ at different applied potential at 298 K](image)

Fig. 5. Recovery ratio for the electrodeposition of palladium from 3M HNO$_3$ at different applied potential at 298 K (Unit: Potential, V vs Ag/AgCl)

The influences of nitric acid concentration on the cathodic deposition of palladium (II) (5mM) were investigated at a constant applied potential of −0.1V, and the results are shown in Fig. 6. When there is no stirring, the curves obtained from 1M and 3M HNO$_3$ are close to each other and a slightly higher curve was got from 0.1M. However, the mean current efficiency for the electrodeposition of palladium from 0.1M, 1M and 3M HNO$_3$ are 65%, 51% and 29%, respectively. The current efficiency of electrolysis decreases as the nitric acid concentration increases, which could be due to the reduction of nitric acid or H$^+$ ions. When stirring was introduced during electrolysis in 3M HNO$_3$, the electrodeposition rate of palladium increased substantially, and near 100% recovery ratio of palladium was achieved within 2 h. Evidently, stirring could greatly increase the electrodeposition rate of palladium in from nitric acid solutions.
Fig. 6. Recovery ratio for the electrodeposition of palladium from 0.1M, 1M and 3M (with and without stirring) HNO₃ at -0.1V. ; T = 298 K (Unit: Potential, V vs Ag/AgCl)

Fig. 7. SEM images of palladium obtained by electrolysis at Pt electrode in 3M HNO₃ at different magnifications.
The deposit obtained from the electrolysis in 3M HNO₃ was subjected to surface morphological examination by scanning electron microscopy (SEM). As shown in Fig. 7, a thick but uniform electrodeposition of palladium was observed all over the surface of Pt electrode. The clear dendrite morphology of palladium electrodeposition shows free dendrite growth, thin dendrite arms as well as side branch. The deposit was loose and could be scraped off from Pt plate easily, offering us the convenience to recover metallic palladium from nitric acid media after direct electrolysis.

4. Conclusions

In this work, the electrochemical behavior of palladium (II) in nitric acid medium at platinum electrode was investigated using various electrochemical techniques. UV-vis absorption curves demonstrated that palladium (II) in various concentration nitric acid had optical absorbance ranging from 400~450 nm and showed a spectral red-shift resulting from the formation of different nitrato-complexes. By analyzing the cyclic voltammogram of palladium (II) in nitric acid, a series of electrochemical reactions associated with palladium were recognized. According to Tomes criterion, the reduction of palladium (II) in nitric acid at Pt electrode was irreversible, SEM images of palladium obtained by electrolysis reveal the dendrite growth in all cases, which is uniform all over the entire surface of Pt electrode. The recovery ratios of palladium at different nitric acid concentration were high, and the faradic efficiency of electrolysis decreased with increasing nitric acid concentration, which is probably due to the reduction of nitric or H⁺ ions. Stirring could facilitate the reduction of palladium (II) in relatively low nitric acid concentration.

Acknowledgements

Projects supported by the Major Research Plan of the National Natural Science Foundation of China (No. 91026019 and No. 91126006).

References


