

IRON FORMATION IN GOLD AND PALLADIUM CATHODES

T. Ohmori

Catalysis Research Center, Hokkaido Univ.
Kitaku, Sapporo, 060 Japan

M. Enyo

Hakodate National College of Technology
Tokura-cho, Hakodate, 042 Japan

ABSTRACT

Investigation of some reaction products possibly produced by electrolyzing with Au and Pd electrodes in Na_2SO_4 , K_2CO_3 , and KOH light water solutions was made. The electrolysis was performed for 7 days with a constant current of 1 A. After the electrolysis the elements accumulated in the electrode were analyzed by means of AES. In every case a notable amount of Fe atoms were detected together with a certain amount of excess energy evolution, being in the range of 9×10^{15} to 1.8×10^{16} atoms/cm² for Au and of 1.2×10^{15} to 4.0×10^{16} atoms/cm² for Pd. The isotopic abundance of these Fe atoms was measured by means of SIMS, which was 6.5, 77.5, and 14.5% for ⁵⁴Fe, ⁵⁶Fe and ⁵⁷Fe, respectively, at the top surface of Au electrode, obviously different from the natural values. For Pd electrode, a considerable increase in the contents of ⁵⁴Fe and ⁵⁷Fe was observed.

INTRODUCTION

We recently observed the production of Fe atoms reaching about 10^{16} atoms/cm² (true area) together with the excess heat evolution of several hundred mW at Au cathode [1,2]. In order to verify that such a Fe atom production is responsible for some nuclear transmutation, it is absolutely necessary to investigate the isotopic abundance of these Fe atoms.

For this reason we made the determination of the isotopic abundance of Fe product together with its quantification with Au and Pd electrodes after the electrolysis in light water electrolyte solutions. In this work, we also measured the excess heat and checked its correlation with the amount of Fe atoms produced.

EXPERIMENTAL

Five quartz (Fe<0.3 ppm) electrolytic cells were used. These electrolytic cells were in the form of flat bottomed cylinder (about 20 cm² x 15 cm) with a 5 cm thick silicone rubber stopper holding a test electrode, a counter electrode, a thermocouple and a quartz glass inlet tube for H₂ gas, which were cleaned carefully with hot mixed acid (1:1 H₂SO₄, HNO₃), rinsed with MQ water ultrasonically. The test electrode was suspended by an Au lead wire (0.03 cm diam.) for Au electrode or by a Pd lead wire (0.03 cm diam.) for Pd electrode, which was sealed with a thin teflon film without the extremity. The cells were placed in the air thermostat whose temperature was regulated at around $21 \pm 1^\circ\text{C}$. The working electrodes used were cold worked Au plates (5 cm² app. area, 0.1 mm thick, 99.99% purity, Fe< 1 ppm), or cold worked Pd plates (5cm² app. area, 0.1 mm thick, 99.95% purity, Fe< 5 ppm), whose surfaces were scraped with a cleaned glass fragment edge and then washed with methyl alcohol and MQ water. The roughness factor of the electrode determined from the measurement of double layer capacitance by the galvanostatic

transient method [3] was 2.0. The counter electrode was 1 x 7 cm, 80-mesh platinum net (99.98% purity, Fe < 16 ppm). The electrolyte solutions used were 0.5 M Na₂SO₄, K₂CO₃ and KOH which were prepared from Merck sprapur grade chemicals. The volume of the electrolyte solution used was 100 ml. The electrolysis was conducted galvanostatically for 7 days by a constant current of 1 A. Before the electrolysis the Au electrode was kept at RHE by passage of H₂ into the cell. During the electrolysis MQ water was added to make up for the solution loss every 24 hours.

In order to identify the elements present in Au electrodes after the electrolysis and determine these atomic abundances, AES and SIMS measurements were carried out. For the AES measurement the electrode sample after washing with MQ water was placed on a Ni plate holder in a chamber in a vacuum of 2.0 x 10⁻⁸ Torr. Argon ion bombardment was performed under 99.9995% argon atmosphere of 2.5 x 10⁻⁵ Torr. The SIMS measurement was made in a vacuum of 5 x 10⁻⁹ Torr. by the O₂⁺ irradiation.

RESULTS

Fig. 1 shows typical AES spectra from the top to the several 10 layers of Au electrode after the electrolysis in Na₂SO₄ solution. In the spectrum of the top surface (no A⁺ bombardment treatment), Fe and O signals were observed in addition to Au spectral signals.

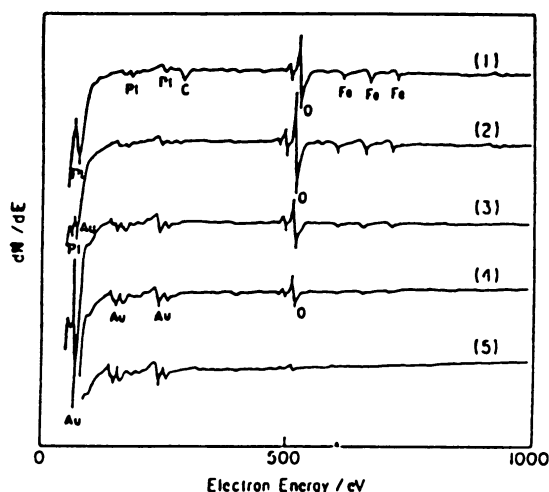


Fig. 1. AES spectra of Au electrode after electrolysis in Na₂SO₄ solution; bombardment time: 0 sec. (1), 30 sec. (2), 120 sec. (3), 180 sec. (4), & 600 sec. (5).

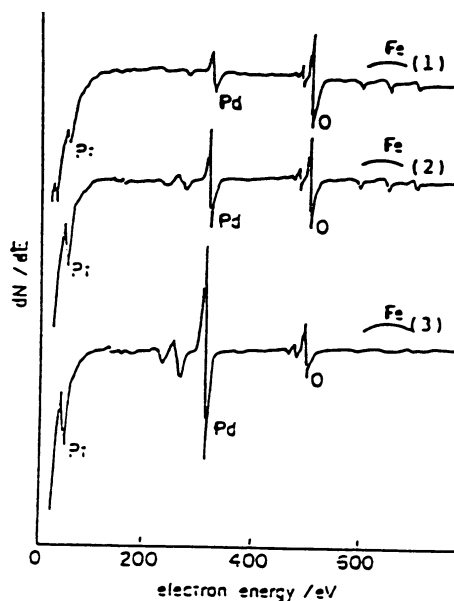


Fig. 2. AES spectra of Pd electrode after electrolysis in Na₂SO₄ solution; bombardment time: 0 sec. (1), 60 sec. (2), & 180 sec. (3).

On carrying out A⁺ bombardment, the Fe and O signals decline and disappear after several minutes of the bombardment. Fig. 2 shows typical AES spectra for Pd electrodes after the electrolysis in Na₂SO₄ solution. In this case Fe, O and Pt signals were observed, the strength of Pt signal tending to increase with bombardment time in this time region. The Fe and O signals were observed for every Au and Pd electrodes independent of the nature of the electrolyte. The O signal always appears together with the Fe signals and the intensity ratio of Fe to O is nearly the same as that of the spectrum obtained on a pure Fe plate. Perhaps, traces of O₂⁺ contained in the AES chamber bind with Fe atoms during the A⁺ bombardment. We considered that the number of O atoms estimated from O signal is equal to the number of Fe atoms covered with O atoms, assuming that each O atom binds for each Fe atom, and added the number of O atoms to the number of Fe atoms estimated from the Fe signal itself, when estimating the total amount of Fe atoms from the AES spectra.

The distribution of Fe atoms from the top surface to the inner layers of the electrode estimated from the results in Fig. 1 and Fig. 2 is shown in Fig. 3 and Fig. 4, respectively. For Au electrode the content of Fe atoms on the top surface amounts to 44%. The amount of Fe atoms, in this case, becomes maximum (about 60%) at several mono-layers from the surface and the distribution extends down to about 80 mono-layers (corresponding to about 5 min. of the bombardment time). Whereas for Pd electrode the maximum content of Fe is about 45% (top surface) and its distribution extends down to 150 mono-layers. It is noticeable that a large amount of Pt is also accumulated in the bulk of Pd electrode. The amounts of Fe atoms produced in Au and Pd electrodes in every electrolyte solutions range between 1.0×10^{15} and 1.8×10^{16} atom/cm² for Au electrode and between 1.2×10^{15} and 4.0×10^{16} atom/cm² for Pd electrode.

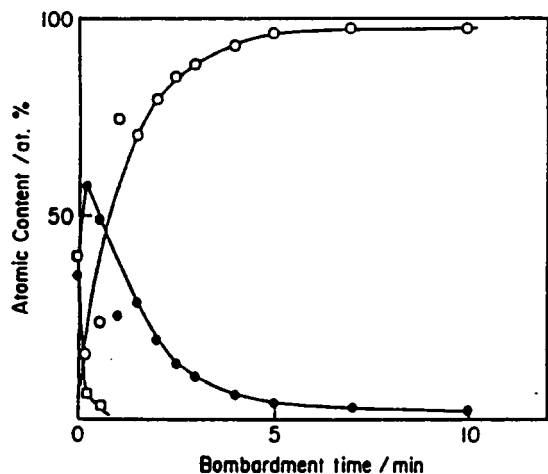


Fig. 3. Distribution profile of Fe and Pt atoms in Au electrode after electrolysis in Na₂SO₄ solution: Fe (●), Pt (□), & Au (○).

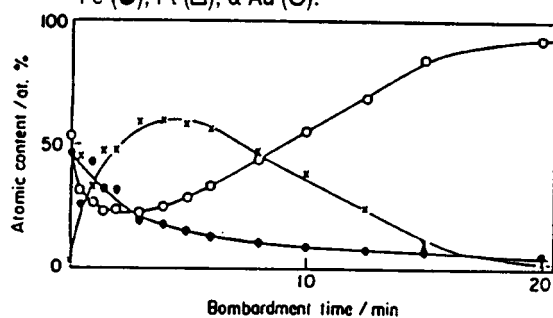


Fig. 4. Distribution profile of Fe and Pt atoms in Pd electrode after electrolysis in Na₂SO₄ solution: Fe (●), Pt (x), & Pd (○).

Thus, the maximum total amounts of Fe present in Au and Pd electrodes yield about 17 μ g and 38 μ g, respectively. However, in the case of Au electrode without any mechanical treatment, the amount of Fe atoms produced at the same electrolysis condition is smaller by one - two orders of magnitude. This result suggests that the production of Fe atoms is strongly influenced by the stress of the surface crystal lattice.

Fig. 5 shows the relationship between the amounts of Fe atoms and the mean excess energies obtained for Au electrodes in every electrolyte solutions. Although the data are rather scattered, there is a proportionality between these two terms. This supports strongly that the production of Fe atoms is related to the excess heat evolution observed.

SIMS spectrum was measured for each scan (up to 15 scans) for Au and Pd electrodes after the electrolysis in Na₂SO₄ solution. Fig. 6 and Fig. 7 show the profiles of the isotopic abundance of Fe atoms in Au and Pd electrodes, respectively. The Fe atoms detected at 15 scans correspond to those existing in the depth around 180 mono-layers from the top surface. For Au electrode, the contents of the particles with mass numbers 54, 56, 57, and 58 corresponding to Fe isotopes obtained from the spectrum of first scan are 6.5, 77.5, 14.5, and 1.5%, respectively, clearly different from the natural isotopic abundance of Fe atom.

In particular, the difference is remarkable for the particles with mass number 57, whose content is about 6.6 times the natural ⁵⁷Fe content. On the contrary, the content of the particles with mass number 56 is decreased by 15.5% from the natural ⁵⁶Fe content. Whereas, for Pd electrode, the rates of the particles with mass numbers 54, 56, 57, and 58 are 7.8, 85.4, 6.2 and 0.6%, respectively, different from these natural value to some extent. Such a departure becomes significant with the particles present in more inner layers of the electrode. Eventually, for Au electrode the content of the particles of mass number 57 after 10 scans reaches about 25%, being about 11 times the natural ⁵⁷Fe content.

Similar results should be obtained also from the analysis of the signals of mass numbers of 70, 72, and 73 corresponding to FeO, if all the particles with mass numbers 54, 56, and 57, are of Fe atoms. The signal intensity ratios of 57 to 56 and of 73 to 72 obtained are plotted against every scan numbers for Au electrode in Fig. 8. Although the plots are rather scattered, we can see that these ratios are, on the whole, in agreement with each other. Therefore, the change of the content of mass numbers 54, 56, and 57 from the natural value, shown in Fig. 6 is not due to FeH formation but probably due to some nuclear transmutation to produce Fe atoms.

As can be seen from Fig. 6 and Fig. 7, there is unambiguous difference in the isotopic abundance change between Au and Pd electrodes. In the former case, the increase of ^{57}Fe is significant, while, in the latter case, the increase of ^{54}Fe is noticeable. This suggests that the nuclear transmutation proceeds through somewhat different processes for different metals.

The possibility of the formation of Fe atoms from the impurities of chemical reagents or of the cell materials would be negligible because of the following reasons; (i) the number of Fe atoms from the electrolyte reagent should be at most 7×10^{14} atoms, e.g., in 100 ml of 0.5 M Na_2SO_4 (Merck spurapur grade reagent, $\text{Fe} < 0.01$ ppm,) solution, and (ii) the number of Fe atoms coming from the impurities in Au cathode and Pt anode materials would be negligible judging from the purity of these materials as have already mentioned. Hence, the amount of Fe atoms produced in Au electrodes in this experiment is at least 1 - 2 orders of magnitude larger than the values estimated above. Even if all impurity Fe atoms are accumulated in an Au electrode they could not give such clear Fe AES signals as those shown in Fig 1. From this point of view, most of the ^{56}Fe atoms, which being still the major isotopic component, are considered to be the product of nuclear transmutation together with ^{54}Fe and ^{57}Fe atoms.

The isotopic abundances of Mg, Si, K and Ti, obtained from the SIMS spectrum of first scan are shown to Table 1. As seen, the isotopic abundances of these elements are in agreement with these natural ones. Therefore, these atoms can be regarded as the impurities from the electrolyte reagents. The isotopic abundance of Pt atoms accumulated in Pd electrode was close to

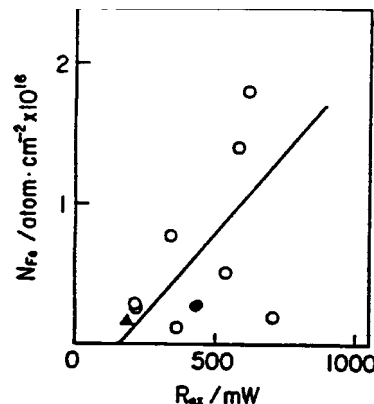


Fig. 5. Plots of the total amount of Fe atoms against the mean excess energy for Au electrode: Na_2SO_4 (O), K_2CO_3 (●), & KOH (▲).

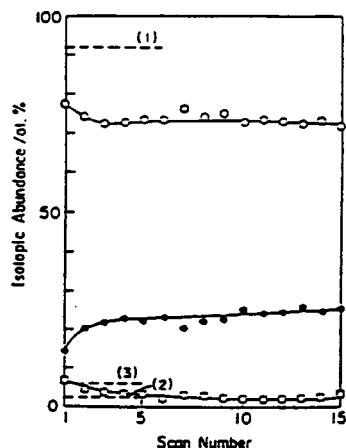


Fig. 6. Profile of the isotopic abundance of Fe atoms in the Au electrode. Solid line: the content of the particles on mass number 56 (O), 57 (●), & 54 (□). Dotted line: natural isotopic abundance levels of ^{56}Fe (1), ^{57}Fe (2), & ^{54}Fe (3).

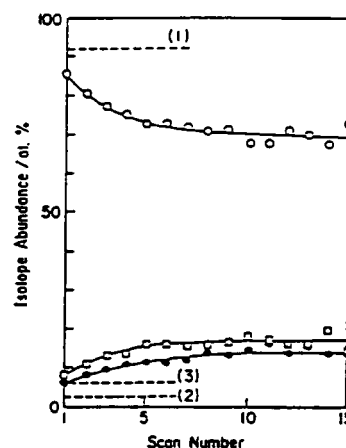


Fig. 7. Profile of the isotopic abundance of Fe atoms in the Pd electrode. Solid line: the content of the particles on mass number 56 (O), 57 (●), & 54 (□). Dotted line: natural isotopic abundance levels of ^{56}Fe (1), ^{57}Fe (2), & ^{54}Fe (3).

