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Kwang-Wook Kim[a]; Eil-Hee Lee[a]; Jae-Hyung Yoo[a]
[a] KOREA ATOMIC ENERGY RESEARCH INSTITUTE, TAEJON, SOUTH KOREA

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A Study on In-Situ Electrolytic Stripping of Uranyl Ion by Using a Closely Packed Glassy Carbon Fiber Column Electrode System

KWANG-WOOK KIM,* EIL-HEE LEE, and JAE-HYUNG YOO
KOREA ATOMIC ENERGY RESEARCH INSTITUTE
YUSONG P.O. BOX 105, TAEJON 305–600, SOUTH KOREA

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ABSTRACT

Uranium(VI) in a tributyl phosphate organic phase was stripped into an aqueous phase by reduction of uranium(VI) to uranium(IV) in a closely packed GC fiber column electrode system. A model for in-situ uranium(VI) electrolytic stripping was suggested for the system. Uranium(VI) electroreduction occurred both in the organic phase and in the aqueous phase of the mixed phases. The uranium stripping yield increased and then became constant with the organic flow rate in the electrolytic system due to an increase of diffusion resistance of uranium ions in the organic phase into the aqueous phase. The aqueous flow rate, on the other hand, did not significantly affect the total uranium(VI) reduction current in the system. Electrolytic stripping was confirmed to be more effective than ordinary stripping without electrolysis.

INTRODUCTION

Waste treatment of heavy-metals-containing solutions from the primary metal industry or the nuclear industry is important because of the volume reduction of waste to be released to the environment or the recovery of reusable resources from them (1, 2). One of the ways to separate selectively a few metal ions from multicomponent solutions or to enhance the separation yield of them is to change the extractabilities of the metal ions toward an organic extractant by controlling the valences of the metal ions electrochemically without adding chemicals which could result in generating secondary wastes and

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changing the stoichiometric concentrations of components in the system. The system for that purpose has an electrolytic extraction step or an electrolytic stripping step in which mass transfers of the metal ions between the organic and aqueous phases are accompanied with the electrolytic reaction of the metal ions (3–5). The system should have a large electrode area in order to change the oxidation states of the metal ions rapidly as well as a large liquid–liquid contact area to accomplish the effective mass transfer of metal ions between two phases at the same time with the electrolytic reaction (5).

In our work an effective electrolytic stripping system with such a large electrode area and a large liquid–liquid contact area in the same space was developed by using a flow-through glassy carbon (GC) fiber column electrode (6) into which two immiscible phases, between which the mass transfer of a metal ion occurred, were fed together. A GC fiber bundle closely packed in a tube acts as a working electrode with a huge electrode surface area, and it also acts simultaneously as a supporter for the two phases fed into the fiber column to be spread thinly and homogeneously among countless clearances between respective GC fiber strands due to capillary action induced by the clearances between fibers, resulting in generating a large and effective liquid–liquid contact area. A flow-through liquid–liquid contactor using a small, closely packed polystyrene fiber bundle has been confirmed to be able to bring about a large liquid–liquid contact area effectively and continuously within the fiber column in our previous works (7–9). Also, the flow-through GC fiber column electrode system is known to be effective for changing the oxidation states of metal ions continuously and rapidly in the aqueous phase because of its huge electrode area (6). Therefore, a GC fiber bundle packed densely in a tube can act as an efficient contactor to generate a very large liquid–liquid contact area for mass transfer and as a large electrode surface area for electrolytic reaction simultaneously.

In this work the stability and performance of an electrolytic stripping system using a GC fiber column bundle were studied with the well-known electrochemical/chemical system U(VI)/U(IV)–tributyl phosphate (TBP) in nitric acid. Prior to the main electrolytic stripping, in order to determine the extent and behavior of reduction of U(VI) to U(IV) in the mixture of organic and aqueous phases, voltammograms of the reduction of U(VI) to U(IV) in the respective phases, including the mixture of aqueous and organic phases, were measured and analyzed. Stripping yields in that system with/without changing the valence of U(VI) to be transferred between the two phases were compared.

EXPERIMENTAL

A schematic diagram of an in-situ electrolytic stripping system with a closely packed GC fiber bundle to be used as a working electrode and a supporter for a

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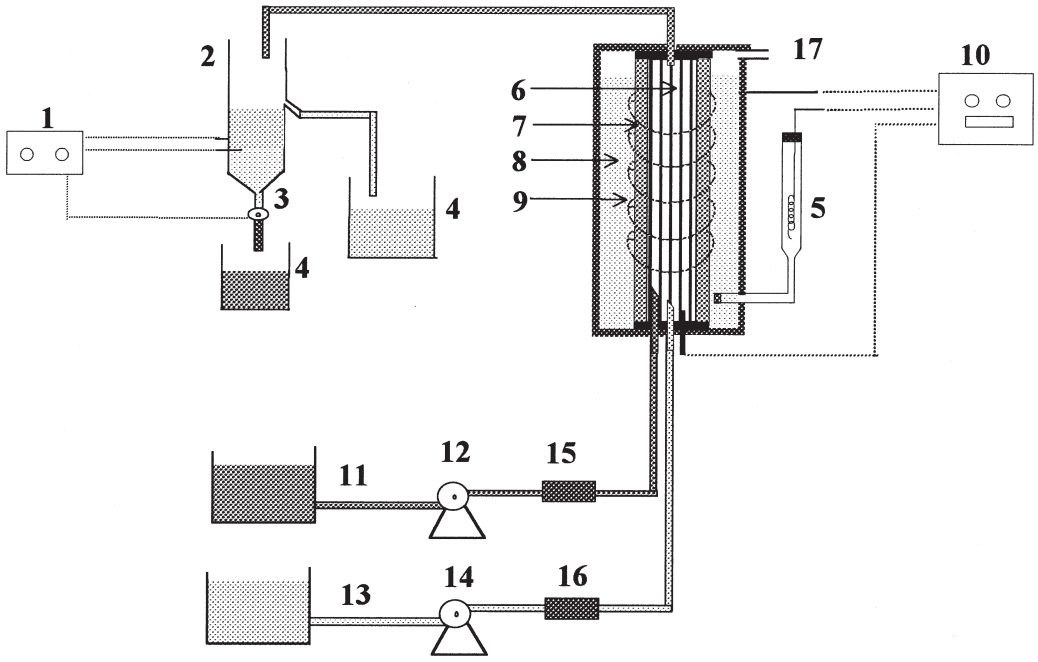
liquid–liquid contactor is shown in Fig. 1. The GC fiber bundle (6) was prepared by closely packing 50 glassy carbon fiber yarns (one yarn consists of about 11,000 fine strings) into a porous glass tube (7) (Corning Vycor glass No. 7930) of 9.3 cm length and 0.8 cm inside diameter. A GC rod of 3 mm diameter was inserted into one end of the fiber bundle in order for the fiber bundle to be connected through a terminal to a potentiostat (10) (Bioanalytical Systems Inc., Model No. BAS 100B/W). A counter solutions (8) of 0.1 N $N_2H_5^+$ + 1.0 N HNO_3, the same as the aqueous stripping solution to be fed into the GC fiber bundle, was filled outside the porous glass tube which was surrounded with the platinum counterelectrode (9). The reference electrode (5) of saturated KCl–Ag/AgCl (SSE) was placed close to the porous glass tube. The aqueous phase (11) of nitric acid and the TBP organic phase (13) containing U(VI) ion



1. Interface Level Controller
2. Organic/Aqueous Phase Separator
3. Solenoid Valve
4. Product Storage Tank
5. Reference Electrode (SSE)
6. Working Electrode (GC Fiber Column)
7. Porous Tube (Membrane)
8. Counter Solution
9. Counter Electrode (Pt)
10. Potentiostat/Data Recording System
11. Aqueous Reservoir
12. Aqueous Pump
13. Organic Reservoir
14. Organic Pump
15. Aqueous Flow Controller
16. Organic Flow Controller
17. Vent

FIG. 1 Schematic diagram of electrolysis system with a glassy carbon fiber column eletrode.

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were simultaneously fed into the fiber bundle through two variable pumps (12, 14) (Ismatec Co. Model No. Regulor 10). The mixture of two phases coming out of the GC fiber bundle went to a separator (2) actuated with a solenoid valve (3) and an interface level controller (1). The phase ratio of the mixture coming out of the system was carefully measured with a mass cylinder.

The chemical system used to test the performance of the electrolytic stripping system was nitric acid solution with 0.1 N neutralized hydrazine ($N_2H_5^+$) for an aqueous phase and 30 vol% TBP (tributyl phosphate)/dodecane with U(VI) of 8.46 g/L and nitric acid of 0.11 N for an organic phase. The organic solution was prepared by mixing 10 g/L U(VI)-containing 1.0 N nitric acid and 30 vol% TBP vigorously with a phase ratio of 1.0 for 10 minutes. The extraction reaction between U(VI) in nitric acid and TBP is well known to be fast. The extraction reaction is expressed as follows (10, 11):

$$(UO2_2^+)_{Aq.} + (2NO_3^-)_{Aq.} + (2TBP)_{Org.} = (UO_2(NO_3)_2 \cdot 2TBP)_{Org.} \quad (1)$$

$$(H^+)_{Aq.} + (NO_3^-)_{Aq.} + (TBP)_{Org.} = (HNO_3 \cdot TBP)_{Org.} \quad (2)$$

In order to observe the reduction characteristics of U(VI) in the aqueous phase, the organic phase, and their mixture in the electrolytic stripping system, the voltammograms of U(VI) reduction in each phase were measured. The stripping yields with/without electrolytic reduction of U(VI) at an applied potential and at several flow rates of each phase were evaluated by analyzing the concentrations of U(VI) and U(IV) in the aqueous phase coming out of the electrolytic system, respectively. The concentration analysis of U(IV) in the aqueous phase was carried out by measuring the absorbance of U(IV) at 645.5 nm without any interference of U(VI) with a spectrophotometer (Shimadzu Co., Model No. UV-160A). The standard solution of U(IV) for the determination of the molar extinction coefficient of U(IV) was prepared by a coulometry system with a column electrode of glassy carbon fibers as a working electrode (6). The total uranium was measured by an ICP (Induced Coupled Plasma Spectroscopy, Jobinyvon Co., Model No. JY 38 Plus).

The experimental parameters and their ranges used in this work are shown in Table 1.

TABLE 1
Experimental Parameters and Their Ranges

	Parameter			
	Phase ratio (Org./Aq.)	Aqueous flow rate (mL/min)	Organic flow rate (mL/min)	Nitric acid (*N*)
Range	0.1–2.5	0.25–2.5	0.1–1.5	0.5–2.0

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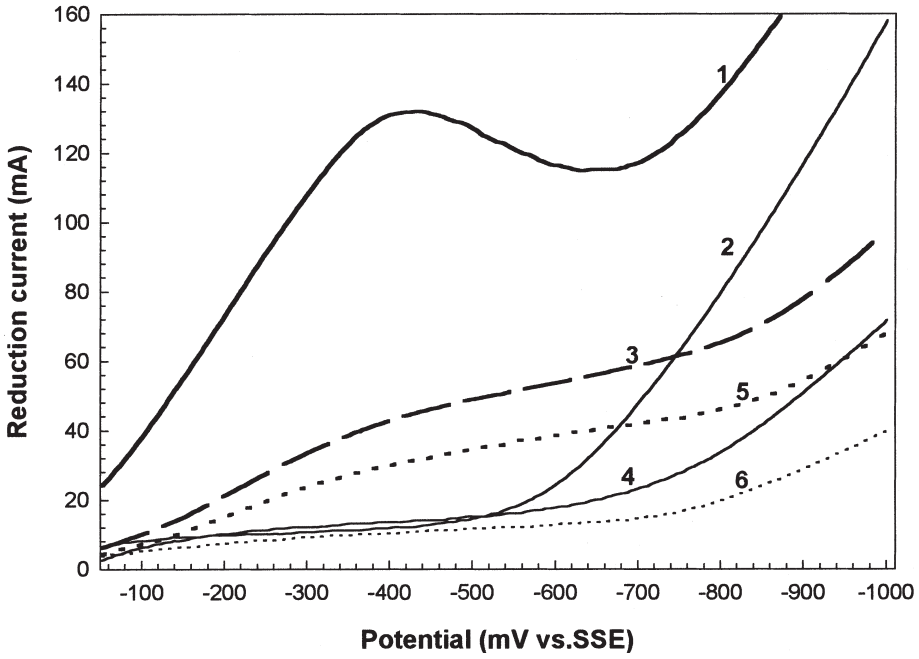

FIG. 2 Voltammograms of U(VI) reduction at GC fiber column electrode. Aqueous system: Curve 1, 5.1 g/L U(VI) in 1.0 N HNO_3 + 0.1 N $N_2H_5^+$; Curve 2, 1.0 N HNO_3 + 0.1 N $N_2H_5^+$. Mixed system: Curve 3, Aqueous phase = 1.0 N HNO_3 + 0.1 N $N_2H_5^+$, Organic phase = 8.46 g/L U(VI) + 0.11 N HNO_3 in 30 vol% TBP; Curve 4, Aqueous phase = 1.0 N HNO_3 + 0.1 N $N_2H_5^+$, Organic phase = 0.11 N HNO_3 in 30 vol% TBP. Organic system: Curve 5, 8.46 g/L U(VI) + 0.11 N HNO_3 in 30 vol% TBP; Curve 6, 0.11 N HNO_3 in 30 vol% TBP. Flow rate: All aqueous phase = 1.60 mL/min, All organic phase = 0.45 mL/min. Scan rate: 3 mV/s.

RESULTS AND DISCUSSION

Figure 2 shows the voltammograms of reduction of U(VI) to U(IV) in aqueous, organic, and their mixed phase together with their respective background voltammograms without U(VI). Curves 1 and 2 are the voltammograms of reduction of U(VI) in an aqueous phase and its background voltammogram. Curve 1 shows a well-developed peak current around −450 mV due to the limiting current of reduction of U(VI), and it rises at more negative potential than −650 mV due to hydrogen gas evolution that is also observed in the same potential range of Curve 2. The reduction reaction of U(VI) in the aqueous solution is known to be irreversible, as follows (11–13):

$$UO_2^{2+} + 2e^- + 4H^+ \rightarrow U^{4+} + 2H_2O, \qquad E_0 = +0.33 \text{ V (SHE)} \quad (3)$$

The relationship between current, flow rate, and concentration of the flow-through electrolytic equipment like that used in this work can be expressed as follows (6, 13–15):

$$I = nFf(C_{in} - C_{out}) \quad (4)$$

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where I, n, F, f, C_{in}, and C_{out} are the current (A) measured between the working electrode and the counterelectrode, the number of electrons involved in the electro-reaction, the Faraday constant (96,500 C), the flow rate of the solution (L/s), the inlet concentration of species in the solution (mol/L), and the outlet concentration of species in the solution (mol/L), respectively. If the system operates at the limiting current throughout the system, the species concentration is zero at all points on the electrode surface. When the solution passes through the system with sufficient residence time in the limiting current state, the outlet concentration, C_{out}, becomes zero (6, 15). The number of electrons involved in the reduction of U(VI) to U(IV), calculated at the limiting current of Curve 1 by using Eq. (4) with zero C_{out}, is about 2.03, that is, very close to 2, the number of electron involved in Eq. (3). This means that this flow-through electrolytic system with a highly packed GC fiber bundle is effective for a continuous change of valance of a metal ion because of its huge electrode area.

Curve 3 of Fig. 2 shows a voltammogram measured when the organic phase with U(VI) and the aqueous stripping solution without any U(VI) were fed into the electrolytic system simultaneously. In other words, it is the voltammogram of reduction of U(VI) in a mixture of aqueous and organic phases. Curve 4 is its background voltammogram without U(VI). The hydrogen evolution currents in Curves 3 and 4 occur around -650 mV, and are a little more negative than those of Curves 1 and 2. Curve 5 is the voltammogram of reduction of U(VI) obtained when only the organic phase containing U(VI) and a small amount of nitric acid of 0.1 N was fed into the electrolytic system without feeding the aqueous stripping solution in the system. Curve 6 is the background voltammogram of the organic phase with the nitric acid only. The reduction current of Curve 5 means that the U(VI) in the organic phase containing U(VI) ion and proton ion can be reduced to U(IV) at the interface between the GC fiber electrode and the organic phase. The reduction of U(VI) in the organic solution containing nitric acid could be considered to have the same reaction form as that in the aqueous solution. A paper (4) showed that the reduction of U(VI) occurred at the interface between an electrode and an organic phase with proton ion and the U(VI) ion. The reduction current patterns of Curves 5 and 6 are similar to those of Curves 3 and 4. No clear limiting currents of the reduction of U(VI) in Curves 3 and 5 are observed, in contrast to Curve 1. The reason could be explained as follows. The IR drops in the mixed system of aqueous and organic phases or only in the organic phase should be larger than that in the aqueous phase and can not be negligible, which is clearly observed in the background voltammogram measured in the mixture of aqueous phase and organic phase without U(VI), indicating a somewhat distorted current–potential relation for hydrogen evolution. Accordingly, the apparent reduction rates, i.e., the kinetic reduction currents of

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U(VI) observed in the mixed system and in the organic phase, are smaller than that observed in the aqueous phase. Moreover, when the mixed phases flow through the GC fiber column electrode, the GC electrode surface could be covered in part by a thin organic film because the viscosity and interfacial tension of the organic phase are higher than those of the aqueous phase and because the organic phase is more hydrophobic toward the GC fiber than the aqueous phase. Such blots of organic film on the electrode could increase the overpotential against the reduction of U(VI) in the aqueous phase so that the reduction current in the aqueous phase becomes low compared with that at the clean GC electrode in the aqueous phase alone. In that case the concentration of U(VI) at the whole electrode surface could not easily be zero due to the organic phase which covers part of the electrode surface.

In order to understand the electrolytic stripping in the flow-through reactor with the mixed phases more quantitatively and qualitatively, a suitable and plausible model of that is necessary, even though it is not perfect. When the organic and aqueous phases are simultaneously fed into the system, they are considered to flow alternately in contact with the surface of the GC fiber electrode, as shown in Fig. 3, because they are immiscible to each other. At that time the ratio of the electrode area portions in contacted with each phase is considered to be equivalent to the phase ratio (organic phase/aqueous phase). The U(VI) in the organic phase in contact with the GC electrode is reduced to U(IV) as described in Curve 5 of Fig. 1, and the U(VI) diffuses to the aqueous phase. When the organic and aqueous phases flow through the GC fiber column in good contact with the GC electrode surface and with enough residence time, the U(VI) and generated U(VI) in the organic phase are backextracted into the aqueous phase as much as the equilibrium concentration of U(VI) and U(IV) between the aqueous and organic phases, respectively, and then the U(VI) transferred into the aqueous phase is again reduced to U(IV) at the interface between the GC fiber electrode and the aqueous phase. Therefore, the

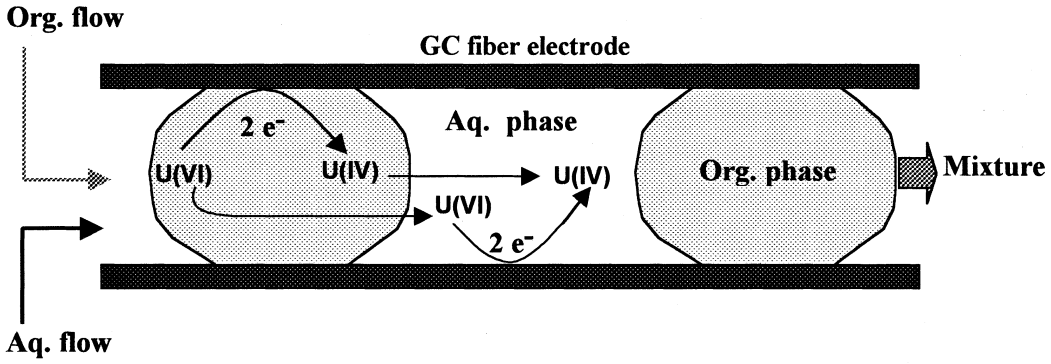

FIG. 3 Conceptual mechanism of electroreduction of U(VI) and mass transfer in aqueous and organic mixed phases at GC fiber column electrode system.

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reduction current of Curve 3 measured in the mixed phase is attributed to the reductions of U(VI) at the aqueous phase/GC electrode interface and at the organic phase/GC electrode interface. In this case, Eq. (4) can be modified for the reductions for both phases as follows:

$$I_{\text{Total}} = nFf_{\text{Org.}}(C_{\text{Org.in}} - C_{\text{Org.out}}) + nFf_{\text{Aq.}}(C_{\text{Aq.in}} - C_{\text{Aq.out}}) \qquad (5)$$

U(VI), C_{in}, and C_{out} of the aqueous phase part of this equation result from the organic phase due to the stripping of U(VI) in the organic phase. The distribution coefficient of U(IV) to TBP is known to be much lower than that of U(VI) to TBP (10, 11). The experimentally observed distribution coefficient of U(VI) of 8.5 g/L in 1.0 N nitric acid to 30 vol% TBP was about 6.3, and that of U(IV) of 4.5 g/L in the same condition was less than 1.0. Therefore, most of the U(IV) generated in the organic phase could be transferred into the aqueous phase if good liquid–liquid contact between the aqueous and organic phases is maintained. As mentioned before, the U(VI) in the aqueous phase transferred from the organic phase by diffusion is also reduced to U(IV) at the electrode. As a consequence, most of the total uranium in the system which existed in the organic phase can finally exist in the aqueous phase as U(IV).

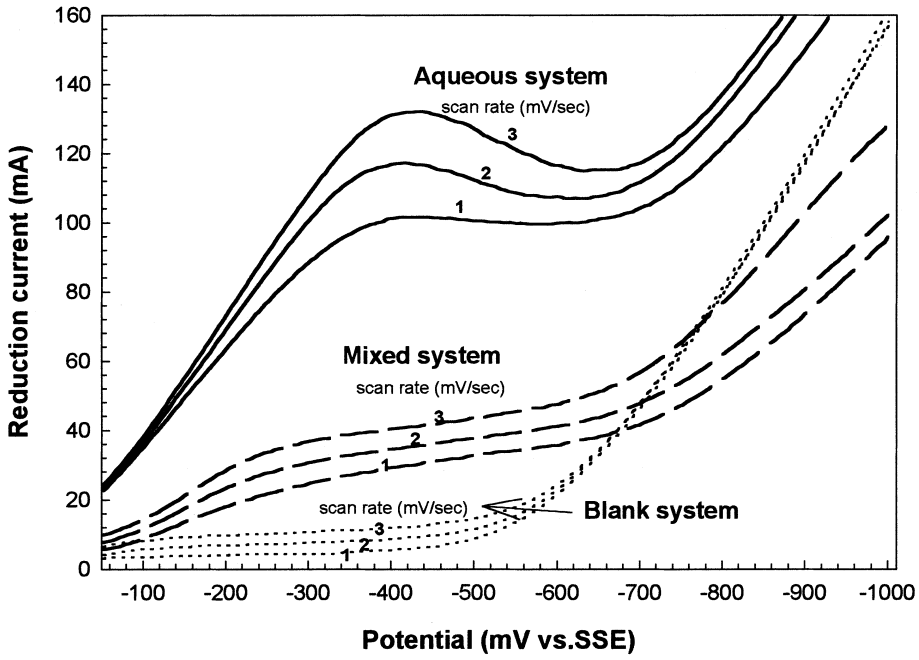

FIG. 4 Effect of scan rate of voltammograms of U(VI) reduction at GC fiber column electrode. Aqueous system: 5 g/L (VI) in 1.0 N HNO_3 + 0.1 N $N_2H_5^+$. Mixed system: Aqueous phase = 1.0 N HNO_3 + 0.1 N $N_2H_5^+$, Organic phase = 8.46 g/L U(VI) + 0.11 N HNO_3 in 30 vol% TBP. Blank system: 1.0 N HNO_3 + 0.1 N $N_2H_5^+$. Flow rate: All aqueous phase = 1.4 mL/min, All organic phase = 0.4 mL /min.

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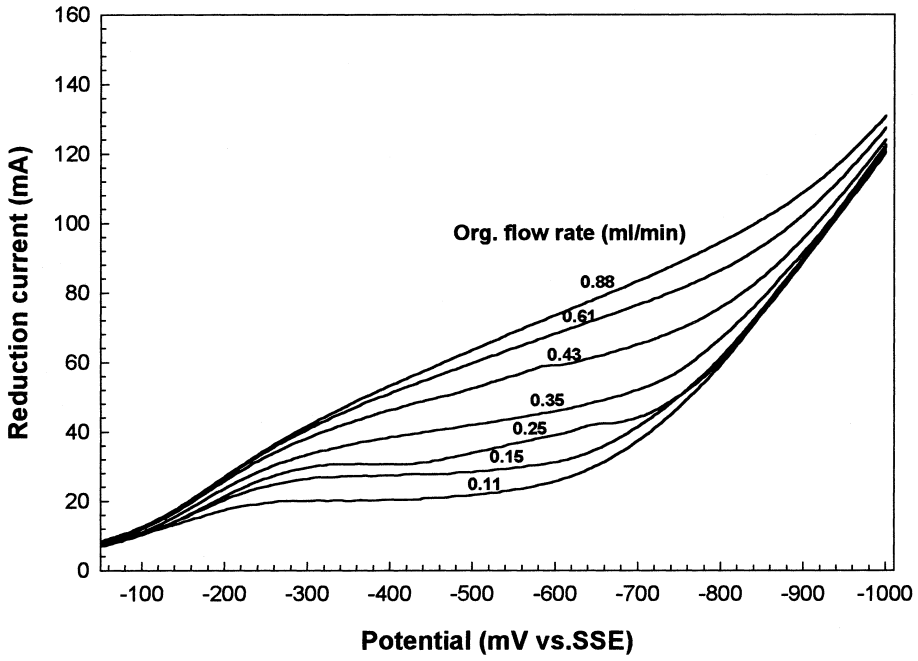

FIG. 5 Effect of the organic flow rate on voltammograms of U(VI) reduction in mixed phases at the GC fiber column electrode. Scan rate: 3mV/s. Mixed system: Aqueous phase = 1.0 N HNO_3 + 0.1 N $N_2H_5^+$, Organic phase = 8.46 g/L U(VI) + 0.11 N HNO_3 in 30 vol% TBP. Aqueous flow rate = 1.4 mL/min.

This means that electrolytic stripping can enhance the stripping yield much more compared with ordinary stripping without the electrolytic reaction. The results about the enhancement of stripping yields resulting from changing the valences of the metal ions will be discussed in more detail at the end of this paper.

Figure 4 shows the effect of scan rates on the voltammograms of reduction of U(VI) in the aqueous and mixed phase. The peak currents in the aqueous phase increase with the scan rate, and the peak potentials also shift a little bit to negative potential with the scan rate, as shown by the results in other work (16). They are typical characteristics of an irreversible reaction of Eq. (3). The plateau regions in the case of the mixed phase look like diffusion-limited currents, and they increase in magnitude with an increase of scan rate, even though the limiting currents are not as clear as those in the voltammogram in the aqueous solution.

Figure 5 shows the effect of the organic flow rate on the voltammograms of reduction of U(VI) in the mixed phases at a fixed aqueous flow rate. The reduction current of U(VI) increased with the organic flow rate. The increase in organic flow rate means an increase of the phase ratio. In ordinary stripping without electrolysis, the concentration of U(VI) in the aqueous phase trans-

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ferred from the organic phase increases with an increase of the phase ratio at a fixed aqueous flow rate. An example of this is shown in Fig. 10. Accordingly, the increase of U(VI) concentration in the aqueous phase can result in an increase of the reduction current of U(VI) in the aqueous phase with respect to Eq. (5), so that the total reduction current of U(VI) observed in the system increases. When the organic flow is much smaller, most of the GC fiber electrode surface is in contact with the aqueous phase. Therefore, the reduction current has a clear plateau, showing a diffusion-limited current similar to that in the aqueous phase, even though the current amplitude is small.

Figure 6 shows the effect of the aqueous flow rate on the voltammograms of reduction of U(VI) at a fixed organic flow rate in the mixed phase where the nitric acid concentration of the aqueous phase is 1.0 N. In contrast to Fig. 5, the aqueous flow rate does not have much effect on the system. An increase of the aqueous flow rate at a fixed organic flow rate can bring about two effects on the reduction current of U(VI) in the system. The first one is a decrease in the reduction current of U(VI) due to the decrease in U(VI) concentration in the aqueous phase according to the decrease in the phase ratio (as shown in Fig. 12). The other one is the increase in the reduction current due to the increase of the aqueous flow rate with respects to Eq. (5). The two effects

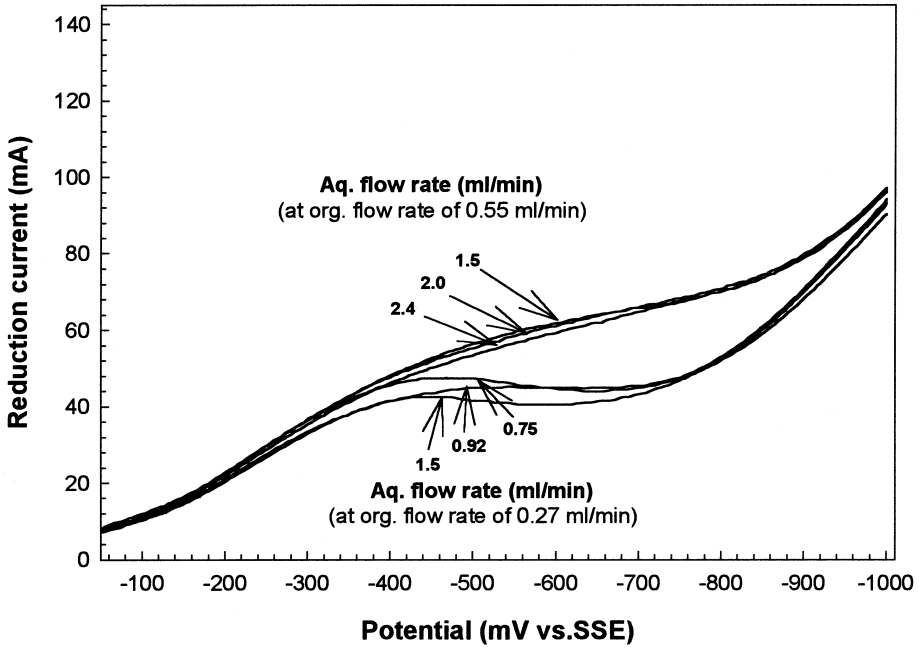

FIG. 6 Effect of the aqueous flow rate on voltammograms of U(VI) reduction in mixed phases at the GC fiber column electrode. Scan rate: 3 mV/s. Mixed system: Aqueous phase = 0.75 N HNO_3 + 0.1 N $N_2H_5^+$, Organic phase = 8.46 g/L U(VI) + 0.11 N HNO_3 in 30 vol% TBP. U(VI) + 0.11 N HNO_3 in 30 vol% TBP.

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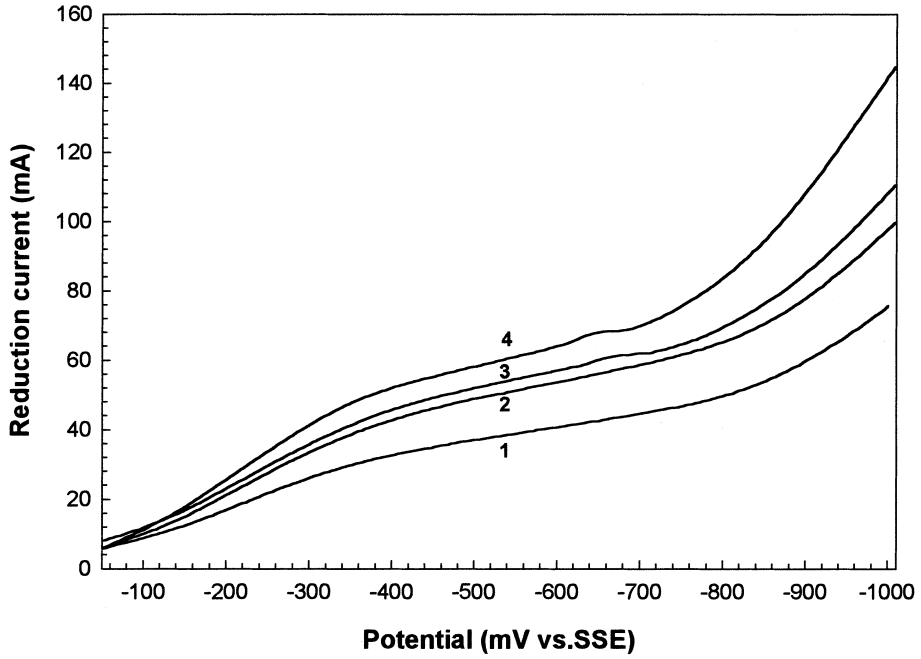

FIG. 7 Effect of the nitric acid concentration of the aqueous phase on voltammograms of U(VI) reduction in mixed phases at GC fiber column electrode. Scan rate: 3 mV/s. Mixed system: Aqueous phase = $x1$ N HNO3 + 0.1 N $N_2H_5^+$, Organic phase = 8.46 g/L U(VI) + $x2$ N HNO_3 in 30 vol% TBP. Curves 1, 2, 3, 4, ($x1$, $x2$): (0.5, 0.04), (1.0, 0.11), (1.5, 0.19), (2.0, 0.28). Flow rate: Aqueous phase = 1.4 mL/min. Organic phase = 0.4 mL/min.

offset each other. Therefore, the apparent change of the reduction current of U(VI) observed in the system with a change of the aqueous flow rate is considered to be small.

Figure 7 shows the effect of nitric acid concentration in the stripping solution of the aqueous phase on the voltammograms of reduction of U(VI) in the mixed phase. The nitric acid concentration in the organic phase depends on that in the aqueous phase, as shown in Eq. (2). Also, the reduction of U(VI) to U(IV) has a strong relation with the proton from the nitric acid, as shown in Eq. (3). Accordingly, an increase of nitric acid in the aqueous stripping solution makes the reductions of U(VI) in the organic and aqueous phases increase. The effect of nitric acid is not as significant, as shown in other papers (16) where the reduction occurred only in the aqueous phase. This could be explained by the fact that the reduction of U(VI) occurs in the mixed system with a higher IR drop and lower conductivity compared with those in the aqueous phase.

Figure 8 shows the concentration of U(IV), the total uranium concentration [U(VI) plus U(VI)] in the aqueous phase coming out of the electrolytic stripping system, and the reduction current of U(VI) as a function of the organic

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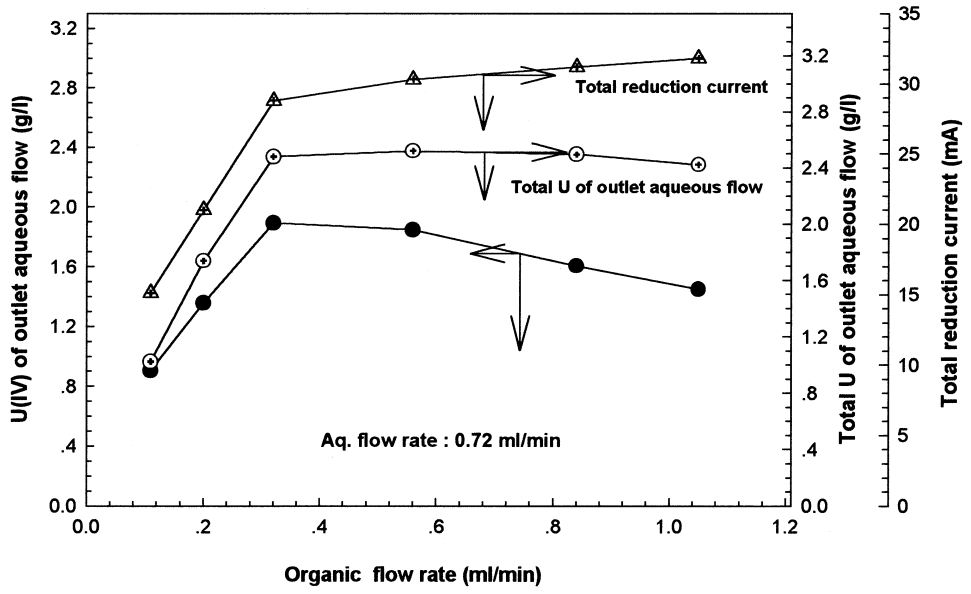

FIG. 8 U(IV) and total U concentration in outlet aqueous flow and total reduction current in the mixed phases at GC fiber column electrode with various organic flow rates. Applied potential: −550 mV vs SSE. Mixed system: Aqueous phase = 1.0 N HNO_3 + 0.1 N $H_2H_5^+$, Organic phase = 8.46 g/L U(VI) + 0.11 N HNO_3 in 30 vol% TBP.

flow rate at a fixed aqueous flow rate with a controlled potential of −550 mV (vs SSE). It shows the diffusion-limited current of Figs. 2 and 4 being applied in the mixed phase with minimum hydrogen gas evolution. The reduction current increases slowly after rising rapidly at first with an increase of the organic flow rate. The U(IV) concentration measured in the aqueous phase shows a peak and then decreases slowly. That can be explained as follows. When the organic flow rate is low (that is, the ratio of the portions of the organic phase in contact with the electrode to those of the aqueous phase is low), the distance for the U(VI) existing originally in the organic phase and the U(VI) generated at the electrode surface in contact with the organic phase to diffuse to the aqueous phase is short, as shown in Fig. 3, so that U(VI) and U(IV) in the organic phase are transferred easily into the aqueous phase. And then, the transferred U(VI) is reduced to U(IV) at the interface between the aqueous phase and the GC fiber electrode. These result in the first rapid rise of concentration of U(IV) in the aqueous phase in Fig. 8. However, as the organic flow rate increases, the portion of the organic phase in contact with the GC fiber electrode increases so that the distance for U(VI) and U(IV) in the organic phase to diffuse into the aqueous phase becomes longer. This results in an increase of the diffusion resistance of U(VI) or U(IV) in the organic phase to the aqueous phase, so that the concentration of U(IV) observed in the aqueous phase becomes lower. In that case, if a longer electrolytic system is used or if the lower

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flow rates of the two phases are selected in order to increase the residence time of the two phases within the electrolytic stripping system, the concentration of U(IV) measured in the aqueous phase coming out of the electrolytic stripping system is considered to get higher. The maximum equilibrium concentration of U(VI) in the aqueous phase of an ordinary stripping system without a change in the valence of the U(IV) to be backextracted increases slowly with the organic flow rate at a fixed aqueous flow rate, as shown in Fig. 9 which was calculated by using the SEPHIS code (17). U(IV) has the same behavior. This possibility for an increase of total uranium concentration to be observed in the aqueous phase due to the increase of the phase ratio is offset by the increase of the diffusion resistance of the U(VI) and U(IV) in the organic phase with the organic flow rate. Therefore, the total uranium concentration measured in the aqueous phase is observed to be almost constant after the first rise. Figure 9 also shows the enhanced stripping yield, due to the electrolysis, calculated on the basis of the results of Fig. 8 compared with that of ordinary stripping without accompanying electroreduction of U(VI), where the enhanced stripping yield was defined as

$$\frac{C_{\text{Aq.Total,U with electrolysis}} - C_{\text{Aq.U(VI) without electrolysis}}}{C_{\text{Aq.U(IV) without electrolysis}}} \times 100$$

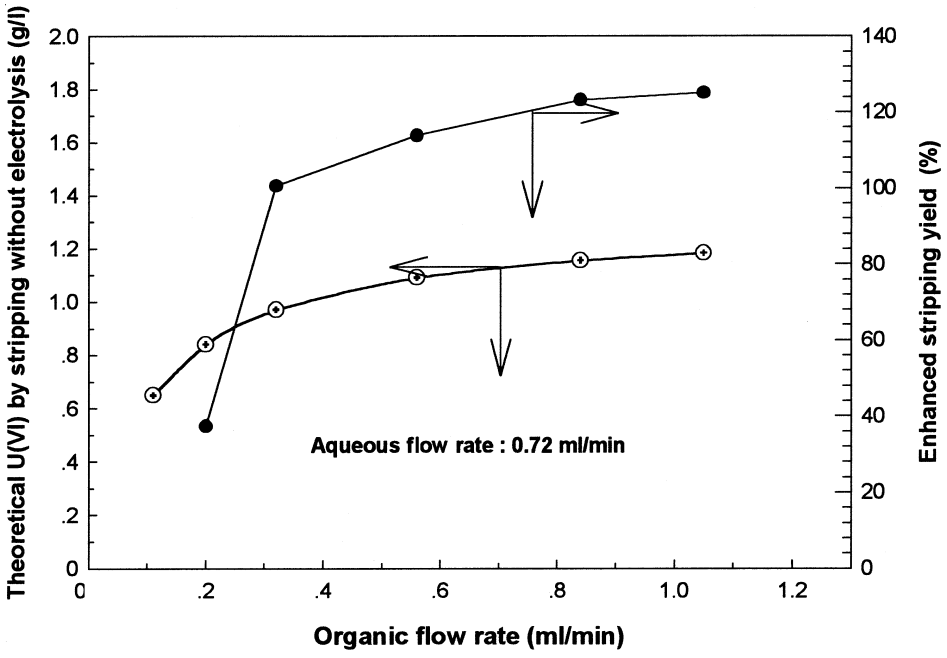

FIG. 9 Theoretical equilibrium U(VI) concentration by stripping without electrolysis and enhanced stripping yield by electrolysis in GC fiber column with various organic flow rates. Mixed system: Aqueous phase = 1.0 N HNO_3 + 0.1 N $N_2H_5^+$, Organic phase = 8.46 g/L U(VI) + 0.11 N HNO_3 in 30 vol% TBP.

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The zero-enhanced stripping yield means no electrolysis effect on stripping. The enhanced stripping yield of uranium increases with the organic flow rate. These results mean that changing the valence of the metal ion in order to change the extractability toward the extractant in the organic phase is effective for increasing the stripping yield.

Figure 10 shows the concentration of U(IV), the total uranium concentration [U(VI) plus U(IV)] in an aqueous phase coming out of the electrolytic stripping system, and the measured reduction current of U(VI) in the system as a function of the aqueous flow rate at a fixed organic flow rate with a controlled potential of −550 mV (vs SSE) being applied. There is nearly no change in the total reduction current of U(VI) in the system, similar to the results of Fig. 6. However, the concentration of U(IV) and the total uranium concentration in the aqueous phase decrease with the aqueous flow rate. This is believed to be mainly due to the decrease of the phase ratio. Figure 11 shows the maximum equilibrium concentration of U(VI) of the aqueous phase in ordinary stripping without electrolysis and the enhanced stripping yield due to electrolysis calculated on the basis of the results of Fig. 9. The concentration of U(VI) of the aqueous phase in ordinary stripping without electroreduction of U(VI) increases with the aqueous flow rate (that is, with a decrease of the

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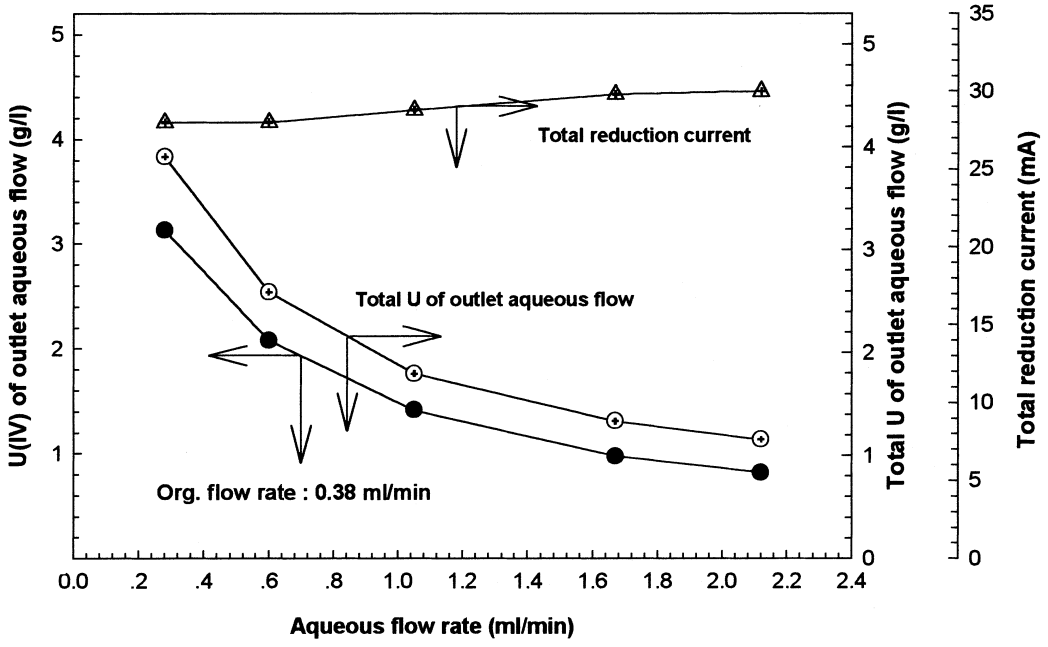

FIG. 10 U(IV) and total U concentration in outlet aqueous flow and total reduction current in the mixed phases at GC fiber column electrode with various aqueous flow rates. Applied potential: −550 mV vs SSE. Mixed system: Aqueous phase = 1.0 N HNO_3 + 0.1 N $N_2H_5^+$, Organic phase = 8.46 g/L U(VI) + 0.11 N HNO_3 in 30 vol% TBP.

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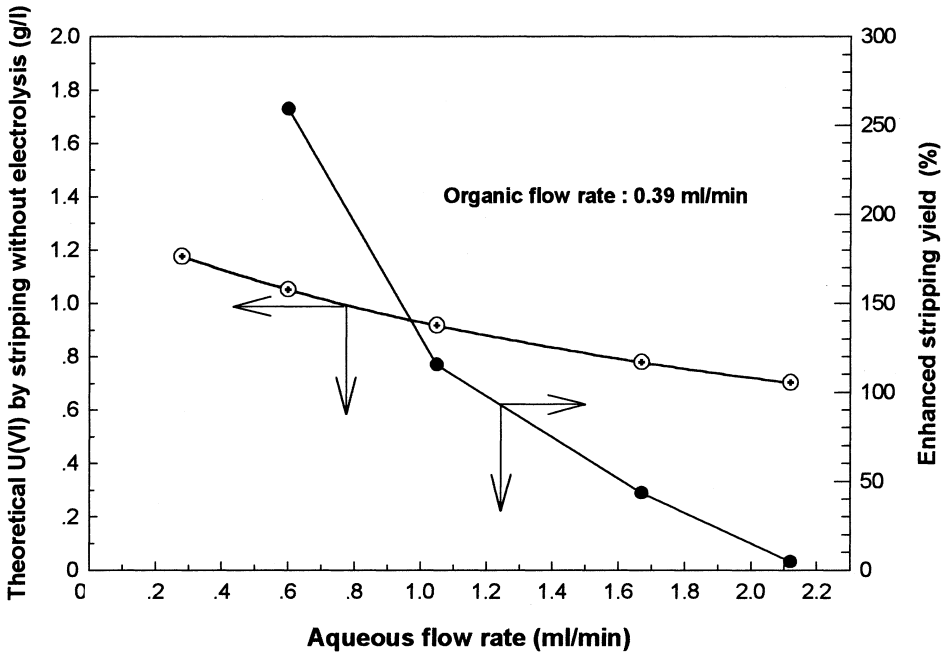

FIG. 11 Theoretical equilibrium U(VI) concentration by stripping without electrolysis and enhanced stripping yield by electrolysis in GC fiber column with various aqueous flow rates. Applied potential: −550 mV vs SSE. Mixed system: Aqueous phase = 1.0 N HNO_3 + 0.1 N $N_2H_5^+$, Organic phase = 8.46 g/L U(VI) + 0.11 N HNO_3 in 30 vol% TBP.

phase ratio). The enhanced stripping yield increases significantly with a decrease of the aqueous flow rate. Figures 9 and 11 indicate the enhanced stripping yield increases at a high phase ratio.

CONCLUSION

In the electrolytic stripping of U(VI) using a closely packed GC fiber column electrode into which aqueous and organic phases are fed simultaneously, the measured total reduction current of U(VI) is attributed to the reductions of U(VI) at the interfaces between the GC electrode and the aqueous and organic phases. The aqueous flow rate had little effect on the total reduction current of U(VI) in the system. The stripping yield of uranium first increases rapidly and then slowly with an increase of the organic flow rate because of an increase of diffusion resistance of U(VI) and U(IV) ions in the organic phase into the aqueous phase. A significantly enhanced stripping yield by electrochemically changing the valence of U(VI) to U(IV) was obtained when the phase ratio was high rather than low. Electrolytic stripping was confirmed to be more effective than ordinary stripping without electrolysis.

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