

DETECTION OF IRON ATOMS ON GOLD ELECTRODES USED FOR ELECTROLYSIS OF NEUTRAL AND ALKALINE H₂O AND D₂O SOLUTIONS

Tadayoshi Ohmori and Michio Enyo

Catalysis Research Center,
Hokkaido University, Kita 11 Nishi 10,
Kitaku, Sapporo, 060 Japan

ABSTRACT

Detection of any products possibly produced during the excess heat evolution by electrolysis was attempted on Au electrodes, in parallel with the excess heat observations. The electrolytes used were K₂CO₃, Na₂CO₃, Na₂SO₄, KOH and NaOH. The electrolysis was performed for 7 days with a constant current of 1 A. The electrode surface was then analyzed by means of AES spectroscopy. In every solutions a notable amount of Fe atoms were detected, being in the range of 1.1 to 9.9 x 10¹⁶ atoms. These values are much larger than those contained as impurities in the reagents used (ca. 7 x 10¹⁴ atoms for Na₂SO₄) or possibly originated from the cell materials. The mean excess heat observed was in the range of 187 to 723 mW. The amounts of Fe atoms observed were approximately proportional to the total amounts of the excess energy observed during the electrolysis. These results suggest that the iron formation reaction may be responsible for the excess heat evolution.

INTRODUCTION

The identification of any product caused by the cold fusion reaction is essential to conclude whether this reaction really exists or not. Several authors have reported that T or Ca atoms were detected in the electrolysis in Ni/K₂CO₃/ H₂O systems [1-2].

In addition, the latter author claimed detection of Sr in Ni/RbCO₃/ H₂O system [3]. These results suggest that various types of nuclear fusion reactions might be taking place in the electrolysis in various metal/electrolyte systems.

In the previous work we have observed evaluation of the excess heat ranging from 0.2 to 0.9 W during the electrolysis with Sn, Au, Ni and Ag electrodes in various alkali metal salts (K₂CO₃, Na₂SO₄, etc.) / H₂O systems [4-5]. It may then be conceivable that any nuclear fusion reaction products, apart from neutron, He and T, are formed at the electrode.

In this study, we tried to detect such products on Au electrode after the electrolysis in alkali-metal sulfates, carbonates and hydroxides / H₂O and D₂O systems using AES spectroscopy.

EXPERIMENTAL

The electrolytic cell used was a flat-bottomed cylinder made of quartz glass (ca. 23 cm² x 15 cm, Fe < 0.3 ppm, nominal) with a 5 cm-thick silicone rubber stopper holding a test electrode, a counter electrode, a thermocouple, and a quartz glass inlet tube for hydrogen gas. The cell was placed in an air thermostat

whose temperature was regulated at $21 \pm 1^\circ\text{C}$; the variation was periodical with 10 cycles/h. The precision of the solution temperature measurement was 0.03°C . The working electrode used is a Au sheet (5 cm^2 area, 0.1 mm thick, 99.99% purity, $\text{Fe} < 1\text{ ppm}$), whose surface was scraped with edge of a cleaned glass fragment and then washed with acetone, methyl alcohol and MQ water. The true surface area determined from the double layer capacitance [6] was 10.0 cm^2 . The counter electrode was a $1 \times 7\text{ cm}$, 80-mesh platinum net (99.98% purity, $\text{Fe} < 16\text{ ppm}$). The working and counter electrodes were placed near the bottom of the cell to minimize the temperature gradient in the electrolytic solution by stirring with H_2 and O_2 bubbles evolved from these electrodes. The electrolysis cell was cleaned carefully with hot mixed acid ($1:1\text{ H}_2\text{SO}_4 + \text{HNO}_3$) and then rinsed with MQ water ultrasonically and finally rinsing for ca. 10 times with MQ water before conducting the electrolysis. The electrolytic solutions used were $0.5\text{ M K}_2\text{CO}_3$, Na_2CO_3 , Na_2SO_4 , KOH and NaOH which are prepared from Merck suprapure grade chemicals. Heavy water was also obtained from Merck (99.8% purity) which was doubly distilled under vacuum. The volume of electrolytic solution used was 100 ml.

An electric heater used for measuring the calibration curve between solution temperature and input power was a $0.3\text{ mm}\phi$ diam., 1.6Ω nichrome spiral, connected to copper wires at both ends, which was inserted into a Pyrex-glass tube (6 mm diam., 15 cm long) containing silicone oil and set in the middle position of the cell. During the measurement, the solution was stirred by H_2 with the same flow rate as the rate of the evolution of H_2 and O_2 gases during the electrolysis.

The electrolysis was conducted galvanostatically for 7 days with a constant current of 1 A, and the variations of the applied cell voltage and the solution temperature growth were monitored by penrecorders.

RESULTS AND DISCUSSION

Excess heat

Fig. 1 shows a typical calibration curve between input power of the electrolysis cell and solution temperature. As seen, a very reproducible linear relationship was obtained up to 20°C . The cell constant k calculated from the gradient was $3.25 \pm 0.04^\circ\text{C}/\text{W}$. The rates of excess heat evolution R_{ex} in H_2O and in D_2O solutions were determined from the solution temperature growth ΔT , cell voltage E and the polarization current I by the following equation [6], respectively.

$$R_{\text{ex}} = \Delta T/k - (E - 1.48)I \quad (1)$$

$$R_{\text{ex}} = \Delta T/k - (E - 1.54)I \quad (2)$$

where the values of 1.48 and 1.54 are the thermoneutral potentials for H_2O and D_2O decomposition reactions, respectively.

Fig. 2 shows typical variations of the solution temperature with polarization time obtained in $\text{Na}_2\text{SO}_4/\text{H}_2\text{O}$ and $\text{Na}_2\text{CO}_3/\text{H}_2\text{O}$ systems. The variations of the cell voltage were also shown in this figure. As seen, the increase of the solution temperature in Na_2SO_4 was larger than in Na_2CO_3 although the cell voltages were nearly the same with each other. The difference was essentially unchanged during the whole period of polarization. This result indicates that noticeable amount of excess heat is produced in the $\text{Au}/\text{Na}_2\text{SO}_4/\text{H}_2\text{O}$ system.

The excess heat obtained in various solutions was listed in Table 1. The maximum excess heat observed was 914 mW (in $\text{K}_2\text{CO}_3/\text{D}_2\text{O}$), which corresponded to 17.2% of the input power (EI 1.481). The mean excess heat evolved during 7 days of polarization in 11 kinds of electrolyte systems was in the range of 204 to 723 mW, the amounts of which seemed to be rather independent of the nature of electrolytes. These values of excess heat well reproduced the results reported previously in

Au/K₂CO₃, Na₂CO₃ and Li₂SO₄/H₂O systems [4-5].

The results of the excess heat measurement on Au and Pt electrodes in H₂SO₄/H₂O solutions are listed in Table II. The excess heat was negative, but very close to 0.0 in every case; it can be regarded that no excess heat was evolved. No observation of excess heat in electrolysis in H₂SO₄ solutions without exception supports reliability of our measurements of excess heat.

The total excess heat evolved during 7 days of polarization ranged between 130 and 437 KJ in the electrolyte systems shown in Table I. This means that at least several moles of reaction products should be produced during the electrolysis if the excess heat is caused by any conventional chemical reactions. However, no such large amounts of the reaction products were obtained except for H₂ and O₂, suggesting that some nuclear fusion reaction might be responsible for the excess heat.

The reaction products

Fig. 3 shows AES spectra from the Au electrode surface after 7 days of polarization in Na₂SO₄/H₂O system. In the spectrum on the top-surface (no Ar⁺ ion bombardment), Fe and O signals were observed other than Au ones. On carrying out Ar⁺ ion bombardment, the intensity of Fe and O signals decreased while that of Au signals increased, and the former signals disappeared completely after 2 minutes of bombardment. Fig. 4 shows similar AES spectra obtained on the Au electrode used in Na₂SO₄/D₂O system. The Fe and O signals were again observed in this case, whose intensity was somewhat larger than those in Na₂SO₄/H₂O system. Such Fe and O signals were observed in every electrolyte systems used, while no signals other than Fe, O and Au were detected. As seen from Fig. 3 and Fig. 4, the O signal is present together with the Fe signals and the ratio of the signal intensity of these species is not much different in every spectra observed. This suggests that these O atoms are present only on Fe atoms. Perhaps, they are contained originally in Ar gas as impurity and bound with surface Fe atoms during the Ar⁺ ion bombardment. Therefore, the atomic contents of O on Au surfaces estimated from O signals can be replaced by those of Fe, assuming that O atoms bind with Fe atoms with the ratio of 1:1, so that the contents of Fe can be estimated by summing up the number of Fe and O atoms.

It is interesting to see the distribution of Fe atoms in the layers close to the electrode surface and to estimate the total amounts of Fe atoms. The number of iron atoms, N_{Fe}, sputtered from the surface by Ar⁺ ion bombardment was estimated by the following equation [6].

$$N_{Fe} = f_{Fe} \times N_{Ar^+} = \frac{f_{Fe} \times I_{Ar^+} \times t}{1.6 \times 10^{-19}} \quad (3)$$

where N_{Ar⁺} is number of Ar⁺ ion bombarded per unit surface area, I_{Ar⁺} is its current density, f_{Fe} is the sputtering yield for Fe, and t is a duration of the bombardment. In this case I_{Ar⁺} was 21 μA/cm₂ and f_{Fe} was estimated at 2.4 [7]. The number of layers sputtered was estimated roughly by dividing N_{Fe} with 10¹⁵.

The distributions of Fe atoms in the layers close to the surface, as calculated on the basis of the results in Fig. 3 and Fig. 4, are shown in Fig. 5. The content of Fe atoms in the top layer of the surface amounts to 78 and 44 at.% in Na₂SO₄/D₂O and Na₂SO₄/H₂O solutions, respectively. The Fe atoms distributed down to several ten layers. Similar results were obtained in other electrolyte systems. The total numbers of Fe atoms formed on Au electrodes in each electrolyte system, ranging between 1.1 × 10¹⁶ and 9.9 × 10¹⁶ atoms, are listed in Table III together with the mean excess heat. These values correspond to 1 - 10 layers of Fe atoms. The total amounts of Fe atoms against the mean excess heat in every electrolyte systems are plotted in Fig. 6. Although the data obtained were rather scattered, it is seen that the total

amounts of Fe atoms is likely to be proportional to the mean excess heat. This result may suggest that the Fe is produced along with the excess heat evolution.

The possibility of the Fe atoms coming from impurities in chemical reagents or impurities of cell materials are considered unlikely because of the following reasons; (i) the number of Fe atoms from the reagent impurity is believed to be at most 7×10^{14} atoms, e.g., in 100 ml of 0.5 M Na_2SO_4 (Merck suprapure grade agent) solution, and (ii) the number of Fe atoms from the quartz material by its dissolution during 7 days of electrolysis should amount only 10^{11} atoms. Hence, the amount of Fe atoms actually formed on Au electrode is roughly 2 orders of magnitude larger than the values estimated above. Even if all the Fe atoms as impurities were deposited on the Au electrode it cannot give the Fe signals shown in Fig. 3 and Fig. 4.

Further, nearly the same amounts of Pb, Cd, Cu, Co, Ni, Mn, Ti and Zn as that of Fe are contained as impurities in Na_2SO_4 , but no signal other than Au, O and Fe was detected in AES spectra.

From the considerations presented above, we believe that there is a high possibility that the formation of Fe atoms is caused by a nuclear fusion reaction. However, no reaction scheme may be suggested at the present stage. It may only be mentioned that O, H and/or D atoms might be taking part in the present case, judging from the independence of the Fe atom production upon alkali-metal ions.

REFERENCES

- [1] M. Srinivasan, A. Shyam, T.K. Sankaranarayanan, M.B. Bajpai, H. Ramamurthy, U.K. Mukherjee, M.S. Krishnan, M.G. Nayar and Y.P. Naik. Presented at 3rd Annual Conf. Cold Fusion, Nagoya, Japan, October 21 - 25 (1992).
- [2] R.T. Bush, *Fusion Technol.*, vol 21, p 163 (1992).
- [3] R.T. Bush and R. Eagleton, presented at 4th Annual Conf. Cold Fusion, Lahaina Hawaii, December 6 - 9 (1993).
- [4] T. Ohmori and M. Enyo, presented at 3rd Annual Conf. Cold Fusion, Nagoya, Japan, October 21 - 25 (1992).
- [5] T. Ohmori and M. Enyo, *Fusion Technol.*, vol 24, p 293 (1994).
- [6] T. Ohmori, *Electroanal. Chem.*, vol 157, p 159 (1983).
- [7] A. Takeuchi, K. Tanaka, I. Toyoshima and K. Miyahara, *J. Catal.* vol 40, p 94 (1975).
- [8] M. Kaminsky, Atomic and Ionic Impact Phenomena on Metal Surfaces, Springer-Verlag, Berlin, 1965.

FIGURE CAPTIONS

Fig. 1

Calibration curve between solution temperature and input power.

Fig. 2

Variations of input potential and solution temperature with polarization time: (1) and (1') $\text{Na}_2\text{SO}_4/\text{H}_2\text{O}$; (2) and (2') $\text{Na}_2\text{SO}_4/\text{D}_2\text{O}$.

Fig. 3

AES spectra of the Au electrode surface after electrolysis in $\text{Na}_2\text{SO}_4/\text{H}_2\text{O}$ system.

Fig. 4

AES spectra of the Au electrode surface after electrolysis in $\text{Na}_2\text{SO}_4/\text{D}_2\text{O}$ system.

Fig. 5

Distribution of Fe atoms on the Au electrode in the layers close to its surface: (1) $\text{Na}_2\text{SO}_4/\text{H}_2\text{O}$; (2) $\text{Na}_2\text{SO}_4/\text{D}_2\text{O}$.

Fig. 6

Plots of the total amounts of Fe atoms against the mean excess heat:

(○) (●) Na_2SO_4 ; (◇) Na_2CO_3 ; (□) (■) K_2CO_3 ; (▽) NaOH ; (△) (▲) KOH .
Open mark, H_2O solutions; filled mark, D_2O solutions.

TABLE I

Amount of excess heat in various electrolyte systems

system	E (V) %	R _{ex,mean} (mW)	R _{ex,max} (mW)	efficiency
Na ₂ SO ₄ /H ₂ O	4.88	215	300	4.4
Na ₂ SO ₄ /H ₂ O	5.09	535	849	10.5
Na ₂ SO ₄ /H ₂ O	5.07	723	805	14.5
K ₂ CO ₃ /H ₂ O	4.95	281	417	5.7
K ₂ CO ₃ /H ₂ O	5.10	461	573	9.0
Na ₂ CO ₃ /H ₂ O	5.20	204	285	3.9
NaOH/H ₂ O	4.82	391	470	8.1
KOH/H ₂ O	4.51	526	815	11.7
Na ₂ SO ₄ /D ₂ O	5.15	523	770	10.2
K ₂ CO ₃ /D ₂ O	5.29	689	914	13.0
KOH/D ₂ O	5.11	187	280	3.7

TABLE II

Amount of excess heat in 0.5 M H₂SO₄/H₂O systems

electrode	E (V)	AT _{ex} (°C)	R _{ex} (mW)
Au	3.10	-0.03	-9
Au	3.10	-0.04	-12
Au	2.83	-0.03	-9
Pt	2.95	-0.10	-30

TABLE III

Amount of Fe atoms and mean excess heat in various electrolyte systems

system	NFe (atom)	R _{ex} ,mean (mW)
Na ₂ SO ₄ /H ₂ O	3.0 x 10 ¹⁶	215
Na ₂ SO ₄ /H ₂ O	3.1 x 10 ¹⁶	723
K ₂ CO ₃ /H ₂ O	3.1 x 10 ¹⁶	281
K ₂ CO ₃ /H ₂ O	1.8 x 10 ¹⁶	461
Na ₂ CO ₃ /H ₂ O	1.5 x 10 ¹⁶	204
NaOH/H ₂ O	1.1 x 10 ¹⁶	391
KOH/H ₂ O	6.5 x 10 ¹⁶	526
Na ₂ SO ₄ /D ₂ O	9.9 x 10 ¹⁶	523
K ₂ CO ₃ /D ₂ O	3.8 x 10 ¹⁶	689
KOH/D ₂ O	1.5 x 10 ¹⁶	187

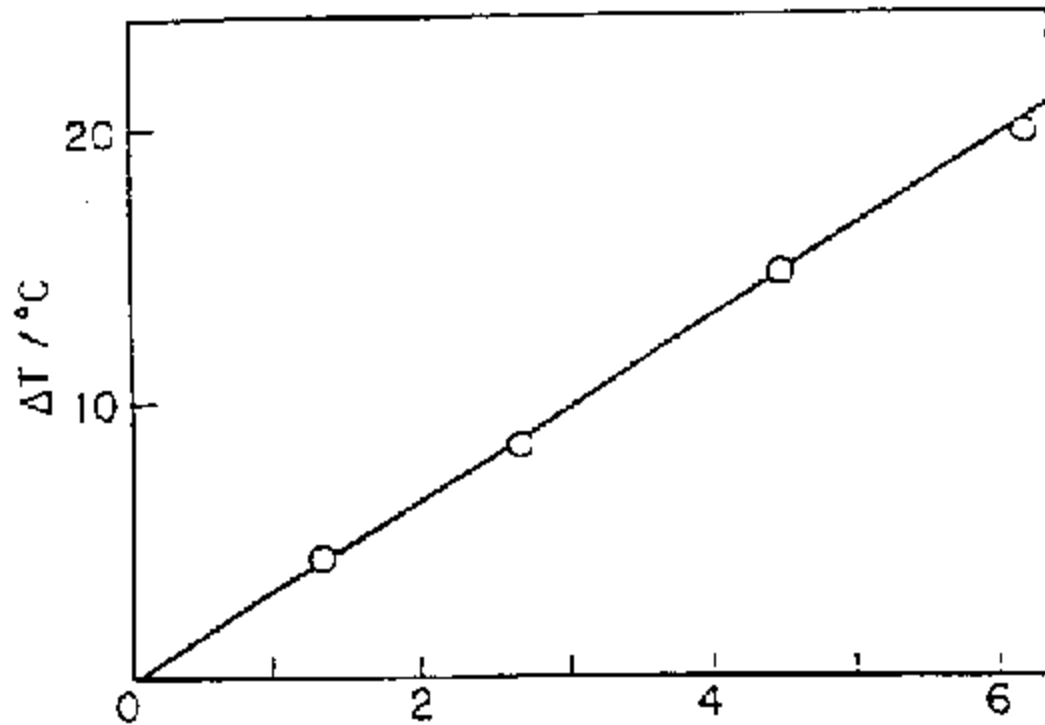


Figure 1 P / W

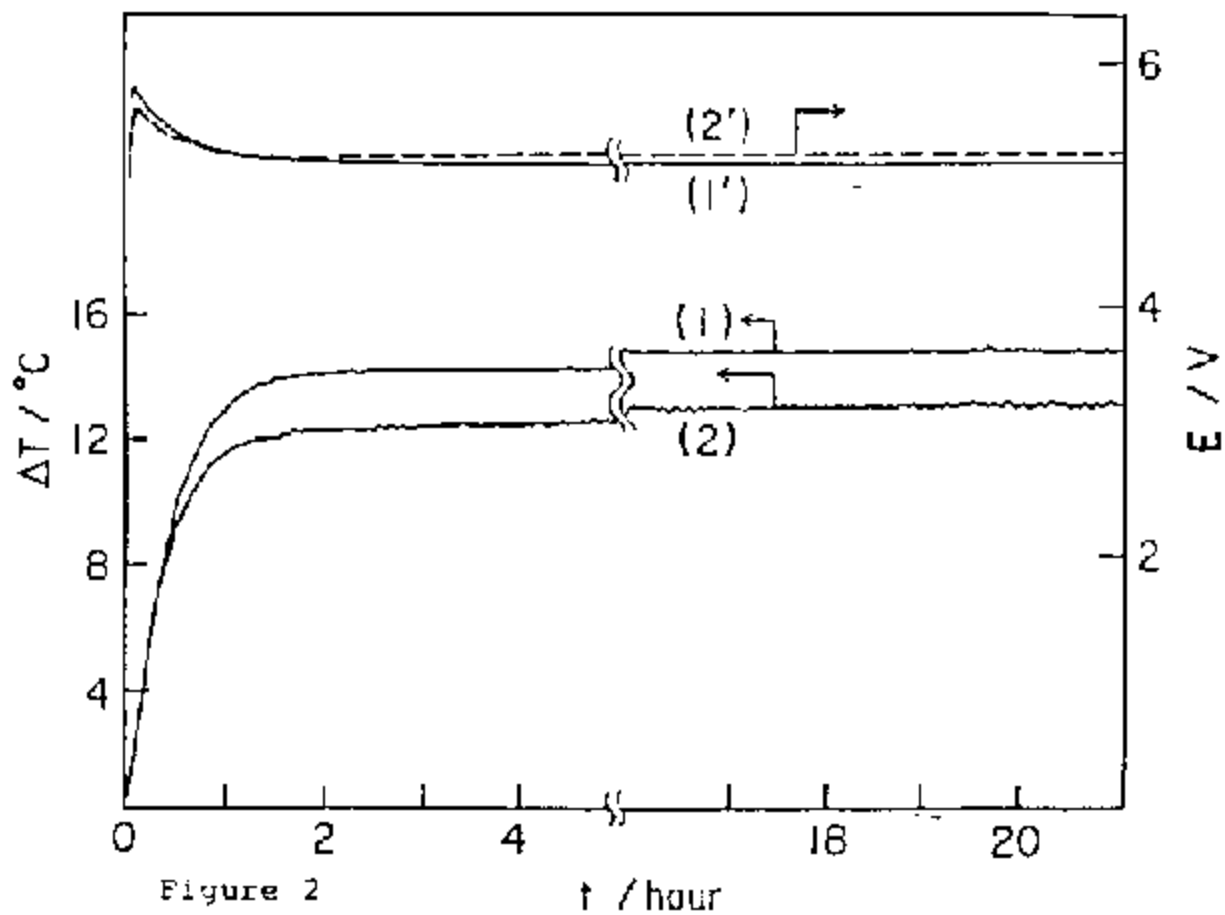


Figure 2

t / hour

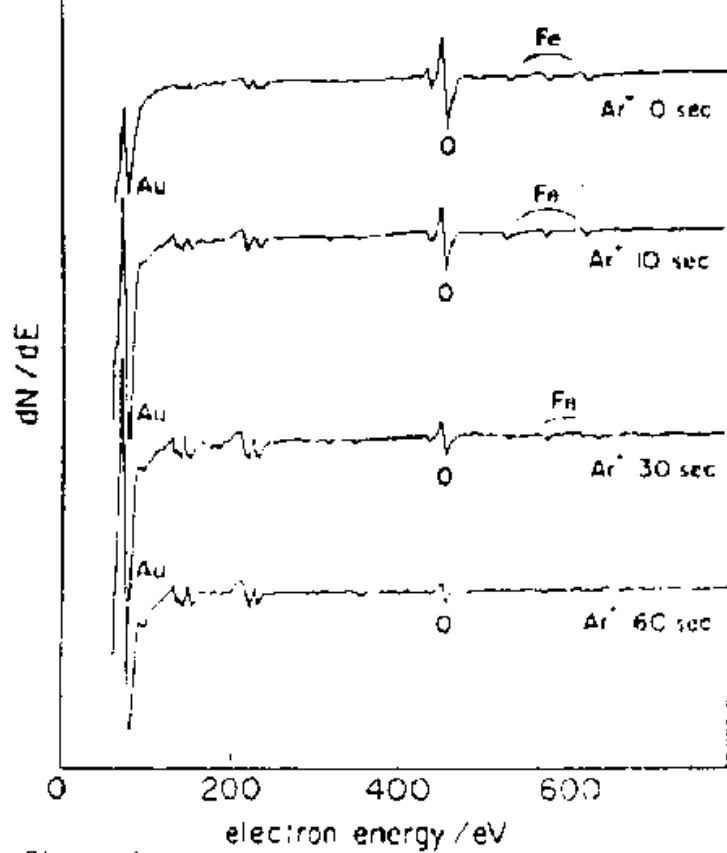


Figure 3

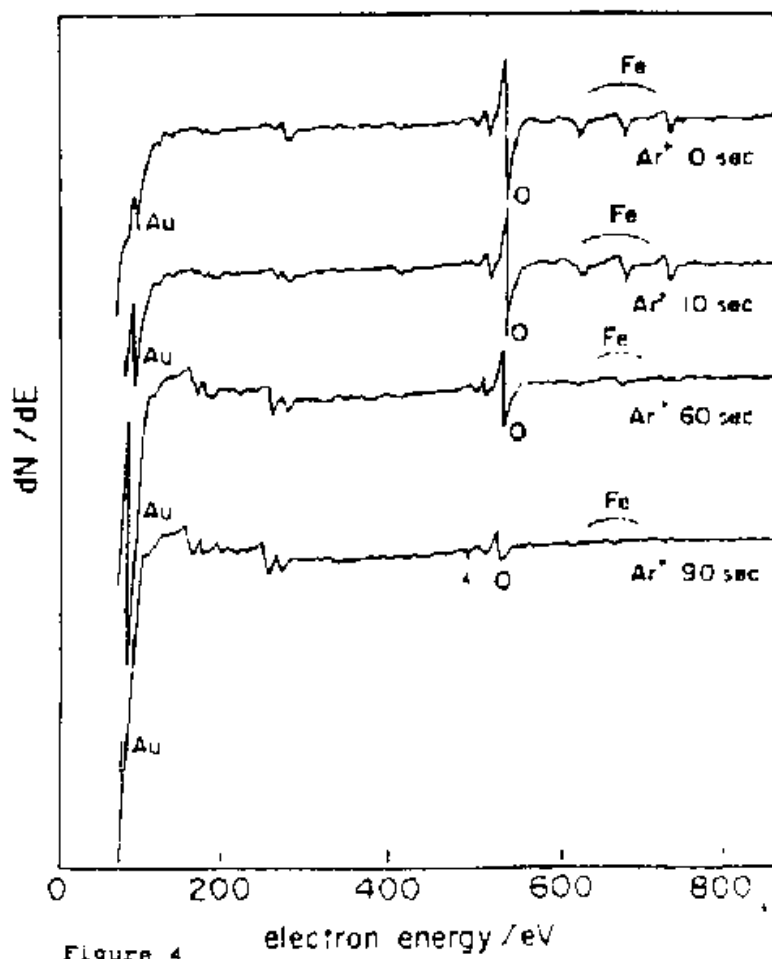


Figure 4

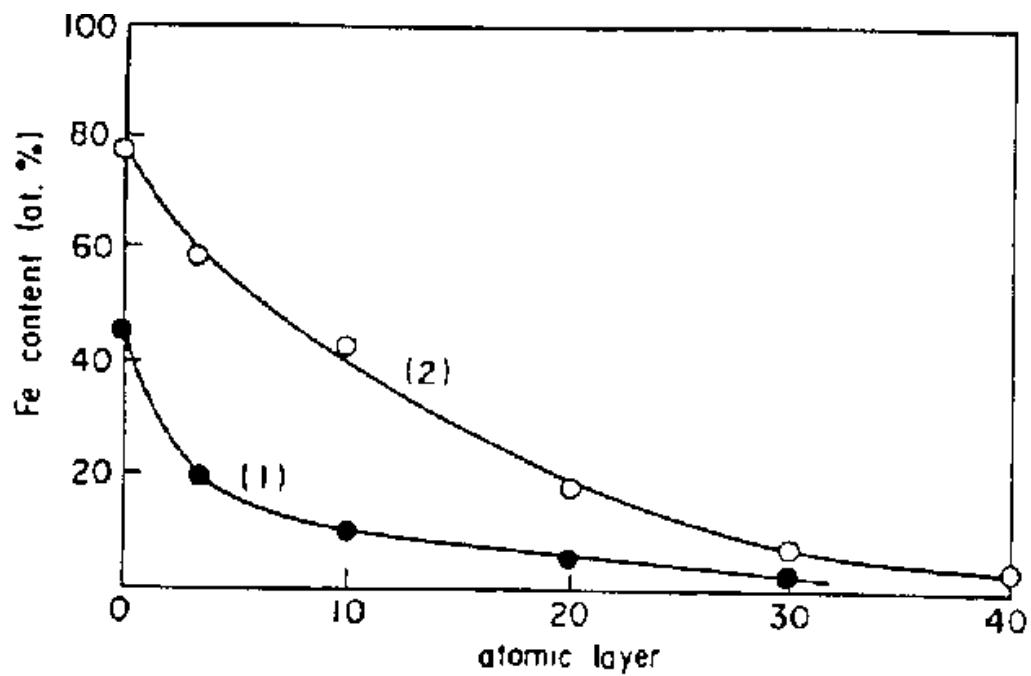


Figure 5

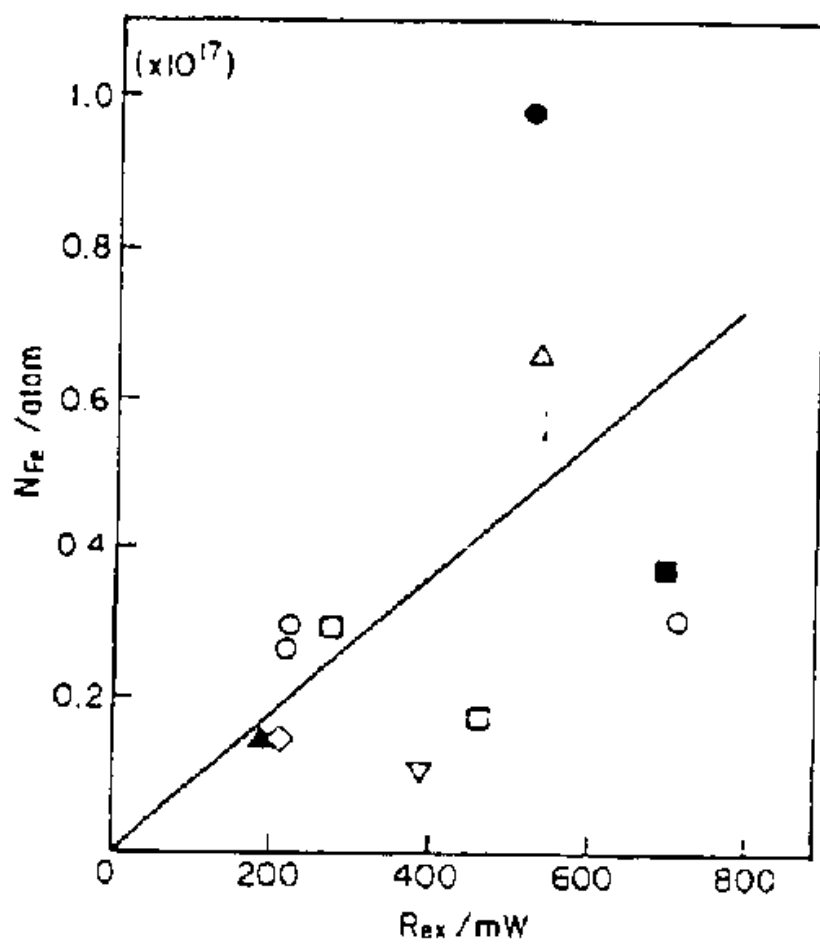


Figure 6