



# Electrolysis of plutonium nitride in LiCl–KCl eutectic melts

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## Abstract

The electrolysis of plutonium nitride, PuN, was investigated in the LiCl–KCl eutectic salt with 0.54 wt% PuCl<sub>3</sub> at 773 K in order to understand the dissolution of PuN at the anode and the deposition of metal at the cathode from the viewpoint of the application of a pyrochemical process to nitride fuel cycle. It was found from cyclic voltammetry that the electrochemical dissolution of PuN began nearly at the theoretically evaluated potential and this reaction was irreversible. Several grams of plutonium metal were successfully recovered at the molybdenum electrode as a deposit with a current efficiency of about 90%, although some fractions of the deposited plutonium often fell from the molybdenum electrode. © 2000 Elsevier Science B.V. All rights reserved.

## 1. Introduction

Uranium and plutonium nitrides are potential advanced fuels having an advantage in plutonium breeding or actinide burning because of their high thermal conductivity, high melting point and high metal density [1]. In JAERI, studies have been made for the application of the pyrochemical process to the nitride fuel cycle system from the thermodynamic considerations [2]. The pyrochemical reprocessing, which has been developed for the dense fuel cycle at ANL [3,4], gives the possibility of reducing the fuel cycle cost drastically. The recycling of <sup>15</sup>N-enriched nitrogen gas, which should be used in the fabrication of nitride fuels for the suppression of the formation of <sup>14</sup>C, would become feasible by use of the pyrochemical process. Information on the electrolysis of various nitrides such as actinides, lanthanides, alkali metals, alkaline earths etc. is, however, meager although it is necessary in developing the pyrochemical process for nitride fuels.

Kobayashi et al. [5] elucidated the dissolution of uranium mononitride, UN, by voltammetry and successfully recovered uranium metal by electrolysis of UN in the LiCl–KCl eutectic melt containing uranium trichloride, UCl<sub>3</sub>. On the other hand, Rogozkin et al. [6] recovered about 0.5 kg of uranium metal as a cathode deposit by the electrolysis of UN in the UCl<sub>3</sub>–LiCl–KCl melt. As for plutonium nitride, PuN, Campbell [7,8] reported the thermodynamic properties of PuN by electromotive force measurement in the LiCl–KCl melt containing plutonium trichloride, PuCl<sub>3</sub>. However, there are no reports in which the dissolution behavior of PuN in the LiCl–KCl melt are discussed in relation with the electrolysis.

In the present work, the dissolution of PuN in the PuCl<sub>3</sub>–LiCl–KCl melt was investigated by voltammetry for fundamental understanding of the electrolysis of PuN in the melt. Pu metal recovery at the solid cathode by the electrolysis of PuN was studied in order to ascertain the applicability of the pyrochemical process to the nitride fuel cycle.

## 2. Experimental

Plutonium mononitride, PuN, was prepared by carbothermic reduction of plutonium dioxide, PuO<sub>2</sub> [9].

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The mixture of PuO<sub>2</sub> and graphite powder with a C/PuO<sub>2</sub> molar ratio of 2.5 was heated at first in N<sub>2</sub> gas stream at 1823 K and then in 92%N<sub>2</sub>–8%H<sub>2</sub> mixed gas stream at 1723 K. The product was subjected to chemical and X-ray diffraction analyses.

Plutonium trichloride was prepared by the chlorination of Pu metal with CdCl<sub>2</sub> in Cd–LiCl–KCl at 773 K. The details of the procedure were described in the preceding paper [10]. Polarographic grade LiCl–KCl eutectic salt and CdCl<sub>2</sub> were obtained from Anderson Physics Laboratory, and cadmium (99.999%) was supplied from Soekawa Chemicals.

The scheme of the electrochemical cell used is shown in Fig. 1. A cage (i.d.: 10 mmφ, o.d.: 12 mmφ, depth: 15 mm) made of tungsten (99.95% up) was served as a working electrode. A few pieces of plutonium mononitride pellets were placed in the W cage. The counter electrode used was a wire (1 mmφ) made of molybdenum (99.95% up). A silver–silver chloride electrode with 1.00 wt% of AgCl in the LiCl–KCl eutectic salt was used as a reference electrode. The temperature of the molten salt was measured by a calibrated chromel–alumel thermocouple and controlled at 773 ± 0.5 K. Cyclic voltammograms were obtained using a voltammetric analyzer (BAS CV-50W) at the scan rate of 0.02 V s<sup>-1</sup>. The concentrations of PuCl<sub>3</sub> in the LiCl–KCl eutectic

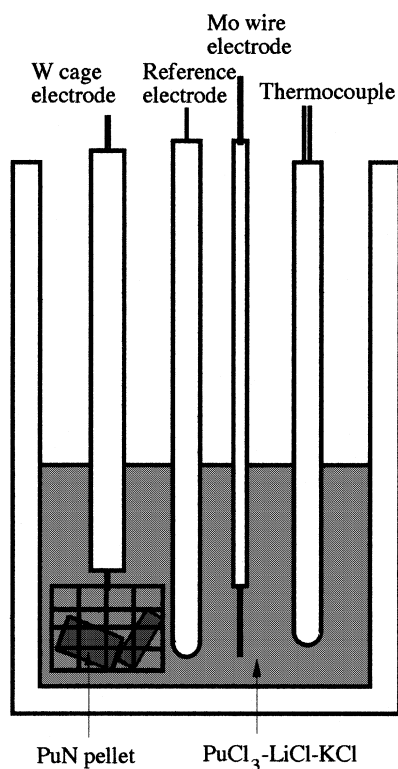


Fig. 1. Electrochemical cell.

were determined by ICP-AES after voltammetric measurements.

The electrolysis of PuN was performed under potential- or current-control by using a potenti/galvanostat coulometer (Hokutodenko, HAB-501). As for the potential-controlled electrolysis, the potential of the cathode (Mo wire electrode) vs. the reference electrode was fixed at –2.00 V. On the other hand, the current between the cathode and the anode (W cage electrode) was kept constant, –10 or –20 mA for the current-controlled electrolysis. After the quantity of electricity reached 100–300 C, the Mo wire electrode was taken out from the salt. Since the electrodeposit on the wire was a mixture of Pu metal and the salt, it was put in an aluminosilicate crucible and heated at 1073 K for 3.6 ks. The slag was separated from the mixture and the residue was analyzed by X-ray diffractometry.

The sample preparation, voltammetric measurements and electrolysis were carried out in gloveboxes with an atmosphere of argon gas purified to the levels of 0.5–2 ppm of oxygen and 2–5 ppm of moisture.

### 3. Results and discussion

#### 3.1. Voltammetric studies

A cyclic voltammogram of PuN in the W cage electrode immersed in the LiCl–KCl eutectic salt with 0.54 wt% of PuCl<sub>3</sub> at 773 K in the potential range of –0.5 to –1.0 V vs. the Ag/AgCl reference electrode is indicated in Fig. 2. The apparent equilibrium potential, at which anodic current was observed, is around –0.88 V. It could be attributable to the reaction represented by the following equation:

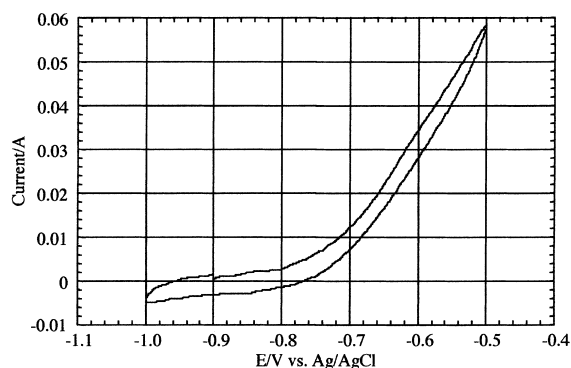
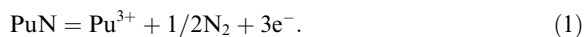
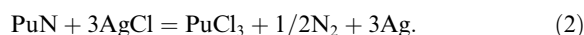


Fig. 2. Cyclic voltammogram of PuN in PuCl<sub>3</sub>–LiCl–KCl melt at 773 K. Working electrode: PuN pellet in a tungsten cage. PuCl<sub>3</sub> concentration: 0.54 wt%. Scan rate: 0.02 V s<sup>-1</sup>.

In contrast to the anodic current, no cathodic current flowed in the voltammogram. The reversibility of the reaction could be evaluated by the analysis of the Tafel plot,  $\eta = a + b \ln i$ , on current–potential curve [11]. Here,  $\eta$  and  $i$  are the overpotential and current density, respectively, and  $a$  and  $b$  are characteristic constants of the material. When the anode potential was scanned from the equilibrium potential,  $-0.88$  to  $-0.5$  V,  $a = 0.52$ ,  $b = 0.078$  and transfer coefficient,  $\alpha = 0.34$ , were obtained. This result indicates that reaction (1) is irreversible.

The observed equilibrium potential was interpreted by comparison with the theoretical redox potential of PuN as discussed below. Since the Ag/AgCl electrode was used as a reference electrode, the overall chemical reaction at the working electrode (W cage electrode) could be expressed as



The redox potential of PuN,  $E_{\text{PuN-Ag/AgCl}}$ , referring to the Ag/AgCl equilibrium is described as Eq. (3) by using standard Gibbs free energies of formation of PuCl<sub>3</sub>, PuN and AgCl,  $\Delta G_{\text{PuCl}_3}^0$ ,  $\Delta G_{\text{PuN}}^0$  and  $\Delta G_{\text{AgCl}}^0$ , respectively. In the equation,  $a_{\text{PuCl}_3}$  is the activity of PuCl<sub>3</sub> in the LiCl–KCl melt,  $a_{\text{AgCl}}$  the activity of AgCl in the LiCl–KCl melt of the reference electrode, and  $p_{\text{Cl}_2}$  and  $p_{\text{N}_2}$  are the partial pressures of Cl<sub>2</sub> gas and N<sub>2</sub> gas in the LiCl–KCl melt, respectively, and  $R$  is the gas constant, and  $T$  the temperature in K, and  $F$  the Faraday constant.

$$\begin{aligned} E_{\text{PuN-Ag/AgCl}} = & \Delta G_{\text{PuCl}_3}^0/3F - \Delta G_{\text{PuN}}^0/3F \\ & - \Delta G_{\text{AgCl}}^0/F + (RT)/(3F) \ln a_{\text{PuCl}_3} \\ & + (RT)/(6F) \ln p_{\text{N}_2} \\ & - (RT)/F \ln a_{\text{AgCl}}. \end{aligned} \quad (3)$$

The values of  $\Delta G_{\text{PuCl}_3}^0$ ,  $\Delta G_{\text{PuN}}^0$  and  $\Delta G_{\text{AgCl}}^0$  are  $-767\,700$ ,  $-232\,200$  and  $-86\,370$  J mol<sup>-1</sup>, respectively, at 773 K [12,13].  $a_{\text{PuCl}_3}$  and  $a_{\text{AgCl}}$  are  $3.6 \times 10^{-6}$  and  $3.90 \times 10^{-3}$ , respectively, as the concentration and activity coefficient of PuCl<sub>3</sub> are 0.54 wt% (0.087 mol%) and 4.1  $\times 10^{-3}$  and those of AgCl are 1.00 wt% (0.390 mol%) and 1, respectively [13,14]. Therefore,  $E_{\text{PuN-Ag/AgCl}}$  is expressed as follows:

$$E_{\text{PuN-Ag/AgCl}} = -0.864 + 0.0111 \ln p_{\text{N}_2}. \quad (4)$$

The apparent equilibrium potential,  $-0.880 \pm 0.005$  V, observed in the voltammogram is slightly lower than the potential evaluated theoretically. If the difference between the apparent and theoretical values is only caused from  $p_{\text{N}_2}$ , this value is calculated to be 24 kPa. Although the present measurement was carried out under the atmosphere of high purity argon gas, N<sub>2</sub> gas was that

which was generated by the electrolysis of PuN. Accordingly, the apparent equilibrium potential obtained could be understood as a reasonable value by considering the equation of theoretical equilibrium potential and  $p_{\text{N}_2}$ . The exact contribution of  $p_{\text{N}_2}$  on the redox potential should be further investigated since  $p_{\text{N}_2}$  was not determined in the present study.

### 3.2. Electrolysis of PuN

The redox potential,  $E_{\text{PuCl}_3\text{-Ag/AgCl}}$ , of Pu<sup>3+</sup>/Pu in the LiCl–KCl eutectic salt with 0.54 wt% of PuCl<sub>3</sub> at 773 K is  $-1.73 \pm 0.01$  V vs. the Ag/AgCl reference electrode [10]. It means that the potential difference between the Mo and reference electrodes must be  $-1.8$  V or lower in order to recover Pu metal on the Mo working electrode. Therefore, in the potential-controlled method, the constant potential of  $-2.00$  V was applied between the Mo and reference electrodes.

Fig. 3 shows the change of the anode potential and the current during the potential-controlled electrolysis. The current rose up to about  $-60$  mA at the beginning of electrolysis, but quickly fell down to  $-10 \pm 1$  mA. It may be caused by the diffusion of Pu<sup>3+</sup> in the salt. Then, the current increased gradually to  $-110 \pm 10$  mA. Before the electrolysis, the anode potential showed a constant value,  $-0.880 \pm 0.005$  V, which indicates that PuN is chemically stable in the salt. The anode potential shifted more positively to facilitate the dissolution of PuN when  $-2.0$  V was applied between the Mo and reference electrodes, and PuN started to be electrodisolved as Pu<sup>3+</sup> at the anode. The change of the electric current during the electrolysis is considered to be caused by the increase of cathode area accompanied by the accumulated deposition of Pu. The anode potential shifted more positively with the increase of current as can be understood from the relation between the current and the anode potential shown in Fig. 2. The oscillation

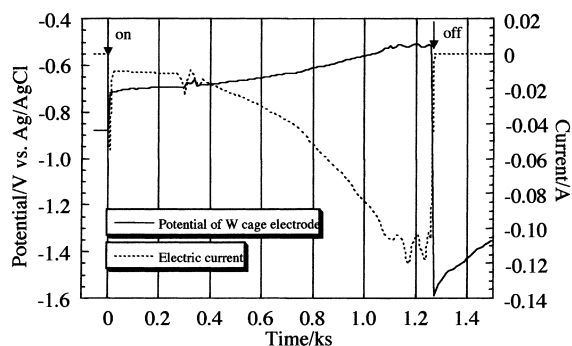


Fig. 3. Time-courses of potential of the W cage electrode and current under the potential-controlled electrolysis for run 1. PuCl<sub>3</sub> concentration: 0.54 wt%. Potential of the Mo electrode:  $-2.0$  V.

of electric current was observed during the electrolysis around  $t = 1.2$  ks, which might be caused by the fact that some fractions of the deposit were peeled off and the cathode area became small. When the electrolysis was completed,  $t = 1.26$  ks, the anode potential changed largely, but did not return to the initial value. It might be probable that the anode potential shifted toward  $E_{\text{PuCl}_3\text{-Ag}/\text{AgCl}}$  since the fall of Pu metal from the cathode might be suspended in the salt and partly adhere to the surface of the anode. In other runs, the equilibrium potentials of the anodes before the electrolysis were likewise located between  $E_{\text{PuN-Ag}/\text{AgCl}}$  and  $E_{\text{PuCl}_3\text{-Ag}/\text{AgCl}}$ . Fig. 4(a) shows the deposits on the Mo wire electrodes. The electrodeposits were mixtures of Pu metal and the LiCl–KCl salt as pasty cakes.

The electrodeposits in the current-controlled method are shown in Fig. 4(b). The deposits were also mixtures of Pu metal and the LiCl–KCl salt. In each operation, the cathode and anode potentials were  $-1.90 \pm 0.10$  V and  $-1.65 \pm 0.07$  V, respectively, at the beginning of the electrolysis and then changed up to  $-1.73 \pm 0.02$  V and  $-0.70 \pm 0.03$  V, respectively. From the comparison of the results of voltammetric analysis, this indicates that PuN was always electrodisolved at the anode and Pu metal was deposited at the cathode. The potential shifts during the electrolysis may be due to the increment of the cathode area in analogy with the case of the potential-controlled electrolysis.

In all runs, the concentration of  $\text{PuCl}_3$  in the melt was confirmed by ICP-AES to be approximately constant. The current efficiency at the anode is estimated to be about 90% by considering the relation between the change of weight and the accumulated amount of coulomb number.

The electrodeposit, a mixture of Pu metal and the LiCl–KCl eutectic salt, was heated at 1073 K for 3.6 ks to separate Pu metal from the salt.  $\alpha$ -Pu metal was identified as a major phase in the product by X-ray diffraction analysis, but minor chloride phases were still observed. Further investigation is necessary for complete separation of Pu metal from the electrodeposits.

#### 4. Conclusion

Plutonium metal was recovered on the solid cathode in gram order amount by the electrolysis of PuN in the LiCl–KCl eutectic salt. This result suggests a possibility for practical use of pyrochemical reprocessing for nitride fuels though there are still remaining problems such as the effect of  $p_{\text{N}_2}$ , the formation of PuNCl and the separation of Pu from the deposit etc.

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#### Appendix A

The redox potential of PuN,  $E_{\text{PuN-Ag}/\text{AgCl}}$  is derived as follows.

Gibbs free energies of  $\text{PuCl}_3$ , PuN and AgCl represented by  $\Delta G_{\text{PuCl}_3}$ ,  $\Delta G_{\text{PuN}}$  and  $\Delta G_{\text{AgCl}}$ , respectively, are expressed as Eqs. (A.1)–(A.3):

$$\Delta G_{\text{PuCl}_3} = \Delta G_{\text{PuCl}_3}^0 + RT \ln \left( a_{\text{PuCl}_3} / p_{\text{Cl}_2}^{3/2} \right), \quad (\text{A.1})$$

$$\Delta G_{\text{PuN}} = \Delta G_{\text{PuN}}^0 + RT \ln \left( 1 / p_{\text{N}_2}^{1/2} \right), \quad (\text{A.2})$$

$$\Delta G_{\text{AgCl}} = \Delta G_{\text{AgCl}}^0 + RT \ln \left( a_{\text{AgCl}} / p_{\text{Cl}_2}^{3/2} \right). \quad (\text{A.3})$$

Total energy change of the chemical reaction,  $\Delta G_{\text{Total}}$ , is regarded as Eq. (A.4) taking into account the above relations:

$$\Delta G_{\text{Total}} = \Delta G_{\text{PuCl}_3} - \Delta G_{\text{PuN}} - 3\Delta G_{\text{AgCl}}. \quad (\text{A.4})$$

The redox potential of PuN,  $E_{\text{PuN-Ag}/\text{AgCl}}$ , referring to the Ag/AgCl equilibrium is described as Eq. (A.5) inserting Eqs. (A.1)–(A.3):

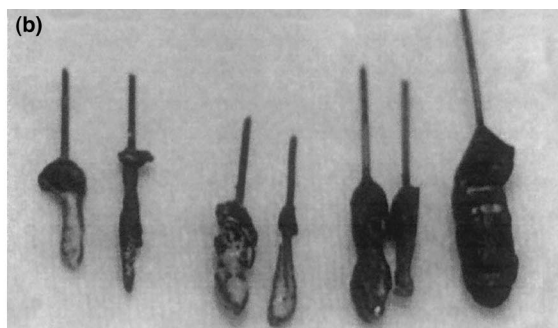
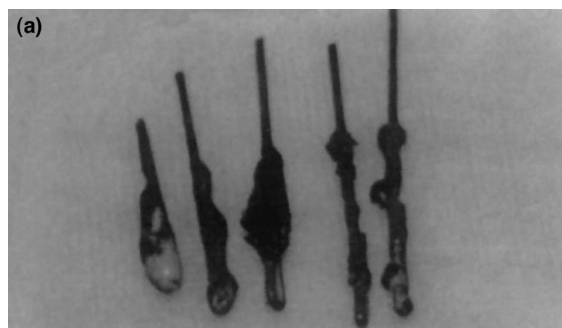


Fig. 4. (a) Deposits obtained by potential-controlled electrolysis. (b) Deposits obtained by current-controlled electrolysis.

$$\begin{aligned}
 E_{\text{PuN-Ag/AgCl}} &= \Delta G_{\text{Total}}/3F \\
 &= \Delta G_{\text{PuCl}_3}^0/3F - \Delta G_{\text{PuN}}^0/3F - \Delta G_{\text{AgCl}}^0/F \\
 &\quad + (RT)/(3F) \ln a_{\text{PuCl}_3} + (RT)/(6F) \ln p_{\text{N}_2} \\
 &\quad - (RT)/F \ln a_{\text{AgCl}}.
 \end{aligned}
 \tag{A.5}$$

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