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Kinetics of the electrodissolution of metallic uranium

L. S. Rodrigues, N. A.-Falleiros, C. A. L. G. de O. Forbicini*

Comissão Nacional de Energia Nuclear-SP, Instituto de Pesquisas Energéticas e Nucleares, Caixa Postal 11049-Pinheiros, 05422-970 – São Paulo, Brasil

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The kinetics of the anodic dissolution of metallic uranium in 1, 2, 3, and $4 \text{ mol} \cdot \Gamma^{-1} \text{ HNO}_3$ solutions at 30 °C were studied by potentiostatic polarization. The dissolved uranium was determined by polarography and the anodic dissolution rates by the initial rate method. It was observed that the dissolution rate increases with the applied potential, but is independent of the HNO₃ concentration, because it is a zero order reaction. A mechanism for the anodic reaction was proposed based on the adsorption theory.

Introduction

Metallic uranium is one of the heaviest metals and its thermal conductivity is similar to that of iron.¹ Because of its great reactivity, it reacts with almost all the elements of the periodic table, except with the noble gases.² The uranium reactions in the presence of oxygen, nitrogen and water are the most important and WILKINSON¹ has discussed the corrosion mechanisms in details. Its high density is essential for the operation of some reactors (as gas cooled reactor), presenting as advantages the simple cycle and the low costs involved.^{2,3}

To attend the restrictions imposed in the 90's for the use of high-enriched uranium (HEU) in material testing reactor (MTR), many concepts of fuel elements and irradiation targets were developed, containing higher concentration of low-enriched uranium (LEU), as the metallic foil targets. These targets may provide the same 99 Mo (99m Tc precursor, used in medicine) yield as the highly enriched UO₂.

The fuel elements and irradiation targets have been dissolved by chemical process, generating high quantities of waste. As electrolysis can be used in the dissolution of different fuel elements and targets, either in basic or acid solutions,⁵ the reprocessing via electrolytic dissolution would be an important alternative, due to its selectivity, low waste generation and short time dispensed.

MANCE⁶ has studied the effect of temperature in the kinetic reaction of anodic dissolution of metallic uranium in citric acid. However, no studies were found about the anodic dissolution of metallic uranium in nitric acid solution. For this reason, the corrosion behavior of metallic uranium in nitric acid media is known only qualitatively.⁷

In this work some initial kinetic studies were developed to understand the mechanisms of the anodic dissolution of metallic uranium in nitric acid media.

Experimental

The metallic uranium samples were obtained from an uranium bar produced at Institute of Energetic and Nuclear Researches (IPEN), by reducing UF₄ with metallic Mg. The samples were embedded in an acrylic resin as shown in Fig. 1. The sample surfaces (0.56 cm²) were polished with 400, 600 and 1000 SiC sandpapers, dried in hot air blast, before being submitted to the electrochemical experiments.

The experiments were performed in a jacketed borosilicate cell (Fig. 2), with an electrical stirrer, thermometer and a thermostatic bath, connected to an EG&G PAR 273A Potentiostat/Galvanostat as indicated in Fig. 3. An Ag/AgCl reference electrode and a Pt wire auxiliary electrode were used.



Fig. 1. Scheme of a test sample; metallic sample (1) and spindle of stainless steel (2)

* E-mail: cforbici@net.ipen.br

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Fig. 2. Scheme for electrochemistry experiments; electrochemical cell (1); working electrode (2); reference electrode and capillary (3); counter electrode: Pt rod (4); potentiostat/galvanostat (5); computer (6); printer (7)



Fig. 3. Electrochemical cell used for the potentiostatic polarization experiments of metallic uranium

The potentiostatic experiments were developed with aerated 1, 2, 3 and 4 mol· 1^{-1} HNO₃ solutions, at 30 °C. Each experiment used 700 ml solution and 3 ml sample aliquots were collected at every 300 seconds for the determination of uranium by polarography.

Results and discussion

The anodic current density transients for the potentials 600 and 650 mV (Ag/AgCl) applied to uranium submitted to potentiostatic polarization in 4 mol· 1^{-1} at 30 °C, are shown in Fig. 4. At the beginning, a gradual current increase is observed, until the steady state is reached. This occurs probably due to the dissolution of corrosion products, that provides a cathodic protection to uranium.



Fig. 4. Anodic current density transients of metallic uranium (0.56 cm^2) in aerated and stirred (f=5 Hz) 4 mol·1⁻¹ aqueous solutions of HNO₃, determined by potentiostatic polarization at 30 °C

[HNO ₃], mol·l ⁻¹	E, (Ag–AgC 600 mV							Cl) 650 mV					
	0	600 s	900 s	1200 s	1500 s	1800 s	0	600 s	900 s	1200 s	1500 s	1800 s	
1.00 2.00 3.00 4.00	0 0 0 0	0.95 1.30 1.14 1.08	1.52 1.68 1.75 1.67	2.85 2.63 2.94 2.29	3.41 3.88 3.71 3.41	4.35 4.42 4.69 4.02	0 0 0 0	2.01 2.10 1.99 2.08	2.66 3.63 3.32 3.15	4.05 4.42 5.08 4.36	5.01 5.93 5.47 5.57	5.73 7.72 6.89 6.22	

Table 1. Concentration of metallic uranium anodically dissolved in HNO₃ at 30 °C (in $\times 10^4$ mol·l⁻¹)



Fig. 5. Uranyl nitrate $[UO_2(NO_3)_2]$ concentration as a function of potentiostatic polarization time of uranium (0.56 cm²) in stirred (f = 5 Hz) and aerated aqueous solutions of 1, 2, 3 and 4 mol·1⁻¹ HNO₃ at 30 °C

The concentrations of dissolved metallic uranium are shown in Table 1. The results were reproducible, being below the standard error of the method used (<10%).

Figure 5 shows the curves obtained from the data of Table 1. The curves have a 2nd degree polynomial tendency, probably due to the exposed surface of uranium to the HNO_3 solution as a function of the pits resulted from the acid attack. It was also observed that the uranium anodic dissolution rate increases at high potencials applied.

The anodic dissolution rates were obtained by the initial rate method, from the data showed in Fig. 6. These rates were converted to current densities (i) using Faraday's law,

i = zFdn/dt

where z is the number of electrons transferred, F is the Faraday's constant and dn/dt is the uranium dissolution rate.

The data presented in Table 2 were used to calculate the uranium anodic dissolution reaction order in HNO_3 solution (Fig. 6). The average rates have a relative standard deviation lower than that set by polarographic analysis:

 $i_{600\text{mV/Ag-AgCl}} = (0.040 \pm 0.003) \cdot 10^4 \text{ A} \cdot \text{m}^{-2} \text{ (c.v.=8.3\%)}$

and

 $i_{650 \text{ mV/Ag-AgCl}} = (0.090 \pm 0.006) \cdot 10^4 \text{ A} \cdot \text{m}^{-2} \text{ (c.v.=}6.7\%).$

The dissolution rate presented a reaction order equal to zero, thus does not depend on the HNO_3 concentration at the conditions studied. In fact, HNO_3 solutions can cause passivation of uranium and its dissolution rate increases with temperature raising and with decreasing acid concentration. A mechanism may be proposed for the anodic dissolution rate based on the adsorption theory. Five steps are necessary that the surface reaction occurs: (1) diffusion of the reagents to the surface, (2) adsorption of reagents on the surface, (3) reaction in the surface, (4) desorption of the products, (5) diffusion of the surface products.

Any of these steps or a combination of them can be the determining reaction rate. For very fast reactions, as the charge transfer, the rate can be limited by the diffusion to or from the surface, but can be increased by vigorous stirring. Many times, the reaction rate is determined by the step 2 or by the combination of steps 3 and 4.

The elementary steps are:

$$A + S \xrightarrow{k_d} AS$$

$$AS \xrightarrow{k_d} A + S \qquad (1)$$

$$AS \xrightarrow{k_r} \text{products}$$

where k_a is the adsorption rate constant of specimen A on the metallic surface, k_d is the desorption rate constant and k_r is the product formation rate constant.

Table 2. Current densities of metallic uranium in HNO3 solutions at 600 and 650 mV (Ag–AgCl) at 30 $^{\circ}{\rm C}$

[HNO ₃],	$i, \times 10^{-4} \mathrm{A}\cdot\mathrm{m}^{-2}$				
mol·l ⁻¹	600 mV	650 mV			
1.00	0.0364	0.0857			
2.00	0.0442	0.0831			
3.00	0.0416	0.0961			
4.00	0.0390	0.0935			



Fig. 6. Anodic current density variation of uranium (0.56 cm²) submitted to potentiostatic polarization in function of HNO₃ concentration at 30 °C

The reaction rate is $v = k_a c_{AS}$, where c_{AS} is the A specimen concentration on the uranium surface. As the total concentration of active sites on the uranium surface is constant, and θ is the fraction of the surface covered by specimen A, so $c_{AS} = c_S \theta$. The reaction rate can be written as $v = k_r \theta$.

At steady state, the rate becomes:

$$v = \frac{k_a k_s c_A}{k_a c_A k_d + k_r} \tag{2}$$

If the decomposition rate is greater than the adsorption/desorption rate, then a reagent film coats the surface and a first order reaction occurs.

When the decomposition rate is very low related to the adsorption and desorption rates, the reaction will be of first order at low reagent concentration. If the surface is partially coated by the reagents, a zero order reaction occurs, because the reaction rate depends on the concentration of A.

On the uranium surface, several secondary and successive anodic and cathodic reactions⁷ may occur: At the anode:

$$U(s) = U^{3+}(ad) + 3e$$
 (3)

 $U^{3+}(ad) + 2NO_{3}^{-}(ad) = UO_{2}(ad) + 2NO^{+}(aq) + e$ (4)

$$2NO^{+}(aq) + 2H_2O(l) = 2NO_3^{-}(aq) + 4H^{+}(aq)$$
 (5)

$$UO_2(ad) = UO_2^{2+}(ad) + 2e$$
 (6)

$$UO_2^{2+}(ad) + 2NO_3^{-}(ad) = UO_2(NO_3)_2(aq)$$
 (7)

$$O_2(g) = 2O(ad) \tag{8}$$

$$2O(ad) + 2e = 2O^{2-}(ad)$$
(9)

$$U^{3+}(ad) + 2O^{2-}(ad) = UO_2(ad) + e$$
 (10)

At the cathode:

$$2H^{+}(aq) + 2e = H_{2}(g)$$
 (11)

$$NO_{3}^{-}(aq) + 2H^{+}(aq) + 2e = NO_{2}^{-}(aq) + H_{2}O$$
 (12)

$$UO_2^{2+}(ad) + 2e = UO_2(ad)$$
 (13)

where (ad) means adsorbed, (aq) aqueous, (g) gaseous, (l) liquid, and (s) solid. The X-ray photoelectric spectroscopy (XPS) analysis has showed the existence of many oxides, such as UO_2 and U_2O_3 , on the uranium surface when submitted to the potentiostatic polarization in 4 mol·l⁻¹ HNO₃, showing that the above proposed anodic reactions occur. The cathodic reactions are already established in the literature.⁹ A vigorous hydrogen evolution was observed and the Griess test confirmed the presence of NO_2^- in the anolite. Reaction (6) may be the slowest reaction step of the process, because UO_2 is a ceramic compound and, therefore, a poor electric conductor.

Conclusions

The anodic dissolution of metallic uranium is a zero order reaction, being independent of the HNO_3 concentration at the conditions studied.

Several competitive and successive secondary reactions may occur during the uranium anodic dissolution in nitric acid media and the determining rate of the reaction is the oxidation of U(IV) to U(VI).

The anodic dissolution rate of metallic uranium increases with the applied potential.

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