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Electrolytic Dissolutions of UO_2 and SIMFUEL in Carbonate Solutions at Several pHs

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***Abstract*—**Electrolytic dissolution characteristics of UO_2 and SIMFUEL electrodes were studied at several potentials in carbonate solutions of a high concentration at several pHs. The electrolytic uranium dissolution was much affected by a corrosion product of UO_2CO_3 generated at the electrode during the dissolution in carbonate solution. The corrosion product distorted the voltammogram at UO_2 and SIMFUEL electrodes in the potential region of oxygen evolution and increased the overpotential of oxygen evolution at the electrode. The effective dissolution in a carbonate solution could be obtained at an applied potential such as +4 V (vs SSE) or more which had an overpotential of oxygen evolution high enough to rupture the corrosion product on the electrode surface.

***Keywords*—**Anodic, Electrolytic, Dissolution, SIMFUEL, Uranium dioxide, Carbonate

I. INTRODUCTION

A process, called COL (Carbonate-based Oxidative Leaching), has been recently introduced as a way to manage spent nuclear fuel with enhanced proliferation resistance and environmentally-friendliness concept.[1] In the process, uranium of spent nuclear fuel is selectively leached from the spent nuclear fuel in the form of uranyl peroxo carbonato complex ion of $UO_2(O_2)_xCO_{3y}^{-z}$ in a carbonate solution containing H_2O_2 as a salt-free oxidant [1]-[6], while most of fission product elements including TRU elements being undissolved and then being precipitated together because of their very low solubility in the alkali carbonate condition. The dissolved uranium complex ion can be recovered as UO_4 by acidification of the uranium solution in the process, and all the salts including carbonate used in the process could be recycled without generation of secondary wastes. The chemical dissolution of uranium oxide by using hydrogen peroxide in carbonate media is simple, but the oxidative dissolution reaction of UO_2 by hydrogen peroxide is exothermic so that the solution temperature rises during the dissolution, which results in a rapid consumption of H_2O_2 in the carbonate solution because the hydrogen peroxide is easily self- decomposed in the alkaline media at the elevated temperature. Electrolytic dissolution can be alternative to the chemical dissolution using hydrogen peroxide because it can rule out the problems caused by using H_2O_2.

Many works on the anodic dissolution of UO_2 or SIMFUEL (SIMulated spent nuclear FUEL) have been carried out to date for understanding the dissolution or corrosion characteristics of U or TRU elements of the UO_2 or SIMFUEL in the aqueous solutions under geological conditions in the case of direct disposal of spent nuclear fuel.[7]-[13] So, the previous papers by other researchers have been mainly focused on the dissolution phenomena of the UO_2 or SIMFUEL surfaces in the bicarbonate or NaCl solutions at pH 8 to 10 and near the corrosion equilibrium potential where the dissolution just begin to occur rather than at the high potential ranges where the dissolution occurs substantially and rapidly.

In this work, the anodic dissolution characteristics and rates of UO_2 and SIMFUEL were evaluated and compared in the potential ranges over oxygen evolution in the carbonate solutions of a high concentration at several pHs.

II. EXPERIMENTAL

The anode used in this work was prepared by connecting a UO_2 or SIMFUEL pellet of 8.2mm in diameter and 10 mm in length and a stainless steel rod of the same diameter as a terminal lead and inserting them into a Teflon sleeve with tight sealing. The SIMFUEL pellet was fabricated with the 16 metal oxides and their weight percents chosen on the basis of the main components of a PWR spent fuel calculated by the ORIGEN code (33,000 MWd/MT) at Korea atomic energy research institute. The counter and reference electrodes were Pt wire and Ag/AgCl (Silver-Silver chloride Electrode (SSE) in 3M KCl), respectively. The working electrode was set into a cell of 50 mL without a membrane with the electrode open surface being upward to prevent the oxygen gas generated at high potential from covering the surface. The open pellet surface to be used as the working electrode was polished with several steps of emery paper (No 400, 800, and 1200) and 0.5μm gamma alumina, then cleaned in a sonicator, and finally thoroughly washed with ultrapure water. In order to measure the dissolution rates of uranium at applied constant potentials, the solution was sampled at regular intervals. The measurements of voltammograms and dissolution rates at the potential range of -1.5V to +4.5 V (vs SSE) were carried out with a potentiostat (Zahner IM6) in 0.5 M Na_2CO_3 solutions at several pHs controlled with HNO_3 and NaOH. All the voltammograms in this work were measured at a scan rate of 20 mV/sec. The concentrations of uranium and other metals in the

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solution were analyzed by an ICP (Induced Coupled Plasma spectroscopy; Jobiny von JY 38 Plus). After the dissolution experiments, a 1mm thickness of the open surface of the working electrode was cut off for ex-situ analyses with an electron probe microanalyzer (EPMA, JEOL JXA 8600 with EDX detector) with SEM (Scanning Electron Microscope).

III. RESULTS AND DISCUSSION

In order to know the dissolution characteristics of UO_2 itself or UO_2 of the major component in SIMFUEL, it is necessary to understand the general dissolution mechanism of UO_2. The dissolution of UO_2 begins with the oxidation of stochiometric UO_2 to $UO_{2.33}$, as shown in (1). Then, the oxidation and dissolution of $UO_{2.33}$ occurs as UO_2^{2+}. The dissolution can be accelerated or be blocked depending on the solution condition affecting the solubility of UO_2^{2+} species in the solution. In the neutral non-complexing solution, the dissolved UO_2^{2+} can change to a corrosion product of $UO_3 \cdot xH_2O$ at the surface due to the low solubility of UO_2^{2+}, which results in the suppression of the dissolution. On the other hand, in a carbonate solution, UO_2^{2+} forms uranyl carbonate complex ions such as $UO_2(CO_3)_x^{y-}$ that have a much higher solubility in the solution, which accelerates the dissolution while preventing the formation of $UO_3 \cdot xH_2O$ at the surface. However, in the carbonate solution of high concentration, other corrosion product of UO_2CO_3 can occur on the surface, which also blocks the dissolution [12-17].

$$UO_2 \rightarrow UO_{2+x} \rightarrow UO_{2.33} \rightarrow \overset{(UO_3 \cdot xH_2O)_{surface}}{\overset{\uparrow}{(UO_2^{2+})_{surface and bulk}}} \text{ or } \overset{(UO_2CO_3 \cdot xH_2O)_{surface}}{\overset{\uparrow}{(UO_2(CO_3)_x^{y-})_{surface and bulk}}} \quad (1)$$

Fig. 1 shows cyclic voltammograms at UO_2 and SIMFUEL electrodes in a 0.5 M Na_2CO_3 solution at pH 11.6 in the potential window of -1.5 to +1.5 V. The current of the voltammogram at the SIMFUEL electrode was much higher than that at the UO_2 electrode. The typical peaks observed at UO_2 electrode, which were observed by other workers, were not clearly developed at the SIMFUEL electrodes. The inset box of Fig.1 shows the consecutive cyclic voltammograms at UO_2 electrode in a 0.5 M Na_2CO_3 at pH 11.6 in the potential window of -1.5 to +1.5 V. The respective peaks at UO_2 electrodes in the inset box can be explained as follows. The peak 1 is ascribed to the oxidation of non-stochiometric species of UO_{2+x} at grain boundary, which is due to incomplete reduction during fuel fabrication, up to $UO_{2.33}$. The peak 2 is ascribed to the general oxidation of stochiometric grain UO_2 at grain up to limiting composition $UO_{2.33}$, where O^{2-} ions are incorporated into the interstitial sites, and the peak 3 is attributed to the oxidation of the UO_{2+x} layer at the surface made at peak 2 to soluble specie of UO_2^{2+}. Above this peak 3, a corrosion product deposit of $UO_3 \cdot 2H_2O$ can occurs in the neutral non-complexing solution. However, in the carbonate solution like in this work, such a corrosion product does not form. In the carbonate solution of over pH 11 where only CO_3^{2-} exists, the dissolved uranium ion,

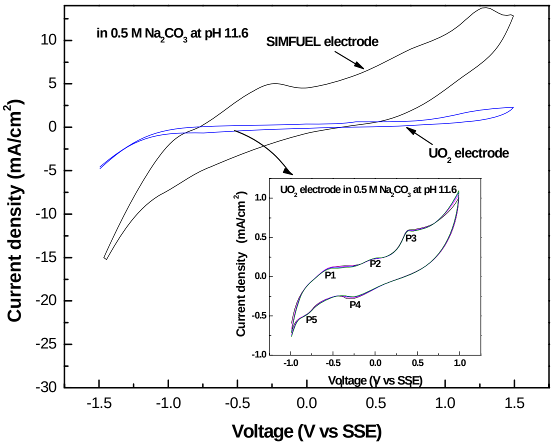

Fig. 1 Cyclic voltammograms at a UO_2 and SIMFUEL electrodes in the potential window of -1.5 V to +1.5 V in a 0.5 M Na_2CO_3 solution.

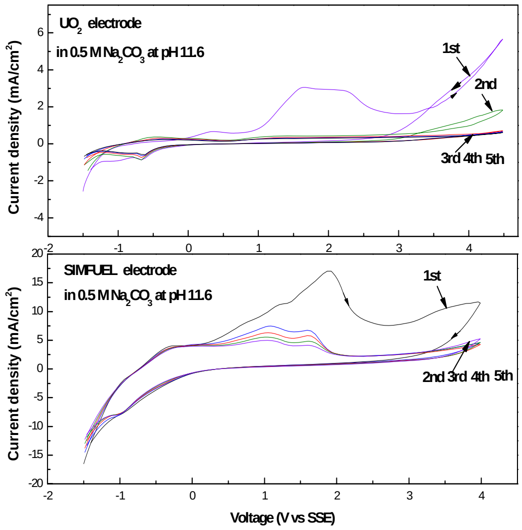

Fig. 2 Cyclic voltammograms at a UO_2 and SIMFUEL electrodes in the potential window of -1.5 V to +4.5 V in a 0.5 M Na_2CO_3 solution.

UO_2^{2+} complexes with the CO_3^{2-} ion to produce the uranyl tri-carbonato complex of $UO_2(CO_3)_3^{4-}$ with a high solubility like (2). The overall dissolution oxidation of UO_{2+x} in the CO_3^{2-} solution in the peak 3 region can be expressed as shown in (3).

$$UO_2^{2+} + 3CO_3^{2-} = UO_2(CO_3)_3^{4-} \quad (2)$$

$$UO_{2+x} + 3CO_3^{2-} + x\,H_2O = UO_2(CO_3)_3^{-4} + 2x\,OH^- + (2-2x)\,e^- \quad (3)$$

The peak 4 is attributed to the reduction of peak 2. Peak 5 is attributed to the reduction of $UO_2(CO_3)_3^{4-}$ or the corrosion product at the surface generated after the peak 3 region.

The big charging current at SIMFUEL electrode in Fig.1 is considered to be ascribed to the presence of metallic particles (Ru, Pd, Mo) as known epsilon-particles and the trivalent rare earth elements acting as dopants in the UO_2 lattice, which result in an increase in electronic conductivity [13], [17]. The unclear development of peaks, compared with those at the UO_2

electrode, is considered to be a result of an increase in the non-stochiometric metal oxides in the SIMFUEL matrix and the partial dissolution of the metal oxides of which the SIMFUEL consists such as Mo oxide. In this work, Mo oxide among the metal oxides of the SIMFUEL was experimentally confirmed to be partially dissolved.

Fig. 2 shows the consecutive cyclic voltammograms at the SIMFUEL electrode in a 0.5 M Na_2CO_3 solution at pH 11.6 in the potential window of -1.5 to +4.0 V. In contrast to the results in Fig.1, a very big peak appeared in the potential between +1.5 and +2.5 V where the oxygen evolution normally vigorously occurred, and the current after the peak decreased and then rose again. The peak 6 around +1.5 V rapidly disappeared with the repeat of cyclic scan. The rapidly-rising current over +1 V is ascribed to the oxygen evolution with water oxidation reaction of (4). The appearance of the big peak between +1.5 and +2.5 V at the first scan and the current decrease with cyclic scan are considered to be a result of the deposition of corrosion product such as UO_2CO_3 which is accumulated to block the electrode surface [10]-[16], resulting in suppression of the oxygen evolution and an increase in the overpotential of the oxygen evolution reaction. It brings about the peak in the potential region of the oxygen evolution and makes the potential of oxygen evolution shifted more in the positive direction. The deposition of UO_2CO_3 at the electrode is known to occur according to (5) to (7). When the voltammograms at UO_2 and SIMFUEL electrodes in 0.1 M NaCl was measured in the same potential ranges of Fig. 2, although they are not present in this work, the oxygen evolution current starting from about +1.0 V linearly increased with the potential without any meaningful change in the cyclic voltammogram up to +4.5 V, which is quite different from the results of Fig. 2. This means that there was no effect of corrosion product such as UO_2CO_3 at the electrodes in the NaCl solution.

$$2H_2O = O_2 + 4H^+ + 4e^- \tag{4}$$

$$UO_2 + HCO_3^- = U^V(HCO_3)_{ads} + e^- \tag{5}$$

$$U^V(HCO_3)_{ads} + OH^- = (UO_2CO_3)_{ads} + e^- + H_2O \tag{6}$$

$$UO_2(CO_3)_{ads} + 2CO_3^{2-} = UO_2(CO_3)_3^{4-} \tag{7}$$

Fig. 3 shows the dissolution rate of the uranium of the UO_2 and SIMFUEL electrodes at several applied potentials in a 0.5 M Na_2CO_3 solution. The dissolution almost linearly increased with time at each applied potential, which are not present in this work. The dissolution rate was evaluated from the change of uranium concentration in the solution with time. The dissolution rate at 0.0 V was almost zero. In the applied potential range of +0.5 V to +4 V, the dissolution rate was the highest at +1.0 V and steadily increased with applied potential. Finally, it drastically increased at +4.5 V. The dissolution behavior can be explained with the results of the cyclic voltammogram in Fig. 2. The decrease in the dissolution rate and the sluggish increase after +1 V is considered to be due to the corrosion product generated at the electrode surface. The dissolution rate rapidly increased after +4 V where the oxygen evolution current rose again, as shown in Fig.2. Table 1 shows the current efficiencies of the UO_2 and SIMFUEL at the several applied potentials. The dissolution current efficiencies at the UO_2 and SIMFUEL, on the whole, have no much change before +4.0 V, or not significant change, if any. However, they rapidly increased at the potential of more than +4.0 V.

These results reveal that an overpotential of the oxygen evolution high enough to break the UO_2CO_3 deposit layer hindering the dissolution on the electrode surface can accelerate greatly the dissolution of UO_2 and SIMFUEL electrodes.

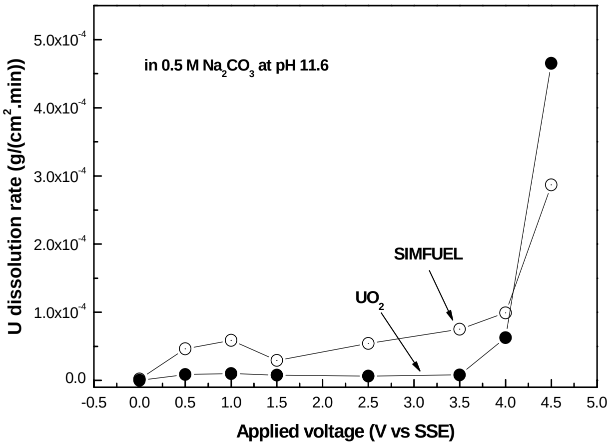

Fig. 3 Dissolution rate of uranium of UO_2 and SIMFEL electrodes at several applied potentials in 0.5 M Na_2CO_3 solution.

TABLE 1
CURRENT EFFICIENCIES OF DISSOLUTIONS OF A UO_2 AND SIMFUEL ELECTRODES AT SEVERAL APPLIED VOLTAGES

Applied Potential (V vs SSE)	Current efficiency (%)	
	UO2	SIMFUEL
+0.5	13.1	29.2
+1.5	13.4	30.1
+2.5	21.7	36.8
+3.5	23.9	43.6
+4.0	70.2	46.8
+4.5	87.1	67.3

Fig. 4 shows the dissolution rate of a UO_2 and SIMFUEL electrodes at 1.0 V (vs SSE) in carbonate solutions with a carbonate concentration of 0.5 M at several pHs. The dissolution rate of uranium increased with a decrease of pH in the carbonate solution, and rapidly increased at pH of less than 10 where there was less effect of the deposition of corrosion product of UO_2CO_3 on the electrode, because of the dissolution of UO_2CO_3 as ions in the pH condition where HCO_3^- ions existed. Table 2 shows the current efficiency of the UO_2 dissolution calculated with the total supplied currents and the measured amount of dissolved uranium. The current efficiency decreased with an increase of pH in the carbonate solution because the corrosion product of UO_2CO_3 deposited at the surface suppressed more the dissolution of UO_2 itself in higher pH solution.

From all the above results, it can be said that the general electrolytic dissolution characteristics of uranium at UO_2 and SIMFEUL electrodes are similar.

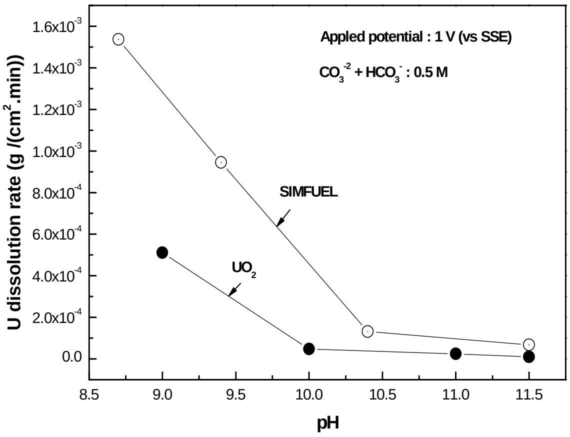

Fig. 10 Dissolution rate of a UO_2 electrode at +1.0 V (vs SSE) in carbonate solutions at several pH at a constant carbonate concentration of 0.5 M.

TABLE II
CURRENT EFFICIENCIES OF URANIUM DISSOLUTION AT UO_2 AND SIMFUEL ELECTRODE IN CARBONATE SOLUTIONS WITH CONSTANT CARBONATE CONCENTRATION OF 0.5 M AT SEVERAL PHS

UO_2		SIMFUEL	
pH	Current efficiency (%)	pH	Current efficiency (%)
9.0	70.2	8.7	86.7
10.0	45.8	9.4	88.5
11.0	32.1	10.4	64.7
11.6	18.0	11.6	46.1

IV. CONCLUSIONS

Electrolytic uranium dissolution of UO_2 and SIMFUEL were affected by a corrosion product of UO_2CO_3 generated at the electrode surfaces during the dissolution in the carbonate solution. The corrosion product distorted the voltammogram in the potential region of oxygen evolution and increased the overpotential of oxygen evolution at the electrode. Effective dissolution of the UO_2 and SIMFUEL electrode in the carbonate solution could be obtained at an applied potential such as + 4 V (vs SSE) or more which had an overpotential of oxygen evolution high enough to rupture the corrosion product on the electrode surface, and the Current efficiency increased with a decrease of pH in the carbonate solution.

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