

Electrolytic Reduction of Palladium in DBSO/Ionic Liquid System

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1. Introduction

This research is to develop a source technology for a treatment of radioactive and decontamination waste produced from the nuclear fuel cycle process by using ionic liquids. Ionic liquids easily dissolve organic or inorganic compounds, therefore feasibility studies on ionic liquids application for high level wastes treatment was conducted. Ionic liquids are being evaluated as an alternative to the conventional diluent, n-dodecane, in aqueous reprocessing, and as a substitute to the traditional high-temperature molten salts in the non-aqueous reprocessing of spent nuclear fuels [1].

As a part of the research to recover platinum group metals from nitric acid, the extraction and electrolytic reduction of palladium was studied using dibutyl sulfoxide (DBSO) as an extractant in the ionic liquid, 1-butyl-3-methylimidazolium bis(trifluoromethanesulfonyl)imide (C_4mimTf_2N). The feasibility of the Extraction and Electrodeposition (EX-EL) process was demonstrated.

2. Experimental

2.1 Chemicals and equipment

All the chemicals and reagents used in the study were of analytical grade and used without further purification. Ionic liquid, C_4mimTf_2N , and DBSO were procured from Sigma-Aldrich. To remove the water and volatile impurities, C_4mimTf_2N was dried under a reduced pressure at 373 K, and the residual water concentrations measured using a Karl Fisher moisture content meter (Metrohm 831 KF Coulometer) were below 100 ppm.

2.2 Experimental method

The extraction experiment was carried out by equilibrating the organic phase (0.03~1 M DBSO in C_4mimTf_2N) and the aqueous phase (1,000 ppm of

palladium in the desired HNO_3 concentration) with a phase ratio of 1:1 at 298 K. After equilibration, Pd concentration in the aqueous phase was determined by ICP-OES (Model No. PQ 9000 Elite), and the distribution ratio of palladium (D_{Pd}) was calculated.

All electrochemical experiments were carried out in a three-electrode cell. For cyclic voltammetric measurements, a glassy carbon (cylindrical, SA = 0.07 cm²) and a platinum wire were used as a working electrode and a counter electrode, respectively. As a quasi-reference electrode, a platinum wire was used. Cyclic voltammograms of the ionic liquid solutions were recorded using ZIVE SP2 (WonA Tech) equipped with Smart Manager program.

3. Results and discussion

The distribution ratio of palladium in solutions of 0.03 to 1 M DBSO/ C_4mimTf_2N as a function of concentration of nitric acid is shown in Fig. 1. The extraction mechanism of palladium into C_4mimTf_2N can be best represented by a cation exchange reaction.

A plot of $\log D_{Pd}$ vs. DBSO concentration results in straight lines with a slope 2.3 from 0.05 M nitric acid feed and 1.0 from 5 M nitric acid feed.

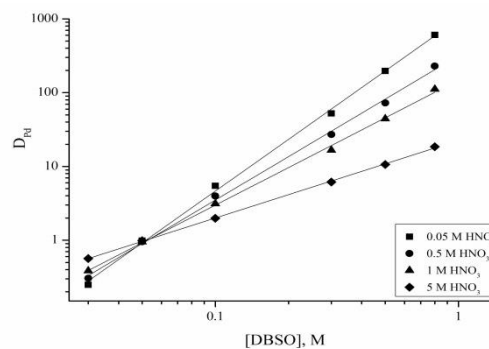


Fig. 1. Distribution ratio of palladium at varying DBSO concentrations extracted from HNO_3 feed into C_4mimTf_2N .

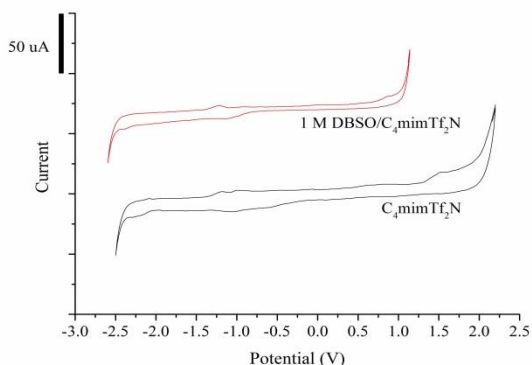


Fig. 2. Cyclic voltammogram of C_4mimTf_2N and 1 M DBSO/ C_4mimTf_2N at 298 K.

The results indicate that, in high acidity, palladium is coordinated with 1.0 DBSO molecules, compared with 2.3 molecules in low acidity, due to competition between palladium and hydrogen ions.

The cyclic voltammogram (CV) of C_4mimTf_2N at 298 K on glassy carbon electrode is shown in Fig. 2. C_4mimTf_2N exhibits a window of 4.5 V. The CV of 1 M DBSO/ C_4mimTf_2N is also shown in the same figure. Although the addition of DBSO shifts the peak potential anodically with a cathodic stability up to -2.5 V, it is sufficient for enabling the reduction of metallic ions into metal state.

30 mM of palladium ion was extracted from 0.5 M nitric acid using 1 M DBSO/ C_4mimTf_2N . The CV for the reduction of Pd(II) in this solution on glassy carbon working electrode at the scan rate of 10 mV/s is shown in Fig. 3. The CV consists of a reduction wave occurring at a peak potential of -1.1 V, and oxidation wave occurring at peak potential of -0.7 V. The results from the CV experiments at various scan rates and temperatures indicate that a reduction of Pd(II) takes place through a quasi-reversible single-step two electron transfer reaction.

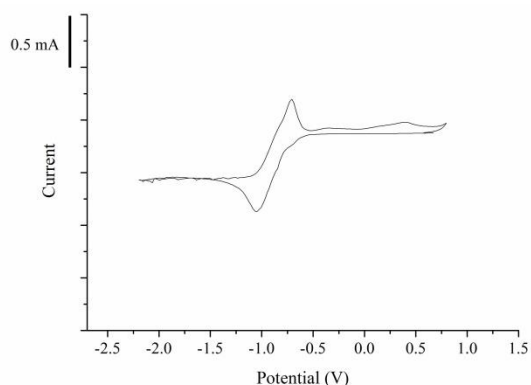


Fig. 3. Cyclic voltammogram of 1M DBSO/ C_4mimTf_2N containing 30 mM $PdCl_2$ after extraction.

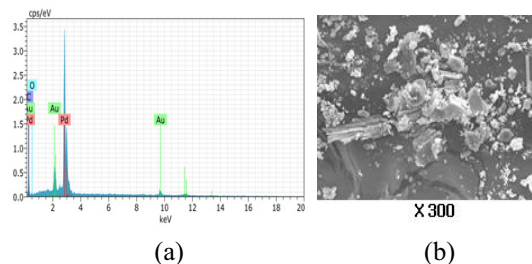


Fig. 4. (a) EDS Analysis, (b) SEM photograph.

The cathodic peak current (i_p^c) depends linearly on square root of scan rate ($v^{1/2}$), which confirms that the reduction of Pd(II) is diffusion controlled.

Electrodeposition experiments of Pd ions extracted from 0.5 M nitric acid using 1 M DBSO/ C_4mimTf_2N were carried out at -1.0 V potential. The current response for the potentiostatic electrolysis was stable throughout, and black and dense particles were deposited on the glassy carbon electrode. The XRD pattern and EDS of such deposit confirmed the palladium deposited in metallic form (Fig. 4).

4. Conclusion

The extraction and electrochemical behavior of palladium in the new media, 1 M DBSO/ C_4mimTf_2N , were investigated, and the feasibility of the Extraction-Electrodeposition (EX-EL) process was demonstrated. Lower distribution coefficient was obtained from higher acidity, and palladium ion formed a complex with less DBSO molecules in higher acidity.

The redox potential of palladium was obtained from DBSO/ C_4mimTf_2N containing palladium either dissolved or extracted. The result of potentiostatic electrodeposition showed palladium recovery process using ionic liquid was feasible.

ACKNOWLEDGEMENT

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REFERENCES

- [1] X.Q. Sun, H.M. Luo and S. Dai, Ionic liquids-based extraction: A promising strategy for the advanced nuclear fuel cycle, *Chemical Reviews* 112, 2100-2128 (2012).