

## Study of the Effect of Hydrazine Form and Titanium Electrode Condition on Reduction of Uranium(VI) in Nitric Acid

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### 질산중의 우라늄(VI) 환원에 대한 하이드라이진 형태와 티타늄 전극상태의 영향연구

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#### Abstract

Voltammogram analysis of U(VI) reduction at electrochemically non-pretreated/pretreated Ti electrodes in nitric acid and hydrazine( $\text{N}_2\text{H}_4$ )/protonated hydrazine( $\text{N}_2\text{H}_5^+$ ) media was done in order to determine the effect of hydrazine form and Ti electrode condition on the reduction of U(VI) in nitric acid. In the case of non-pretreated Ti electrode, the reduction in nitric acid and hydrazine mono-hydrate solution needed a high activation overpotential and was affected by the ratio of hydrazine to nitric acid rather than by only absolute amount of hydrazine because of the decrease of solution conductivity and increase of  $iR$  drop, which were caused by proton consumption in the solution by the hydrazine. In the case of pretreated Ti electrode in nitric acid and protonated hydrazine solution, the reduction current peaks of U(VI) were clearer and higher enough to perform a kinetic analysis, compared with the case with the non-pretreated Ti electrode at the same potential, and the behavior was strongly affected by nitric acid. The presence of hydrazine was important in the reduction of U(VI) at the pretreated Ti electrode for preventing the reoxidation of U(IV), but the concentration of protonated hydrazine was not.

#### 요 약

질산 용액중의 우라늄(VI) 환원에 대한 하이드라이진 형태 및 티타늄 전극상태 영향을 알기 위하여, 질산 및 하이드라이진( $\text{N}_2\text{H}_4$ ) / 하이드라이진 양이온( $\text{N}_2\text{H}_5^+$ ) 용액중의 전기화학적 미-처리 / 처리 티타늄 전극에서 우라늄환원에 대한 voltammogram 해석을 수행하였다. 질산 및 하이드라이진 양이온 계를

사용한 전기화학적 미처리 티타늄 전극에서의 우라늄 환원은 그 전극에 존재하는 산화막에 의해 높은 활성화 과전압을 보이며, 하이드라이진에 기인한 질산용액중 수소이온의 소모에 의해 용액전도도의 감소 및 IR저항의 증가 때문에 하이드라이진의 절대 농도보다는 하이드라이진/질산 농도 비에 의해 영향을 더 받았다. 질산 및 하이드라이진 양이온 제를 사용한 전기화학적 처리 티타늄 전극에서의 우라늄환원 전류는 같은 전위에서 전기화학적 미처리 티타늄전극에 비해 속도론을 해석하기에 충분히 분명하며, 높은 피크를 보였으며 질산에 의해 크게영향을 받았다. 용액중에 하이드라이진 양이온의 존재는 생성된 우라늄(IV)의 재산화 방지를 위해 중요하지만 그 농도는 우라늄 이온의 환원에는 영향을 미치지 않았다.

### 1. Introduction

An efficient electrolytic method for the preparation of  $U(IV)^{(1-4)}$  in nitric acid solution is important in the hydrometallurgy of uranium ores, the preparation process of starting material for uranium dioxide and the *in-situ* electro-partitioning part of PUREX process which involves the solvent extraction accompanied by the reduction of  $Pu(IV)$  to  $Pu(III)$  by  $U(IV)$ . Reductants such as ferrous sulfamate and hydroxylamine nitrate etc.<sup>(5-6)</sup>, were widely employed in these processes to control the oxidation state of uranium. These chemical methods, however, not only have the disadvantage of increasing the amount of waste but also the excess reagents may interfere with the subsequent steps of the process. Furthermore, ferrous sulfamate can bring about severe process corrosion<sup>(1-3)</sup>. Since the electrochemical method shows promise in the development of simple and remote-controlled operations as well as overcoming the drawbacks of chemical methods, the direct electrolysis methods for controlling the oxidation state of uranium and/or other actinide elements have been studied by several investigators<sup>(2-9)</sup>.

Because Ti is highly resistant to corrosion in nitric acid media,<sup>(1, 2, 7)</sup> a Ti cathode is usually used for the reduction of  $U(VI)$  in an electrolytic pulsed column or in an electrolytic mixer-settler of solvent extraction process. The electrolyte in these cases is generally a mixture of nitric acid and hydrazine which functions as a stabilizer for  $U(IV)$  and an electron-donor for the anode.<sup>(1, 2, 8, 9)</sup> In order to control or simulate such an *in-situ* electrolytic separation processes for

uranium and/or plutonium, the reduction kinetics of  $U(VI)$  must be determined. However, few data have been reported on the reduction kinetics of  $U(VI)$  at a Ti electrode, because difficulties in obtaining a clear and reproducible voltammogram tolerable for wave-analysis are caused by the potential of the reduction of  $U(VI)$  being close to that of hydrogen evolution<sup>(1, 4)</sup> and by the fact that oxide film at the Ti electrode surface disturbs the reduction of  $U(VI)$ . The oxide film exists still on the Ti electrode even after physical polishing of the electrode.<sup>(10)</sup> Also, there is variation in published works as the optimum form of hydrazine. In some works, hydrazine mono-hydrate ( $N_2H_4 \cdot H_2O$ ) is directly used<sup>(11-13)</sup>, while protonated hydrazine in nitric acid ( $N_2H_5^+$ ), neutralized hydrazine, is used in the others.<sup>(2, 14)</sup> Therefore, it is necessary to evaluate the effect of the form of hydrazine on the reduction of  $U(VI)$  at the electrode.

In this work, voltammogram analysis of reduction of  $U(VI)$  at non-pretreated/pretreated Ti electrode in nitric acid and hydrazine( $N_2H_4$ )/protonated hydrazine( $N_2H_5^+$ ) media was done in order to know the effect of hydrazine form and Ti electrode condition on reduction of  $U(VI)$  in nitric acid. Here, the non-pretreated Ti electrode means a Ti electrode polished physically with fine emery papers but without any electrochemical treatment.

### 2. Experimental Procedure

A rectangular-shaped working electrode of  $1 \text{ cm}^2$  was prepared by tightly embedding all sides of Ti plate of 3mm in thickness into epoxy resin except

one side. The open side was polished with emery papers (No. 120, 240, 400, and 600) and alumina powder of 0.1  $\mu\text{m}$  and 0.5  $\mu\text{m}$ , and washed with distilled water and alcohol, and dried. However, the Ti electrode was used without any electrochemical pretreatment for the non-pretreated Ti electrode experiments.

The effect of the pretreatment of Ti electrode on the reduction of U(VI) was investigated by the cathodic polarization method described in our previous work.<sup>(10)</sup> The surface condition of the Ti electrode affects the voltammetric results, and hence, careful pretreatment of the electrodes is required; the Ti electrode after polishing with emery papers was polarized at a sufficient negative potential, e.g.  $-1.0$  V vs. Ag-AgCl/sat. KCl (SSE) reference electrode for 40 minutes before each run.

The electrolytic cell was composed of cathodic and anodic chambers equipped with 4 standard baffles, having the size of 10cm in inner diameter and 10cm in height, respectively. The voltammogram was recorded at  $25 \pm 0.5^\circ\text{C}$  with aid of a platinum counter electrode and a saturated calomel electrode (SCE) going toward the nearest position beside the working electrode (1–2mm from the surface of working electrode) through Luggin capillary filled with 2 N nitric acid. The potential was controlled by a potentiostat (EG&G Co. Model no. 362).

All chemicals used were of reagent grade. Uranyl nitrate hexahydrate  $\text{UO}_2(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  was dissolved in nitric acid of 0.5 to 2.0M to obtain  $(0.6-2.3) \times 10^{-1}$  M of U(VI). The concentration range of hydrazine mono-hydrate was 0.025–0.8M.

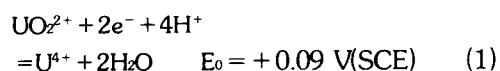
### 3. Results and Discussion

#### 3.1. Reduction of U(VI) at Non-Pretreated Ti Electrode

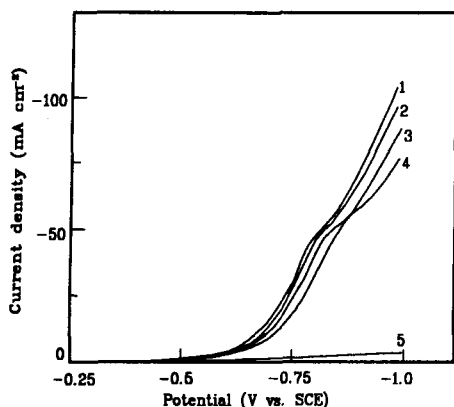
Fig. 1 and Fig. 2 show the effect of hydrazine on the reduction of U(VI) at a non-pretreated Ti electrode in nitric acid of 0.5 and 1.0M, respectively.

Most of current-potential curves have inflection points which are due to the limiting current of the reduction of U(VI). Rapid increases of currents just after the inflection points are thought to result from hydrogen evolution. The current below the inflection point is due to the reduction of U(VI). Intensive gas bubbles were observed at more negative potential than one showing inflection points, but there was no gas bubble before the inflection points. These observations are similar to ones of other workers.<sup>(2, 4)</sup>

The reduction of U(VI) should ideally occur at about  $+0.09$  V (vs. SCE) but the apparent currents of reduction of U(VI) were observed at more negative potential than  $-0.3$  V (vs. SCE). It means that the reduction of U(VI) at the Ti electrode needs a high overpotential of about 0.4 V. The redox reaction of uranium showing disproportionation step is known to be irreversible below the oxygen generation potential as follows.<sup>(1-4)</sup>

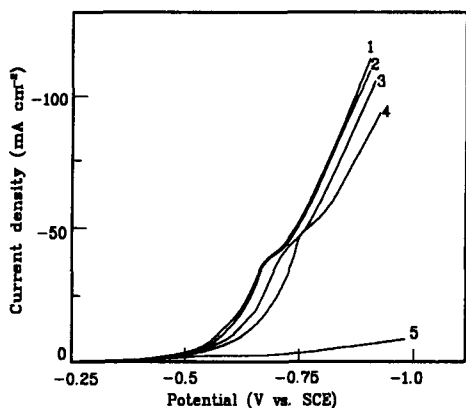


The irreversible electro-reaction usually has a characteristic of slow electron transfer through the electrode toward solution so that it needs some overpotential for current passing, which is called, the activation overpotential. The shift of reduction potential of U(VI) to negative direction by such an overpotential caused the reduction potential of U(VI) to get close to that of hydrogen evolution so that the reduction current of U(VI) was overlapped with one of hydrogen evolution at more negative potential after the inflection points. Such high overpotential and observed low reduction current of U(VI) were attributed to presence of an oxide film at the Ti electrode which hindered the reduction of U(VI) and hydrogen evolution.<sup>(10)</sup> As a consequence, the correct analysis of reduction peaks of U(VI) for kinetic data becomes difficult because of unclear reduction peak of U(VI) in the voltammograms. From these kinds of voltammograms, however, the effect of hydrazine on the reduction of U(VI) and the general characteristics



Electrolyte : 1-5 :  $1.26 \times 10^{-1} \text{ M UO}_2^{2+} + 0.5 \text{ M HNO}_3 + x \text{ N}_2\text{H}_4$   
 $\text{N}_2\text{H}_4 \text{ (M)} : (1) 0.025, (2) 0.05, (3) 0.1, (4) 0.2, (5) 0.8$   
 Scan rate ( $\text{mV s}^{-1}$ ) : 0.5  
 Mixing rate (rpm) : 348

Fig. 1. Voltammograms of the Reduction of U(VI) at Non-Pretreated Ti Electrode With Change of Hydrazine Concentration in 0.5M HNO<sub>3</sub>.



Electrolyte : 1-5 :  $1.26 \times 10^{-1} \text{ M UO}_2^{2+} + 1.0 \text{ M HNO}_3 + x \text{ N}_2\text{H}_4$   
 $\text{N}_2\text{H}_4 \text{ (M)} : (1) 0.05, (2) 0.1, (3) 0.2, (4) 0.4, (5) 0.8$   
 Scan rate ( $\text{mV s}^{-1}$ ) : 0.5  
 Mixing rate (rpm) : 348

Fig. 2. Voltammograms of the Reduction of U(VI) at Non-Pretreated Ti Electrode With Change of Hydrazine Concentration in 1.0M HNO<sub>3</sub>.

of the reduction of U(VI) could be analyzed.

The current-potential curves of voltammograms of Fig. 1 and Fig. 2 were observed to be affected much not by an absolute concentration of hydrazine but by the amount relative to nitric acid i.e., concentration ratio of hydrazine to nitric acid. The currents decreased slightly with increase of the ratio of less than 0.5, but dropped drastically at the ratio of more than 0.5. Over the ratio of 1.0, the reduction current was experimentally not observed and some yellow compound was observed to precipitate into the solution. The compound might be thought to be a complex form of uranium hydroxides. These results are thought to be due to the following three reasons. Firstly, the hydrazine should exist in the type of  $\text{N}_2\text{H}_5^+$  in acid solution so that it consumes much proton of the acid solution to become  $\text{N}_2\text{H}_5^+$ . The equilibrium relationship between hydrazine and nitric acid is as follows.<sup>(15)</sup>

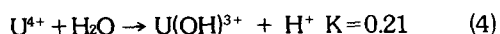


When nitric acid and hydrazine coexist in the solution, there must be equilibriums among the those components to satisfy the above conditions. As the proton concentration in a solution decreases due to the protonation of hydrazine, the currents for reduction of U(VI) and hydrogen evolution should decrease, because the proton is involved in the reduction of U(VI) of equation (1). Secondly, the electrolytic conductivity of solution decreases according to the decrease of proton concentration due to the hydrazine becoming  $\text{N}_2\text{H}_5^+$ . Table 1 shows that the conductivity of the solution decreases with increase of hydrazine at fixed concentrations of nitric acid. It consequently brings about the increase of  $iR$  drop (ohmic resistance) between the working electrode and the reference electrode<sup>(16)</sup>. It hinders the reduction at working electrode and the diffusivity of ions in the solution.

**Table 1. Electrolytic Conductivity ( $S\ cm^{-1}$ ) of Nitric Acid and Hydrazine Mono-Hydrate Media**

HNO <sub>3</sub> (N)	N <sub>2</sub> H <sub>4</sub> ·H <sub>2</sub> O (N)					
	0	0.01	0.025	0.05	0.1	0.2
0.25	115.8	104.9	99.7	88.2	68.4	37.4
0.5	—	206	197.2	177.3	153.4	112.3
1.0	363	357	344	335	299	276
2.0	664	636	623	612	595	552
3.0	792	778	766	756	744	713

Thirdly, the ratio of hydrazine mono-hydrate to nitric acid approaches 1, the concentration of proton in the solution gets to a very low level so that U(VI) is liable to precipitate in solution as forms of hydroxides such as  $UO_2(OH)^+$ ,  $(UO_2)_2(OH)^{3+}$ ,  $U_3O_8(OH)^+$ , etc.<sup>(17, 18)</sup> The hydrolysis of U(IV) can also occur in such condition of proton concentration of 0.5 N as follows.<sup>(19)</sup>



Therefore, the amount of uranium ion in the solution becomes low so that the reduction current at the electrode decreases.

In summary, the proton consumption due to the fact that the hydrazine should exist in the form of  $N_2H_5^+$  brings about above three phenomena which affect the reduction of U(VI) simultaneously one another. Finally it causes the reduction of U(VI) to be inactive. Therefore, the proton concentration is a very predominant factor affecting the reduction of U(VI).

Fig. 3 shows the effect of nitric acid on the reduction of U(VI). With increase of nitric acid, the currents rise exponentially, and the potentials showing the inflection points shifts to more positive direction and the inflection points become clear. These can be also explained by equation (1) i.e., the reduction of U(VI) becomes active with increase of the proton concentration in the solution.

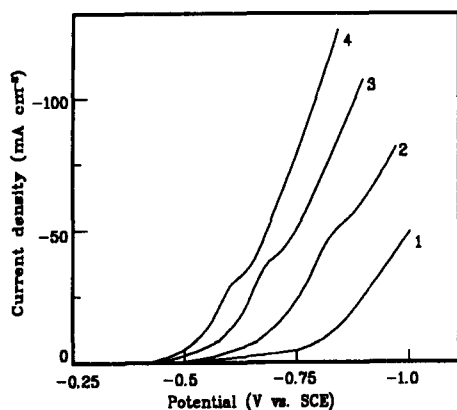
From these results, it can be noted that the voltammograms obtained at the non-pretreated Ti electrode in nitric acid with hydrazine are insufficient

for application to kinetic analysis because of unclear peaks for the voltammogram analysis.

### 3.2. Protonation of Hydrazine in Nitric Acid Solution

As mentioned above, the hydrazine itself consumes proton ion to form  $N_2H_5^+$  in the solution. It affects the reduction of U(VI) severely. Accordingly, if the hydrazine mono-hydrate is used directly in some process accompanied with mass transfer of uranium by TBP(Tri-butyl phosphate) such as in the PUREX process, its concentration should be carefully determined as a suitable value relative to nitric acid, the ratio of hydrazine to nitric acid, to have little effect on the process, because the change of proton concentration due to hydrazine might cause the change of distribution coefficient of U(VI) to TBP and the reduction of U(VI).

When the protonated hydrazine of  $N_2H_5^+$  applied, there is no disturbance on proton concentration in a solution and the process can be more easily controlled. So, the ambiguity of the change of proton concentration in a system can be removed. Instead, one additional step is required in the process to protonate the hydrazine with nitric acid in advance. Benefit of the option would depend on the situation. In the study of sensitive electro-kinetic analysis of U(VI), the protonated hydrazine is thought to be more effective than the hydrazine mono-hydrate in determining the effect of the hydrazine on the reduction of U(VI). Therefore, a basic experiment for the neutralization of hydrazine with nitric acid was performed. Fig. 4 shows a titration curve of nitric acid by hydrazine. The experimental midpoint of the titration curve showing the complete neutralization is coincided well with the theoretical equivalent point to satisfy equation(2) and (3). The experimental pH value is about 4.5 at the end point. The theoretical pH value is 4.25. The equations (2) and (3) are considered to be effective for the estimation of neutral point of mixture of nitric acid and hydrazine theoretically.



Electrolyte : 1-4 :  $1.26 \times 10^{-1} \text{ M UO}_2^{2+} + x \text{ HNO}_3 + 0.1 \text{ M N}_2\text{H}_4$   
 $\text{HNO}_3 \text{ (M)} : (1) 0.25, (2) 0.5, (3) 1.0, (4) 2.0$   
 Scan rate ( $\text{mV s}^{-1}$ ) : 0.5  
 Mixing rate (rpm) : 346

Fig. 3. Voltammograms of the Reduction of U(VI) at Non-Pretreated Ti Electrode With Change of  $\text{HNO}_3$  Concentration in 0.1M Hydrazine.

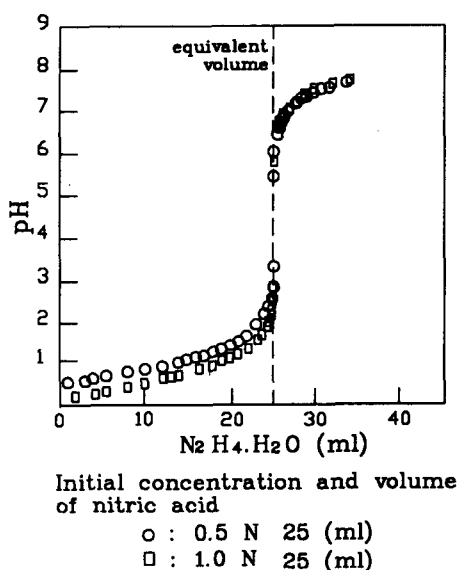
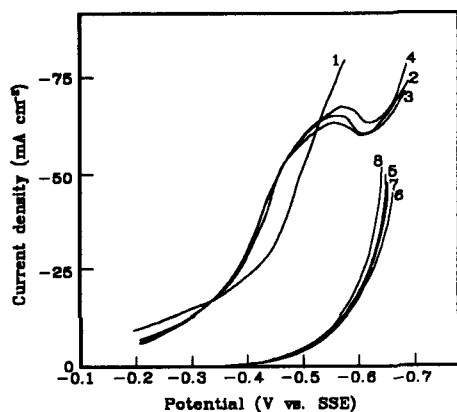


Fig. 4. Titration Curve for the Neutralization of Hydrazine by Nitric Acid.

### 3.3. Reduction of U(VI) at Pretreated Ti Electrode

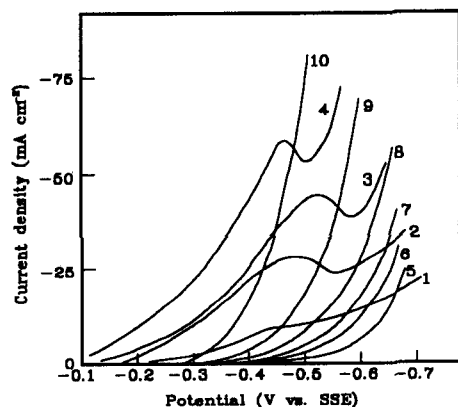
Fig. 5 shows the effects of protonated hydrazine on the reduction of U(VI) in 1.0M nitric acid at a pretreated Ti electrode obtained according to the previous work<sup>(10)</sup> where the existence of oxide film on non-pretreated Ti electrode was confirmed and its effect on the reduction of U(VI) was described quantitatively. Compared with the results obtained at the non-pretreated Ti electrode in Fig. 2, the reduction current of U(VI) at pretreated Ti electrode is much higher at the same potential and the peak shapes are clearer. These peaks provide enough information for kinetic analysis. Large reduction current without peak for the reduction of U(VI) was observed in the absence of hydrazine. Reduction peaks, however, were clearly observed in the presence of the protonated hydrazine and the voltammograms were almost independent in the concentration range of hydrazine from 0.1 to 0.4M. This can be attributed to an instantaneous reoxidation of U(VI) to U(IV) at the electrode surface, which results in a cyclic electro-redox between U(VI) and U(IV) in the vicinity of the electrode surface. In the presence of the hydrazine, on the other hand, the reduction peak of U(VI), whose peak potential does not depend on the concentration of hydrazine, can be observed. These results imply that the U(IV) in nitric acid solution can be enough stabilized at a low hydrazine concentration of 0.1M and that neither U(IV) nor U(VI) forms a complex with hydrazine. It should be noted that the reduction of U(VI) in the hydrazine free solution takes place at slightly more negative potential than that in the solution with hydrazine. (compare curve 1 with curves 2-4 of Fig. 5) It might be considered to be attributable to the effect on the reduction of U(VI) by the adsorption of hydrazine at the electrode surface.

Fig. 6 shows the effect of the nitric acid concentration on the reduction of U(VI) at pretreated Ti



Electrolyte : 1-4 :  $1.68 \times 10^{-1} \text{ M } \text{UO}_2^{2+} + 1.0 \text{ M } \text{HNO}_3 + x \text{ N}_2\text{H}_5^+$   
 5-8 :  $1.0 \text{ M } \text{HNO}_3 + x \text{ N}_2\text{H}_5^+$   
 $\text{N}_2\text{H}_5^+ \text{ (M)} : (1,5) 0, (2,6) 0.1, (3,7) 0.2, (4,8) 0.4$   
 Scan rate ( $\text{mV s}^{-1}$ ) : 0.4

Fig. 5. Voltammograms of the Reduction of U(VI) and Hydrogen Evolution at Pretreated Ti Electrode With Change of Protonated Hydrazine Concentration in 1.0M  $\text{HNO}_3$ .



Electrolyte : 1-4 :  $1.68 \times 10^{-1} \text{ M } \text{UO}_2^{2+} + x \text{ HNO}_3 + 0.1 \text{ M } \text{N}_2\text{H}_5^+$   
 5-10 :  $x \text{ HNO}_3 + 0.1 \text{ M } \text{N}_2\text{H}_5^+$   
 $\text{HNO}_3 \text{ (M)} : (1) 0.25, (5) 0.5, (2,6) 0.75, (3,7) 1.0,$   
 (8) 0.5, (4,9) 2.0, (10) 3.0  
 Scan rates ( $\text{mV s}^{-1}$ ) : 0.2

Fig. 6. Voltammograms of the Reduction of U(VI) and Hydrogen Evolution at Pretreated Ti Electrode With Change of  $\text{HNO}_3$  Concentration in 1.0M Protonated Hydrazine.

electrode. The peak current for the reduction of U(VI) increases and the reduction wave shifts to more positive direction with increase of nitric acid concentration. The effect of the nitric acid concentration on the hydrogen evolution reaction is more remarkable than that of the hydrazine on the reduction of U(VI). With more than 3 M  $\text{HNO}_3$ , high hydrogen evolution current disturbs the measurement of the voltammogram for the reduction of U(VI). Such a high apparent hydrogen evolution current may include currents not only due to hydrogen evolution but also due to a reduction of nitrous ion<sup>(20)</sup> which is produced as an intermediate species of the reduction of nitric acid even in the presence of the hydrazine. It is noteworthy that in voltammograms 1 and 2 of Fig. 6 observed in the solution of 0.25–0.75M  $\text{HNO}_3$ , the cathodic final rise due to the hydrogen evolution increases more slowly and shifts to more negative direction, compared with the respective background voltammograms. This is attributable to the possibility of adsorption of uranous hydroxide on the surface of Ti electrode, because uranous ion produced may form easily as hydroxide in 0.5M  $\text{HNO}_3$ . The adsorption of uranous hydroxide may change the surface condition of the electrode, hindering the reduction of proton like the hindrance of the oxide film on the reduction of U(VI).

#### 4. Conclusion

- 1) In the reduction of U(VI) at non-pretreated Ti electrode in nitric acid and hydrazine mono-hydrate solution, the reduction needed a high activation overpotential and was affected by the concentration ratio of hydrazine to nitric acid rather than by absolute amount of hydrazine because of the decrease of solution conductivity and increase of  $iR$  drop, which were caused by proton consumption in the solution by the hydrazine.
- 2) Nitric acid is more significant on the reduction of U(VI) than the hydrazine mono-hydrate when the

ratio of hydrazine mono-hydrate to nitric acid was below 0.5.

- 3) In the reduction of U(VI) at pretreated Ti electrode in nitric acid and protonated hydrazine solution, the reduction current peaks of U(VI) were clearer and higher enough to perform the kinetic analysis, compared with ones from the non-pretreated Ti electrode at the same potential. The existence of hydrazine was important in the reduction of U(IV) for the prevention of reoxidation of U(IV), but the concentration of hydrazine had no effect on the uranium reduction.
- 4) Peaks of voltammograms were disappeared at nitric acid above 3M by being overlapped with the currents of vigorous side reaction of hydrogen evolution or the reduction of nitrous ion..

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