*Journal of Alloys and Compounds, 206* (1994) 249–253
*JALCOM 1056*

# Electrode reactions of uranium during electrolysis of its oxide in a molten fluoride mixture

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(Received September 20, 1993; in final form November 11, 1993)

## Abstract

Current density–potential curves have been obtained for the electrolysis of uranium oxide in a molten fluoride mixture, *i.e.* $BaF_2$–$CaF_2$–LiF–$UF_4$, at 1200 and 1250 °C. Three kinds of reduction were found to occur at the cathode: (1) $U^{4+}+e^- \rightarrow U^{3+}$; (2) $U^{3+}+3e^- \rightarrow U$; (3) $U^{4+}+4e^- \rightarrow U$. The reduction of $U^{3+}$ to U was found to be relatively fast from analysis of the current density–potential curves and from X-ray photospectroscopic analysis of uranium species present in solidified salts.

## 1. Introduction

It is considered that the pyro-electrochemical process is the most effective way to recover uranium metal from spent oxide fuel. High purity uranium metal can be obtained by electrolysis at temperatures higher than the melting point of uranium metal. In this case, molten fluoride mixtures were used as the electrolyte, because of their low vapor pressure. Research on the electrolysis of uranium oxide has been carried out by others at Knolls Atomic Power Laboratory [1–3]. Their experimental results for electrolysis were different from the theoretical estimates of the amount of reduction, because the product yield and coalescence of the uranium metal were poor [2, 3]. In the 1960s, research was carried out at the U.S. Bureau of Mines to design electrolytic cells [4, 5]. In these studies, Kesterke and coworkers reported that over 1000 g of high purity metal was obtained in some tests, and the compartment cell was excellent as an electrolytic cell.

Several electrode reactions of uranium were investigated at temperatures less than 1000 °C in corrosion studies of the materials for molten salt breeder reactors. Jenkins *et al.* [7] estimated the U(IV)/U(III) ratio in a molten LiF–$BeF_2$–$ZrF_4$ system by voltammetric measurements. Clayton *et al.* [8] reported that U(IV) was reduced to U(0) through two steps: one was the reduction of U(IV) to U(III), and the other was the reduction of U(III) to U(0). Their standard electrode potentials for the U(IV)/U(III) and U(III)/U(0) couples were $-1.41$ and $-1.81$ V respectively.

In our previous study, electrolysis of uranium oxide was carried out to investigate a suitable fluoride mixture [6]. It was found that the coalescence and purity of the uranium metal produced in the molten fluoride mixture of the $BaF_2$–$CaF_2$–LiF–$UF_4$ system were superior to the results with the fluoride composite investigated by the US Bureau of Mines. Thus, fundamental knowledge of the electrolytic reaction of uranium oxide was accumulated in these previous studies.

In the present study, the cathodic reductions of uranium ions for the electrolysis of uranium oxide in a molten fluoride mixture of $BaF_2$–$CaF_2$–LiF–$UF_4$ were estimated at 1200 and 1250 °C, which are above the melting point of uranium metal. The cathodic reactions were clarified from current density–potential curves. Since the experimental temperatures were very high and reference electrodes could not be used, the cathodic potentials were measured against the anode, which had a large area, so that polarization effects could be neglected. The reaction products in molten salt samples quenched during electrolysis were examined by X-ray photospectroscopy (XPS).

## 2. Experimental details

### 2.1. Material

The electrolytes used in this study were (in weight per cent) $45.5BaF_2$–$19.5CaF_2$–10LiF–$25UF_4$ and $45.5BaF_2$–$19.5CaF_2$–10LiF–$25UF_4$ (saturated with $UF_3$). The composition of the first fluoride mixture was chosen based on the results of our previous study [6]. The $BaF_2$, $CaF_2$ and LiF were regent-grade chemicals, and

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0925-8388/94/$07.00
*SSDI* 0925-8388(93)01056-A

these fluorides were premelted before the experiments. Mixtures of 99.9% $UF_4$ (supplied by Sumitomo Metal Mining Co., Ltd.) and 99.9% $UO_2$ were added to other electrolytes, and the $UF_3$ used in this study was a reagent prepared by reacting $UF_4$ with U metal in advance.

### 2.2. Apparatus

The apparatus consisted of reaction, vacuum and helium gas introduction systems. The electrolytic cell was installed in the reaction system and was the same as that used in a previous study [6]. The cathode consisted of a tantalum rod but acted as an uranium electrode under electrolysis, because the tantalum was covered with a liquid uranium deposit. The graphite crucible doubled as the anode and the electrolyte vessel. The effective surface area of the anode was about 100 times the cathode area. The surface area of the cathode remained constant, as a result of dropping of liquid uranium metal into a collection crucible under the cathode. The temperature of the molten salt was measured using a Pt–PtRh thermocouple fitted with a BN cap. A recorder linked to the voltammeter was used to record the current and cell voltage.

### 2.3. Procedure

30 g of uranium oxide and 200 g of the fluoride mixture were placed in the graphite crucible. The graphite crucible was connected to a crucible holder which had the movable cathode and the thermocouple. The assembled electrolytic cell was put in the electric furnace and dried for 10 h *in vacuo* at 400 °C.

The fluoride mixture was then melted after backfilling with helium gas. The helium flow was maintained at 1 l $min^{-1}$ during the electrolysis. The temperature of the electrolyte was held at 1200 or 1250 °C.

The cathode was then lowered into the electrolyte to the desired depth, and a direct current was passed between the anode and cathode to electrolyze the uranium oxide. The electrolytic current and voltage were increased gradually, and these values were recorded continuously.

The electrolyte was sampled from the molten salt near the cathode surface using an alumina tube. The samples were analyzed by XPS to determine the valence of the uranium species. This analysis was carried out for two samples; one was sampled at low voltage (about 1 V) and the other was sampled at high voltage (about 4–5 V).

When the uranium oxide was depleted by the electrolysis, the electrolytic cell was quenched to room temperature after raising the cathode and thermocouple from the electrolyte. The purity of the uranium metal obtained was determined by absorption photospectrometry.

## 3. Results and discussion

### 3.1. Cathodic reaction of uranium

It was reported previously that uranium metal was obtained in a molten fluoride mixture at high applied voltage, and the purity of the metal was 99.5% [6]. No uranium metal was deposited at cell voltages of less than 2.0 V. In the present study, although it is impossible to measure the standard reduction potential without using a reference electrode, it was possible to estimate the electrode reactions.

The current density–potential curves obtained during the electrolysis of uranium oxide in the molten fluoride of $BaF_2$–$CaF_2$–LiF–$UF_4$ at 1200 and 1250 °C are shown by the full lines in Figs. 1 and 2 respectively. Both curves show a gradual increase in current density up to about −1.0 V, a shoulder at potentials between

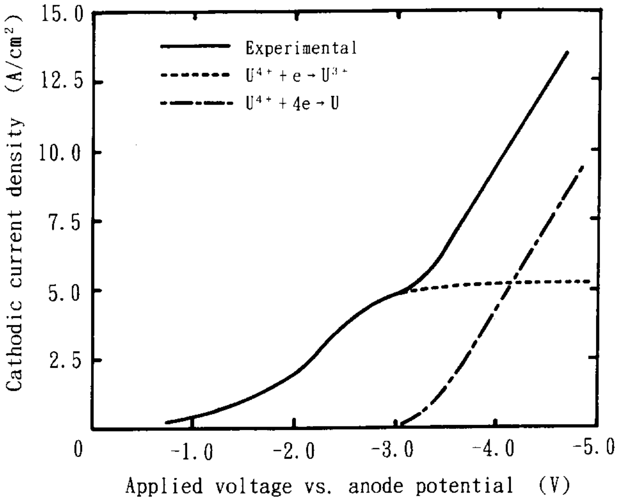

Fig. 1. Current density–potential curve of $UO_2$ electrolysis at 1200 °C.

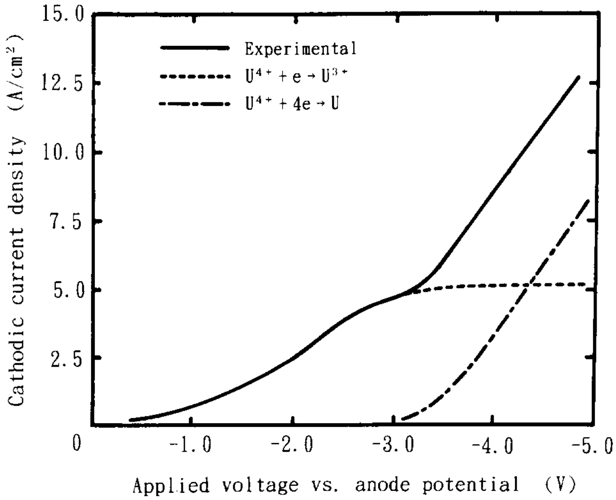

Fig. 2. Current density–potential curve of $UO_2$ electrolysis at 1250 °C.

$-2.0$ and $-3.0$ V, and then the current densities increase linearly with voltages higher than $-3.0$ V. These figures differed very little in the curves for the two experimental temperatures.

In the electrolysis of uranium oxide, three possible reactions at the cathode are as follows: (1) $U(IV)+e^- \rightarrow U(III)$; (2) $U(III)+3e^- \rightarrow U(0)$; (3) $U(IV)+4e^- \rightarrow U(0)$. Since uranium metal could not be obtained at cell voltages of less than 2.0 V, it is inferred that, in Figs. 1 and 2, the shoulders in the curves between $-2.0$ and $-3.0$ V appeared as a result of cathodic reaction (1). If the reaction (2) or (3) occurred, uranium metal would have to be obtained electrochemically. The increase in current density from the potential of $-3.0$ V, which indicates a cathodic limit, cannot be attributed with certainty to reaction (2) or to reaction (3).

Therefore, to determine which reactions occur, the electrolysis of uranium oxide was carried out in molten fluoride mixture saturated with $UF_3$, and the values of the current density and cell voltage were measured at a temperature of 1200 °C. The current density–potential curve obtained are shown in Fig. 3. A new cathodic peak appeared at a potential of about $-3.0$ V. This peak was not observed in the electrolysis in the molten fluoride mixture of $BaF_2$–$CaF_2$–LiF–$UF_4$; however, it appeared when $UF_3$ was added to the mixture, and uranium metal was deposited at this voltage. Thus, it is inferred that this peak indicates the occurrence of reaction (2), and electrode reaction (3) occurred at the cathodic limit above $-3$ V in Figs. 1 and 2.

In Figs. 1 and 2, the shoulders for the reduction of U(IV) to U(III) were analyzed by the reaction kinetics at electrode. The limiting current densities were estimated by extrapolation of experimental data. These values are represented by the broken lines in Figs. 1 and 2.

Plots of the applied voltage against $\ln(i/i_d-i)$ are shown in Figs. 4 and 5 respectively; $i_d$ represents the limiting current density and $i$ is the electrolysis current density. The plots can be regarded as straight lines. The slopes of the lines obtained were almost the same at 1200 and at 1250 °C. The slopes of both lines were calculated by the least-squares method.

Strictly, there is a slight deviation of the plots from the line in Figs. 4 and 5. This deviation generally indicates a slow electrode reaction. This effect is described by the Bulter–Volmer equation. Therefore, it is inferred that the rate of electrode reaction (1) is slow. Since the slope is equal to $-(RT/\alpha nF)$, where $R$ represents the gas constant, $F$ is Faraday's constant and $\alpha$ is a transfer coefficient, and electrode reaction (1) is a one-electron reaction, *i.e.* Nernst's value $n$ is unity, $\alpha$ can be estimated to be 0.24 and 0.27 in Figs. 4 and 5 respectively.

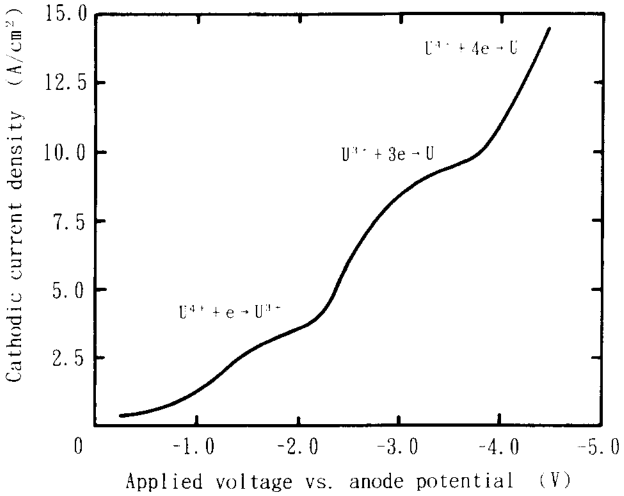

Fig. 3. Current density–potential curve of $UO_2$ electrolysis in molten salt saturated with $UF_3$ at 1200 °C.

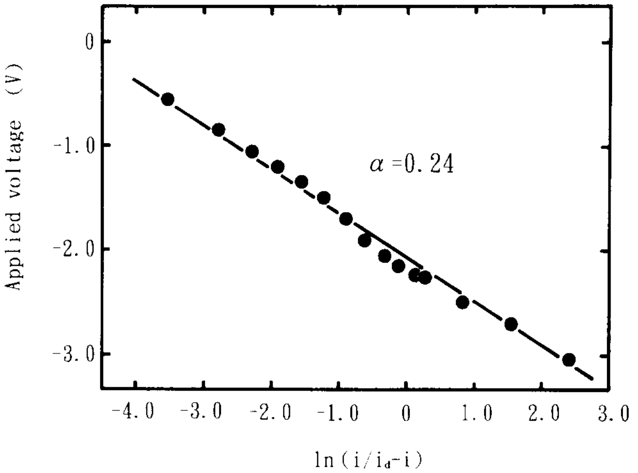

Fig. 4. Dependence of applied voltage on $\ln(i/i_d-i)$ at 1200 °C.

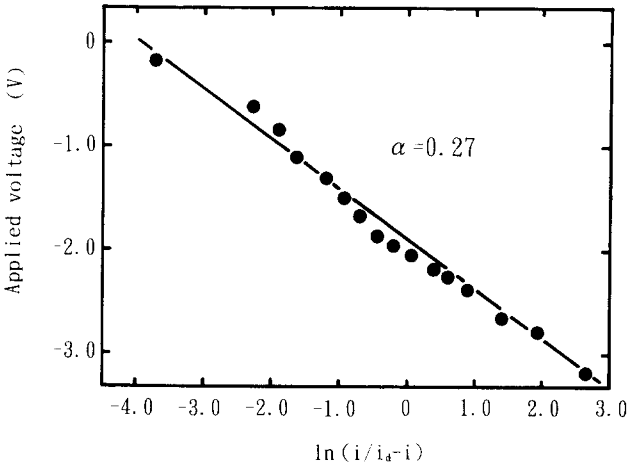

Fig. 5. Dependence of applied voltage on $\ln(i/i_d-i)$ at 1250 °C.

It is known that the product of $\alpha$ and $FE$ ($E$ is the overvoltage of the electrode reaction) indicates the degree of lowering of the activation energy of the electrode reaction, resulting from the applied cell voltage. Our experimental values of $\alpha$ are quite small compared with unity. This indicates that $\alpha$ limits the rate of reaction (1).

If it is supposed that the rate of electrode reaction (2) is fast compared with reaction (1), it can be interpreted that the shoulders resulting from the electrode reduction of $U^{3+}$ ions to the metal would not appear in the current density–potential curves in Figs. 1 and 2, because reaction (1) determines the rate of reduction of the uranium ions on the cathode.

### 3.2. Analysis of solidified salt

The XPS spectra obtained during electrolysis of solidified salt samples at voltages of 1 and 4 V, just before the electrolysis was finished, are shown in Fig. 6. These spectra were compared with standard samples containing $UF_4$ or $UF_3$ [6]. As shown in the spectra, the difference in binding energy of U $4f_{7/2}$ between these peaks is about 1 eV, and this difference is enough to distinguish both samples.

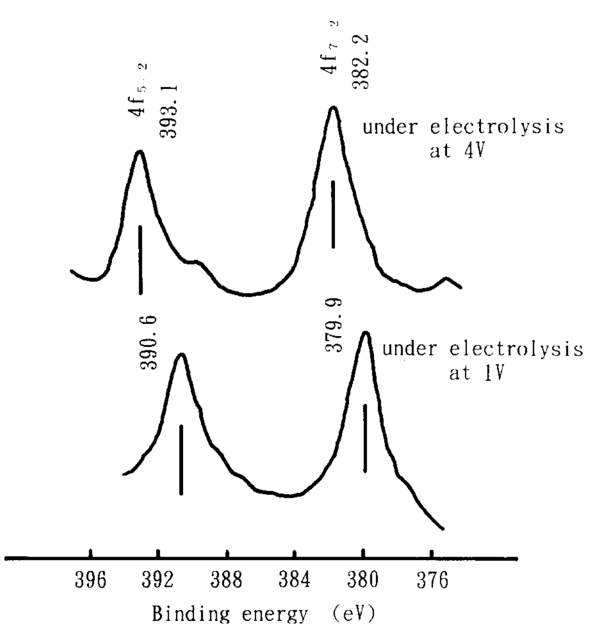

Fig. 6. XPS spectra of U $4f_{5/2}$ and $4f_{7/2}$ for quenched salts.

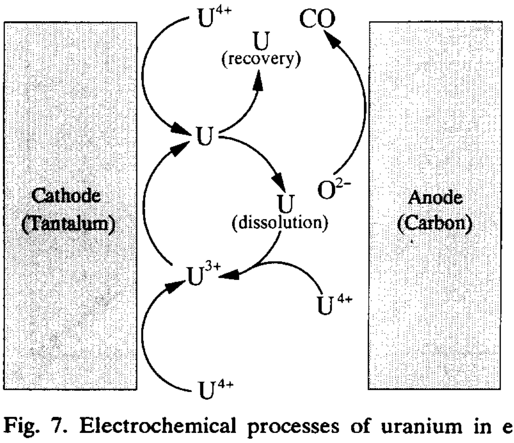

Fig. 7. Electrochemical processes of uranium in electrolysis of $UO_2$.

The identification showed that the sample electrolyzed at 4 V contained tetravalent uranium and that electrolyzed at 1 V contained trivalent uranium. Since the valence of uranium in the molten fluoride remains tetravalent at high cell voltages, it is considered that $U^{3+}$ formed by reaction (1) was quickly reduced to U metal. Also, it was inferred that $U^{3+}$ was not reduced to U metal at low cell voltages, because the concentration of $U^{3+}$ in the molten fluoride increased.

## 4. Conclusions

The electrode reactions in the electrolysis of uranium oxide were clarified by analyses of current density–potential curves. An illustration of the electrode reactions is shown in Fig. 7. It can be concluded that the order of the electrochemical series of cathodic reactions for uranium ions is as follows:

$$U^{4+} + e^- \longrightarrow U^{3+} \qquad (1)$$

$$U^{3+} + 3e^- \longrightarrow U \qquad (2)$$

$$U^{4+} + 4e^- \longrightarrow U \qquad (3)$$

However, the standard electrode potential of these reactions could not be determined in the present study. In addition, it was inferred that reaction (2) was faster than reaction (1) from analyses of the shoulder in the current density–potential curves and the XPS analyses of the salt samples.

## Acknowledgment

We would like to thank Prof. Dr. K. Taniguchi of Osaka Electro-Communication University for his guidance of the measurements by XPS analysis.

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