

The Mechanism of Mediated Electrochemical Dissolution of Semiconducting Metal Oxide Particle

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ABSTRACT

The dissolution of plutonium dioxide (PuO_2) is of a fundamental importance from the point of view of energy as well as environment. In this work the mechanism of mediated electrochemical dissolution of semiconducting plutonium dioxide (PuO_2) particles in nitric acid (HNO_3) was studied on the basis of experimental kinetics published so far. It was found that the rate-controlling reaction is an interfacial electron transfer process between the solid tetravalent plutonium $\text{Pu}^{4+}(\text{s})$ and an aqueous metal ion such as reductive $\text{U}^{4+}(\text{aq})$ or oxidative $\text{Ce}^{4+}(\text{aq})$ ion. The rupture of covalent bond of Pu-O of the possible $[\text{PuO}_4]^{4-}$ cluster in the (110) plane of the cubic PuO_2 lattice by electron transfer is decisive for the dissolution process. The role of HOMO and LUMO of the $[\text{PuO}_4]^{4-}$ cluster is discussed with regards to the oxidative and reductive dissolution respectively.

Keywords: mediated electrochemical dissolution, plutonium dioxide, mechanism

1 INTRODUCTION

The mechanism of electrochemical dissolution of semiconductor electrode was discussed by Gerischer and Mind in their classic paper nearly half a century ago [1]. They stressed the role of the hole in the valence band and an electron in the conduction band in the anodic and cathodic dissolution respectively. They pointed out that the hole in valence band means the rupture or weakening of the bonding orbital. An electron added to the conduction band means the weakening of nonbonding or antibonding orbital.

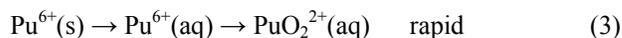
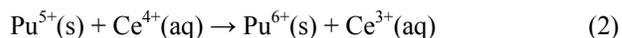
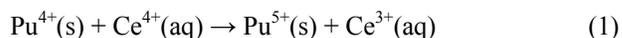
On the other hand the mechanism of the mediated electrochemical dissolution of semiconducting metal oxides has not been discussed in spite of the scientific as well as technological importance of the electrochemical process. The mediated electrochemical dissolution refers to the electron transfer reaction between a semiconducting metal oxide and an aqueous metal ion which can be generated or regenerated by an electrochemical reaction, whereas an electrochemical dissolution refers to the anodic or cathodic dissolution of semiconductor electrode.

The purpose of this work is to discuss the mechanism of the mediated electrochemical dissolution of semiconducting PuO_2 particle. The dissolution of PuO_2 is of a great interest from the point of view of electrochemistry because the metal oxide can easily be reduced as well as oxidized by usual metal ions due to the existence of 5f orbitals of Pu.

2 DISCUSSION

2.1 Mechanism of Mediated Electrochemical Oxidative Dissolution of PuO_2

Although PuO_2 is inert even in concentrated HNO_3 , the metal oxide is well-known to oxidatively dissolve in 4 M HNO_3 in the presence of a powerful oxidizing metal ion, ~ 0.1 M Ce^{4+} ($\text{Ce}^{4+}/\text{Ce}^{3+}$: $E^\circ = 1.72$ V). The mechanism of the oxidative dissolution will be represented by the following reaction sequence on the basis of the kinetics and mechanism of the oxidative dissolution of uranium oxides, UO_2 and U_3O_8 in HNO_3 [2,3,4].



,where $\text{Pu}^{4+}(\text{s})$ indicates the surface solid ion which is not a defect. $\text{Pu}^{5+}(\text{s})$ and $\text{Pu}^{6+}(\text{s})$ indicate the oxidized surface ion which are supposed to be a defect. The defect, $\text{Pu}^{6+}(\text{s})$ is considered to be labile because of the rupture of the Pu-O covalent bond by the electron transfer by means of an interfacial electron tunneling. So the surface defect ion will be readily ejected into aqueous solution. That is, the possible rate-controlling step should be the interfacial electron transfer reactions (1) and (2). We will assume for simplicity in the following argument that the reaction (1) is rate-controlling.

The half reaction of the redox reaction (1) is represented as



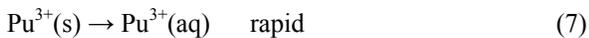
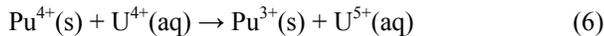
The above half reaction does correspond to neither the ionization reaction of an isolated metal ion nor the emission of electron from the valence band of the metal oxide. The reaction (1) is interpreted as the unique ionization reaction which corresponds to the creation of the transient surface hole in the valence band. The surface transient hole, a small polaron, could also be conducted to the bulk semiconductor. However, the transient surface ion will transiently be

remained there and have a larger probability of being ejected into solution according to the reaction (2) and (3) because the small polaron is a heavy hole in the ionic crystal.

The dissolution of PuO₂ in HNO₃ in the presence of Ce⁴⁺ is well-known to have a maximum velocity at 4 M HNO₃. The rate of the dissolution decreases rapidly to 1 M below 4 M and to 15 M above 4 M by as much as over 10² times [5,6]. The predominant species around 4 M HNO₃ seems to be a neutral tetranitrato complex Ce(NO₃)₄. On the other hand a hexa-hydrated/nitrato complex cation and a hexanitrato complex anion are predominant in 1 M and 16 M HNO₃ respectively. The reason for the maximum rate of the dissolution at 4 M HNO₃ could be the least tunneling barrier for an electron due to the least obstructing effect by ligands.

2.2 Mechanism of Mediated Electrochemical Reductive Dissolution of PuO₂

As the Pu⁴⁺ ion has the vacant 5f valence orbital, the ion can be relatively easily reduced to Pu³⁺. So, it is reasonable to select the tetravalent uranium as the promoter of the dissolution of PuO₂ in HNO₃. We earlier investigated the effect of the aqueous U⁴⁺ ion (U⁵⁺/U⁴⁺, U⁶⁺/U⁵⁺: E°=0.38 V, 0.16 V) on the dissolution of PuO₂ in HNO₃ and could successfully confirm the effect on the dissolution of PuO₂; at 90°C, 3-5 M HNO₃ in the presence of 0.2 M U⁴⁺ and hydrazine (N₂H₄) as a stabilizer of U⁴⁺ [7,8]. The mechanism of the reductive dissolution will be represented by analogy with the oxidative dissolution of PuO₂ as follows:



As the U⁵⁺(aq) is a unstable intermediate, it will rapidly react with the O²⁻(s) and form UO₂⁺(aq). The UO₂⁺(aq) should also reduce Pu⁴⁺(s) to Pu³⁺(s) at the surface of PuO₂ by means of an electron transfer.

The important step for the reductive dissolution is,



The above reaction is also unique. The reaction does correspond to neither the reduction of a free Pu⁴⁺ ion nor the ejection of an electron to the conduction band of the semiconductor. That corresponds to the electron transfer reaction to the surface Pu⁴⁺(s) for creating the transient surface polaron(an electron). The polaron could conduct into the bulk semiconductor. However, the polaron is relatively heavy. So that the Pu³⁺(s) will be transiently remained at the crystal surface and dissolved into aqueous solution as in the case of the oxidative dissolution of PuO₂.

2.3 The Electronic Structure of PuO₂ in Terms of the Mechanism of Mediated Electrochemical Dissolution

The valence electronic structure of PuO₂ is controversial in spite of many experimental studies using a spectroscopy such as XPS and XAS as well as theoretical computations. We would like to propose here the qualitative valence molecular orbital diagram for PuO₂ on the basis of the mechanism of dissolution of PuO₂. We could speculate on the electronic structure of PuO₂ from the dissolution mechanism and the crystal structure as follows:

1) PuO₂ is of the cubic crystal of CaF₂ type and eight O²⁻ ions are arranged in the cubic symmetry to central Pu⁴⁺. However, [PuO₄] cluster is a reasonable choice because oxygen has two unpaired electrons. The planar [PuO₄]⁴⁺ cluster in the (110) plane may be the best choice because an electron is more delocalized in a plane than other structures.

2) The formal charge of Pu is nearly +4 as understood from the mechanism of the dissolution.

3) 5f orbitals participate to molecular orbital to some extent. Two electrons occupy a bonding orbital, HOMO of 5f character and the orbital is broken by the oxidative electron transfer to the aqueous ion. LUMO of [PuO₄]⁴⁺ cluster is of 5f and an antibonding character. The reductive dissolution takes place by one electron transfer to the LUMO.

We propose the tentative molecular energy level diagram of PuO₂ on the basis of above consideration (Figure 1).

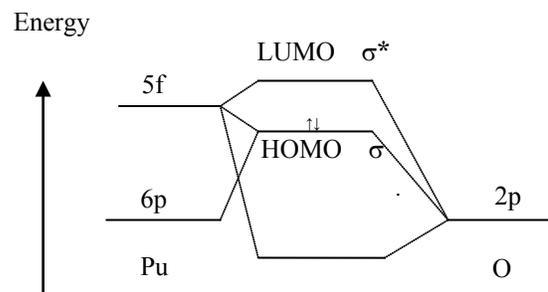


Fig. 1: The molecular orbital energy diagram of planer [PuO₄]⁴⁺ cluster in the (110) plane.

The participation of the 6p as well as 5f orbital to HOMO will be necessary in order to make the HOMO to be a bonding orbital.

3 CONCLUSION

The nuclear energy is expected to play an important role for preventing the global warming. The mediated electrochemical dissolution of PuO₂ is one of the key technologies in the nuclear engineering. The author believes that the microscopic view on the dissolution of semiconducting PuO₂ particle will help to connect the isolated nuclear science with the global nano science and technology.

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