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Electrodeposition of ruthenium, rhodium and palladium from nitric acid and ionic liquid media: Recovery and surface morphology of the deposits

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ABSTRACT

Electrodeposition is a promising technique for the recovery of platinum group metals with unique surface morphologies. The electrodeposition of palladium, ruthenium and rhodium from aqueous nitric acid, and non-aqueous 1-butyl-3-methylimidazolium chloride ionic liquid medium was studied at stainless steel electrode. The surface morphology and elemental composition of the resultant deposit were probed by scanning electron microscopy (SEM) and energy dispersive X-ray (EDS) analysis. Deposits with diverse surface morphologies and metal compositions were obtained by varying the composition of the electrolytic medium and applied potential. The results demonstrate the possibility of tailoring the morphologies of PGMs by controlling the composition and potential needed for electrodeposition.

1. Introduction

Lighter platinum group metals (or platinoids) namely, ruthenium, rhodium and palladium find several applications in various industries [1,2]. The natural availability of the platinoids in earth crust is very low; whereas their consumption in industries is very high due to their advantageous properties such as catalytic nature, high-temperature conductivity, corrosion resistance, etc. This disparity has escalated the market price of platinoids exponentially over the years. Among the platinoids, palladium and ruthenium are widely used as cheaper substitutes to rhodium and platinum [3]. Besides, there are no alternatives to these costly metals. This situation compels the material chemists to improve the properties of these materials with minimal metal content to meet the desired applications.

Spent nuclear fuel is a valuable resource of man-made noble metals [4]. Significant quantities of platinum group metals (PGMs) namely, palladium, rhodium, ruthenium are produced as by-products of nuclear fission in a nuclear reactor. Most of the isotopes of fission PGMs are non-radioactive. There are two sources available for the recovery of PGMs from spent nuclear fuel. They are the high-level liquid waste (HLLW) and the spent nuclear fuel itself. Among the various approaches, electrochemical method is one of the easiest and promising techniques for the recovery of PGMs due to its simplicity and accessibility of reduction potential of PGMs [5,6]. Moreover, this method does not demand the addition of external reagents, which is indeed desirable for the management of HLLW. In addition, the electrochemical method offers several ways of tuning the surface morphology and composition of metal deposits [7]. The deposit with the required morphology can be obtained by manipulating the parameters such as applied potential/current, electrolyte, electrodes, concentration of metal ion, temperature, additives/modifiers, duration, etc. [7]. In this perspective, we have studied the feasibility of recovering fission platinoids from nitric acid medium [8–10], from non-aqueous ionic liquid medium [11–13] and by extraction–electrodeposition (EX–EL) procedure [14,15]. However, we have not investigated in detail the surface morphology of the resultant deposits.

Some reports on the surface morphology of the platinoid electrodeposits are available in literature. Sun et al. [16] reported the electrodeposition of palladium(II) from a basic aluminium chloride + 1-methyl-3-ethyl imidazolium chloride ionic liquid. The palladium deposit was black and finely divided powder when platinum wire gauze acted as cathode [16]. Bando et al. [17] reported the electrodeposition of palladium from 1-n-butyl-1-methylpyrrolidinium bis(trifluoromethylsulfonyl)imide ($bmPyNTf_2$) ionic liquid on a Ni substrate. At lower cathodic currents smooth and bright deposits were observed while higher

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Table 1
Recovery of platinoids from bmimCl ionic liquid by electrodeposition. Working electrode: SS plate (6 cm^2); reference electrode: Pd wire; *T*: 373 K. All metals are taken in equal concentration in binary/ternary solutions.

Metal ion present in bmimCl	Applied potential vs. Pd (V)	Duration (h)	Amount of metal initially present in the electrolyte (g)	Amount of metal finally recovered in the deposit (g)	Total recovery (%)
Pd(II)	−0.85	2	0.157	0.037	*23.4*
	−1.05	2	0.157	0.072	*45.8*
	−1.20	2	0.157	0.080	*51.0*
Rh(III)	−1.70	25	0.054	0.014	*26.6*
Ru(III)	−1.80	30	0.056	<0.001	No deposit
Ru(III)[a]	−1.0	3	0.03	0.003	*10.1*
Pd(II)–Rh(III)	−0.73	12	0.451	0.109	*24.2*
	−1.20	12	0.458	0.128	*28.4*
	−1.70	12	0.458	0.167	*34.9*
Pd(II)–Ru(III)	−1.00	3	0.066	0.009	*13.7*
	−1.50	3	0.066	0.012	*18.3*
Rh(III)–Ru(III)	−1.7	20	0.065	<0.001	No deposit
Pd(II)–Rh(III)–Ru(III)	−0.85	8	0.052	0.0121	*23.3*
	−1.05	8	0.052	0.014	*26.9*
	−1.25	8	0.052	0.015	*28.7*
	−1.50	10	0.052	0.018	*34.3*

[a] Deposited from $bmimPF_6$.

cathodic currents resulted in black and powdery deposits [17]. Katayama et al. [18] reported the electrodeposition of nonoscale palladium from hydrophobic $bmPyNTf_2$ ionic liquids. The morphology was smooth when $[PdCl_4]^{2-}$ was electrolysed from $bmPyNTf_2$ as compared to $[PdBr_4]^{2-}$ in $bmPyNTf_2$. Raz et al. [19] reported the electrodeposition of ruthenium on silicon from a solution of 4 mM $RuCl_3$ in $bmimPF_6$ medium. Electrodeposition of ruthenium was reported to be initiated as grains in 10 min that became a compact and dense deposit in 1 h and became coarse granulated with an extended period (2 h) of electrolysis. Mann et al. [20] reported the electrochemical deposition of ultrathin ruthenium films on Au(1 1 1) from bmim-DCA (dicyanamide) ionic liquid. We reported the electrodeposition of Ru(III) from $bmimPF_6$ and $bmimNTf_2$ ionic liquids at a constant potential of −0.8 V [13].

Considering the importance of exotic morphologies and applications of platinoids in industries, it is vital to recover the man-made noble metals from nuclear wastes with the required morphologies. The present paper attempts to probe the surface morphology of

i) palladium, rhodium and ruthenium electrodeposited from 1-butyl-3-methylimidazolium chloride ionic liquid (Section 3.1);
ii) palladium, rhodium and ruthenium electrodeposited from nitric acid medium and simulated high level liquid waste (Section 3.2);
iii) palladium from tri-n-octylmethylammonium nitrate (TOMAN) medium by EX–EL procedure (Section 3.3).

The effect of various parameters such as the composition of electrolytic medium, applied potential, duration of electrolysis on the recovery and surface morphology was studied and the results are reported in this paper.

Table 2
The onset and cathodic peak potentials of Pd(II), Rh(III) and Ru(III) present is various media derived by cyclic voltammetry at stainless steel working electrode (0.1 cm^2); Reference electrode: Pd wire; *T*: 373 K (for bmimCl) and 298 K (for nitric acid and TOMAN). E_pc^1 – first cathodic peak potential, E_pc^2 – second cathodic peak potential.

Medium	Platinoid ion	Onset of cathodic current V (vs. Pd)	Cathodic peak potential V (vs. Pd)		Reference
			E_pc^1	E_pc^2	
bmimCl ionic liquid	Pd(II)	−0.65	−0.96	−1.35	[13]
	Rh(III)	−1.29	−1.60	–	[12,13]
	Ru(III)	−0.10	−0.47	−0.60	[13]
		−1.08	−1.37	–	[13]
	Ru(III)[a]	0.00	−0.23	–	[13]
		−0.60	−0.80	–	[13]
	Pd(II)–Ru(III)	−0.16	−0.45	−0.65	[13]
		−0.88	−1.41	–	[13]
	Pd(II)–Rh(III)	−0.41	−0.65	–	[13]
		−0.76	−1.2	–	
	Rh(III)–Ru(III)	−0.61	−0.95	−1.26	[13]
	Pd(II)–Rh(III)–Ru(III)	−0.63	−1.03	−1.23	[13]
Nitric acid	Pd(II)	−0.5	–[b]	–	[8–10]
	Rh(III)	−0.36	−0.69	–	[10]
	Ru(III)	−0.45	−0.70	–	[10]
	Pd(II)–Rh(III)–Ru(III)	−0.40	−0.62	–	[10]
0.5 M TOMAN/$CHCl_3$	Pd(II)	−0.50	−1.70	–	[15]

[a] Medium was $bmimPF_6$.
[b] Pd(II)/Pd(0) cathodic wave merges with H^+/H_2 reduction wave.