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Electrolytic extraction of palladium from nitric acid and simulated high-level liquid waste

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ABSTRACT

Electrochemical behavior of palladium (II) nitrate in nitric acid medium and simulated high-level liquid waste has been investigated to explore the feasibility of recovering this potentially useful fission product from high-level liquid waste. The cyclic voltammogram of palladium (II) in nitric acid medium at stainless steel electrode consists of a cathodic wave occurring at an onset of –0.4 V (vs. Pd) due to the irreversible reduction of palladium (II) to metallic palladium at 298 K. The recovery of palladium was quantitative at nitric acid concentrations ranging from 1 to 4 M, however, the recovery from simulated high-level liquid waste (SHLLW) solution was only 30% due to the interferences of various ions present in SHLLW. The faradic efficiency of electrolysis lowered with increase in nitric acid concentration and only silver was found to get co-deposited to the extent of 5% along with palladium from SHLLW solution.

Keywords: Palladium; Fission product; Nuclear waste; Voltammetry; Electrodeposition

1. Introduction

Ruthenium, rhodium and palladium are noble metals. These platinum group metals (PGMs) have unique and potentially useful properties such as high catalytic activity, electrical conductivity, chemical inertness, etc. Currently, there is a huge demand for these metals in various industries owing to their superior physical and chemical properties. However, the abundance of these metals in the earth crust is very low. The price of PGMs in global market is escalating steeply and it is likely to increase further due, partially, to the heavy demand of PGMs and, largely, to the increased cost of mining from already depleted natural resources. This situation compels the metallurgists to either discover other metal alloy substitutes for these noble metals or look for alternate sources that are abundant and easily accessible. One such source is the spent nuclear fuel [1–3].

Significant quantities of platinum group metals (Ru, Rh, Pd) are formed as fission products during nuclear reactor operation. Recovery of these man-made PGMs from spent nuclear fuel was envisaged as early as in 1970s [1]. The projected estimates [3] of PGMs indicate that about 2500–3000 tonnes of fission PGMs will be produced by the year 2030 as a result of nuclear reactor operations world-wide and only 7000 tonnes of natural reserves will be left in the same period.

PUREX process is being adopted for the recovery of uranium and plutonium from spent nucelar fuel dissolver solution and the raffinate rejected after extraction is called as high-level liquid waste, HLLW [4], which contains PGMs (70% soluble in HLLW) existing in the form of complex nitrates. Among these fission PGMs, palladium exhibits a less complex solution-chemistry

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and a well-established electrochemical behaviour. In addition, all the isotopes of palladium present in the spent nuclear fuel are non-radioactive [^{104}Pd (17 wt%), ^{105}Pd(29 wt%) ^{106}Pd(21 wt%) ^{108}Pd(12 wt%) ^{110}Pd(4 wt%)) except ^{107}Pd (17 wt%)] isotope, which is a soft β-emitter with a half-life of 6.5×10^6 y and its radioactivity can be tolerated for several industrial applications [3]. Due to these features, there is an increased interest in the recovery of palladium from HLLW.

Several separation methods such as ion exchange [5], non-aqueous methods [6], etc. have been reported for the recovery of palladium. Excellent reviews in this regard by Kolarik and Renard [7–9] and Pokhitonov et al. [10] detail the methods reported to date for the separation and recovery of fission platinoids. Among various procedures, electrochemical method for the recovery of palladium is simple and congenial for scaling-up operation. This method does not demand addition of any reagents for the recovery and hence does not generate any secondary waste. Koizumi et al. [11] and Kirshin et al. [12] studied the electrolytic recovery of PGMs from nitric acid solutions and reported the efficiency of the process in the presence of various interfering ions like uranium. Recently, we reported the redox behavior of palladium (II) in nitric acid media at platinum electrode, the diffusion coefficient and its recovery from nitric acid medium [13]. However, from the process point of view and for scaling-up operations, platinum electrode is unsuitable. Therefore, the present study deals with the electrochemical behavior of palladium (II) nitrate in nitric acid medium and simulated high-level liquid waste (SHLLW) at stainless steel electrode, to explore the feasibility of recovering the potentially useful fission product, palladium, from high-level liquid waste. The cyclic voltammetry of palladium (II) at stainless steel electrode, effect of applied potential and [HNO_3] on the recovery of palladium has been reported. The characterization of the deposit by X-ray diffraction and surface analysis by scanning electron microscopy are also reported in this paper.

2. Experimental

2.1. Material

All the chemicals and reagents used in the present study were of analytical grade. Palladium (II) nitrate in nitric acid medium (~10% w/v) was procured from Arora Matthey, Kolkata, India. Nitric acid was procured from S.D. Fine Chemicals, Mumbai, India and was diluted to appropriate concentrations and estimated by titrimetry. Voltammetric studies were performed using a stainless steel wire electrode (surface area = 0.1 cm^2) with platinum as counter electrode and palladium as quasi-reference electrode. Since, the standard reference electrodes are not compatible with ~4 M nitric acid medium, the potentials were recorded against palladium as quasi-reference. Therefore electrolytic extraction was performed using stainless steel plates (surface area = 6 cm^2) with platinum plate as counter electrode and palladium as quasi-reference electrode. All the studies were performed at 298 K.

2.2. Instrumentation

All electrochemical studies were performed using Autolab (PGSTAT-030) equipped with an IF 030 interface. A Philips field effect scanning electron microscope (SEM), model XL 30, with energy-dispersive spectrometer (EDS) working at 30 kV was used to examine the surface morphology and elemental composition of the deposit. X- ray diffraction pattern of the deposited samples were obtained using Philips 1011 X-ray diffractometer with Cu K_α radiation. The amount of palladium deposited on the electrode was determined from the increase in weight of working electrode as well as by estimating palladium present in the solution before and after the electrolysis using ICP-OES. Faradic efficiency was calculated from the ratio of palladium deposited to the palladium deposit expected from the quantity of coulombs passed into the solution.

3. Results and discussion

3.1. Cyclic voltammetry of Pd (II) in HNO_3

Palladium (II) nitrate in nitric acid medium results in the formation of coordinate complexes of the type, $[Pd(NO_3)_x]^{(2-x)}$ $x = 0$–4, and their composition in solution depends upon the concentration of nitric acid [13–15]. Fig. 1 shows the cyclic voltammograms of 4 M nitric acid and its solution with palladium (II) nitrate (20 mM) recorded at a stainless steel electrode at a scan rate of 0.1 V/s at 298 K. It is observed that nitric acid exhibits an electrochemical window of 1.2 V (from –1.1 V to 0.1 V) (vs. Pd). The onset of palladium reduction occurs at a potential of –0.4 V (vs. Pd) and the corresponding anodic wave is insignificant during scan reversal. Controlled potential electrolysis at –0.5 V (vs. Pd) results in the deposition of metallic palladium. In addition, it is also observed from the cyclic voltammogram of palladium (II) that there is a steep increase in cathodic current when the potential is more negative than –0.6 V. This could be due to the underpotential reduction of H^+ resulting in the evolution of hydrogen gas at working electrode. The catalytic activity of palladium favoring underpotential evolution of hydrogen has been well-established [16]. Moreover, the possible reduction of nitrate ion may also occur at these potentials [17]. Thus, the presence of palladium (II) ion, even in small quantity, in electrolytic medium lowers the cathodic stability of nitric acid from –1.1 V to –0.5 V, i.e. by 600 mV, due to the underpotential reduction of H^+, while the anodic stability fairly remains the same. A similar phenomenon is also observed in a cyclic voltammogram of palladium(II) in simulated high-level liquid

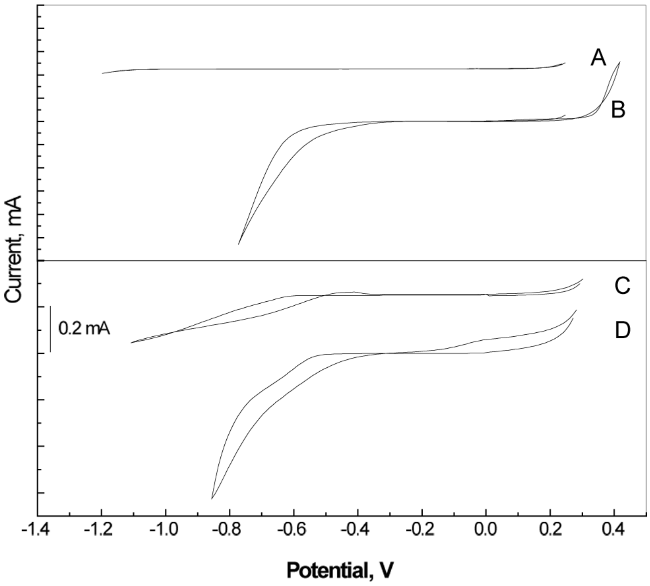

Fig. 1. Cyclic voltammograms of 4 M HNO_3 and simulated PHWR high-level liquid waste in the presence and absence of palladium recorded on a stainless steel electrode. Counter electrode: platinum, reference electrode: palladium wire. T = 298 K, A — 4 M HNO_3, B — 20 mM $Pd(NO_3)_2$ in 4 HNO_3, C — PHWR simulated high-level liquid waste without $Pd(NO_3)_2$, D — PHRW simulated high-level liquid waste with 20 mM $Pd(NO_3)_2$.

waste solution, shown in Fig. 1. The study indicates that palladium (II) in SHLLW undergoes an irreversible two-electron transfer to metallic palladium at stainless steel electrode at potentials more negative than –0.4 V (vs. Pd).

3.2. *Optimization of electrode potential*

The concentration of nitric acid in high-level liquid waste varies from 3 to 4 M. To explore the recovery of palladium from HLLW, experiments were carried out at various applied potentials to determine the optimum potential required for the recovery of palladium from 4 M nitric acid. Fig. 2 shows the coulombic charge vs. time curves for the electrodeposition of palladium from 4 M HNO_3 at various applied potentials. It is observed that when the applied potential is –0.4 V (vs. Pd) the total coulombic charge consumed for the reduction is insignificant. A similar behavior is also observed when the applied potential is –0.45 V. There was no significant deposit even after 8 h. However, when the applied potential is –0.5 V or more negative, a remarkable increase in the passage of coulombic charge as shown in Fig. 2 is observed, resulting in significant deposition of palladium. After 6–7 h of electrolysis, the recovery of palladium is quantitative (100%). However, in order to minimize the complications arising from non-faradaic reductions of nitrate and H^+ ions by the reactions shown in Eqs. (1)–(4), which are also likely to occur at similar potentials [18], it is desirable to carryout electrolysis at an optimum potential of –0.5 V (vs. Pd)

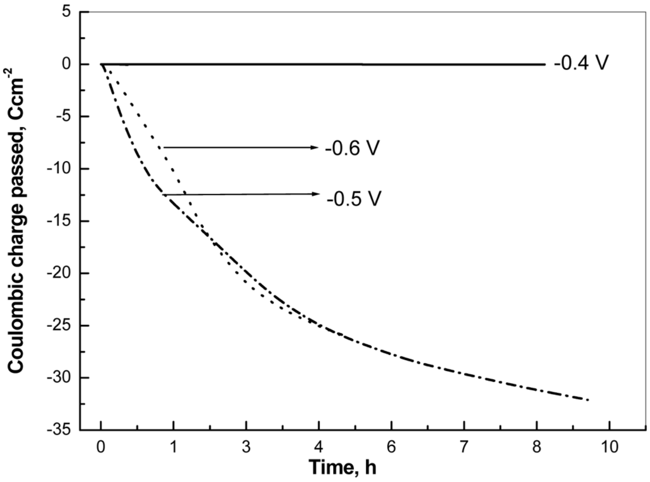

Fig. 2. Plot of coulombic charge passed in the solution against time for electrodeposition of palladium from 4 M nitric acid medium at various potentials. Working electrodes: stainless steel (area = 6 cm^2), counter electrode: platinum, reference electrode: palladium wire, T = 298 K.

$$NO_3^- + 2H^+ + 2e^- = NO_2^- + H_2O \tag{1}$$

$$2H^+ + 2e^- = H_2 \tag{2}$$

$$HNO_2 + 4H^+ + 2e^- = NH_2OH + H_2O \tag{3}$$

$$2NO_3^- + 12H^+ + 10e^- = N_2 + 6H_2O \tag{4}$$

3.3. *Effect of nitric acid concentration*

Previously, we studied the effect of nitric acid concentration on the electrolytic extraction of palladium [13]. The results showed that recovery of palladium was quantitative and independent of nitric acid in the concentration range 1–4 M. However, the faradic efficiency dropped from 76% to 53%, when the concentration of nitric acid increases from 1 M to 4 M, due to the undesirable reductions of H^+ and NO_3^- ions with increase in nitric acid. The SEM images of the deposits, shown in Fig. 3, indicate the dendritic growth of palladium on stainless steel surface. The SEM images also support the fact that the dendritic palladium has larger surface area, which enhances the catalytic activity of palladium, favoring underpotential evolution of hydrogen and lowers the faradic efficiency of palladium deposition.

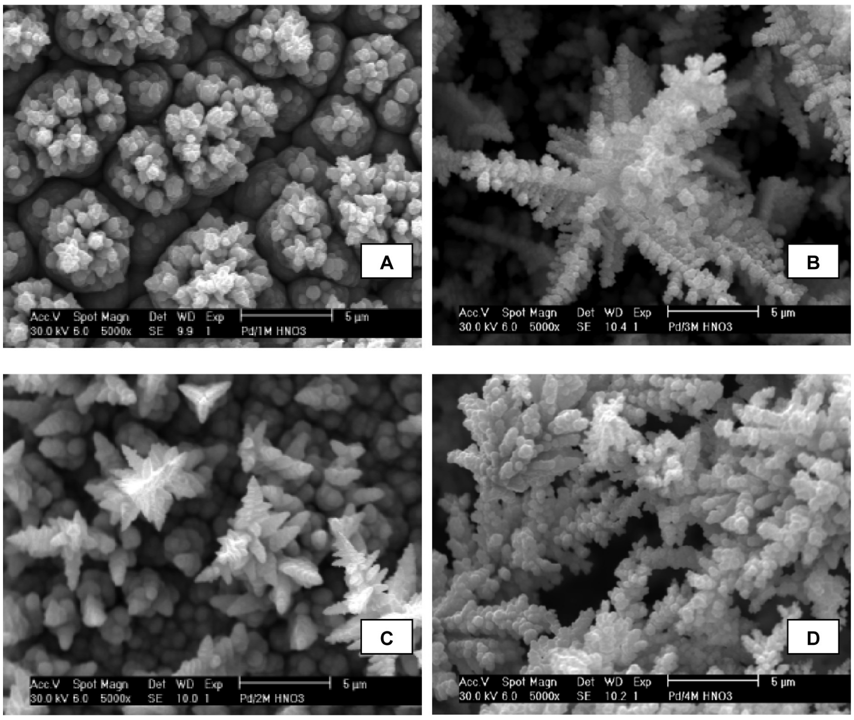

Fig. 3. SEM images of palladium deposit obtained by constant potential electrolysis (–0.5 V vs. Pd) on stainless steel plate from different nitric acids. A — 1 M HNO_3, B — 2 M HNO_3, C — 3 M HNO_3, D — 4 M HNO_3. T = 298 K, time = 8 h.

3.4. *Electrolytic extraction of palladium from simulated high-level liquid waste*

The compositions of simulated high-level liquid waste obtained from pressurized heavy water reactor (PHWR) and fast breeder reactor (FBR) are shown in Table 1 [19]. Electrolysis was performed in a two-compartment electrolytic cell shown in Fig. 4. Compartment A consists of stainless steel working electrode and palladium quasi-reference electrode immersed in a solution of simulated HLLW. Compartment B contains platinum counter electrode immersed in 4 M nitric acid. Fig. 5 shows the coulombic charge vs. time plot for the electrolysis of PHWR simulated high-level waste solution at a potential of –0.5 V in the presence and absence of palladium. A similar result was also obtained for the electrolysis of simulated high-level liquid waste of fast reactor. It is observed that the quantity of coulombs passing in the solution is low

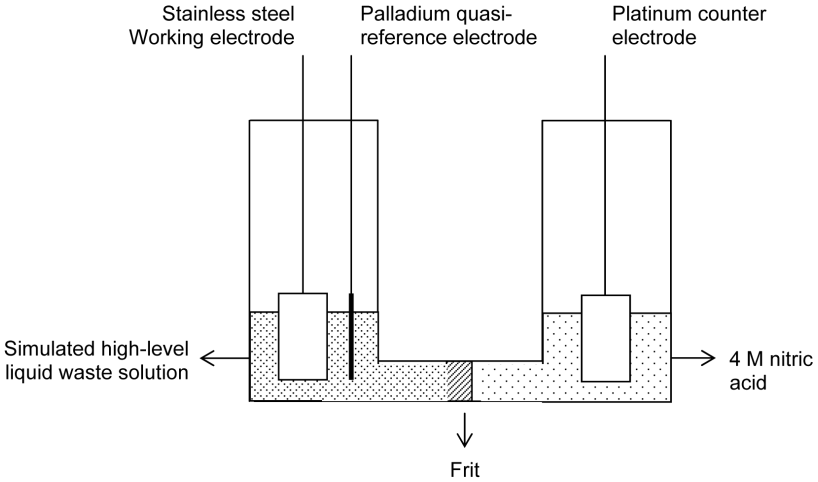

Fig. 4. Schematic diagram of a two-compartment electrolytic cell employed for the electrodeposition of palladium from simulated high-level liquid waste. Left side of the frit is compartment A and right side is compartment B.

Table 1
Elemental compositions of simulated high-level liquid waste (HLLW) from pressurized heavy water reactor and fast breeder reactor spent fuel [19]

	PHWR (6500 MWd/Te)	FBR (80,000 MWd/Te)
Element	Elements present (g/L)	Elements present (g/L)
Antimony	0.01	0.01
Barium	0.31	0.41
Cadmium	0.02	0.04
Cerium	0.54	0.69
Cesium	0.55	1.12
Chromium	0.1	0.1
Dysprosium	0.001	0.005
Europium	0.02	0.31
Gadolinium	0.02	0.07
Iron	0.5	0.5
Lanthanum*	0.26	0.48
Molybdenum	0.73	1.09
Neodymium	0.86	1.131
Nickel	0.1	0.1
Palladium	0.27	0.6
Promethium	0.24	0.34
Promethium	0.03	0.05
Rhodium	0.13	0.26
Rubidium	0.08	0.06
Ruthenium	0.46	0.81
Samarium	0.17	0.05
Selenium	0.01	0.01
Silver	0.02	0.13
Sodium	3.01	3
Strontium	0.19	0.14
Technetium	0.18	0.26
Tellurium	0.1	0.16
Terbium	0.001	0.01
Tin	0.02	0.02
Uranium	18.33	2.64
Yttrium	0.1	0.08
Zirconium	0.77	0.89
Acidity, M	4.0	4.0

La* — added for Y, Pm, Te, Dy
Tc, Mo — not added
Co — added for Ni
Pd — added for Ru, Rh, Rb
Sn, Sb, Te — not added due to poor solubility
Excess palladium taken to study the feasibility of electrolytic extraction

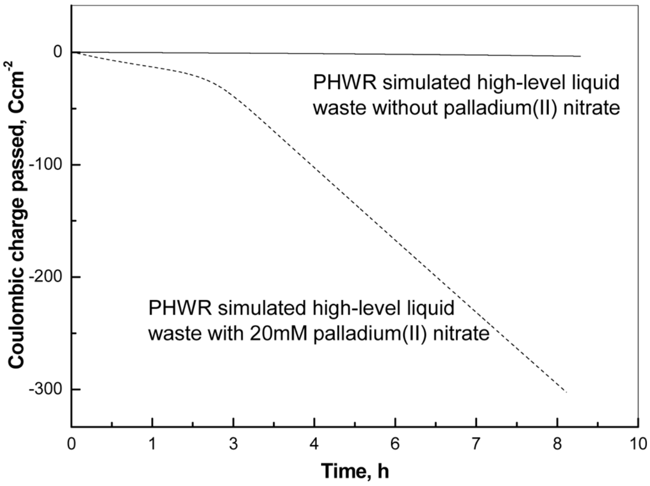

Fig. 5. Comparison of coulombic charge passed vs. time curves for the electrolysis of simulated high-level liquid waste in the presence and absence of palladium. Working electrode: stainless steel, counter electrode: platinum, reference electrode: palladium. T = 298 K.

in the initial stages of electrolysis (from 0 to 3 h) and it increases with increase in time. During this period a significant amount of palladium was found to be deposited on stainless steel electrode. This was followed by a steep increase in the quantity of coulombs passing into the solution. However, on this occasion the deposition of palladium was negligible. This indicates that the initial deposition of palladium on stainless steel electrode modifies the electrode surface and favors the underpotential reductions of other non-faradaic reactions at the modified electrode. Therefore the electrolysis was terminated in 5 h and the recovery was around 30%, which remained the same even after 8 h.

The X-ray diffraction pattern of the deposit is shown in Fig. 6. This shows that along with palladium, silver

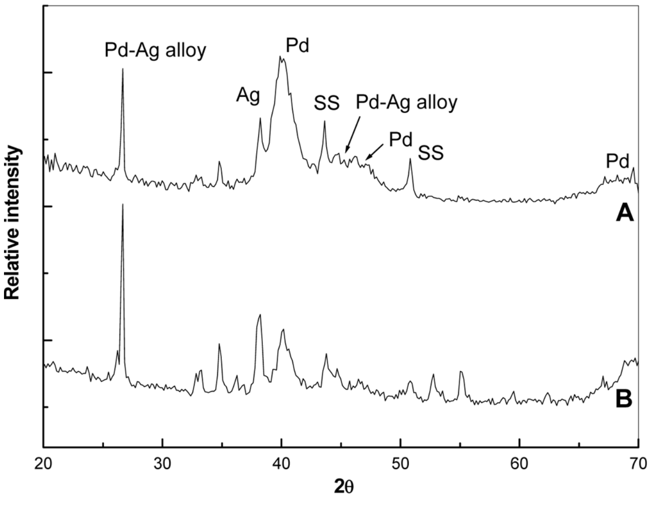

Fig. 6. XRD pattern of deposits obtained on stainless steel plate from the electrolysis of PHWR (A) and FBR (B) simulated high-level liquid waste solutions.

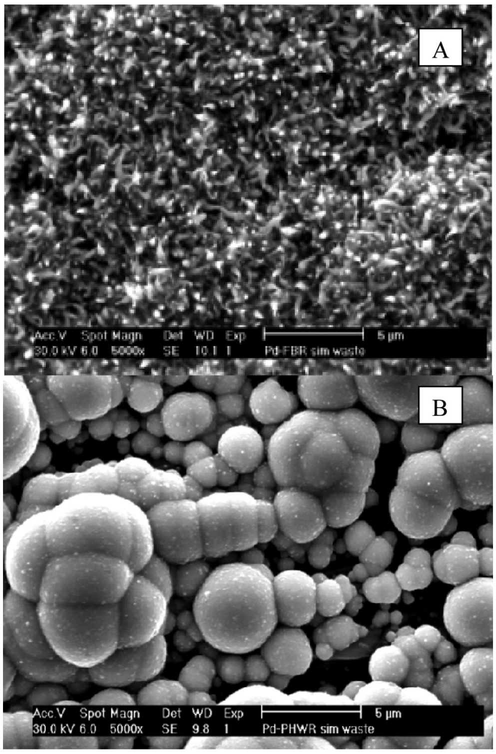

Fig. 7. SEM images of deposit from FBR (A) and PHWR (B) simulated high-level liquid wastes.

is also deposited during electrolysis, as its reduction requires less negative (–0.3 V) potential [13] than the potential required for palladium deposition. Fig. 7 shows the SEM images of deposit obtained from the electrolysis of FBR and PHWR simulated high-level liquid wastes. The images display fine fibril like structures in the deposit obtained from FBR-SHLLW and particle like deposit from PHWR-SHLLW solution. SEM-EDS (Energy dispersive X-ray spectroscopy) characterization of the deposit revealed the co-deposition of silver to the extent of 5% (the concentration of silver is low in HLLW, Table 1) along with palladium from both the PHWR and FBR simulated high-level liquid wastes. Other metal deposits are not observed in the analysis.

4. Conclusions

Palladium (II) ion in simulated high-level liquid waste undergoes an irreversible single step two-electron reduction to insoluble palladium metal at stainless steel electrode at an optimum potential of –0.5 V (vs. Pd). Electrochemical recovery of palladium from 1 M to 4 M nitric acid was quantitative, but the faradaic efficiency lowered with increase in concentration of nitric acid. Initial deposition of palladium on stainless steel electrode, catalyzes the underpotential reduction of H^+ and other ions present in SHLLW at the modified surface, which seems to limit the recovery of palladium to ~30% and also lowers the faradaic efficiency. Silver is the only element co-deposited to the extent of 5% along with palladium. The study explored the pertinent complications arising from a multi-component system, namely high-level liquid waste that hinders the quantitative extraction of palladium, in spite of the fact that palladium is a noble metal.

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