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Electrolytic reduction mechanism of Np(V) and the effect of coexisting nitric acid

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Abstract. The behaviors of reduction of NpO₂⁺ by controlled potential electrolysis were studied, and a unique time course of electrolysis current was observed. It was concluded that NpO₂⁺ was reduced by two reduction processes, which were the chemical reaction with Np³⁺ and the electrocatalytic reduction by adsorbed hydrogen atom on platinum electrode surface. The time courses of current for controlled potential electrolysis of NpO₂⁺ under various conditions of the solution were investigated, and the effects of the concentration of H⁺ and NO₃⁻ on electrolysis behavior were explained by proposed reduction mechanisms. The Np⁴⁺ was prepared from NpO₂⁺ in 3 mol dm⁻³ HNO₃ by electrolytic reduction at the potential where evolution of hydrogen gas and reduction of NO₃⁻ were inhibited. The electrolysis efficiency could be improved.

1. Introduction

The actinide elements from U to Pu exist as trivalent to hexavalent ions in acidic aqueous solution [1]. The control of the oxidation state of an actinide ion to the desired one is required for the efficient chemical separation or the precise determination of the ion. Electrolysis is promising for the adjustment of the oxidation state, since it does not require the addition of special chemical reagents, and electrolytic potential can be controlled precisely resulting high selectivity. Bulk electrolysis based on the reversible electrode reactions such as NpO₂²⁻/NpO₂⁺ and Np⁴⁺/Np³⁺ couples [2,3] was applied to control the oxidation state of Np. On the other hand, it is not simple to control the oxidation state by utilizing an irreversible electrode reaction process such as Np⁵⁺/NpO₂⁺ couple that accompanies breaking or formation of Np-O bond. In order to attain the quantitative electrolytic reduction of NpO₂⁺ of which overpotential is large, the ordinary batch electrolysis was conducted at considerably negative potential where H₂ evolution occurred [2,4]. The authors developed a novel method for the rapid preparation and speciation of Np ions based on flow-through electrolysis at a column electrode(s) [5]. This electrolysis method enabled to reduce NpO₂⁺ to Np⁵⁺ rapidly, but Np⁴⁺ could not be prepared from NpO₂⁺ unless otherwise the two-step column electrode system was used. In the two-step system, NpO₂⁺ was reduced to Np³⁺ at the 1st column electrode, and then Np³⁺ was oxidized to Np⁵⁺ at the 2nd column electrode. In this connection, it is well known that similar procedure which is electrolytic reduction of PuO₂²⁺ to Pu³⁺, followed by electrolytic oxidation of it to Pu⁴⁺ can be applied to preparation of Pu⁴⁺.
Minor actinides such as Np, Am and Cm are α emitters and some isotopes of them are of long half-life. The efficient recovery of the minor actinides from high-level radioactive waste (HLW) in a nitric acid solution and the transmutation of them have been studied to reduce the environmental impact by disposal of HLW. A number of works has been performed to develop the partitioning methods of minor actinides from HLW [6]. The precise adjustment of the oxidation states of Np ions is one of important factors in the efficient recovery of Np. Though the electrolysis methods described above is expected to be also applicable to the preparation of the oxidation states of Np ions in HLW solutions of nitric acid, the electrolysis at the potential available for the reduction of NpO$_2^+$ overlaps with that for the reduction of NO$_3^-$ [7] as well as evolution of H$_2$. Since the side reactions lower the electrolytic efficiency of reduction of NpO$_2^+$, and Np ions, especially Np$^{4+}$, form stable complexes with NO$_3^-$ of high concentration, the electrolytic adjustment of the oxidation state of Np ion is not easy.

In the present study, the details of irreversible electrode reduction process of NpO$_2^+$ were investigated by controlled potential bulk electrolysis at a platinum or gold electrode, and the reduction mechanisms were elucidated. The preparation of Np$^{4+}$ in nitric acid media by controlled potential electrolysis was examined on the basis of the investigation.

2. Experimental

2.1. Electrochemical measurements
Bulk electrolysis of Np ions was carried out employing a cylindrical glass cell of 20 mm in inner diameter and 40 mm in height with a cylindrical counter electrode compartment of 50 mm in inner diameter and 40 mm in height separated by an electrolysis diaphragm made of sintered glass. Gold or platinum gauze (80 mesh, 60 × 20 mm) was used as the working electrode. A platinum wire (0.5 mm in diameter, 30 mm long) and a silver-silver chloride electrode, SSE, with 1 M (=mol dm$^{-3}$) lithium chloride were employed as the counter and the reference electrodes, respectively. Lithium chloride was used to avoid the generation of a precipitate of KClO$_4$. The sample solution (9 ml) was electrolyzed with stirring at a rate of 500 rpm by a magnetic stirrer and purging nitrogen gas after the deaeration by bubbling nitrogen gas for 15 min.

A potentiostat and a function generator (HA501 and HB105, respectively, Hokuto Denko Co. Ltd.), an X-Y recorder (model 3036, Yokogawa) and an X-T recorder (type 3056, Yokogawa) were used for the electrochemical measurements. All electrochemical measurements were performed at 25 ± 0.5 °C.

2.2. Spectrophotometric measurements
The concentrations of NpO$_2^+$, Np$^{4+}$ and Np$^{3+}$ in a sample solution of perchloric acid were determined based on the absorption peaks at 980, 960 and 786 nm, respectively [8]. The absorption peak around 722 nm of Np$^{4+}$ was used for a solution of high concentration of nitric acid. The UV-VIS spectrophotometry system consisting of a light source, a spectrometer, optical fibers and a cuvette holder (USB4000, DH2000, P400-VIS/NIR and CUV-UV, respectively, Ocean Optics, Inc.) were employed for spectrophotometry.

2.3. Chemicals
Neptunium-237 dioxide powder of a chemical purity higher than 99.99% (supplied by CEA, Fontenayaux-Roses, France) was dissolved with 10 ml of concentrated nitric acid, and the solution was heated to almost dryness. The residue was dissolved in 1 M HNO$_3$ solution, and the stock solution of Np in HNO$_3$ was obtained. Five ml of 60% HClO$_4$ was added to 10 ml of the nitric acid solution containing Np, and the solution was heated to almost dryness at a temperature of the fuming of perchloric acid. The fuming procedure was repeated three times. The residue obtained was dissolved in 1 M HClO$_4$, and the stock solution of NpO$_2^{2+}$ in HClO$_4$ was obtained. The concentration of Np in the stock solutions was determined by controlled potential coulometry [9]. The concentrations of NpO$_2^+$, Np$^{4+}$ and Np$^{3+}$ coexisting in the prepared NpO$_2^{2+}$ stock solution were determined spectrophotometrically to be less than 0.4, 0.05 and 0.1%, respectively, of that of NpO$_2^{2+}$. 

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3. Results and discussion

3.1. Reduction mechanisms of NpO$_2^+$ at gold and platinum electrodes

Current-time ($i$-$t$) curves during the controlled potential electrolysis of reduction of 3 $\times$ 10$^{-3}$ M NpO$_2^+$ in 1 M HClO$_4$ were measured at a gold gauze electrode (curves 1 and 2) or a platinum gauze electrode (3 and 4) as shown in Fig. 1. Though the ordinary $i$-$t$ curve shows that of a first-order reaction (i.e., the concentration of the reactant and the current decay exponentially with the time during the electrolysis [10]), the time courses of $i$ in Fig. 1 showed unique shapes. When the electrolysis at a gold electrode was carried out by applying -0.10 V versus SSE, only a small current that was close to the background current was observed for 30 min from the beginning of electrolysis (see, curve 1). The electrolytic current due to reduction of NpO$_2^+$ became larger gradually with the increase of $t$. The $i$-$t$ curve showed maximum when $t$ was about 85 min, and then decreased to the level of a residual current. The concentrations of NpO$_2^+$, Np$^{4+}$ and Np$^{3+}$ in the solution after the completion of the electrolysis were determined by spectrophotometry, and the product was found to be the mixture of Np$^{3+}$ and Np$^{4+}$. NpO$_2^-$ was not found. Total quantity of electricity, $Q$, consumed during the electrolysis after correction of residual current was 3.26 C that agreed well with the theoretical value (3.35 C) calculated from the concentrations of reduction products (Np$^{4+}$: 74%, Np$^{3+}$: 26%).

![Figure 1. Current – time relationships for the reduction of NpO$_2^+$ during controlled potential electrolyses. Solution: 3$\times$10$^{-3}$ M NpO$_2^+$ + 1 M HClO$_4$. Electrode: (1, 2) gold or (3,4) platinum gauze. Applied potential: (1) -0.1, (2) -0.125, (3) -0.04 or (4) -0.07 V versus SSE.]

The small current at the initial period of electrolysis indicates that reduction of NpO$_2^+$ cannot be attributed to a direct electrode reaction. The electrolysis time for the completion of the reduction of NpO$_2^+$ was shorter when the applied potential, $E$, was more negative (cf., curves 1 and 2). The time course of $i$, however, did not depend on $E$ when $E$ was more negative than -0.175 V versus SSE. Since the redox potential of Np$^{4+}$/Np$^{3+}$ couple is -0.13 V versus SSE, the results of the present work indicate that the coexistence of Np$^{3+}$ affects with the reduction of NpO$_2^+$. The reduction of Np$^{4+}$ to Np$^{3+}$ is expected to proceed when $E$ is negative as -0.175 V. Therefore, it is considered that NpO$_2^+$ is reduced to Np$^{4+}$ not by the direct electrode reaction but by the chemical reaction of NpO$_2^+$ and Np$^{3+}$. The redox processes of NpO$_2^+$ is shown in Scheme 1. Initially, small amount of Np$^{4+}$ coexists in a solution of NpO$_2^+$ through the disproportionation of NpO$_2^+$ [11] expressed as Eq.(3). The Np$^{3+}$ is reduced to Np$^{3+}$ by the electrode reaction of Eq. (2) at this potential range. Then Np$^{3+}$ reduces NpO$_2^+$ by the chemical reaction of Eq. (1). The resulting Np$^{3+}$ is reduced to Np$^{3+}$ by the electrode reaction of Eq. (2) again.

In the case of the electrolysis at a platinum gauze electrode, although the $i$-$t$ (curves 3 and 4 in Fig. 1) had a peak similarly to that at a gold electrode, the current at the beginning of the electrolysis was fairly large compared with that at a gold electrode. The large initial current was observed when $E$ was...
-0.07 V versus SSE where the reduction of H$^+$ to the hydrogen atom adsorbed on the platinum electrode surface [12], Pt-H$_{ads}$ [Eq. (4)] was observed by voltammetry. Therefore, it was considered that NpO$_2^+$ was reduced by Pt-H$_{ads}$ [Eq. (5)]. Here, it is well known that Pt-H$_{ads}$ is quite active [13,14]. The Np$^{4+}$ produced by the reaction of Eq. (5) is reduced to Np$^{3+}$ by electrode reaction of Eq. (2), and the chemical reaction of Eq. (1) follows similarly to the electrolysis at a gold electrode. It was observed that the electrolysis time required to complete the reduction of NpO$_2^+$ was longer when total concentration of Np was lower. This phenomenon can be explained by the disproportionation of Eq (1). The details of the reaction processes of the electrolytic reduction of NpO$_2^+$ were discussed in the previous paper [15].

\[
\begin{align*}
\text{NpO}_2^+ + \text{Np}^{3+} + 4\text{H}^+ & \rightarrow 2\text{Np}^{4+} + 2\text{H}_2\text{O} & \text{chemical reaction (1) in solution} \\
\text{Np}^{4+} + e^- & \rightarrow \text{Np}^{3+} & \text{electrode reaction (2) at Au and Pt} \\
2\text{NpO}_2^+ + 4\text{H}^+ & \rightarrow \text{Np}^{4+} + \text{NpO}_2^{2+} + 2\text{H}_2\text{O} & \text{disproportionation (3) in solution} \\
\text{Pt} + \text{H}^+ + e^- & \rightarrow \text{Pt-H}_{ads} & \text{adsorption of hydrogen atom on platinum (4)} \\
\text{NpO}_2^+ + \text{Pt-H}_{ads} + 3\text{H}^+ & \rightarrow \text{Np}^{4+} + 2\text{H}_2\text{O} + \text{Pt} & \text{electrocatalytic reaction (5)} \text{ at Pt}
\end{align*}
\]

**Scheme 1**

### 3.2. Effect of the concentration of H$^+$

Since the HLW solution usually contains high concentration of acid(s), the reduction of NpO$_2^+$ in the presence of 1 to 5 M H$^+$ was investigated. The $i$-$t$ curves in Fig. 2 were observed during the reduction of NpO$_2^+$ by controlled potential electrolysis at a platinum electrode. The $E$ applied was -0.05 V versus SSE. The time courses of $i$ depended on the concentration of HClO$_4$, and the time required to complete the reduction of NpO$_2^+$ became shorter when the concentration of HClO$_4$ was higher. The $Q$ of these 5 electrolyses in Fig. 2 coincided to 2.65 ± 0.02 C after correction of background current. The spectrophotometric measurement of the electrolyzed solution of 1 M HClO$_4$ indicated that the solution contained 95% of Np$^{4+}$ and 5% of Np$^{3+}$.

![Figure 2](image_url)

**Figure 2.** Effect of the concentration of HClO$_4$ on the reduction of NpO$_2^+$ at a platinum electrode.

Solution: (1) 1, (2) 2, (3) 3, (4) 4 or (5) 5 M HClO$_4$ + 3×10$^{-5}$ M NpO$_2^+$, $E$: -0.05 V versus SSE.

The effect of the concentration of HClO$_4$ on the time required to complete the electrolytic reduction of NpO$_2^+$ can be explained by considering the participation of both H$^+$ and Pt-H$_{ads}$ in the reduction of
The reduction of NpO$_2^+$ due to reactions of Eq. (1) and (5) is accelerated when the concentrations of H$^+$ and Pt-H$_\text{ads}$ are higher. Here, the concentration of Pt-H$_\text{ads}$ is higher when the concentration of H$^+$ is higher [Eq. (4)].

The agreements of $Q$ values for different acidity can be explained by independency of the composition of the reduction products that is mixture of Np$^{4+}$ and Np$^{3+}$ on the acidity of the solution, because the formal redox potential of Np$^{4+}$/Np$^{3+}$ was little affected by the concentration of H$^+$. 

3.3. Reduction of NpO$_2^+$ in the presence of NO$_3^-$

The $i$-$t$ curves in Fig. 3 were observed during the electrolytic reduction of NpO$_2^+$ at a platinum gauze electrode in a solution containing 1 M H$^+$ and various concentrations of ClO$_4^-$ and NO$_3^-$ . The $E$ applied was -0.05 V versus SSE. The electrolysis time required to complete the reduction of NpO$_2^+$ became larger when the concentration of NO$_3^-$ was higher. The $Q$ for the reduction of NpO$_2^+$ decreased from 2.67 C (curve 1) to 2.52 C (curve 5) with the increase of the concentration of NO$_3^-$ from 0.05 to 1 M.

![Figure 3. Effect of the concentration of NO$_3^-$ on the electrolytic reduction of NpO$_2^+$.](image)

Solution: 1M H$^+$(ClO$_4^-$ + NO$_3^-$) + 3×10$^{-3}$ M NpO$_2^+$. $E$: -0.05 V versus SSE. Concentration of NO$_3^-$: (1) 0.05, (2) 0.1, (3) 0.2, (4) 0.5, (5) 1.0 M

The complex formation constants, $K$, of Np$^{4+}$ and NpO$_2^+$ with NO$_3^-$ were reported to be log $K_1 = 0.34$ [16] and -0.55 [17], respectively, indicating that Np$^{4+}$ forms much more stable complex with NO$_3^-$ than NpO$_2^+$. The complex formation of Np$^{4+}$ disturbs its electrolytic reduction to Np$^{3+}$ [Eq.(2)] , and hence the longer electrolysis time is required to complete the reduction of NpO$_2^+$ in the presence of NO$_3^-$. The decrease of $Q$ observed when the concentration of NO$_3^-$ was high supports the negative shift of the formal potential of Np$^{4+}$/Np$^{3+}$ due to the complex formation of Np$^{4+}$ with NO$_3^-$.

When the electrolysis was carried out at a platinum electrode in a solution containing HNO$_3$ of concentration higher than 1 M, a considerable current due to the reduction of NO$_3^-$ flowed together with that due to the reduction of NpO$_2^+$. Time courses of $i$ and concentrations of NpO$_2^+$ and Np$^{4+}$ in 3 M HNO$_3$ solution observed during the electrolysis at -0.05 V versus SSE are shown in Fig. 4. A large background current due to the reduction of NO$_3^-$ was observed, and the current became larger progressively with the electrolysis time. Though the reduction current of NpO$_2^+$ could not be observed clearly because of the large background current, it was found that more than 99% of NpO$_2^+$ was reduced to Np$^{4+}$ with the electrolysis at -0.05 V for 220 min. The electrolysis efficiency was calculated to be 36.8% from $i$ during the electrolysis for 220 min.
The reduction of NO$_3^-$ at a platinum electrode has been widely investigated. de Groot et al. [7] reported that NO$_3^-$ was reduced at a platinum electrode to which a potential more negative than ca. +0.4 V versus RHE (that is equivalent to ca. +0.1 V versus SSE) was applied. They also reported that the adsorption of NO$_3^-$ on a platinum surface took place, and inhibited the reduction of NO$_3^-$ itself when the electrode potential was in the range between ca. +0.2 and +0.4 V versus RHE (ca. -0.1 and +0.1 V versus SSE). Hence, the electrolysis current due to the reduction of NO$_3^-$ is considered to be lowered at this potential range. However the reduction of NO$_3^-$ is no longer inhibited by the adsorption of NO$_3^-$ at potentials more negative than +0.1 V versus RHE (ca. -0.2 V versus SSE) where adsorption of hydrogen is dominant on the platinum surface, causing the extensive reduction of NO$_3^-$ and evolution of H$_2$. Therefore, the bulk electrolysis of the solution containing high concentration of HNO$_3$ at such extra negative potential decreases the electrolysis efficiency. The reduction of NpO$_2^{+}$ to Np$^{4+}$ can be achieved successfully by the electrolysis at $E$ sufficiently positive as that in the experiment of the present paper.

![Figure 4](image_url)

**Figure 4.** Time courses of $i$ (solid line) and the concentration of NpO$_2^+$ (■) or Np$^{4+}$ (●) during the controlled potential electrolysis at a platinum gauze electrode in 3 M HNO$_3$. $E$: -0.05 V versus SSE. Solution: 3×10$^{-3}$ M NpO$_2^+$ + 3 M HNO$_3$. Broken line: background current without Np.

4. Conclusions
The electrolytic reduction of NpO$_2^+$ at a gold or platinum electrode was found to occur through chemical reaction with Np$^{3+}$ which was produced from Np$^{4+}$ by the electrode reaction. NpO$_2^+$ was also reduced through the reaction with the hydrogen atom adsorbed on the platinum electrode surface. These two reduction processes take place competitively at a platinum electrode, and the reduction is completed more rapidly at a platinum electrode than at a gold electrode. The coexisting of NO$_3^-$ in a solution retarded the reduction of NpO$_2^+$, because production of Np$^{3+}$ from Np$^{4+}$ by electrode reaction was disturbed by complex formation of Np$^{4+}$ with NO$_3^-$. Preparation of Np$^{4+}$ in a solution with high concentration of NO$_3^-$ could be achieved by the electrolysis at a platinum electrode when a potential available for the evolution of H$_2$ was applied, though the electrolysis time required was relatively long.

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