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Electrochemical behavior of rhodium(III) in 1-butyl-3-methylimidazolium chloride ionic liquid

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Abstract

Electrochemical behavior of rhodium(III) chloride in 1-butyl-3-methylimidazolium chloride was investigated by various electrochemical transient techniques at glassy carbon working electrode at different temperatures (343–373 K). Cyclic voltammogram of rhodium(III) in bmimCl consisted of a surge in reduction current occurring at a potential of −0.48 V (vs. Pd) is due to the reduction of Rh(III) to metallic rhodium and a very small oxidation wave occurring at −0.1 V. Increase of scan rate increases the peak current and remarkably shifts the cathodic peak potential (E_p^{c1}) in negative direction indicating the irreversibility of electroreduction of rhodium(III). The diffusion coefficient of rhodium(III) in bmimCl (~10^{-9} cm^2/s) was determined and the energy of activation (~25 kJ/mol) was deduced from cyclic voltammograms at various temperatures. The cathodic (τ_r) and anodic (τ_o) transition times were measured from chronopotential transients and the ratio τ_o/τ_r was found to be 1:7. Electrowinning of rhodium from bmimCl medium results in a deposition of metallic rhodium with lower (20–25%) Faradaic efficiency. A separation factor of rhodium from co-existing noble metal fission product palladium in bmimCl was determined during electrodeposition.

Keywords: Room temperature ionic liquid; Voltammetry; Fission rhodium; 1-Butyl-3-methylimidazolium chloride; Electrowinning; Separation factor

1. Introduction

Rhodium is a noble metal. At present, there is a huge demand for rhodium and its compounds in various industries owing to its unique physical and chemical properties [1]. The abundance of rhodium in the earth crust is very low and occurs only in few countries. The price of rhodium in international market is escalating steeply and it is likely to increase further due, partially, to the heavy demand of rhodium and largely to the increased cost of mining from already depleted natural resources. This cost and the added costs arising from separation, purification up to conversion of rhodium in to a required form may become exorbitant after few decades and further mining would be an unworthy exercise and uneconomical for trading rhodium in global market. It is therefore necessary to look for other alternate sources of rhodium that is abundant and easily accessible. One such source is a spent nuclear fuel [1–3].

Rhodium is one of the by-products of nuclear fission reaction and therefore spent nuclear fuel is a valuable resource of man-made rhodium [1–3]. Significant quantities of platinum group metals (PGMs, palladium, rhodium, ruthenium) are produced as fission products in nuclear reactor and ^{103}Rh is the major non-radioactive isotope produced by fission reaction [1]. The fission yield of other rhodium isotopes, ^{102}Rh and ^{102m}Rh with half-life of 2.9 years and 0.57 years is very low and may vanish if the fuel is cooled over three decades. It was estimated that by the year 2030 AD, the amounts of man-made rhodium produced by nuclear reactor operation all over the world will match with the amounts of rhodium available at that instant in the earth crust [1]. Therefore, recovery of rhodium from spent nuclear fuel may provide appreciable incentives in view of its growing demand and widespread applications in various chemical, pharmaceutical and electronic industries [4,5].

PUREX process is being adopted for the recovery of uranium and plutonium from spent fuel dissolver solution and the raffinate obtained after extraction is known as high-level liquid waste (HLLW), which contains more than 70% of PGMs

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coexisting with other fission products in the form of complex species [1,4]. Excellent reviews by Kolarik et al. [4–6] details the methods and materials reported to date for the recovery of valuable platinoids from spent nuclear fuel, industrial applications of fission platinoids and the behavior of fission platinoids in HLLW. Even though rhodium exists only in trivalent oxidation state, the co-ordination chemistry of fission rhodium(III) in HLLW was reported to be as complex as fission ruthenium [4]. Due to this, the extraction of rhodium from nitric acid medium representing HLLW by several solvents proven for palladium extraction were found to be ineffective, and the basic chemistry of rhodium in HLLW is still lacking [4]. Furthermore, the direct electrochemical recovery of rhodium from HLLW also displayed several complications and the recovery was reported to depend strongly on several factors such as aging of the solution, nature of complex, concentration of nitric acid, etc. [7–9].

Room temperature ionic liquids (RTILs) [10] are emerging novel fluids for possible applications in nuclear fuel cycle. RTILs hold several promises in reprocessing of spent nuclear fuel as an alternative to traditional diluent, *n*-dodcane, in aqueous reprocessing [11,12] and as a substitute for high temperature molten salts in non-aqueous reprocessing [13–17]. Recently we reported a new process *Ex*traction-*EL*ectrodeposition (EXEL)—recovery through direct conversion to solid form by electrolysis has been demonstrated for uranium and palladium from nitric acid medium [11,12]. We have also explored the feasibility of using 1-butyl-3-methylimidazolium chloride as electrolytic medium for the recovery of fission palladium and reported the instantaneous nucleation model for the electrodeposition of palladium at glassy carbon working electrode [14]. However, to the best of our knowledge the electrochemical behavior of fission rhodium in the ionic liquid, 1-butyl-3-methylimidazolium chloride, was not reported in literature. Furthermore, recovery of fission rhodium by pyrochemical process, which employs high temperature molten salt, was also not available in literature, while, the co-deposition behavior of noble metals (palladium, rhodium) during electrowinning of uranium by oxide-electrowinning process was studied [18]. Therefore, the aim of the present paper is to report the electrochemical behavior of rhodium(III) chloride in 1-butyl-3-methylimidazolium chloride (bmimCl) by various transient electrochemical techniques, and to report the co-deposition behavior of fission palladium during electrowinning of rhodium.

2. Experimental

2.1. Materials

All the chemicals used in this study were of analytical AR grade. 1-Butyl-3-methylimidazolium chloride (bmimCl) was prepared by the procedure described elsewhere [19] and characterized by CHNS analysis, melting point measurement (341 K) and IR spectroscopy. Rhodium(III) chloride ($RhCl_3·3H_2O$) and palladium chloride were procured from Arora Matthey, Kolkata and Ranbaxy, Chennai, India, respectively.

2.2. Voltammetry of rhodium(III) chloride in bmimCl

A solution of rhodium chloride (~60 mM) in bmimCl was prepared by dissolving a required quantity of rhodium chloride ($RhCl_3·3H_2O$) in bmimCl (5 g), which was taken in an air-tight beaker. This beaker was kept in an oil bath maintained at a temperature of 373 K. After 25–30 h of heating for complete dissolution, a cherry red coloured solution was obtained and it was transferred in to an electrolytic cell maintained at a desired temperature under argon atmosphere. In voltammetric measurements, glassy carbon acted as the working (cylindrical, $SA = 0.47\ cm^2$) and counter electrodes, and palladium wire acted as quasi-reference electrode. The potential of quasi-reference electrode is −0.8 V against Cl^-/Cl_2 standard as internal reference. All the voltammetric data were obtained after IR compensation. Electrodeposition was conducted on a stainless steel (3 cm × 4 cm) plate with stainless steel (or graphite) acted as counter electrode and palladium wire acted as quasi-reference electrode. After the deposition, the plate was washed extensively with acetone and deionized water before subjecting it for morphological examination by scanning electron microscopy.

2.3. Instrumentation

Cyclic voltammograms of the solutions were recorded using Autolab (PGSTAT-030) equipped with an IF 030 interface. UV–vis absorption spectrum was obtained using Shimadzu UV–vis spectrometer model 2500. A Philips field effect scanning electron microscope (SEM), model XL 30, with energy-disperse spectrometer (EDS) working at 30 kV was used to examine the surface morphology and elemental composition of the deposit. EDXRF pattern of the deposit was obtained by using Jordan Valley's EX 3600 energy dispersive X-ray fluorescence spectrometer.

3. Results and discussions

3.1. Rhodium(III) in bmimCl

Rhodium(III) is a d^6 ion. It forms a low spin octahedral complex resulting in two absorption bands in the UV–vis spectrum that are attributed to $^1A_{1g}$ to $^1T_{1g}$ and to $^1T_{2g}$ transitions [20]. These bands are reported to occur at the λ_{max} of 310 nm and 395 nm for rhodium hexa-aqua complex and shifted bathochromically to ~410 nm and ~515 nm for rhodium chloro-complexes [21–23]. The UV–vis absorption spectrum of rhodium(III) chloride in bmimCl is shown in Fig. 1. Dissolution of $RhCl_3$ in bmimCl results in a highly viscous solution. The UV–vis absorption spectrum was recorded after heating the solution to ~373 K with bmimCl as reference at the same temperature. The absorption spectrum consists of two absorption bands occurring at the λ_{max} of 363 nm and 465 nm and is comparable with the absorption bands observed for a solution of rhodium(III) chloride in 6.0 M HCl. In chloride medium, rhodium(III) ion is speciated in to various chloro-complexes and at concentrations >4 M Cl^-, most of the rhodium was reported