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TRITIUM GENERATION AND LARGE EXCESS HEAT EVOLUTION BY ELECTROLYSIS IN LIGHT AND HEAVY WATER–POTASSIUM CARBONATE SOLUTIONS WITH NICKEL ELECTRODES

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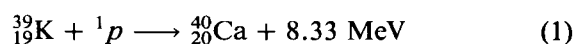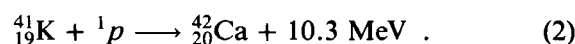*Kita-15, Nishi-7, Kita-ku, Sapporo, 060, Japan*

The generation of tritium was quantitatively measured in an electrolytic cell with a nickel cathode and a platinum anode in potassium carbonate-light and heavy water solutions. Simultaneously, the evolution of a large amount of excess heat (70 to 170% for the input power) was observed during electrolysis of these solutions. The tritium generation by electrolysis provides some of the most conclusive evidence for so-called cold fusion, along with the calcium generation described in a previous paper. On the basis of the current experiments and the knowledge of the kinetics of a hydrogen evolution reaction in an alkaline solution, the nuclear reactions taking place are worth mentioning.
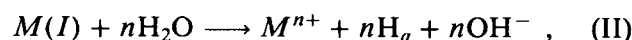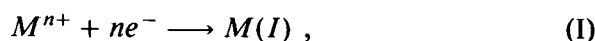
I. INTRODUCTION

The evolution of extraordinarily large excess heat (200 to 360% for the input power) and the production of calcium ions were observed during the electrolysis of a potassium carbonate solution of light water by using a porous nickel cathode.[1] It was concluded that the main cause of such large excess heat might be the following nuclear reactions of potassium and a proton, both of them being the intermediates of the hydrogen evolution reaction[2]:

$$^{39}_{19}K + {}^1p \longrightarrow {}^{40}_{20}Ca + 8.33 \text{ MeV} \tag{1}$$

and

$$^{41}_{19}K + {}^1p \longrightarrow {}^{42}_{20}Ca + 10.3 \text{ MeV} . \tag{2}$$

As has been shown in the preceding paper,[2] the hydrogen evolution reaction on the low overvoltage metals, i.e., platinum group metals, silver, gold, titanium, nickel, and so forth, is composed of the following elementary steps in the solution of alkali metal, alkaline earth metal, Co^{2+}, and other cations:

$$M^{n+} + ne^- \longrightarrow M(I) , \tag{I}$$

$$M(I) + nH_2O \longrightarrow M^{n+} + nH_a + nOH^- , \tag{II}$$

and

$$2H_a \xrightarrow{\quad} H_2 , \tag{III}$$

where M^{n+}, $M(I)$, and H_a denote the metallic cation, the intermediate of the intermetallic compound formed between the cation and the electrode metals, and that of adsorbed or absorbed hydrogen species on or in the electrode, and $\xrightarrow{\quad}$, rate determining, respectively. It has been shown in the cases of platinum and nickel cathodes[2,3] that intermediate $M(I)$ accumulated in the surface layer of the cathode whose thickness attained more than 100 monolayers. It is naturally expected that the intermediate $M(I)$ was undergoing cold fusion with another intermediate H_a being in the solid solute form in the vicinity.

The tritium generation during electrolysis of a heavy water solution of LiOD was reported in the first paper for cold fusion proposed by Fleischmann and Pons[4] and after that many efforts have been made to confirm

it around the world. Two years after the statement by Fleischmann and Pons, Mills and Kneizys[5] proposed that such an excess heat evolution due to electrolysis took place in a light water solution of K_2CO_3 on a nickel cathode. That was reexamined by Noninski.[6] In parallel with these experimental studies, Bush predicted the nuclear fusion between potassium and hydrogen,[7] but mentioned nothing about the chemical state of these reactants and their supplying route. The experimental result obtained by Srinivasan et al.[8] indicates that tritium is generated even in light water solutions of Li_2CO_3 and K_2CO_3 as well as in a heavy water solution and their mixture of a light and heavy water solution on a nickel cathode. There are some possibilities of other nuclear reactions and other causes of heat evolution in these electrolytic systems besides reactions (1) and (2). The aim of this work is to observe tritium generation during the electrolysis in order to find positive evidence of cold fusion.

II. EXPERIMENTS

II.A. Electrolytes

Electrolytes used for the observation of tritium generation were 0.5 mol/ℓ K_2CO_3 (Cicca, Extrapure) solutions of light water and deuterium oxide (Merck deuteration degree not >99.8%). The light water described here means a subterranean one that was pumped up in the campus (tap water) of Hokkaido University and purified twice by ion exchange and distillation.

II.B. Electrolytic Cell and Electrolysis

The structure of the electrolytic cell and the material of the porous nickel cathodes (0.05 cm³ ± 10%, for example, 1.0 × 0.5 cm in size, and 0.1 cm in thickness) were nearly the same as in the previous work,[1] except for the main part of the cell vessel, which was made of quartz glass and not cooled directly by any air or water stream during electrolysis. Moreover, during electrolysis, the electrolyte (20 ml) was not stirred by hydrogen bubbling.

A mercury thermometer (0 to 50 ± 0.05°C) was used for the measurement of the electrolyte's temperature in the cell. The electrolysis was carried out in a dark chamber made of a lead wall of 10-cm thickness, which was settled in an air-conditioned room at 20 ± 1°C.

The electrodes were polarized galvanostatically and at that time the potential difference between the cathode and the anode in response to the current and the electrolyte's temperature were recorded. A heavy water electrolyte was used for the experiment for comparison. The input power W_{input} was estimated on the basis of the following equations:

$$W_{input} = I \cdot (E - 1.48) \text{ for a light water electrolyte}$$

(3)

or

$$W_{input} = I \cdot (E - 1.54) \text{ for a heavy water electrolyte },$$

(4)

where I means the electrolytic current and E means the potential difference between the test electrode and the counter electrode. In each experiment, electrolysis was carried out for 6 to 26 h.

II.C. Tritium Measurement

After electrolysis, the amount of tritium in the electrolyte was measured by means of a liquid scintillation analyzer (Packard-CA 2550), which is down in the second basement of a building to keep the background value low and not fluctuating, and the amount was expressed as the normalized generation rate of ^3t, becquerel-value per 20 ml (volume of the electrolyte), but the decrease of the electrolyte's volume due to electrolysis (maximal 3.5 ml) in each run was taken into account. All radioactivity measurements of the samples were counted in the energy region of emission rays, 0 to 18.6 keV. The comparison of the energy spectrum between the experimental samples and the standard sample of ^3t revealed that the counts per minute (cpm) observed in the region of 0 to 18.6 keV was due to the disintegration of ^3t. Checking the shape of the spectrum, the ^3t amount of each sample was determined by cpm values in the region of 0 to 18.6 keV. The efficiency of the count against the disintegration rate per minute (dpm) of ^3t, i.e., cpm/dpm, was determined to be 0.34 by use of the standard ^3t sample. The counting vials were made of glass of low ^{40}K content, and volumes were ~20 ml. The samples for the tritium measurement were prepared by the following procedure. Each sample of the electrolyte in the amount of 1 ml was mixed with 10 ml of a scintillator (Packard, Ultima Gold). A duration for each tritium measurement of the sample was 30 min. The background value of this scintillation analyzer, which was usually kept very stable and found to be 4.4 ± 0.4 cpm in the energy region of emission rays, 0 to 18.6 keV, by use of 1-ml distilled water instead of the subject solution, was checked before each measurement.

II.D. Excess Heat Measurement

The cell constant was found to be 11.0 ± 0.1°C/W in the same vessel of quartz glass that was filled with 20.0 ± 0.05 ml of the electrolyte and put in the dark chamber as described earlier, but a nichrome wire heater with a resistance value of 10 Ω was settled in the cell instead of the cathode. The cell constant was reciprocally proportional to the volume of the electrolyte in the region, 15 to 20 ml. The excess heat (E-H) was determined as the following ratio of the increase in the electrolyte temperature due to electrolysis ΔT_{elec} measured at each final moment of the electrolysis to that evaluated from the cell constant ΔT_{heat} at the same input power W_{input}

for both ΔT's, where the effect of decrease of the electrolyte's volume due to electrolysis (maximal 3.5 ml) on the cell constant was taken into account:

$$\text{E-H} = (\Delta T_{elec} - \Delta T_{heat})/\Delta T_{heat} \ . \tag{5}$$

III. RESULTS AND DISCUSSION

Some experimental results observed in 0.5 M K_2CO_3 solutions of light and heavy water, are summarized in Table I. In the series of these experiments, a cathode was used for the electrolysis, which had been polarized more than 100 h before this series. The experiment numbers in Table I and also in the following table denote the order of execution of the experiments. The experiments from 0, 0', 1 to 3 and from 0'', 4 to 5 in Table I were continued one after another without interruption except for renewing the electrolyte.

It is quite apparent from Table I that ^3t is generated certainly during the electrolysis in both cases of light and heavy water solutions. But, the experimental result does not indicate that the generation rate of ^3t is simply corresponding to the atomic fraction of deuterium of each solution. Incidentally, a little value of Bq/20 ml of experiment 0' may be mainly due to the radioactivity of ^{40}K contained in the solution, but not due to ^3t, because of its little natural content.

The results of experiments 1, 2, and 3 show the possibility that the cathode had included some amount of tritium before these experiments. Another series of experiments with a new cathode were carried out to observe the results not affected by the history of a cathode and to eliminate this concern. Moreover, in these experiments, the cathode was left at the rest potential in the electrolyte a certain time denoted by t_{rest} after electrolysis, because just after switching off the polarizing current, the cathode continued to generate hydrogen gas and there was the possibility to change the tritium concentration of the electrolyte. The results thus obtained by use of a new cathode are shown in Table II. It is obvious from Tables I and II that the results did not show any simple relationship between the amount of ^3t generation and the other factors, i.e., polarization current I, input power W_{input}, and rest time t_{rest}, but comparison of the amount of ^3t with the value of the excess heat reveals a roughly linear relation between them. Each electrode cut off from the same material may show the specific slope of the relation (see Fig. 1). Besides, it is found that there is no essential difference of the results between worn and new electrodes shown in Tables I and II, respectively, and the results are hardly affected by t_{rest} longer than 20 h.

The excess heat observed in the present work was roughly equal to a half of that in the previous work.[1]

TABLE I

Generated Amount of Tritium and E-H During Electrolysis in 0.5 M K_2CO_3 Solutions of Light and Heavy Water by Use of a Worn Cathode Before This Series of the Experiments

Experiment Number	Solution	I (A)	E (V)	Duration (h)	W_{input} (W)	$T_{in\ cell}$ (°C)	E-H (%)	^3t (Bq)
Accuracy (±)		0.001	0.01	5 min	≤5%	0.15	≤5	≤5%
0	H_2O[a]							0.00
0'	H_2O[b]	0		22				0.31[c]
1	H_2O	0.300	−3.29	6	0.54	36.0	169	9.13[c] (36.5)[d]
2	H_2O	0.300	−3.48	6	0.60	35.2	130	8.23[c] (32.9)[d]
3	H_2O	0.300	−3.57	22	0.63	35.5	124	6.33[c] (6.91)[d]
0''	D_2O[e]							32.3[c]
4	D_2O	0.300	−3.70	26	0.65	35.0	110	426[c] (393.2)[d]
5	D_2O	0.400	−4.19	26	1.06	40.1	72	54.9[c] (50.7)[d]

[a]Pure water.
[b]Electrolyte with the nonpolarized cathode.
[c]Bq denotes the amount of ^3t generated in 20 ml electrolyte.
[d]Bq[c] for 24 h.
[e]Electrolyte without any electrode.

TABLE II

Generated Amount of Tritium and E-H During Electrolysis in 0.5 M K_2CO_3 Solution
of Light Water by Use of a New Cathode

Experiment Number	Solution	I (A)	E (V)	Duration (h)	W_{input} (W)	$T_{in\ cell}$ (°C)	t_{rest} (h)	E-H (%)	^3t (Bq)
Accuracy (±)		0.001	0.01	5 min	≤5%	0.15	5 min	≤5	≤5%
0	H_2O[a]								0.00
0′	H_2O[b]	0	0						0.00
1	H_2O	0.350	−3.76	26	0.80	36.0	20	82	1.59[c] (1.47)[d]
2	H_2O	0.400	−3.83	24	0.94	38.5	74	78	2.60[c] (2.60)[d]
3	H_2O	0.440	−3.90	21	1.07	38.7	46	108	2.88[c] (3.29)[d]
4	H_2O	0.250	−3.38	26	0.48	32.0	73	127	3.24[c] (2.99)[d]

[a]Pure water.
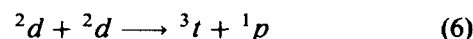[b]Pure water with the nonpolarized new cathode.
[c]Bq denotes the amount of ^3t generated in 20 ml electrolyte.
[d]Bq[c] for 24 h.

Such a decrease of the excess heat might be due to the change of the experimental conditions described earlier. Especially, the omission of cooling the cell affected the rates of the nuclear reactions. It seems that a rise of temperature in the cell greatly increases the rate of step (III) and diffusion of potassium in the electrode rather than that of step (I) on the basis of the comparison of the activation energy among these steps and consequently decreases the densities of the intermediates, especially $M(I)$ accumulated in the surface layer
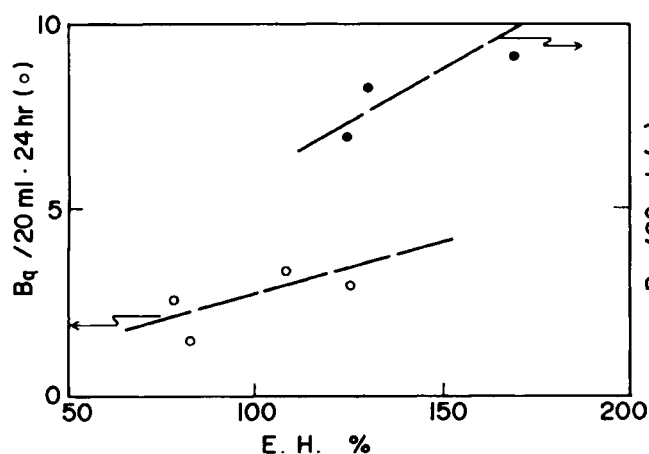

Fig. 1. Relations between generation rate of ^3t and evolved E-H during electrolysis concerning the results of experiments 1, 2, and 3 in Table I (●) and experiments 1 through 4 (o) in Table II.

of the cathode. The activation energy of step (I) on nickel was determined to be 3 kcal/mol from the results of the galvanostatic transient study,[2] but that of the overall reaction on nickel and the self-diffusion of potassium quoted from the literature,[9] were at 8 to 14 and 9.8 kcal/mol in the temperature range of 0 to 60°C, respectively.[10]

The experimental results just described reveal that tritium was generated during the hydrogen evolution by electrolysis on a nickel cathode of light and heavy water solutions of potassium carbonate. The following reactions were presented as the most likely ones to generate ^3t:

$$^2d + {}^2d \longrightarrow {}^3t + {}^1p \tag{6}$$

and

$$^2d + {}^2d + {}^2d \longrightarrow {}^3He + {}^3t . \tag{7}$$

It may easily be imagined that the hydrogen intermediate of deuterium (D_a) expressed by H_a in the elementary step (II) can be formed in the solid of the electrode metal at the boundary layer and occurs in reactions (6) (Ref. 4) and (7) (Ref. 11). If ^3t is not spent for any nuclear reaction, the hydrogen intermediate of tritium T_a formed thusly diffuses to the surface of the nickel cathode and changes to a water molecule almost HTO through a step of the reaction with OH^-, on which the quasi-equilibrium state is held, but not the recombination step (III) because of the recombination mechanism as described earlier. Consequently, hardly any of the fusion product ^3t goes outside the cell as T_2.

On the basis of the results concerning heavy water as well as light water, it was disproved that the evolution of the excess heat during electrolysis was due to only the individual reactions generating ^3t described earlier, because the generation rates of ^3t were far less than that of calcium,[1] even in the electrolyte of heavy water. It may easily be imagined that ^3t is undergoing further nuclear reactions accompanied by intermediates of the expected nuclear reactions and of the hydrogen evolution reaction, for example, ^1n, ^1p, ^2d, ^{3}He, ^{4}He, ^{39}K, ^{41}K, ^{40}Ca, ^{42}Ca, and so forth in nickel.

REFERENCES

1. R. NOTOYA, "Cold Fusion by Electrolysis in a Light Water-Potassium Carbonate Solution with a Nickel Electrode," *Fusion Technol.*, **24**, 202 (1993).

2. R. NOTOYA and A. MATSUDA, "Hydrogen Overvoltage on Platinum in Aqueous Sodium Hydroxide, Part III Intermediates," *J. Res. Inst. Catal., Hokkaido Univ.*, **14**, 198 (1966); see also "Kinetic Study of Electron Transfer Step of Hydrogen Evolution Reaction on Metals in Aqueous Media," Extended Abstracts of 34th Mtg. International Society of Electrochemistry, Erlangen, Germany (1983); see also R. NOTOYA, "Galvanostatic Transient Method for the Study of Electro-Catalysis," *Elektrokhimiya*, **29**, 53 (1993).

3. R. NOTOYA, "Alkali Metallic Intermediate of Hydrogen Electrode Reaction," *Abstracts of 16th Mtg. Hokkaido Branch of Electrochemical Society*, Sapporo, Japan, January 18, 1990.

4. M. FLEISCHMANN and S. PONS, "Electrochemically Induced Nuclear Fusion of Deuterium," *J. Electroanal. Chem.*, **261**, 301 (1989).

5. R. L. MILLS and S. P. KNEIZYS, "Excess Heat Production by the Electrolysis of an Aqueous Potassium Carbonate Electrolyte and the Implications for Cold Fusion," *Fusion Technol.*, **20**, 65 (1991).

6. V. NONINSKI, "Excess Heat During the Electrolysis of a Light Water Solution of K_2CO_3 with a Nickel Cathode," *Fusion Technol.*, **21**, 163 (1992).

7. R. T. BUSH, "A Light Water Excess Heat Reaction Suggests That 'Cold Fusion' May Be 'Alkali-Hydrogen' Fusion," *Fusion Technol.*, **22**, 301 (1992).

8. M. SRINIVASAN et al., "Tritium and Excess Heat Generation During Electrolysis of Aqueous Solutions of Alkali Salts with Nickel Cathode," *Frontiers of Cold Fusion, Proc. ICCF-3*, p. 123, Universal Academy Press.

9. *Chemical Handbook, Fundamental Edition*, Japan Chemical Society, Eds., Vol. 2, Tables 6 through 48, Maruzen Inc., Tokyo, 1984.

10. *Encyclopedia of Electrochemistry of the Elements*, Vol. 9 part A, p. 529, A. J. BARD, Ed., Marcel Deker Inc., New York (1973).

11. A. TAKAHASHI et al., "Excess Heat and Nuclear Products by D$_2$O/Pd Electrolysis and Multibody Fusion," *Int. J. Appl. Electromagnet. Mat.*, **3**, 221 (1992).