

The Fundamentals of Reduction of UO_2^{2+} Ions on a Pt Electrode and Methods for Improving Reduction Current Efficiency

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Abstract : This review article considered the electrochemical reduction of uranyl ions on a Pt surface. Specifically, we focussed on the improvement in its reduction current efficiency. First, this article briefly explained the fundamentals of the reduction of uranyl (UO_2^{2+}) ions on a Pt surface. Namely, they involved the electrochemical behaviour of uranium species, and electrochemical cell configurations for the reduction of UO_2^{2+} ions. In addition, the effects of adsorbed hydrogen atoms were investigated on the reduction of UO_2^{2+} ions. Finally, this article presented the methods for improving current efficiency of the reduction of UO_2^{2+} ions on a Pt surface. Three different kinds of methods are introduced, which include electrochemical surface treatments of Pt electrode involving hydrogenation and anodisation, the use of catalyst poisons, and formation of thin mercury film on a Pt electrode. Moreover, this article provided some clues about how hydrogenation and catalyst poisons work on the reduction of UO_2^{2+} ions.

Keywords : Uranyl ion, Adsorbed hydrogen, Platinum, Electrochemical reduction, Current efficiency.

1. Introduction

One of the basic technologies in the study of actinide compounds is to control the oxidation states of actinide species when studying their chemical reactions and properties in aqueous solutions.¹⁻³⁾ Especially, as uranium oxide is used for a fuel material in nuclear power reactors, much attention has been paid to the study on controlling the oxidation states of the uranium (U) species.⁴⁻⁸⁾ The reduction of the uranyl (UO_2^{2+}) ions, which is a stable U species, has been investigated with the aim of the quantitative analysis of U.⁹⁻¹²⁾ In addition, it is known that the reduction of UO_2^{2+} ions is one of the essential steps in the reprocessing of spent fuels; it has been a concern for the fuel development of the fast breeder reactor, which was designed to use plutonium (Pu) and uranium mixed oxide fuel.

On the other hand, hydrogen evolution generally takes place at the conventional metal electrodes in an acidic solution as well as the electrochemical reduction of UO_2^{2+} ions. Therefore, mercury (Hg), which has a high hydrogen overpotential, had been used as a working electrode for the polarographic or coulometric determination of UO_2^{2+} ions by reducing hydrogen evolution.^{4,5)} However, two main disadvantages,^{11,12)} associated with the use of the Hg-pool electrode, remain in the reduction of the UO_2^{2+} ions to the U^{4+} ions. One is that the experimental arrangement for mixing the contents in the working electrode compartment of the

electrolysis cell is somewhat critical, with both aqueous and Hg phases within each other. The other disadvantage is that Hg dissolves under mildly oxidising conditions.

In addition, in evaluating the electrochemical reactions of chemical species including U ions, it is necessary to employ an electrochemical system coupled with other analysis tools such as an ATR-SEIRA (attenuated total reflectance-surface enhanced infrared absorption) spectrometer, an EQCM (electrochemical quartz crystal microbalance) and a UV/VIS (ultraviolet and visible) spectrometer.¹³⁻¹⁵⁾ However, the Hg-pool electrode is unsuitable for this purpose. For this reason, solid noble metals such as platinum (Pt) and gold (Au) were considered again for the configuration of an appropriate electrode system. Even though the potential range for the reduction of water molecules or proton ions to hydrogen gas and that range for the reduction of UO_2^{2+} ions overlap with each other to some extent on Pt and Au, it was considered that these solid noble metals, especially Pt, are the most appropriate.

The purpose of this article is to overview the reduction of UO_2^{2+} ions on a Pt electrode. First, this article briefly presented the fundamentals of the reduction of UO_2^{2+} ions on a Pt surface. Finally, the methods for improving current efficiency in the reduction of UO_2^{2+} ions on a Pt electrode were introduced.

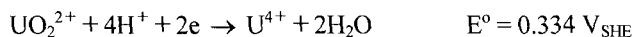
2. Fundamentals of the Reduction of UO_2^{2+} Ions on a Pt Electrode

2.1 Electrochemical behaviour of U species

Most of the electrochemical studies on U ions were carried

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out in aqueous solutions, where two uranium oxidation states, U(IV) and U(VI), are stable. U(VI) is mainly present in the form of UO_2^{2+} ion, whereas U(IV) is in the form of U^{4+} ion. The values of the electrode potential for the various U species are changed with the experimental conditions such as the solution pH. Bard¹⁶⁾ listed the standard electrode potential values of U species for some aqueous media. The resulting standard electrode potentials of major U species are as follows:



Although U^{3+} ions can be prepared by the reduction of U^{4+} ions, it is not stable but it turns into higher valence states (IV and VI) by simultaneously liberating the hydrogen gas from water. From a thermodynamic point of view, it is expected that the reduction of UO_2^{2+} ions into U^{4+} ions spontaneously occurs in the acidic media. However, U^{4+} ions are not observed even in a strong acidic solution, because the reduction rate for UO_2^{2+} ions to U^{4+} ions is too slow from a kinetic viewpoint. On the other hand, UO_2^+ ions are easily generated by the reduction of UO_2^{2+} ions. UO_2^+ ions are chemically stable in the pH range between 2 and 4, whereas they are unstable in a strong acidic solution to disproportionate immediately into U^{4+} ions and UO_2^{2+} ions.^{6,7,17)} It was reported¹⁶⁾ that concentrations of U(V) including UO_2^+ ions can be obtained approximately up to 10^{-3} M in aqueous solutions in the presence of complexing ions or of chelating agents which stabilise U(V) by complex formation.

2.2 Electrochemical cell configurations for the reduction of UO_2^{2+} ions

There are several types of electrochemical cell configurations for reducing UO_2^{2+} ions in an acidic solution. The simplest configuration shown in Fig. 1 is the typical 3-electrode system for investigating the electrochemical behaviour of U species in certain aqueous media.¹⁸⁾ Generally, a working electrode with large surface area is mainly used for the determination of U concentration by measuring the charge equivalent to the total amount of UO_2^{2+} ions reduced to U^{4+} ions.

The second type is designed for the chemical analysis. Fig. 2 depicts an electrochemical cell employed in the reduction of various kinds of U ions for this purpose.^{11,19)} In this case, the working electrode is a cylinder with two to three layers thickness of a strip of Pt gauze. In this system, two factors are taken into consideration for ensuring the accuracy of chemical analysis: One is the separation by a conducting bridge between the working electrode compartment and the counter electrode compartment, and the other is the convection induced by stirring of the solution in the working electrode compartment. The solution in the working electrode compartment is de-aerated by passing nitrogen or argon gas. In addition, the cell system is generally placed in a dark environment to minimize the secondary photochemical reactions.

The third type is a glassy carbon fibre electrode. Since the

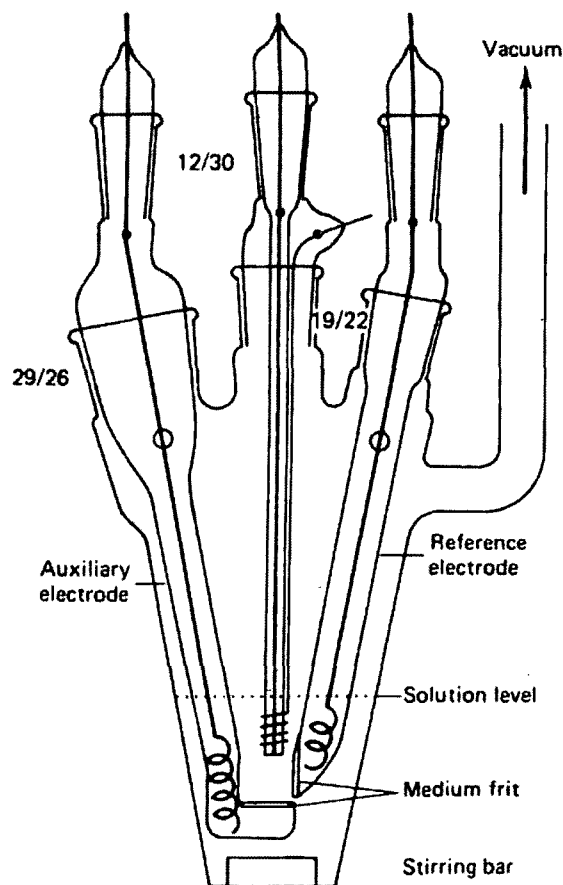


Fig. 1. Three-electrode cell used in electrochemical experiments.¹⁶⁾

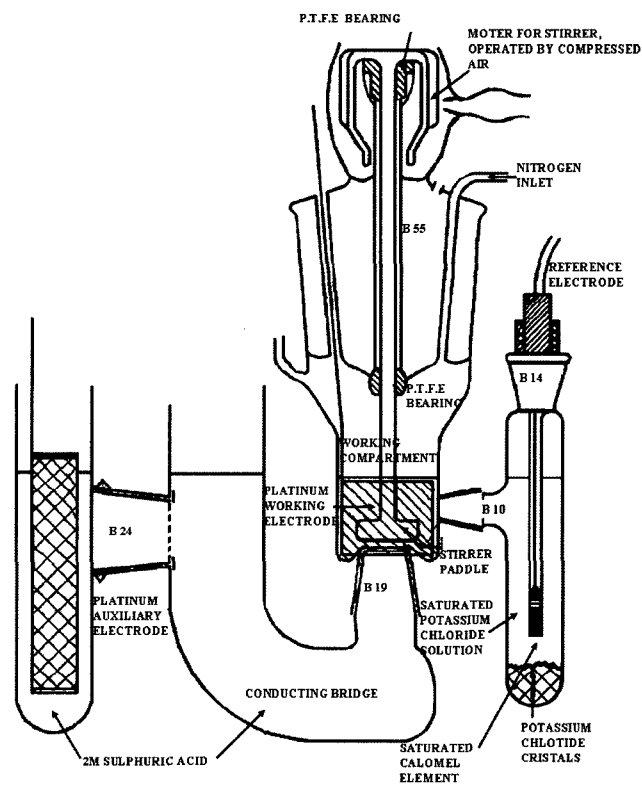


Fig. 2. The coulometric cell for U determination.¹⁷⁾

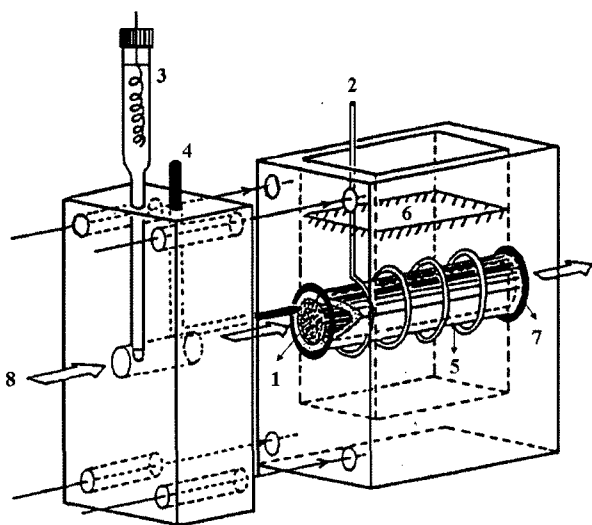


Fig. 3. Column electrode. 1. glass carbon fibre working electrode; 2. Pt counter electrode; 3. reference electrode; 4. contact rod for working electrode; 5. electrolytic diaphragm; 6. outer solution; 7. neoprene seal; 8. sample solution.¹⁸⁾

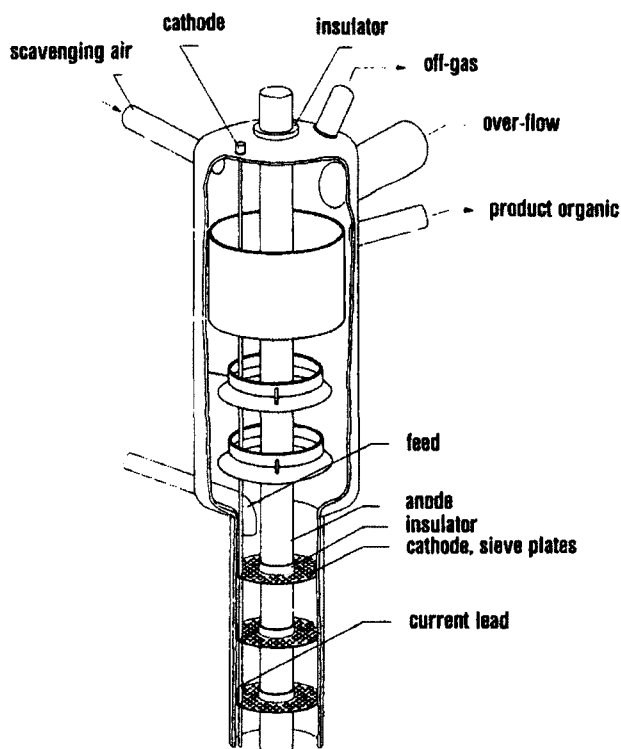


Fig. 4. Electroreduction pulsed column (ELKE).²⁰⁾

Hg-pool electrode has difficulty in the optimisation of the stirring condition and the Hg in the Hg-pool electrode is readily oxidised, the glassy carbon fibre electrode has been developed in order to avoid these disadvantages of this Hg-pool electrode. In this configuration, the glassy carbon fibre is principally used as a working electrode for the prompt determination (within 10 s) of the U concentration in the test samples due to its large exposure area.

The cell configuration for glassy carbon fibre flow

coulometry²⁰⁾ is illustrated in Fig. 3. The working electrode is a bundle of glassy carbon fibre (about 10 μm average diameter), packed in a porous vycor glass cylinder (Corning Co., Ltd.), which is working as an electrolytic diaphragm. The solution flowing through the column electrode is electrolysed at the glass fibre working electrode with a Pt counter electrode, which is placed outside of the porous vycor glass tube. Sometimes a multi-step flow coulometry system²¹⁾ is used for the determination of various ion concentrations at a time with the connection of several column flow cells in a series.

The final type is specially designed for a large-scale reduction system. It was first developed to reduce UO_2^{2+} ions to U^{4+} ions for the purpose of the separation of Pu from the spent nuclear fuel. The diagram in Fig. 4 demonstrates a pilot plant for the reduction of UO_2^{2+} ions to U^{4+} ions.²²⁾ A feature of this system is that no diaphragms are used to separate catholyte and anolyte, since re-oxidation of U^{4+} ions can be sufficiently suppressed by an appropriate anode design alone. On an engineering scale, the applied potential should be high enough to gain the desired reduction reaction rate. In addition, the generated electrode gas should be separated from the liquid phase by means of metal sheets in the top decanter and it should be diluted with air.

2.3 Effects of adsorbed hydrogen atoms on the reduction of UO_2^{2+} ions

It is accepted that the reduction of UO_2^{2+} ions proceeds at an Hg electrode in an acidic medium through the following two steps^{6,7,16)}: First, UO_2^{2+} ions is reduced to UO_2^+ ions ($\text{UO}_2^{2+} + e \rightarrow \text{UO}_2^+$; $E^0 = 0.063 \text{ V}_{\text{SHE}}$), and then the unstable UO_2^+ ions are immediately disproportionated into U^{4+} ions and UO_2^{2+} ions. On the assumption that the electrochemical mechanism does not change with the electrode materials, it was expected that the reduction of UO_2^{2+} ions may occur at a Pt electrode in a similar way to an Hg electrode.^{11,12)}

However, it was revealed that some experimental findings could not be satisfactorily explained by this reduction mechanism; the reduction of the UO_2^{2+} ions shifted toward anodic potentials when the Pt electrode was hydrogenated.²³⁾ Moreover, the reduction of UO_2^{2+} ions was observed to depend upon the hydrogen overpotential of the electrode materials as shown in Fig. 5.²⁴⁾ In this respect, it is noted that Zanella et al.²³⁾ mentioned the assistant role of hydrogen in reducing UO_2^{2+} ions into U^{4+} ions regarding these phenomena. They expected that the adsorbed hydrogen atoms may play some helpful role in the reduction of UO_2^{2+} ions.

Recently, Yeon and Pyun²⁴⁾ investigated the role of adsorbed hydrogen atoms in the reduction of the UO_2^{2+} ions on a Pt surface. They suggested that there exists another pathway for the reduction of UO_2^{2+} ions to U^{4+} ions in addition to the conventional reduction pathway; UO_2^{2+} ions can be reduced to U^{4+} ions not only by the electron transferred from a Pt electrode (direct reduction of UO_2^{2+} ions), but also by hydrogen atoms adsorbed on the electrode (indirect reduction of UO_2^{2+} ions).

Since the adsorbed hydrogen atoms generate during the

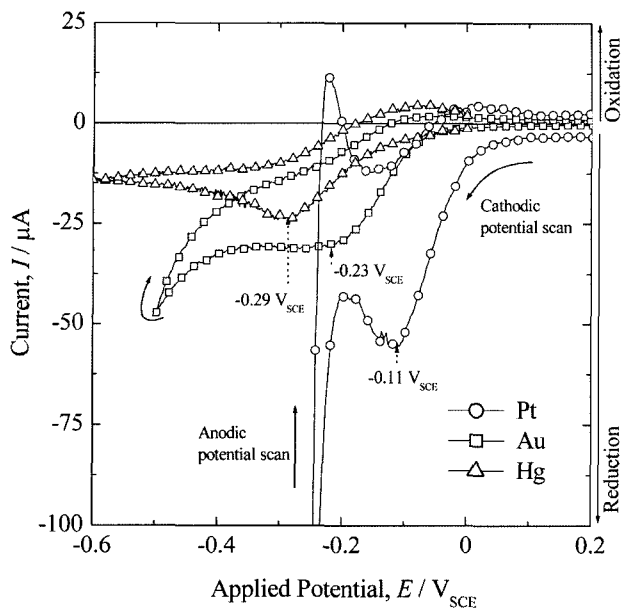


Fig. 5. Cyclic voltammograms for $4.3 \times 10^{-3} \text{M UO}_2^{2+}$ at Pt (O), Au (\square) and Hg (\triangle) electrodes with a scan rate of 100 mV s^{-1} in a 1.0 M HClO_4 Solution.²⁴⁾ The areas of Pt, Au and Hg electrodes were 0.07 , 0.07 and 0.015 cm^2 , respectively.

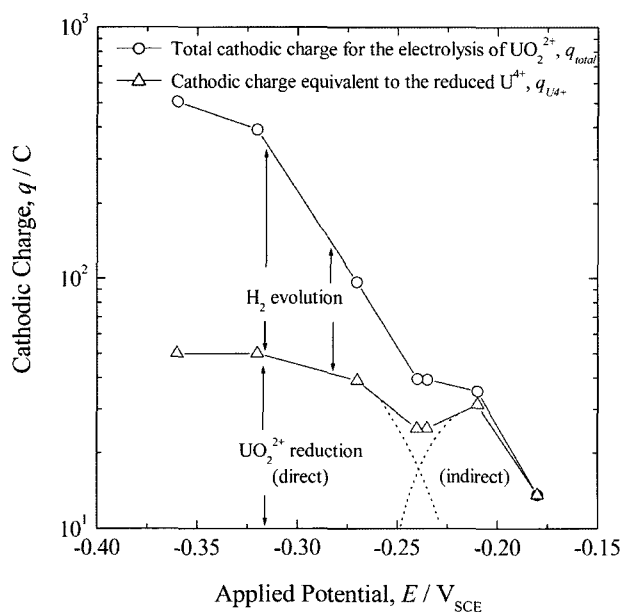


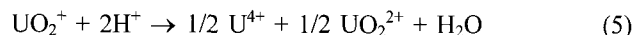
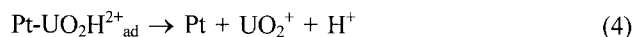
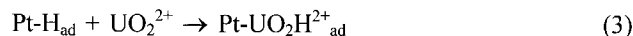
Fig. 6. Plots of the total cathodic charge for the electrolysis of UO_2^{2+} ion (O), q_{total} , and that cathodic charge equivalent to the reduced U^{4+} ion (\triangle), $q_{\text{U}^{4+}}$, against the applied potential E . Reduction of UO_2^{2+} ion was carried out by the chronoamperometric method, and the reduced U^{4+} ion was determined by UV/VIS absorption spectrometric analysis; UO_2^{2+} concentration, 0.02 M ; Pt electrode area, 32.7 cm^2 ; electrolyte, 1.0 M HClO_4 ; electrolysis time, 900 s .²⁴⁾

hydrogen evolution process, it is important to understand the hydrogen evolution mechanism on a Pt surface in advance.

It is generally known²⁵⁻³¹⁾ that the hydrogen evolution reaction (HER) occurs on a Pt surface by the following two-step fast discharge-slow recombination mechanism:



Because the slow recombination in step 2 is the rate-determining step in the HER, the hydrogen atoms generated in step 1 are considered to be stably adsorbed as a form of Pt-H_{ad} . This adsorbed hydrogen atoms may take part in the reduction of UO_2^{2+} ions as follows:²⁴⁾



The effects of the adsorbed hydrogen atoms on the reduction of UO_2^{2+} ions to U^{4+} ions were experimentally examined by the comparison between the total cathodic charge and the cathodic charge equivalent to the concentration of U^{4+} ions during the constant-potential (chronoamperometric) electrolysis of UO_2^{2+} ions coupled with UV/VIS analysis as shown in Fig. 6. This comparison allowed the discrimination of the indirect reduction from the direct reduction in terms of the applied potential and hence, the transition potential from the indirect reduction to the direct reduction of UO_2^{2+} ions could be experimentally determined.

From the presence of the indirect reduction mechanism, it was possible to clearly explain the reason for that shift of the reduction region of UO_2^{2+} ions toward anodic potentials on a hydrogenated Pt electrode. In addition, the change in the reduction potential range of UO_2^{2+} ions with different electrode materials as shown in Fig. 5 was successfully explained in terms of their hydrogen overpotentials.

3. Methods for Improving Current Efficiency of the Reduction of UO_2^{2+} Ions on a Pt Electrode

3.1 Hydrogenation and anodisation of a Pt electrode

Both hydrogenation and anodisation treatments are mainly used to electrochemically modify the surface of electrodes. Whereas hydrogenation means the application of the cathodic potential to the electrode, anodisation indicates the oxidation of the electrode surface by applying an anodic potential. It is generally accepted that the electrodes modified by these treatments exhibit good current efficiencies of the reduction of UO_2^{2+} ions.

Zanello et al.²³⁾ carried out the reduction of UO_2^{2+} ions on a hydrogenated Pt electrode in various inorganic acidic solutions. With the Pt RDE (rotating disk electrode) and the periodic renewed diffusion-layer electrode,³²⁾ treated in $1 \text{ M H}_2\text{SO}_4$ at the potential of $-2.0 \text{ V}_{\text{SCE}}$, it was observed that the reduction region of UO_2^{2+} ions shifted towards anodic potentials, by about $0.1 \text{ V}_{\text{SCE}}$ (as shown in Fig. 7). In addition, the reduction wave of UO_2^{2+} ions was well shaped after hydrogen evolution for 60 min at the potential of $-3.2 \text{ V}_{\text{SCE}}$, but there was no noticeable improvement after 120 min as shown in Fig. 8.

From the results, they developed the following optimum cathodic treatment condition:²³⁾ Applied cathodic current

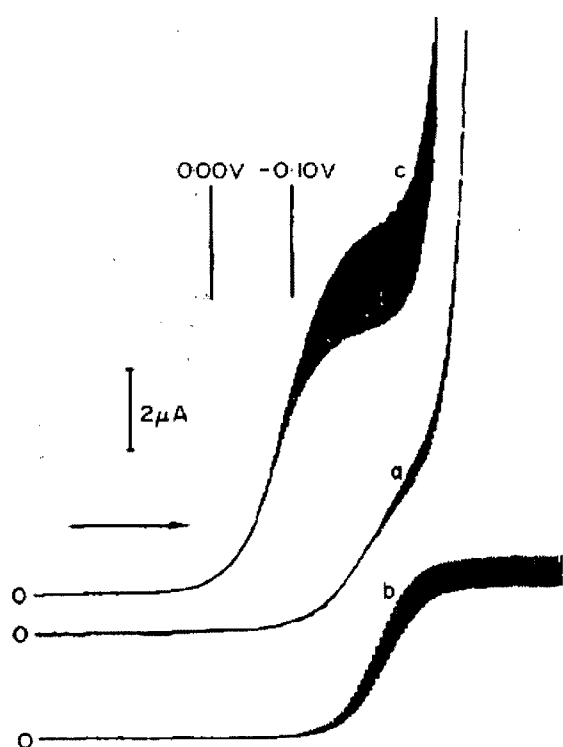


Fig. 7. Voltammograms of 7×10^{-4} M U(VI) after the pretreatment and the subsequent cathodic treatment at -2 V for 1 min (curve c); the same solution polarographed with DME (curve b).²³⁾

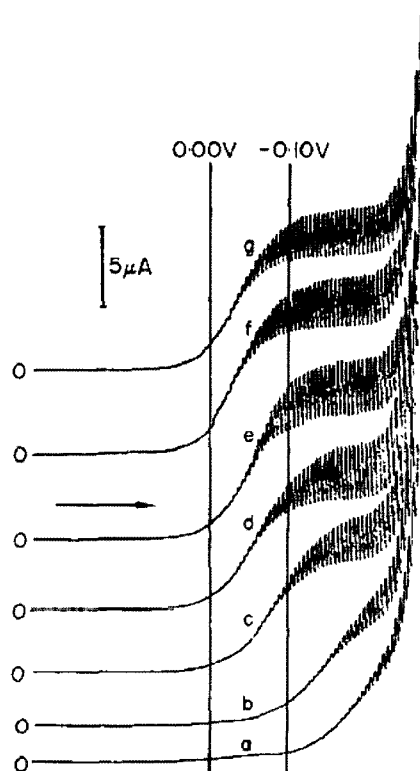


Fig. 8. Voltammograms of 8×10^{-4} M U(VI) in 1 M H_2SO_4 , for increasing duration of cathodic pretreatment: a = 0 min, b = 5 min, e = 15 min, d = 30 min, e = 60 min, f = 120 min, g = 180 min.²³⁾

density of about 7 A cm^{-2} for at least 90 min in a 1 M sulphuric acid deaerated with nitrogen gas. During the voltammetric measurements, it is important to avoid any handling of the solution that may cause the electrode to come into contact with air, because it may lead to the oxidation of adsorbed hydrogen atoms.

In spite of the practical performance of the hydrogenation treatment on the detection of the cathodic wave of UO_2^{2+} ions a Pt surface,²³⁾ it has not been clearly explained how this treatment affects the reduction reaction. However, it was recently proposed²⁴⁾ that hydrogen atoms adsorbed on the electrode surface may take part in the reduction of UO_2^{2+} ions to U^{4+} ions in an acidic solution. In this regard, it is reasonable to think that the hydrogenation treatment puts in a remarkable performance on the reduction of UO_2^{2+} ions by generating adsorbed hydrogen atoms. Something of this sort was found for the reduction of VO^{2+} ions to V^{3+} ions³³⁾.

Burke et al.³⁴⁾ found that the reduction performance of Pt was enhanced by the anodisation treatment in aqueous acidic media. It was reported^{35,36)} that the nature of a Pt oxide film was changed by the anodisation treatment in a 1 M sulphuric acid solution. It was revealed that this anodisation treatment changed the Pt surface film with multilayered oxide phase to the porous type film.³⁵⁻³⁷⁾ This porous layer temporarily exhibited the enhanced catalytic activity due to the increased surface area.^{38,39)}

Gopinath et al.⁴⁰⁾ developed a two-step anodisation treatment for the improvement of the reduction performance of Pt: A Pt electrode was first chemically treated in a hot concentrated sulphuric acid solution saturated with $\text{K}_2\text{Cr}_2\text{O}_7$ for 10 min. After that, the electrochemical anodisation as carried out in a 1 M sulphuric acid solution with an applied potential of $-0.15 \text{ V}_{\text{SCE}}$. It was reported that this treatment considerably shortened the reduction time of UO_2^{2+} ions by increasing the reaction area.

Since Pt is oxidised at potentials higher than $1.2 \text{ V}_{\text{SCE}}$, the surface oxide film readily begins to grow on a Pt surface at the anodisation potentials higher than $1.2 \text{ V}_{\text{SCE}}$. However, the reduction of the UO_2^{2+} ions was hardly affected by this anodisation treatment at the anodisation potentials lower than $1.5 \text{ V}_{\text{SCE}}$, even after many anodic and cathodic (A-C) cycles as shown in Fig. 9.⁴⁰⁾ On the other hand, the reduction of UO_2^{2+} ions substantially enhanced at the anodisation potential of $1.6 \text{ V}_{\text{SCE}}$ even after three A-C cycles.

3.2 Effects of catalyst poisons on the reduction of the UO_2^{2+} ions

The reduction of UO_2^{2+} ions may occur, concurrent with hydrogen evolution on a Pt electrode due to its low hydrogen overpotential. This may cause an inaccurate result in the reduction of the UO_2^{2+} ions to U^{4+} ions when using the coulometric method.

Catalyst poisons, in general, have been used to suppress the hydrogen evolution reaction during the reduction of UO_2^{2+} ions on a Pt electrode. As catalyst poisons and other ions control the hydrogen evolution due to their adsorption interactions with hydrogen atoms adsorbed on a Pt surface,

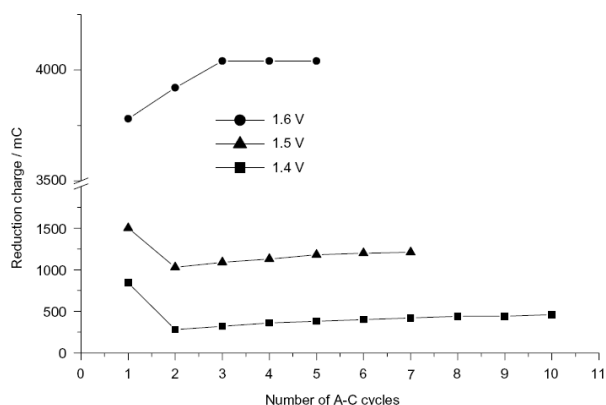


Fig. 9. Amount of reduction charge in the last cathodisation cycle versus the respective number of potentiostatic anodic and cathodic (A-C) cycles.⁴⁰⁾ The Pt wire gauze electrode was anodised in 1 M H₂SO₄ at controlled preselected potential for a period of 15 min and cathodised at a controlled voltage of -0.150 V vs SCE to the background current of 25 μ A. Potentiostatic A-C cycles were performed successively in same electrolyte.

the adsorbed hydrogen atoms should be taken into consideration during the investigation of the roles of poisons and other ions in the reduction of the UO₂²⁺ ions.

In this regard, it was recently proposed²⁴⁾ that hydrogen atoms adsorbed on the Pt electrode surface may reduce UO₂²⁺ ions to U⁴⁺ ions in an acidic solution. Thus, for the optimal reduction condition of UO₂²⁺ ions, catalyst poisons should ensure the presence of sufficient adsorbed hydrogen atoms by retarding the recombination step of adsorbed hydrogen atoms. There are many catalyst poisons that simply suppress hydrogen evolution by the full coverage of the electrode surface.^{41,42)} However, it is hard to find catalyst poisons for this purpose.

A similar case can be easily found on the hydrogen permeation into metals,^{43,44)} which has been investigated intensively in the degradation area of various structural metals (e.g. hydrogen embrittlement cracking).⁴⁵⁻⁴⁷⁾ One part of the adsorbed hydrogen atoms can permeate into metals, and the other part can turn into molecular hydrogen. Therefore hydrogen permeation may be inhibited if the poison atoms fully adsorb on the metal surface, whereas the permeation may be promoted if the poison atoms partially adsorb on the surface to the extent of retarding the recombination step. For this reason, the presence of catalyst poisons in electrolytes can have effects either of promotion or inhibition of hydrogen permeation into metals, depending upon the adsorption behaviour of the poisons, e.g. arsenic, sulfur species, amines and heavy metals.^{11,43)}

The results^{48,49)} on the electro-deposition of metal ions in very dilute solutions indicated that the deposition of sub-monatomic layers of metals on Pt and other inert metal cathodes can occur at potentials appreciably more positive than those predicted by the Nernst equation applicable to an electrode fully covered with the metal being deposited. Therefore some different results may be obtained when one is only expecting the electrode reactions with the known electrode potentials for reduction of metal ions. Thus, the metal ions,

which are deposited on a Pt surface at potentials more negative than needed for the reduction of UO₂²⁺ ions, may give an influence on the reduction of UO₂²⁺ ions as poisons.

From the studies on metal ion poisons,¹¹⁾ it was reported that both bismuth ions (Bi³⁺) and copper (Cu) ions appeared to be effective additives to improve the performance of a Pt electrode in the reduction of the UO₂²⁺ ions. Moreover, Bi³⁺ ions exhibit better performance in the reduction of the UO₂²⁺ ions, compared to Cu ions due to the absence of interfering oxidation states. Accordingly, the reduction of UO₂²⁺ ions could proceed on the Pt working electrode at appreciably less negative potentials in the presence of Bi³⁺ ions.

It is worth mentioning that Bi³⁺ ions would not have the same effects on the reduction of UO₂²⁺ ions in chloride-free perchloric, nitric or sulphuric acid base electrolytes. Macro-amounts of Bi metal would deposit electrochemically in these base electrolytes at more positive potentials. This deposited Bi metal may interfere with the UO₂²⁺ ion reduction. The usefulness of Bi³⁺ ions as a poison in hydrochloric acid base electrolytes depended upon the complexation of the Bi³⁺ ions with chloride ions. This complexation shifted the potential at which macro-amounts of Bi deposit, to more negative values.

Since all metallic and non-metallic ions including catalyst poisons and impurities may adsorb on a Pt surface, it is important to evaluate their interference effects on the reduction of UO₂²⁺ ions. The acceptable maximum concentrations of the foreign ions are listed for the quantitative determination of U concentration in Table 1²³⁾.

3.3 Electro-deposition of thin Hg film on a Pt surface

Pt has an excellent advantage in producing hydrogen gas, because of its low hydrogen overpotential. Nevertheless, the low overpotential of Pt in acidic media becomes an obstacle

Table 1. Concentration tolerance of diverse ions on the determination of U (VI)²³⁾

Cation	Tolerance Limit (mg)	Anion	Tolerance Limit (mg)
Aluminum	100	Acetate	100
Bismuth	0.2	Arsenate	70
Cadmium	30	Borate	70
Calcium	100	Chloride	0.1
Cerium(IV)*	6	Fluoride	20
Chromium(III)	50	Molybdata	0.1
Cobalt(II)	50	Nitrate	100
Copper(II)	0.1	Perchlorate	100
Iron(III)	3	Phosphate	100
Magnesium	100	Vanadate	5
Manganese(II)	100		
Nickel	50		
Silver	5		
Titanium(IV)	10		
Thorium	100		
Zirconium	100		

Initial solution: volume 40 ml, UO₂²⁺ 50 μ g/ml, 1 M H₂SO₄

*E_{1/2} for reduction wave of Ce (IV) \approx + 1.1V.

†E_{1/2} for reduction wave of Fe (III) \approx + 0.04V.

‡Only on prehydrogenated electrode.

§E_{1/2} for reduction wave of V (V) \approx + 0.07V.

to examine the reduction of UO_2^{2+} ions with high current efficiency. In most cases, the potential range for the reduction of UO_2^{2+} ions and that range for the reduction of protons partially overlap with each other. To avoid this overlap by suppressing hydrogen evolution, Pt electrode, coated with Hg with high hydrogen overpotential has been developed. This is the so called Pt-based thin Hg film electrode (TMFE). By employing this electrode, the disadvantages of Hg and Pt electrodes on the reduction the UO_2^{2+} ions were overcome to some extent.⁵⁰⁻⁵²⁾

Three major methods have been developed to coat Hg films on a Pt electrode.⁵⁰⁾ First, Pt is plated with Au used as an amalgam-forming metal, and then covered with Hg.⁵³⁾ Second, Pt is covered with Hg by abrading the Pt surface.⁵⁰⁾ Finally, Hg is electrochemically plated on a Pt surface in an acidic Hg nitrate solution.⁵⁴⁻⁵⁷⁾

Furuya et al.⁵⁸⁻⁶⁰⁾ investigated the hydrogen evolution reaction on Pt-deposited on Au and Cu. In these studies, it was concluded that, when a monolayer Pt is deposited on other metal surfaces, the hydrogen evolution reaction at this sur-

face is just the same in nature as that reaction at the pure Pt. On the other hand, at the surface of thin Hg film-deposited Pt,⁶¹⁾ the potential range for the hydrogen evolution was quite different from that range observed on pure Hg, even when the amount of Hg deposited on Pt was sufficiently large.

Hartley et al.⁵¹⁾ measured the hydrogen overpotential characteristics of Hg film-deposited Pt and pure Pt electrodes, which are shown in Fig. 10. A chemical interaction between Pt and Hg was evident in current-potential behaviour of such electrodes in various stages of preparation.^{54,55)} In addition, Hassan et al.⁶²⁾ investigated the electrochemical performance of a Pt-based thin Hg film electrode (TMFE) with a different amount of deposited Hg; as the amount of deposited Hg increased, the hydrogen overpotential of an Hg-coated Pt electrode shifted in the cathodic direction as shown in Fig. 11.⁶³⁾ There was little change in current and profile for the reduction of UO_2^{2+} ions in a Pt RDE, coated with the Hg films thicker than $50 \mu\text{m}$. The electrode of TMFE exhibited a very low background current, as compared to a Pt electrode. In addition, the potential region for the reduction of UO_2^{2+} ions was clearly observed on TMFE.

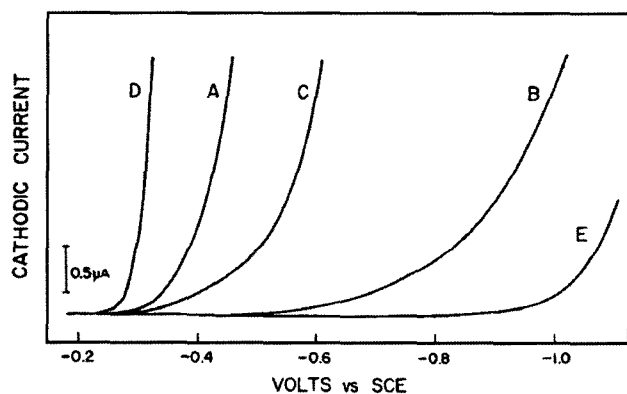


Fig. 10. Hydrogen overpotential characteristics of Hg film and Pt electrodes.⁵¹⁾ (A), bright Pt; (B), $1.3 \mu\text{m}$ Hg film on Pt; (C), film electrode anodically stripped of free Hg; (D), film electrode after anodic removal of free Hg plus interaction compound; (E), hanging Hg drop electrode. Sweep rate: 0.01 Vs^{-1} , de-aerated 0.1 M HClO_4 .

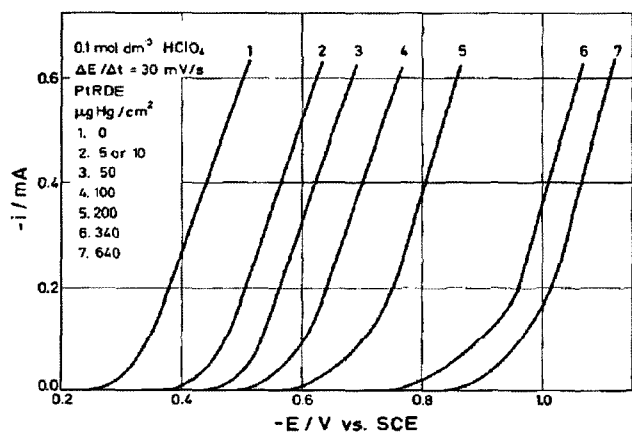


Fig. 11. Current-potential curves for the hydrogen evolution reaction in $0.1 \text{ mol dm}^{-3} \text{ HClO}_4$ at a Pt RDE with different amounts of Hg deposited; scan rate: 30 mVs^{-1} .

4. Concluding Remarks

This review article provided an overview of the electrochemical reduction of uranyl (UO_2^{2+}) ions on a platinum (Pt) electrode with emphasis of the improvement in its current efficiency. First, this article briefly presented the fundamentals of the reduction of UO_2^{2+} ions on a Pt surface. The electrochemical behaviour of uranium species and electrochemical cell configurations for the reduction of UO_2^{2+} ions were described in a comprehensive way. The effects of adsorbed hydrogen atoms were also described on the reduction of UO_2^{2+} ions.

Finally, this article introduced three different kinds of methods for improving current efficiency of the reduction of UO_2^{2+} ions on a Pt surface. Namely, they were electrochemical surface treatments of a Pt electrode involving hydrogenation and anodisation, use of catalyst poisons, and formation of thin mercury film on a Pt electrode. It was proposed that the hydrogenation treatment and catalyst poisons put in a remarkable performance on the reduction of UO_2^{2+} ions by generating adsorbed hydrogen atoms and by retarding the recombination step of adsorbed hydrogen atoms, respectively.

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