

SEPARATION AND UTILIZATION OF FISSION PRODUCTS IN NUCLEAR FUEL CYCLE AS HYDROGEN PRODUCTION CATALYST

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Abstract

Separation and utilization of rare metal fission products (RMFP) in nuclear spent fuel was studied to apply as a catalyst for hydrogen generation by water electrolysis. The RMFP, Pd, Ru, Rh and Tc, etc, are abundant, more than ca. 30kg per metric ton of a typical fast breeder reactor (FBR) spent fuel. The RMFP can be selectively separated from high level liquid waste (HLLW) by catalytic electrolytic extraction (CEE) method. Specific metallic cation such as Pd²⁺, which originate in the solutions, may act as promoters (*i.e.*, Pd_{adatom}) or mediators, thereby accelerating electrochemical deposition of RuNO³⁺, Rh³⁺ and ReO₄⁻ (simulator TcO₄⁻). Current maximum deposition ratios of RMFP by CEE were 95-99% for Pd, 60% for Ru, >99% for Rh, 55% for Re and 25% for Tc, respectively in the nitric acid media. Electro-deposited electrodes were successively dedicated to the water (alkali or sea water) electrolysis tests. The Pd-Ru-Rh-Re mixture deposit electrodes from the solution composition of Pd:Ru:Rh:Re =3.5:4:1:1 showed the lowest initial hydrogen over potential with the highest cathodic currents in the given potential, thereby suggesting to alternate with the existing catalysts for hydrogen generation. The paper will conclusively propose RMFP, generated by nuclear fission reaction, as potential material for hydrogen production in a novel vision to bridge nuclear and hydrogen energy systems.

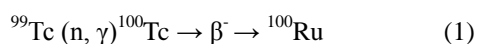
Keywords: fission products, rare metal, nuclear fuel cycle, catalytic electrolytic extraction, hydrogen production

1. Introduction

【RMFP in Nuclear Fuel Cycle】 Towards the ultimate purpose of minimizing radioactive waste from the nuclear fuel cycle, partitioning and transmutation (**P&T**) of actinides (An) and long-lived fission products (LLFP; ⁹⁹Tc, ⁷⁹Se, ¹⁰⁷Pd, etc.) has been investigated. Along this context, extended recycling of rare metal fission products (RMFP; Ru, Rh, Pd, Tc, Se, Te, etc), by utilizing their chemical and radiochemical properties, should be considered as a viable alternative fate (**P&T, U**) [1,2]. The utilization of the RMFP resulting from the transmutation of LLFP can also be envisioned in the future. The most symbolical example of such a

utilization will be stable ruthenium (Ru) resulting from the neutron capture reaction of long-lived radioactive technetium (Tc) in fast breeder reactors or accelerators.

□ □



Typical amounts of RMFPs estimated by ORIGEN-II calculations are shown in Table 1, where Ru and Rh are categorized as short-lived FP. The calculations indicate that the amounts of RMFPs generated are proportional to the burn-up of the irradiated fuel, thus, highly irradiated spent MOX fuel from fast reactor (FR) (burn-up: 150,000 MWd/t, cooling time: 4 y) will contain more than 30 kg of RMFPs per metric ton of U. More than

Table 1 Typical amounts of RMFPs per ton of FR spent fuel

RMFP	Ru	Rh	Pd	Tc	Te	Se	Note
Amount (Kg/HMt)	12.5	3.6	11.1	3.3	2.7	0.2	SF(FR); 150,000MWd/t, Cooled 4 years

*LLFP ($\tau_{1/2} > 10^4$ y); ^{79}Se , ^{93}Zr , ^{99}Tc , ^{107}Pd , ^{126}Sn , ^{129}I , ^{135}Cs
RMFP; Ru, Rh, Pd, Tc, Te, Se, etc

99.9% of RMFP tends to be contained in high level liquid waste (HLLW) by the spent fuel reprocessing.

【Catalytic Electrolytic Extraction for Recovery of RMFP】 Electrolytic extraction (EE), applying to recover RMFP from the HLLW or dissolver solution of spent fuel, has several advantages. For instance, the EE is capable of minimizing the secondary salt and organic radioactive wastes, and of controlling by *in situ* manner under normal temperature, seems to be advantageous for safety and remote / automatization points of view. In general, deposition of Pd^{2+} is easy by the EE, with a deposition ratio more than 95% being constantly attainable. While the deposition of Ru or Re (simulated ion of Tc) suffered significant disturbances in HNO_3 media, the addition of Pd^{2+} remarkably improved their deposition rates even in the highly acidic media. As shown in Fig. 1, the specific EE mechanisms involved were experimentally estimated by the fact that the deposition of Ru and Rh was in the form of metallic *solid solution alloy* with Pd, and the deposition of Re as ReO_3 (and/or ReO_2) in an *island state* on the Pd layers. This

was supported by ESCA analysis (using X-ray photo-emission spectroscopy) and the structural parameters determined by extended X-ray absorption fine structure (EXAFS) curve fitting on the deposits [2]. Recent results reconfirmed huge, around $100\ \mu\text{m}\phi$, island state deposits of ReO_3 . Whereas the deposition ratio of Ru was used to be limited as around 40% in 2.5M HNO_3 , more than 99% of the deposition ratio was achieved when an excess of Pd^{2+} ($\text{Pd}^{2+}/\text{Ru}=1.6$) was added in installments.

Hereupon, Pd^{2+} would accelerate electro-deposition of the other ions as a *promoter* (i.e., $\text{Pd}_{\text{adatom}}$) at the electrode surface or as a *mediator* in the bulk solution, respectively (i.e., **CEE**: Catalytic Electrolytic Extraction). Accordingly, it was suggested that quantitative electro-deposition would require the specific electrolysis manner where Pd should constantly exist at either the surface of electrode or in the bulk solution.

As for separation of RMFP from simulated HLLW, a galvanostatic electrolysis was employed as typical method of the CEE. Metal ions with $E^0 > 0.7\text{V}$ (vs. NHE)

tended to deposit on the cathode, and their deposition ratio was observed to be proportional to the order of the redox potential; $\text{Pd} > \text{Te} > \text{Se} > \text{Rh} > \text{Ru} > \text{Re}$. Mo and Zr were not deposited but co-precipitated as Zr_2MoO_7 at less than 1.5M HNO_3 . ^{98}Mo will be the source of $^{99\text{m}}\text{Tc}$ and ^{93}Zr is one of the target LLFP nuclide of the transmutation. An interaction between Pd^{2+} and TcO_4^- during the EE was previously confirmed [3]. While the deposition of Tc was significantly suppressed with the increase of nitric acid concentration, addition of Pd^{2+} led its electro-deposition to increase

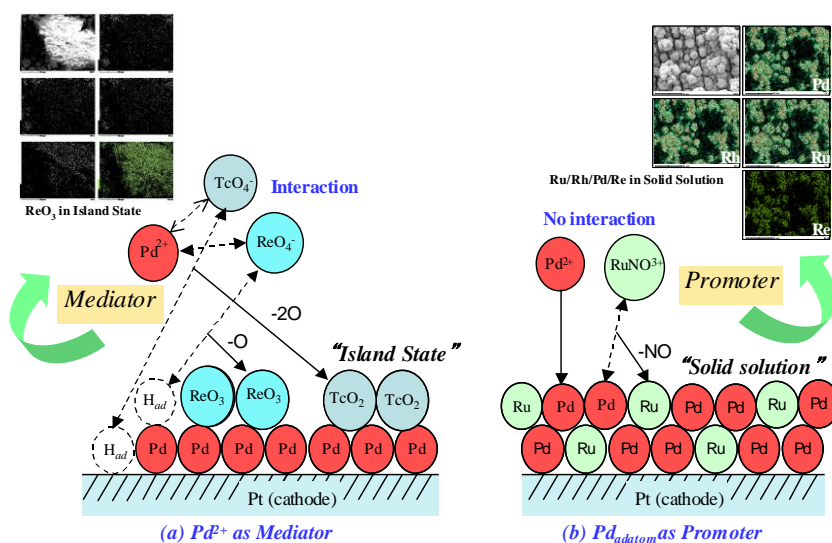
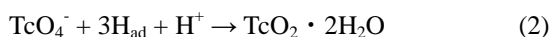


Fig. 1 CEE (Catalytic Electrolytic Extraction) Mechanism

expectedly even though HNO₃ concentration was more than 2M. Namely, Pd²⁺ addition can conquer negative HNO₃ effects, possibly attributing to prevent redissolution of TcO₂ hydrate deposits. Quantitative electro-deposition potential region of TcO₄⁻ was observed to be 0.4V-0.05V (vs. NHE). This agreed well with the hydrogen adsorption-desorption potential region of the smooth Pt electrode, and the maximum deposition was observed near the hydrogen evolution potential. Thus, H_{ad} likely participated in the electro-deposition of TcO₄⁻ in the system (H_{ad} effect).



However, under extremely negative conditions (*i.e.*, <-0.3V), simultaneous hydrogen evolution disturbed the Tc deposition reaction. For a carbon electrode, which had no H_{ad} region in 3M HNO₃, the reduction of TcO₄⁻ to TcO²⁺ was found to be most significant on the contrary [4].

2. Experimental

The cyclic voltammograms (CV) of Pd, Rh, Ru, Re, Pd-Ru and Ru-Rh were measured in a few scan speeds, 50 mV/s, 200 mV/s and 500 mV/s, using Au cathode as working electrode, Pt plate as counter electrode in potential range 0 to 0.8 vs. Ag/AgCl and in 0.5N HNO₃ separately containing of 200 mM of Pd, Rh, Ru, Re for RMFP electrodes.

Typical CV of Pd, Rh, Ru and Re are shown in Fig.2. The reduction peak of Pd²⁺ to Pd was confirmed at about

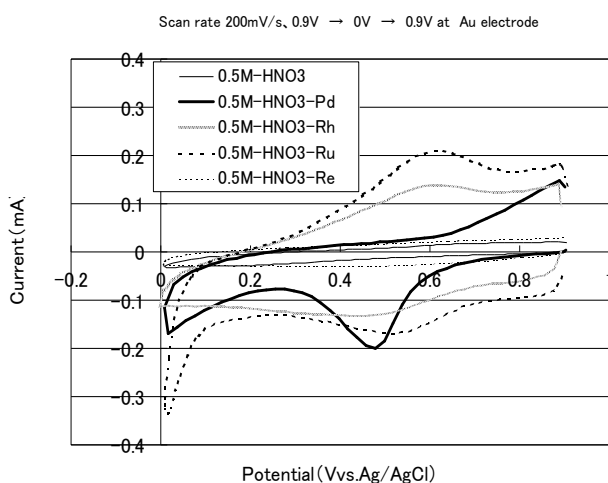


Fig.2 Cyclic Voltammograms of Au electrode in 0.5M HNO₃ separately containing Pd²⁺, Rh³⁺, RuNO₃³⁺, ReO₄⁻ for RMFP electrodes

0.5 V (vs. Ag/AgCl). However, the oxidation peak of Pd to Pd²⁺ was not clear in this potential range. Thus the reaction of Pd²⁺ to Pd might be irreversible in 0.5 M HNO₃ solution. Broad reduction and oxidation peaks were observed for both Rh and Ru. The ReO₄⁻ was electrochemically inactive at the Au electrode as was previously expected.

Based on these fundamental behaviors with CV, electrolysis conditions for RMFP-deposit electrodes were set up as indicated in Table 2 [5]. Experimental cell is shown in Fig.3, where the cation-exchange membrane, nafion-117, separated a catholyte and an anolyte. Both experiments on EE and hydrogen evolution were carried out using the same cell, by just changing the electrolytes, *e.g.*, 0.5 M nitric acid solution for CEE, and 1M NaOH solutions or artificial seawater for hydrogen evolution measurements.

3. Results and Discussions

Table 2 Experimental conditions for RMFP electrodes by Catalytic Electrolytic Extraction

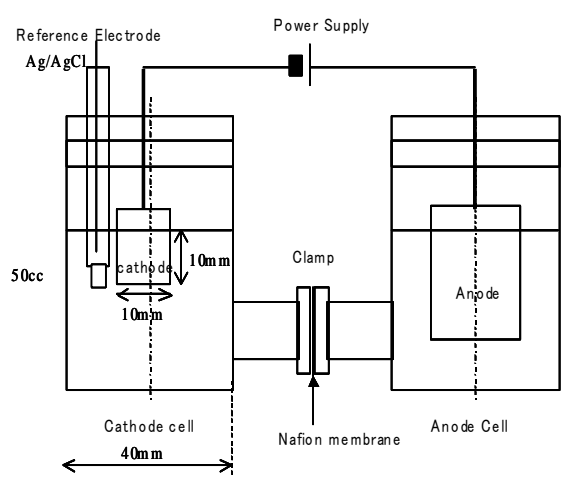


Fig.3 Experimental cell

3.1 Electrochemical Separation

The electrochemical reduction results are shown in Table

3, where “Pd-Ru-Rh-Re (3.5:4:1:1)”, for example, means the quaternary-, Pd-Ru-Rh-Re, deposit Pt electrode obtained from the electrolyte containing Pd, Ru, Rh and Re (Tc) ions in the weight ratio of 3.5:4:1:1, corresponding to the composition of the FR spent fuel indicated in Table 1.

The reduction ratios, calculated from the balance of the ionic concentration during electrolysis, will suggest the maximum deposition ratios of RMFP. The highest and constant reduction ratio of 95-99% was obtained for Pd (Run1-11). The Pd deposit tended to form dendrites, which was easy to be detached by simultaneous hydrogen evolution. The reduction of Rh was similar to Pd, by direct reduction of Rh^{3+} to metal Rh. On the contrary to those, reduction of Ru might proceed by 2 steps like the following reactions;



$$E^0 = 0.255 \text{ V vs. Ag/AgCl}$$

Reduction ratio of it was 14%, but increased up to around 60 % in the presence of coexisting ions especially Pd^{2+} . The reduction of TcO_4^- and ReO_4^- were low around 1.7 % and 16 %, respectively. As previously reported [1,2], the presence of Pd accelerated the deposition of Tc

Table 3 Reduction Ratios of RMFP by Catalytic Electrolytic Extraction

No.	System	Reduction ratio (%)				
		Pd	Ru	Rh	Re	Tc
1	Pd	>99	—	—	—	—
2	Ru	—	14	—	—	—
3	Rh	—	—	>99	—	—
4	Re	—	—	—	16	—
5	Tc	—	—	—	—	1.7
6	Pd-Ru	99.3	60.9	—	—	—
7	Pd-Rh	99	—	84.7	—	—
8	Pd-Re	99.4	—	—	10	—
9	Ru-Rh	—	58.2	32.5	—	—
10	Ru-Re	—	14.5	—	13.5	—
11	Rh-Re	—	—	10	43	—
12	Pd-Ru-Rh-Re(1:1:1:1)	95.7	46	14.5	19	—
13	Pd-Ru-Rh-Re(3.5:4:1:1)	99	11.8	2.1	33.4	—
14	Pd-Ru-Rh-Re(3.5:4:1:1)*1	94.7	16.5	26.6	55.3	—
15	Pd-Ru-Rh-Re(1:1:1:1)	90	35	15	20	—
16	Pd-Ru-Rh-Re(3:1:1:1)*1	50	32	7	12	—
17	Pd-Ru-Rh-Re(5:1:1:1)*1	60.9	54.8	19.8	12.8	—
18	Pd-Ru-Rh-Re(1:3:1:1)	72	13	0	5	—
19	Pd-Ru-Rh-Re(1:5:1:1)	77	10.7	0	0	—
20	Pd-Ru-Rh-Re(1:3:1:1)	85.3	6.8	13.6	9.9	—
21	Pd-Ru-Rh-Re(1:1:3:1)	96.1	39.7	7.7	16.2	—
22	Pd-Ru-Rh-Re(1:1:5:1)	93.8	41.7	6.0	9.9	—
23	Pd-Ru-Rh-Re(1:1:1:3)	93.2	36.5	6.1	9.8	—
24	Pd-Ru-Rh-Re(1:1:1:5)	93.2	32.9	3.7	7.9	—
25	Pd-Ru-Rh-Tc(1:1:1:0.5)	86.3	41.1	13.4	—	26.5

*1 Pd divided addition

as well as Ru in a binary ionic solution. Rh was also found to accelerate the reduction of ReO_4^- in this experiment. It was noted that maximum deposition of Tc, 26.5%, was observed in the result of quaternary deposition system of Pd-Ru-Rh-Tc (1:1:1:0.5). At the initial operation of the CEE, setting low cathode current density, e.g., $2.5mA/cm^2$ with compulsory stirring, was necessary to get a minute and stable deposit of Pd layers, and this procedure was found to be very essential to obtain higher amounts of co-deposits of the other ions in the quaternary deposition system (Run12-25).

Figure 4 shows the element map of the deposit surface with EPMA (Electron Probe Micro Analyzer) in the case of Run17, 19, 22 and 24 in Table 3. In Run14, 16 and 17, Pd^{2+} was added to the catholyte in 5 equal increments to allow Pd to constantly exist either in the bulk solution (as Pd^{2+}) or at the electrode surface (as Pd_{adatom}). The shape of the deposits was not dendrite but became rather spherical in uniformity, likely cohering with fine particles as in Run 17. In the quaternary deposition system, an excess and divided addition of Pd^{2+} resulted in the deposit with almost equal atom composition of metals (Pd-Ru-Rh) at the surface. However, atom numbers of Re at the deposition surface was seemed to be less than others even though its rather higher reduction ratio (Run14).

The amounts of deposit Pd; Rh, Ru and Re metals on the cathode were potentiostatically measured at a few potentials. The amount of deposit Rh metal compared

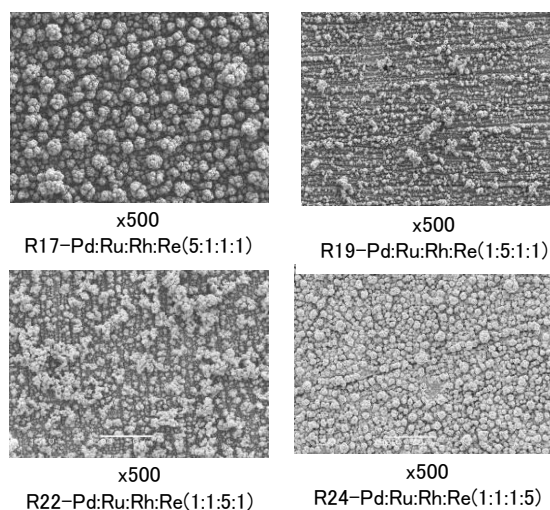


Fig. 4 EDS (EPMA) of the RMFP-deposit Pt Electrodes: Corresponding to Run17, 19, 22 and 24 in Table 3

with that of Ru is shown in Fig.5. At more negatively polarized potentials, the amount of deposit Rh metal was increased. However, that of deposit Ru metal was the lowest at -0.3 V vs. Ag/AgCl. The reduction potential of Rh^{3+} to Rh metal was about 0.553 V vs. Ag/AgCl, far from the H_2 evolution potential. The reduction of $RuNO_3^{3+}$ to Ru metal by Formulae (3) and (4) seems to be comparable with the H_2 evolution reaction.

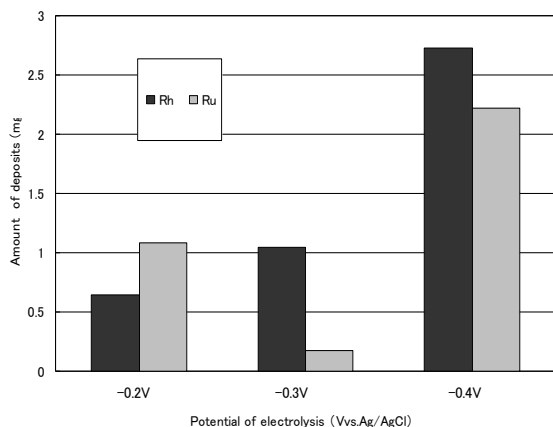


Fig.5 The amount of deposit Rh metal compared with that of Ru metal

3.2 Utilization of RMFP- deposited Electrodes

The cathodic currents corresponding to hydrogen evolution at the given polarized potential ($\phi = -1.25V$ vs. Ag/AgCl) versus initial hydrogen evolution potential ($\phi_{Hinit.}$) are shown in Fig.6. Each data on the figure are corresponding to those occurred in the Table 3. The $\phi_{Hinit.}$ was obtained by the extrapolation of cathodic IE curves. As hydrogen over potential, η , at trace of cathodic currents is given by the deposit electrodes belong to the

$$\eta = | \phi_{Hinit.} - E_H^0 |,$$

1st quadrant will suggest the higher catalytic reactivity comparing to that of the smooth Pt electrode. Among them, the quaternary deposit electrode (Pd-Ru-Rh-Tc (3.5:4:1:1)), those η were less than 0.93V, suggested the highest catalytic reactivity, the same or more even than Pt black electrode up to now. The single deposit electrodes, Pd, Re and Rh, showed lower, but Ru showed higher catalytic reactivity than smooth Pt. It is interesting to note that dual deposit electrode by Rh-Re suggested

significantly high reactivity in spite of each of them showed rather low reactivity.

As the number of atoms at the surface of electrodes is presently unknown, the cathodic currents are correlated to the deposit amount of Ru and Re as shown in Fig.7. The currents were increased with the total amount of deposit Ru and Re, and seemed to be saturated to be ca.150mA (more than twice of that of smooth Pt) by 4 element deposit electrodes, when the total deposition amount of Ru and Re exceeded ca.4mg. The reactivity of 4 element deposit electrodes was superior to that of 2 element deposit electrodes at the same amount of Ru and Re. Such a correlation was, however, never observed with the amount of Pd as shown in Fig.8. In the case of single deposit electrodes, the catalytic reactivity of Ru was significantly higher than that of Pt while those of Re and Pd were less. Therefore, Ru will be one of the dominant elements in causing such a high catalytic reactivity on the mixture deposit electrodes. Pd, on the contrary, must to have played just a role of combining the catalysts. Hereafter, the electro catalytic property of Rh should be clarified, and Re and Tc must be studied to find secure needs in their utilization [6].

The ratio of energy consumption of RMFP-deposit electrode to Pt electrode for H_2 generation was calculated by next equation (5), because amount of H_2 generation

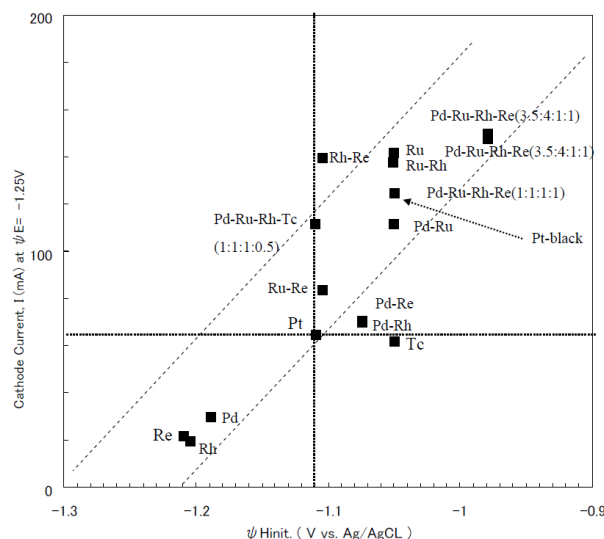


Fig.6 Relation between Cathodic Current Corresponds to Hydrogen Evolution at -1.25V vs. Ag/AgCl and initial hydrogen Evolution potential($\phi_{Hinit.}$) in 1M NaOH

was not measured experimentally.

The ratio of energy consumption

$$= I(V_{H_2}^{NM} + V_{op}^{NM})t / I(V_{H_2}^{Pt} + V_{op}^{Pt})t$$

$$= (V_{H_2}^{NM} + V_{op}^{NM}) / (V_{H_2}^{Pt} + V_{op}^{Pt}) \quad (5)$$

where $V_{H_2}^{Pt}$, $V_{H_2}^{NM}$, V_{op}^{Pt} and V_{op}^{NM} are the potential of hydrogen generation on Pt electrode, the potential of hydrogen generation on various RMFP-deposit electrodes, the over potential on Pt electrode and the over potential on various RMFP-deposit electrodes. $V_{op}^{Pt} = I \times R_{op}^{Pt}$ and $V_{op}^{NM} = I \times R_{op}^{NM}$, therefore

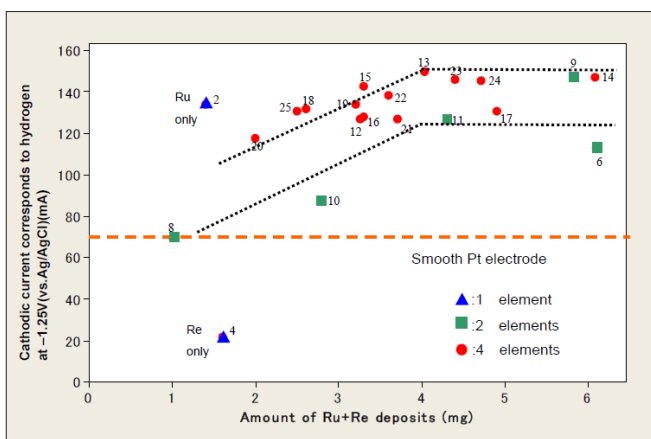


Fig. 7 Relation between Cathodic Current Corresponds to Hydrogen Evolution at -1.25V vs. Ag/AgCl and total amount of Ru and Re on the Electrodes in 1M NaOH

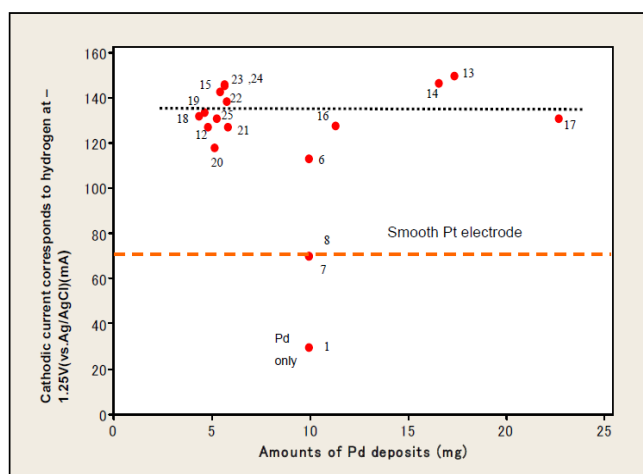


Fig. 8 Relation between Cathodic Current Corresponds to Hydrogen Evolution at -1.25V vs. Ag/AgCl and amount of Pd on the Electrodes in 1M NaOH.

The ratio of energy consumption

$$= (V_{H_2}^{NM} + I \times R_{op}^{NM}) / (V_{H_2}^{Pt} + I \times R_{op}^{Pt}) \quad (6)$$

The ratio of average energy consumption of the RMFP-deposit electrode of Pd-Ru-Rh-Re (5:1:1:1; Run17) for hydrogen generation is calculated to be 95% of that of Pt electrode.

4. Conclusive summary

Electrochemical depositions of Pd, Ru, Rh, Tc and Re in one, two and four elements in the nitric acid solution were carried out. The deposition ratios of Ru, Re and Tc in mixture elements solution significantly increased with the catalytic effect by co-presence of Pd^{2+} and Rh^{3+} . The current maximum deposition ratios of RMFP in the nitric acid were, 95-99% for Pd, 60% for Ru, >99% for Rh, 55% for Re and 25% for Tc, respectively. The Pd-Ru-Rh-Re mixture deposit electrodes from the solution composition of Pd:Ru:Rh:Re = 3.5:4:1:1 showed the lowest initial hydrogen over potential with the highest cathodic currents in the given potential, thereby suggesting to alternate with the existing catalysts. Therefore, RMFP, abundantly generated by nuclear fission reaction, would be a potential material for hydrogen production in a novel vision to bridge nuclear and hydrogen energy systems.

References

- [1] Ozawa, M., Sano, Y. and Shinoda, Y., The Separation of Fission-Product Rare Elements Toward Bridging the Nuclear and Soft Energy Systems, Progress in Nuclear Energy, Vol.40, No.3-4, pp527-538 (2002).
- [2] Ozawa, M., Ishida, M. and Y.Sano, Strategic Separation of Technetium and Rare Metal Fission Products in Spent Nuclear Fuel: Solvent Extraction Behavior and Partitioning by Catalytic Electrolytic Extraction, Radiochemistry, Vol.45, No.4, pp.225-232 (2003).
- [3] Romanovsky, V.N. et al., Research on Extraction of Actinides by Carbamoyl Solutions in Polar Diluents and Electrochemical Extraction of Technetium and Ruthenium, Second Annual Report, (2004).
- [4] Asakura, T., Kim, S-Y., Morita, Y., Ozawa, M. and

Ikegami, T., Selective Separation of Long-lived Fission Products in Nuclear Spent Fuel, JAERI-Conf 20043-011, pp.99-100, Jul (2004).

[5] Ozawa, M., Mizuguchi, K. and Fujita, R., Rare Metal Fission Products in Nuclear Spent Fuel

as Catalysts for Hydrogen Production by Water Electrolysis, 15th World Hydrogen Energy Conference, Yokohama, Japan, June 27-July 2 (2004).

[6] Ozawa, M., Mizuguchi, K., Kawabe, A., Fujita, R. and Sumida, Y., Electrochemical Properties of Rare Metal Fission Product and Re Deposits on Pt Electrode for Electrolytic Hydrogen Production, Global'05, CD-ROM (2005).