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Author(s)	MITUYA, Atusi; ŌBAYASHI, Takeko
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THE BEHAVIOR OF PLATINUM ELECTRODES

Part 1.

Disintegration of the Platinum Anode in Acid Solution

By

Atusi MITUYA and Takeko ŌBAYASHI*)

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I. Introduction

Platinum metal has little ionization tendency. HORIUTI and MITUYA¹⁾, and HORIUTI, KEII and MITUYA²⁾ showed by a theoretical calculation that practically platinum never dissolves into an acid solution from a platinum anode which is kept at the reversible hydrogen electrode potential. On the basis of this conclusion, one of the authors³⁾ designed a vacuum cell for observing the hydrogen electrode process on a mercury cathode under complete exclusion of oxygen, in which the platinum anode was placed over the mercury cathode in the same cell.

FRUMKIN objected this experiment on the ground of supposed disintegration of platinum anode which might result in the contamination of the mercury cathode. A constant progress of contamination has, however, been disproved by the strict reproducibility of observed current—voltage relation repeatedly observed with one and the same cell³⁾.

FRUMKIN⁴⁾ has objected now the above work³⁾ stating that "It is easy to imagine conditions under which platinum will contaminate the solution during the initial periods of contact with it, although the contaminating action will stop later, for instance if we assume that the contamination is caused by the dissolution in acid of the thin oxide layer always existing on the surface of platinum which has been exposed to air for a long time".

If this statement presents itself as a truth, such procedures as pre-electrolysis of the solution, pre-electrolytic purification of the electrodes, and aging of the electrodes, all of which are appreciated

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*) A. M. and T. O.: Department of Chemistry, St. Paul's University (Rikkyo Daigaku), Tokyo.

by many workers[5,6,7], must necessarily be questioned. It is thus doubtful what might have been achieved by the pre-electrolysis of the solution, if platinum metal would have easily contaminated the solution during contact with it.

It is shown as detailed below that the solution in contact with platinum is not at all contaminated except when it is anodically polarized to a certain extent under atomosphere.

II. Experimental

(1) Method of detection of disintegration of platinum and determination of the product of disintegration.

Disks of blank platinum of 99.99% purity as guaranteed by Tanaka Precious Metal Work Co. were bombarded with neutrons in the atomic reactor (J.R.R.-1). One of the disks thus treated and two other untreated platinized platinum disks were carefully worked out to make

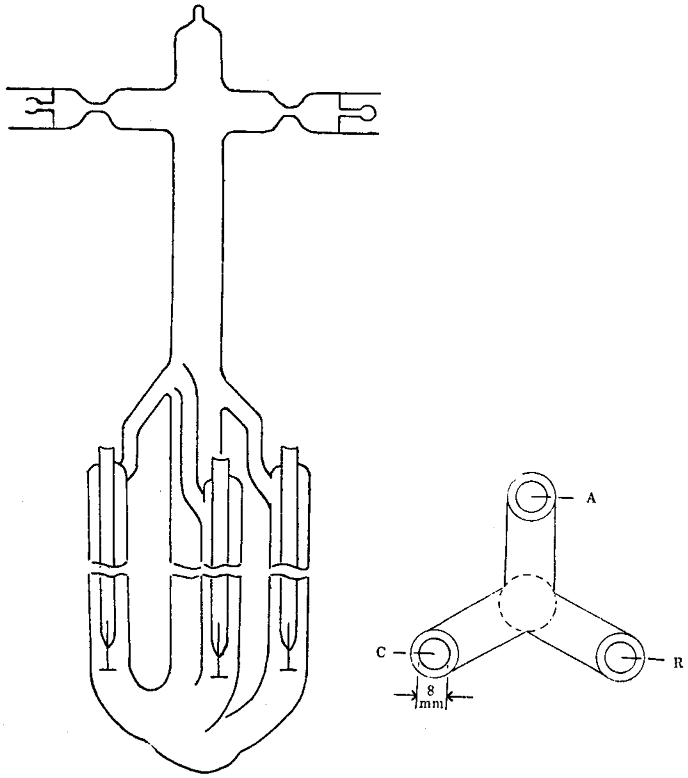

Fig. 1. Electrolytic cell.

an electrolytic cell, as shown in Fig. 1; these three disks were now immersed in purified 0.1N–HCl, and then the activated one was anodically polarized against one of the other two disks under atomosphere. After a recorded time the whole solution was concentrated to 1 c.c., and introduced in the well of a scintillation spectrometer provided with a single channel pulse height analyser, to examine the radioactivity of the solution. The γ-ray spectrograms were also recorded at appropriate times to determine the half-life, so that the product of disintegration of the anode in the solution could be identified by the half life and the energy.

(2) **Preparation of the electrodes.**

Activeted electrode A and two platinized electrodes C and R were treated as follows. Platinized platinum electrodes C and R were electrolytically purified as below, after being platinized, by electrolysis for 30 hours in 0.1N–H_2SO_4 and in 0.1N–HCl both of which had been prepared as described in (3). A current around 100 mA was allowed to pass between C and R first in 0.1N–H_2SO_4 for 30 hrs., the direction being automatically alternated every 30 seconds. These electrodes had now been carefully washed with tri-distilled water and 0.1N–HCl several times, and then subjected to the second electrolysis in 0.1N–HCl in the same manner as the first, except that the total current was kept under 2 mA. After these electrolysis any potential differences could scarcely be found between C and R in 0.1N–H_2SO_4, in 0.1N–HCl, or in tri-distilled water under atomosphere.

The platinum disks to be used as the test electrodes were sealed in a polyethylene sack after being washed, in turn with 5% NaOH alcoholic solution, tri-distilled water, 6N–HNO_3, and tri-distilled water, and were irradiated with neutrons in the atomic reactor JRR-1 of the Japan Atomic Power Research Laboratory. The conditions of the irradiation were as follows:

Reactor output power	40 KW,
Neutron flux	5.1×10^{11} n/cm^2 sec,
Dose rate of the sample	250 mr/hr : at the surface, 1.5 mr/hr : at distance of 1 m.

(3) **Preparation of 0.1N–H_2SO_4 and 0.1N–HCl.**

a) 95% sulphuric acid of analytical grade was distilled under high vacuum without boiling. It was then diluted with tri-distilled water to make $0.1N\text{-}H_2SO_4$ and kept in a polyethylene bottle as a stock.

b) 95% sulphuric acid was added drop by drop to the concentrated hydrochloric acid, both of analytical grade, keeping the latter at 50 C. The evolved HCl-gas was introduced into a glass vessel where it was absorbed in tri-distilled water. The HCl solution obtained was distilled three times successively under atmosphere, and the distillate of about 6N–HCl was stocked in a polyethylene bottle. The 6N-stock was diluted to 0.1N with tri-distilled water and was electrolyzed in a polyethylene bottle provided with two platinum electrodes for purification. The terminal voltage in the electrolysis was 0.2 V and the electrolysis was continued for 70 hrs. The solution was then distilled under high vacuum without boiling and introduced into the electrolytic cell.

(4) Instrumentation.

The instrument used for the analysis was a model 516 scintillation spectrometer provided with a single channel pulse height analyser made by Baird-Atomic Inc. The potential differences between the electrodes were measured and recorded by a vibrating reed electrometer with a recorder, with a sensitivity of 0.1mV/div made by The Takeda Riken Industrial Corporation.

(5) Result.

The test anode was exposed to three-stage anodic treatments in the atmosphere, as listed in Table 1.

TABLE 1. Conditions at the Anodic Treatments of the Platinum Electrode.

Stage	Applied Potential between A–C	Anodic Polarization against R	Time of Duration of Electrolysis	Electrolyte Solution	Mark
1st	0.200 V	0 mV	40 hrs	0.1N–HCl	A
2nd	0.600 V	24 mV	70 hrs	0.1N–HCl	B
3rd	1.200 V	50 mV	70 hrs	0.1N–HCl	C

The analyses of γ-ray spectra were made against the concentrated electrolyte solutions (1 : 30) marked A, B, C of Table 1 and against the platinum cathode. In Figs. 2 and 3, the γ-ray spectrum of ^{137}Cs and of ^{198}Au are shown as standards. These figures agree closely with published data, for example, those listed in the Scintillation Spectrometry Gamma-

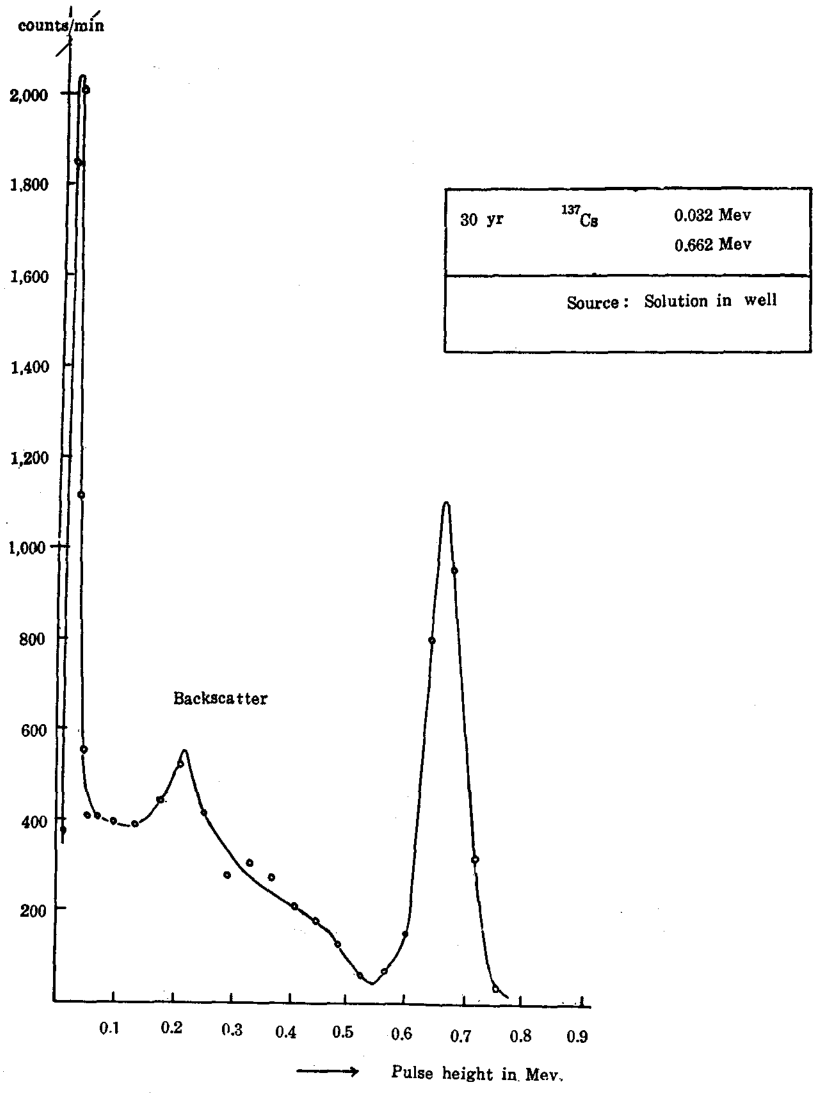

Fig. 2. γ-ray spectrum of ^{137}Cs.

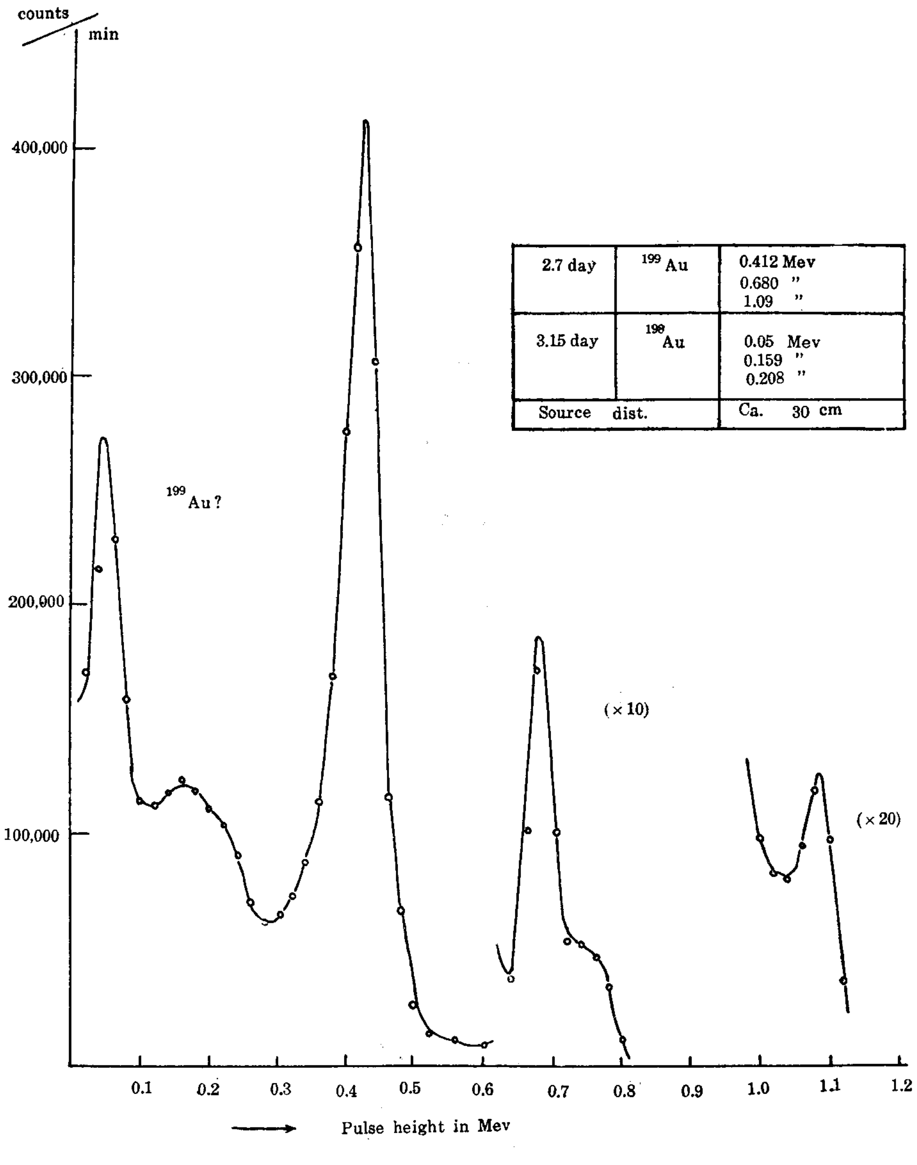

Fig. 3. γ-ray spectrum of ^{198}Au.

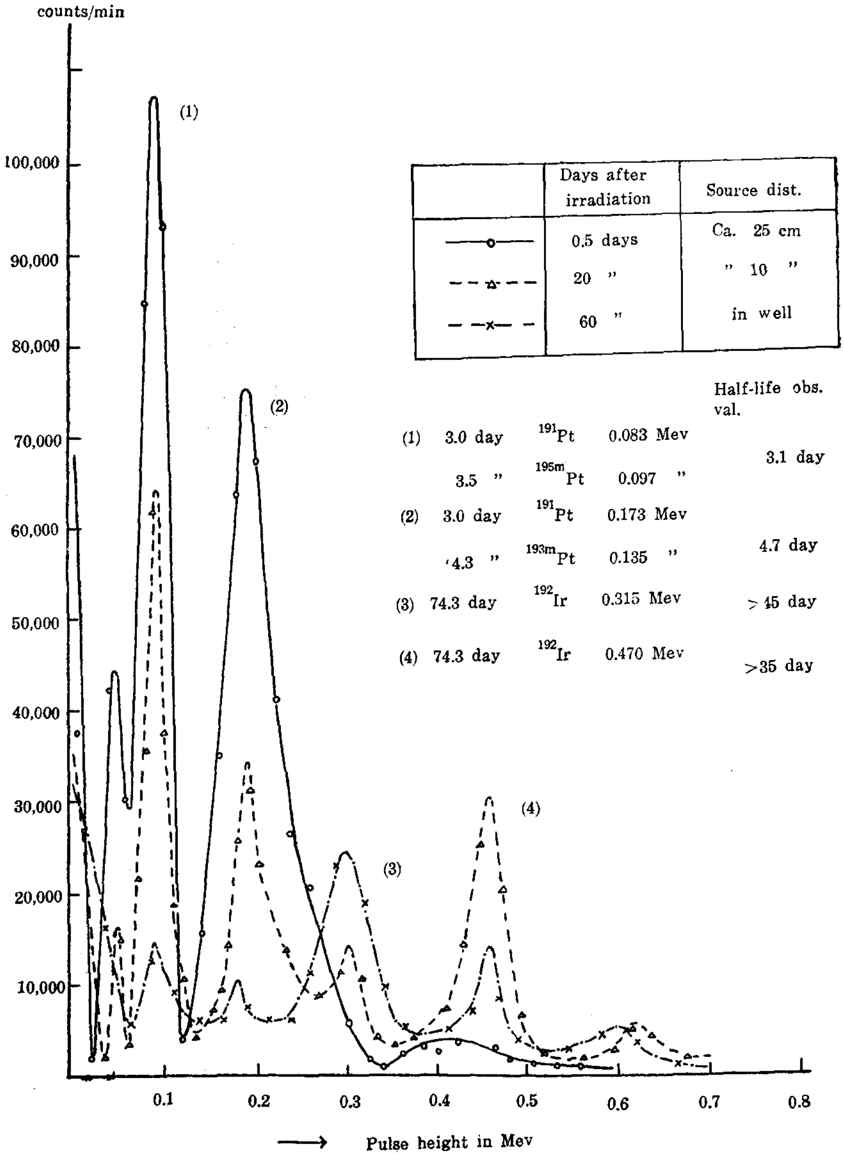

Fig. 4. γ-ray spectra of the Pt-specimen.

Ray Spectrum Catalogue by R. L. Heath*). Fig. 4 shows the γ-ray spectra of an irradiated platinum disk at different times. From these spectral data and the observed half-lives, the atomic species corresponding to the peaks of the spectra can be either determined or inferred. Fig. 5 shows the γ-ray spectra of the electrolyte solutions A, B and C in Table and of the platinum cathode D.

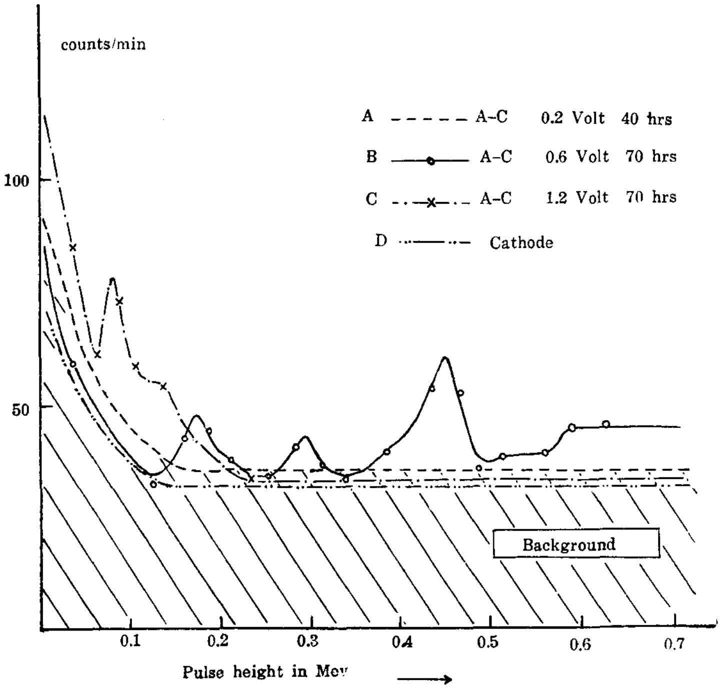

Fig. 5. γ-ray spectra of the solutions and the cathode.

III. Conclusion and Discussion

The 0.1N-HCl did not show any trace of γ-ray irradiation after the 1st stage electrolysis, i.e. no appreciable disintegration or dissolution of the platinum anode occurred (cf. mark A of Fig. 5).

But when the anode was polarized against the reference electrode about +24 mV, the 0.1N-HCl solution showed a γ-ray spectrum of mark B approximately reproducing the peaks of impurities in the platinum metal as seen from Fig. 4.

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When the anodic polarization was further increased to about +50 mV, the γ-ray spectra of the solution showed the existence of platinum in the solution, but not of impurities at all (cf. mark C).

The platinum cathode did not show any trace of γ-irradiation even after the 180 hrs. electrolysis summing up all three stages.

It may be concluded from the above experimental results as follows:

1. Platinum metal as well as its impurities does not disintegrate or dissolved in 0.1N–HCl solution if electrolyzed anodically without polarization.
2. When platinum electrode was anodically polarized by 24 mV, impurities near or at the surface of the platinum go into the solution.
3. The surface layer of the electrode deprived preliminarily of impurities does disintegrate or dissolve at 50 mV anodic polarization.

It follows that no platinum contamination had occurred in the previous work[3], that the disintegration of platinum can occur but not through the new mechanism of FRUMKIN and that it is irrelevant to introduce electrolyte solution after the pre-electrolysis into the cell without redistillation.

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