

## ISOTOPIC DISTRIBUTIONS OF HEAVY METAL ELEMENTS PRODUCED DURING THE LIGHT WATER ELECTROLYSIS ON GOLD ELECTRODE

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### ABSTRACT

Some 100  $\mu\text{g}$  of fine black porous deposits comprised mainly of Au, Hg, Pt, Fe, Si and F were obtained during the cathodic electrolysis on Au electrodes in 0.5 M  $\text{Na}_2\text{SO}_4$  and  $\text{Na}_2\text{CO}_3$  light water solutions for 20-30 days at a current densities  $> 300 \text{ mA/cm}^2$ . The isotopic distributions of these elements other than Au, Pt and F as determined by SIMS analysis were found to deviate from their natural isotopic abundance. The structure of Au electrode surface after the electrolysis revealed very unusual aspects.

### INTRODUCTION

We have observed the production of some 10  $\mu\text{g}$  of Fe with an unusual isotopic abundance ( $^{57}\text{Fe}$ : 14.5 - 25%) on/in Au electrode during the cathodic electrolysis for 7 days at a current density of  $100 \text{ mA/cm}^2$  [1]. More recently, it was found that when the current density was increased up to  $200 - 300 \text{ mA/cm}^2$ , some 100  $\mu\text{g}$  of fine black porous powders were deposited at the bottom of the electrolytic cell from the Au electrode, the main constituting elements of the deposits were Hg, Pt, Fe, Si and F other than Au and, in addition, a small amount of Os was detected in some cases. The isotopic distributions of Hg, Fe and Si contained in the deposits were evidently different from their natural values. This fact suggests strongly the occurrence of some nuclear transmutation reactions. In this report we will describe the experimental procedures and results, and propose some possible reaction schemes.

### EXPERIMENTAL

The electrolytic cell used was made of fused quartz. The working electrodes were cold worked Au plates (about  $2.0 \text{ cm}^2$  in area; 0.1 mm thick; 99.99% purity; Ag: 21 ppm; Pd: 3 ppm; Cu: 1 ppm; Fe, Si, Rh, Pt:  $< 1$  ppm; no detectable Hg, Os and Zn), whose surfaces were scraped with a cleaned glass fragment to make the strained surface. The roughness factor of the electrode determined from the double layer capacitance [2] was around 2.0. The counter electrode was a  $1 \times 7 \text{ cm}$ , 80 mesh Pt net (99.98% purity; Rh: 18 ppm; Pd, Cr, Si: 2 ppm; no detectable Hg, Os and Zn). The electrolytes used were  $\text{Na}_2\text{SO}_4$  and  $\text{Na}_2\text{CO}_3$  from Merck (supra-pure grade; Fe, Zn  $< 0.01$  ppm; no detectable Si, Hg, Os and F for  $\text{Na}_2\text{SO}_4$ ; Si  $< 0.5$  ppm; Fe, Hg  $< 0.05$  ppm; Zn  $< 0.01$  ppm; no detectable Os and F for  $\text{Na}_2\text{CO}_3$ ). The volume of the electrolyte solution used was 100 ml and the concentration was adjusted at 0.5 M. The electrolysis was carried out galvanostatically for 20 - 30 days at a constant current ranging from 1 to 3 A. Before the electrolysis, the working electrode was kept at RHE potential by passage of  $\text{H}_2$  gas into the cell. During electrolysis, Milli Q water was supplied every 24 hours to maintain the total solution amount constant. The deposits obtained were washed with Milli Q water and placed on Ni or Zr plates and the constituent elements of the deposits were analyzed by means of SIMS, AES and EDX. The AES measurement was made with use of an ANEL VA ASS-200 Auger electron spectrometer with 3.0 KeV of beam energy and 2.5  $\text{\AA}$  of filament current. The EDX measurement was conducted with use of an EG &

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GORTEC EEDS-II. The SIMS measurement was carried out with use of a HITACHI IMA-3 ion micro analyzer by  $O_2^+$  ion irradiation (100 nA primary ion current, 12 KeV accelerating voltage) from Hitachi Instruments Engineering Company, Ltd.

## RESULTS AND DISCUSSION

### ANALYSIS OF THE DEPOSITS

Fig. 1 shows the pictures of the deposits placed on a Ni substrate and their SEM image. The deposits are very porous with a lot of fine pores of nm order, and look like pumices. As a typical example, the relative concentrations of the constituent elements of the deposits and electrodes before and after the electrolysis with mass numbers ranging from 1 to 200 estimated from the analysis of SIMS spectra (1st scan) are shown in Fig. 2 (a-d). In this case, the electrolysis was performed in  $Na_2CO_3$  solution for 30 days at a current density of 500  $mA/cm^2$ . We can see from this figure that the major component is Au, besides that, considerable amounts of Hg, Pt, Fe, Si, and F are contained in the deposits and on/in the electrode after electrolysis. In addition, Zn also looks to be present, however the SIMS spectra in that region are possible to be overlapping with  $TiO_2^+$ ,  $SO_2^+$  and  $TiF^+$  so that the quantitative estimation of Zn would be difficult. The considerable amount of C detected here is probably due to some contamination. From the comparison of these results, it is clear that the contents of Hg, Pt, Fe, and F are much higher in the case of the deposits or of the electrode after electrolysis than in the case of the electrode before electrolysis and, especially, the contents of Hg, Pt, and F are much higher in the deposits.

The presence of Hg and Pt was also confirmed by AES and EDX measurements. Fig. 3 and Fig. 4 show AES and EDX spectra of the deposits, respectively. EDX spectra shown here was those of the deposits obtained by the electrolysis in  $Na_2CO_3$  for 20 days at a current density of 800  $mA/cm^2$ . In AES spectra, both Hg and Pt signals are detected in the vicinity of the surface. Inspection of the EDX spectrum of the deposits, on the other hand, we can see only Au signals with Pt shoulders (the widths were a little expanded). However, when subtracting the spectrum of pure Au from the spectrum of the deposits, two pairs of Hg and Pt signals appear in the energy ranges from 9 to 10 and from 11 to 12 keV. The fact that the major constituent element of the deposits is Au suggests strongly that the deposits were produced at Au electrode during the electrolysis.

### ISOTOPIC ABUNDANCE

The isotopic distributions of Hg contained in the deposits and on/in the electrode after electrolysis and the isotopic distributions of Fe, and Si contained in the deposits obtained by SIMS analysis are shown in Fig. 5, Fig. 6, Fig. 7, Fig. 8 from 1st to 15th scans. The data of Fe and Hg on/in the electrode were obtained by the electrolysis in  $Na_2CO_3$  at a current density of 500  $mA/cm^2$  and the datum of Hg in the deposits was obtained in  $Na_2CO_3$  at a current density of 800  $mA/cm^2$ . The datum of Si was obtained by the electrolysis in  $Na_2SO_4$  at a current density of 800  $mA/cm^2$ . The isotopic distributions of these elements reveal significant deviation from their natural isotopic abundance. Thus, for Hg, Fig. 5 and Fig. 6, the isotopic content of  $^{200}Hg$  is 35 - 50%, evidently higher than its natural value of 23.13%, while the content of  $^{202}Hg$ , which being the major component in nature, is reduced from its natural value of 29.80% down to 15-20%. The content of  $^{200}Hg$  has a tendency to increase in the inner part of the deposits or electrode, and the contents of  $^{199}Hg$  and  $^{204}Hg$  in the deposits tend to increase in the surface part. The contents of other isotopes change to some extent. We can see from these results that there is not much difference in the change of the isotopic distribution between Hg in the deposits and on/in the electrode.

For Fe, Fig. 7, the content of  $^{57}Fe$  increases significantly as in the case of Fe produced on Au electrode after electrolysis [1], however, in this case, its ratio ( $^{57}Fe/^{56}Fe$ ) is much higher, exceeding 50% especially in the vicinity of the surface. This ratio has a tendency to decrease in the inner part of the deposits.

The content of Si in the deposits was increased significantly by the electrolysis in  $\text{Na}_2\text{SO}_4$  at a large current density (eg.  $800 \text{ mA/cm}^2$ ), and, in that case, the color of the deposits changes from black to white gray. The signal of Si was clearly observed also by EDX measurement. As seen from Fig. 8, the content of major isotope,  $^{28}\text{Si}$ , in the deposits is decreased down to about 58% from its natural value of 92.2% in the vicinity of the surface. On the contrary, the contents of  $^{29}\text{Si}$  and  $^{30}\text{Si}$  were increased. The extent of the decrease in the content of  $^{28}\text{Si}$  of the deposits prepared in  $\text{Na}_2\text{CO}_3$  at a current density of  $500 \text{ mA/cm}^2$  is a little smaller, the content near the surface being 70-75%. These results show that considerable large amounts of  $^{29}\text{Si}$  and  $^{30}\text{Si}$  are produced preferentially by the electrolysis in  $\text{Na}_2\text{SO}_4$  at a large current density, eg.  $800 \text{ mA/cm}^2$ . As reported already, the isotopic distribution of Si present on/in Au electrode after electrolysis in  $0.5 \text{ M Na}_2\text{SO}_4$  at a current density of  $100 \text{ mA/cm}^2$  was nearly equal to the natural isotopic abundance [3], and in fact, the isotopic distribution of Si present on the Au electrode after the electrolysis in  $\text{Na}_2\text{CO}_3$  for 30 days at a current density of  $500 \text{ mA/cm}^2$  remains to be equal to natural isotopic abundance. Such Si is considered to be fine glass powders produced when scraping the electrode. Therefore, there would be no doubt that  $^{29}\text{Si}$  and  $^{30}\text{Si}$  are produced at Au electrode through some process occurring when the deposits are produced.

#### *SURFACE STRUCTURE OF AU ELECTRODE AFTER ELECTROLYSIS*

**It was found that a lot of craters with various sizes are created** and developed along the scraped lines of the Au electrode surface during the electrolysis, for example, in  $\text{Na}_2\text{CO}_3$  at a current density of  $500 \text{ mA/Cm}^2$  for 30 days. **Each crater has a deep hole.** The size of the largest one reaches about  $20 \mu \text{ m}$  diam. and  $30 \mu \text{ m}$  height. Typical SEM images of the craters are shown in Fig. 9(a-b). From the appearance of the crater, one can imagine that some micro explosion took place at that place. Their outside walls consist of very fine porous substances, very alike to the structure of the deposits shown in Fig. 1(b). In addition, the major element of the deposits was found to be Au from the EDX analysis. Hence, it is very likely that the deposits were spewed out from these craters as the ashes as a result of some partial micro explosion, probably caused by some micro nuclear reactions. The walls inside the crater are constituted by a lot of fine hexagonal crystallites which are assignable Au(111). These crystallites may be considered to be produced by the reconstruction of Au polycrystals owing to the elevated heat evolved locally by the micro explosion. As already described above, we did not detect as much Hg, Pt on/in Au electrode after electrolysis as in the deposits. Perhaps, SIMS analysis was not pin-pointed at the wall of the crater precisely.

#### *REACTION SCHEME*

The amount of deposits obtained by the electrolysis conducted in this experiment was  $0.5 - 1 \text{ mg}$ . The content of Hg in the deposit can be estimated at least at several percent from the result of AES, EDX and SIMS measurement, from which the total amount of Hg produced yields some  $10 \mu \text{ g}$ . On the other hand, even in  $100 \text{ ml}$  of the electrolyte solution of  $0.5 \text{ M Na}_2\text{CO}_3$  containing  $0.05 \text{ ppm}$  of Hg as an impurity, the amount of Hg which must be contained in the deposits as an impurity would be at most  $0.35 \mu \text{ g}$ . In addition, we detected considerable amounts of F by SIMS measurement in every deposits obtained, the amount of which being somewhat larger than the amounts of Hg or Si obtained by the electrolysis at current densities  $< 500 \text{ mA/cm}^2$ . The element, F, would be scarcely present in the environment as long as we do not add it artificially. Hence, it is not understandable that such amount of F is introduced into the electrolytic cell as an impurity. The deviation of isotopic content of Hg, Fe and Si in the deposits strongly suggests that these elements were produced by some nuclear transmutation reaction.

As to the reaction scheme, although it is still far from the completion, we presume on the basis of the results obtained that the nuclear transmutation start by the following reaction,



The Hg atoms thus produced have very high energies, being unstable, then decompose partly to produce Pt, e.g. by the following reaction,



and occasionally, to produce Os by



However the change of the isotopic distribution of Pt is not significant so that the reactions (2) and (3) would not occur pronouncedly (most of Pt present on the deposits is considered to come from the counter electrode.).

On the other hand, we presume that Si and F are produced from Fe, by the following reactions,



The reaction scheme of producing Fe is unambiguous yet, however, at present stage, we presume as follows,



The Xe atoms thus produced are unstable which would cause further fission reaction to produce some elements with smaller atomic numbers.

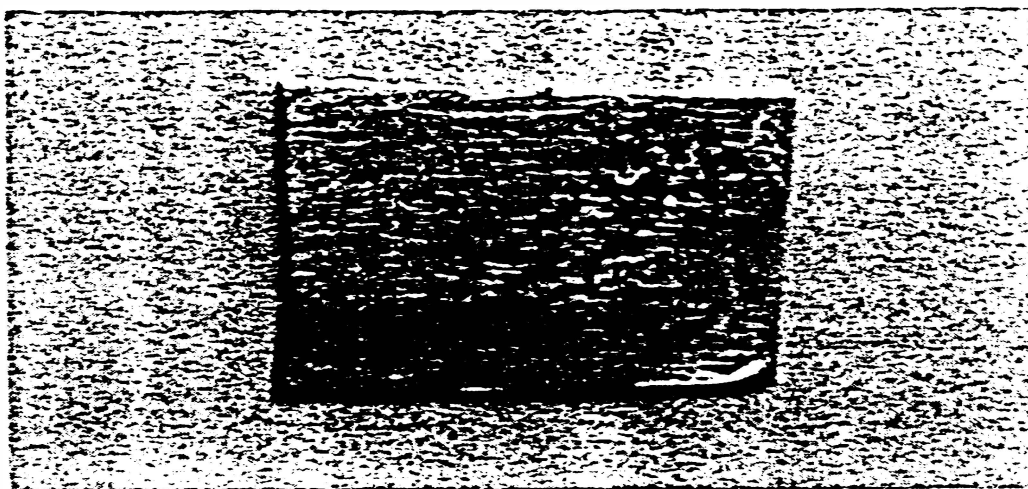
It is very mysterious why such transmutations take place by the electrolysis of light water at a room temperature. It is known that there are small amount of H active sites on Au [4-5] where the hydrogen evolution reaction occurs exclusively by slow recombination mechanism [6-8]. Therefore, at the place where such sites are concentrated (perhaps, it corresponds to the lattice defect), the concentration of H would remarkably increase with increasing hydrogen overpotential, and, in addition, **a considerable amount of micro cracks would be created with high loading of H. As a result of this, extremely strong electric field would be possible to be formed locally at that place.** Under such a condition, some H atoms would have a chance to acquire extremely high kinetic energy and become accessible to Au nuclei enough to cause the nuclear transmutation even instantaneously.

The study of this field is still a starting stage and our concepts concerning the reaction scheme would be far from the completion. In spite of this, there is hardly any doubt that the nuclear transmutation reaction occurs in the electrolysis system at a room temperature from the experimental results obtained here. To elucidate this problem, much more extensive information would be needed.

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( a )



( b )

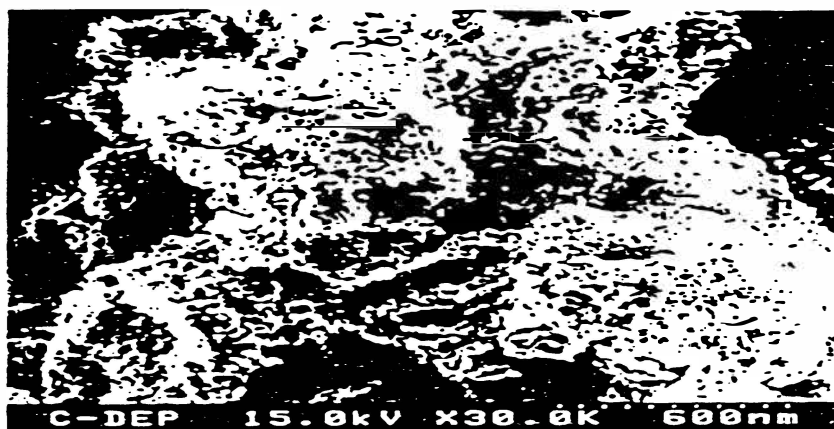


Fig. 1.

(a) Deposits placed on a Ni plate (dark spots mostly distributed at the right hand side) and (b) their SEM image (x 30,000).

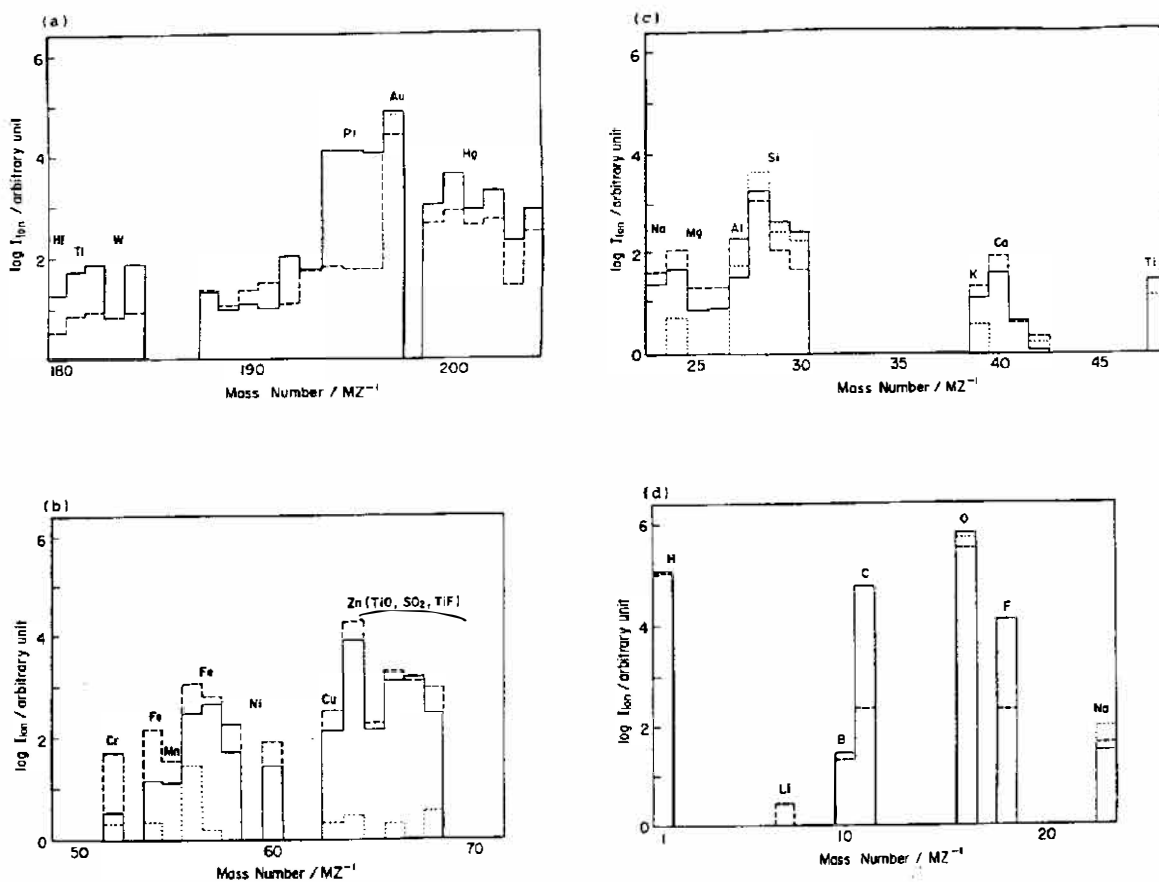


Fig. 2

Relative concentration of the constituent elements of the deposits and of Au electrodes before and after electrolysis. (a) elements with mass number from 180 to 204, (b) elements with mass numbers from 50 to 70, (c) elements with mass numbers from 23 to 48, (d) elements with mass numbers from 1 to 23, (solid line) deposits, (dashed line) electrode after the electrolysis and (dotted line) electrode before the electrolysis. Electrolysis was performed in 0.5 M Na<sub>2</sub>CO<sub>3</sub> solutions for 30 days at a current density of 500 mA/cm<sup>2</sup>.

The value of Zn is that estimated by assuming that all spectra in that mass number range are only attributed to Zn.

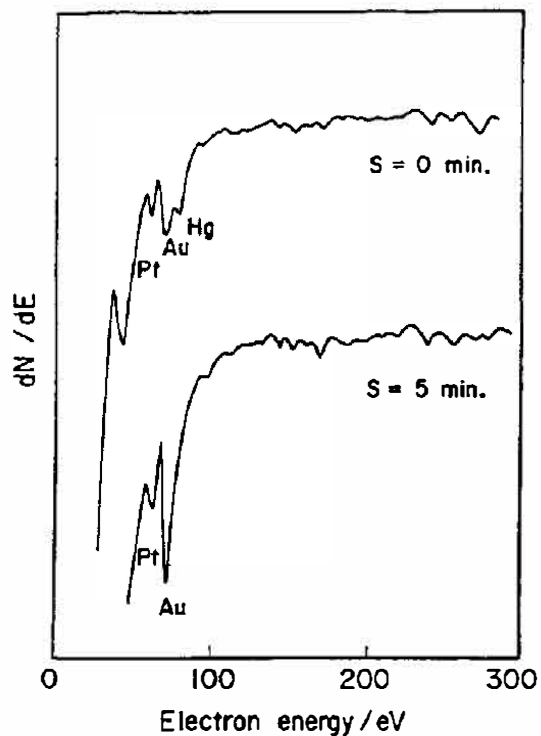


Fig. 3

Typical AES spectra of the deposits, where S means the sputtering time. The deposits were prepared by the electrolysis in 0.5 M  $\text{Na}_2\text{CO}_3$  solution for 30 days at a current density of 500  $\text{mA}/\text{cm}^2$ .

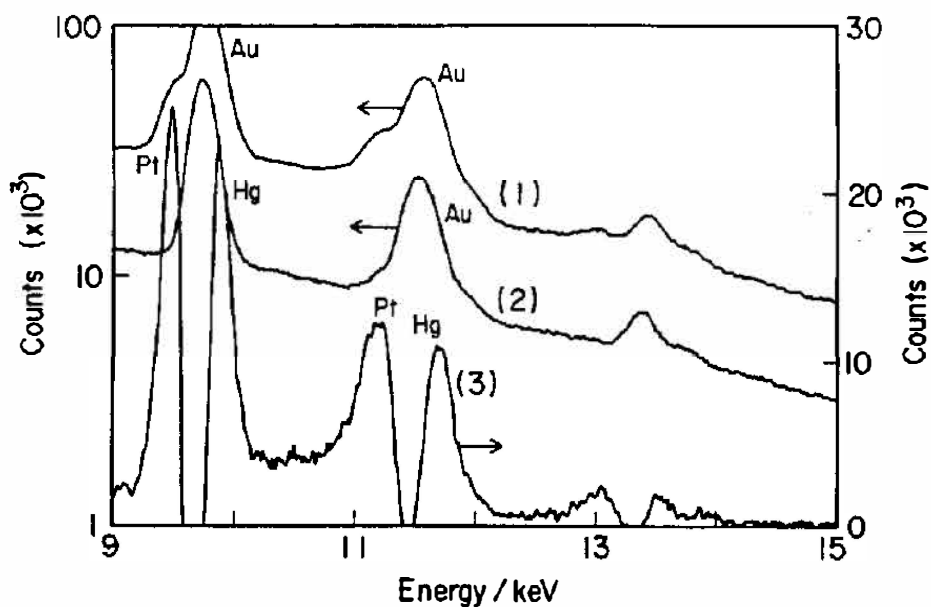


Fig. 4

Typical EDX spectra of the deposits and pure gold and difference spectrum between two spectra. (1) spectrum of the deposits, (2) spectrum of Au electrode before electrolysis and (3) difference spectrum. The deposits were prepared by the electrolysis in 0.5 M  $\text{Na}_2\text{CO}_3$  for 20 days at a current density of 800  $\text{mA}/\text{cm}^2$ .

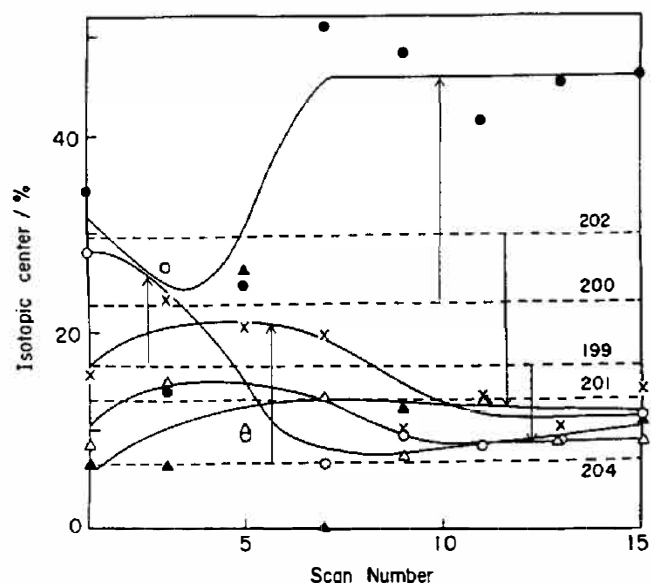


Fig. 5

Isotopic distribution of Hg containing in the deposits, (○) <sup>199</sup>Hg, (●) <sup>200</sup>Hg, (△) <sup>201</sup>Hg, (•) <sup>202</sup>Hg and (X) <sup>204</sup>Hg. Dashed lines show the natural isotopic abundance levels of individual isotopes. The deposits were prepared by the electrolysis in 0.5 M Na<sub>2</sub>CP<sub>3</sub> for 20 days at a current density of 800 mA/cm<sup>2</sup>. In this calculation the isotopic content of <sup>198</sup>Hg was regarded as natural isotopic abundance.

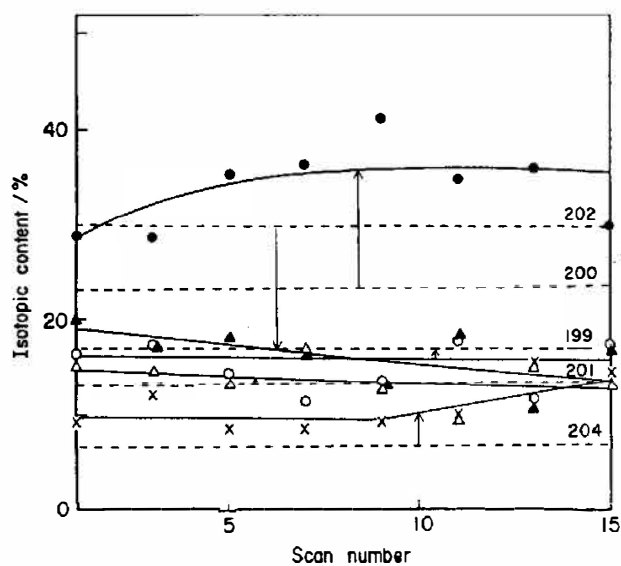


Fig. 6

Isotopic distribution of Hg containing on/in the electrode after the electrolysis, (○) <sup>199</sup>Hg, (●) <sup>200</sup>Hg, (△) <sup>201</sup>Hg, (•) <sup>202</sup>Hg and (x) <sup>204</sup>Hg. Dashed lines show the natural isotopic abundance levels of individual isotopes. The electrolysis were made in 0.5 M Na<sub>2</sub>CO<sub>3</sub> for 30 days at a current density of 500 mA/cm<sup>2</sup>. The deposits were prepared by the same procedures in the case of Fig. 5.



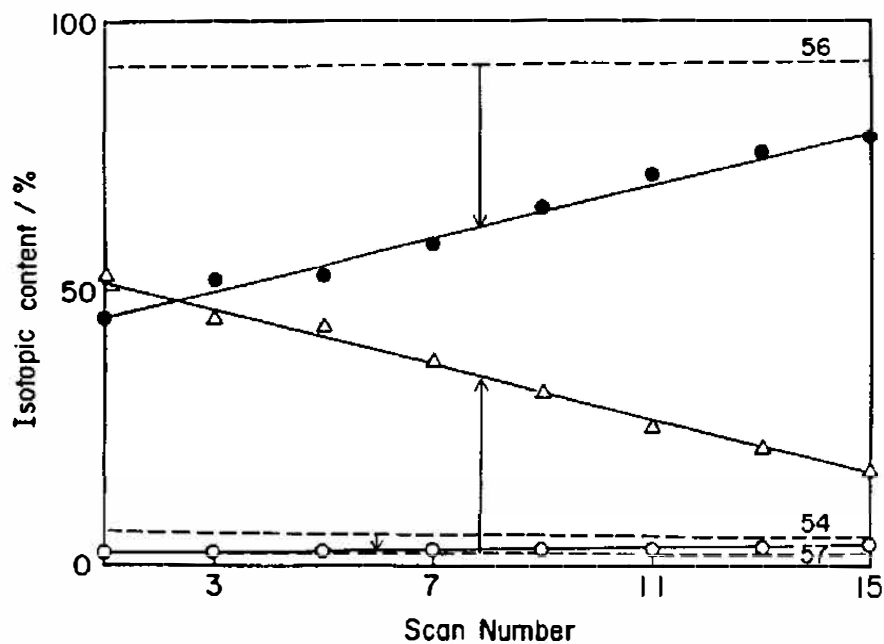


Fig. 7  
Isotopic distribution of Fe containing in the deposits, (○) $^{56}\text{Fe}$  and (●) $^{57}\text{Fe}$ . Dashed lines show the natural isotopic abundance levels of individual isotopes. The deposits were prepared by the electrolysis in 0.5 M  $\text{Na}_2\text{CO}_3$  for 30 days at a current density of 500  $\text{mA}/\text{cm}^2$ .

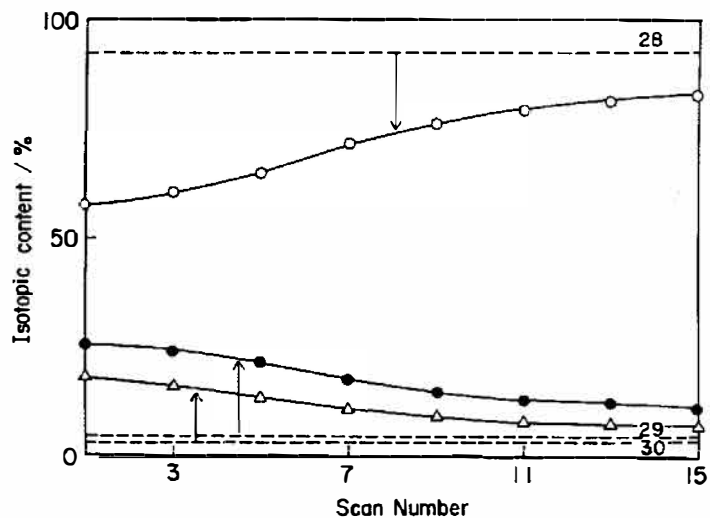


Fig. 8  
Isotopic distribution of Si containing in the deposits, (○) $^{28}\text{Si}$ , (●) $^{29}\text{Si}$  and (○) $^{30}\text{Si}$ . Dashed lines show the natural isotopic abundance levels of individual isotopes. The deposits were prepared by the electrolysis in 0.5 M  $\text{Na}_2\text{SO}_4$  for 30 days at a current density of 800  $\text{mA}/\text{cm}^2$ .

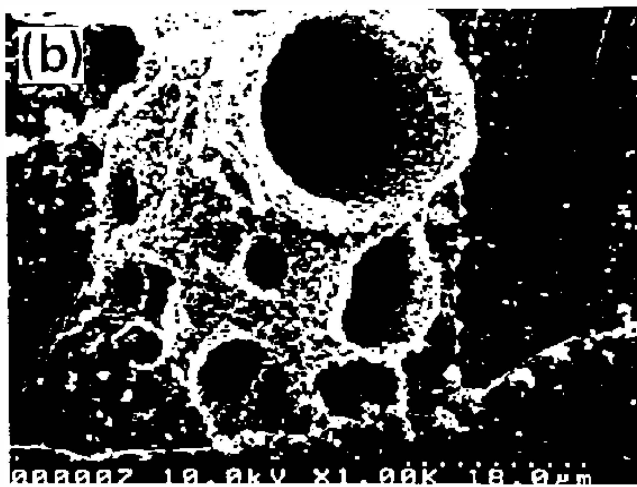
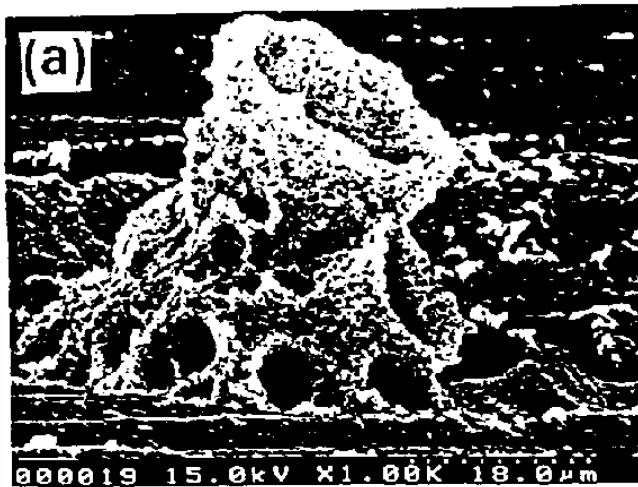


Fig. 9

SEM images of the Au electrode after the electrolysis in 0.5 M  $\text{Na}_2\text{CO}_3$  for 30 days at a current density of  $500 \text{ mA/cm}^2$ , (a) image from upside (x1,000), (b) image from horizontal side (x1,000).