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HEAT MEASUREMENT DURING LIGHT WATER ELECTROLYSIS USING Pd/Ni ROD CATHODES

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ABSTRACT

The heat balance under electrolysis in 1M Li₂SO₄ light water solutions was measured using Pd rods or Pd coated Ni (Pd/Ni) rods for cathode. We detected large excess heat of more than 10% in 6 of 28 experiments. However, in many other experiments, no excess or only small excess heat was observed. In most cases the excess heat was 5% or less. In order to confirm the excess heat, we have to find the reason why these differences take place.

1. INTRODUCTION

In 1989, Fleischmann and Pons observed that the output power much exceeded the input power during electrolysis in heavy water solution containing Li ion so called the cold fusion [1]. More than 13 years has past since then and at the present time the experiments have been made not only in electrolysis, but also glow discharge in gas, gas absorption and discharge in solids [2]-[4]. Various experimental results were reported on such as nuclear products, transmutation (appearance of new elements on the surface of the sample during experiments) as well as excess heat. Fleischmann used Pd as a cathode for electrolysis. Recently materials that are used for cold fusion study are widely spread such as Ni, Ti, W, Pt, Au. However, in many reports, excess heat and nuclear products were not clear and almost nothing, the reproducibility was very poor.

The excess heat generation was reported not only on heavy water electrolysis, but also light water electrolysis. Patterson claimed large excess heat with high reproducibility in light water electrolysis using multi layer beads electrode created by chemical plating of Cu, Ni, Pd and Ni on small synthetic resin balls (1mm diameter) by means of reductant of hydrazine [5][6]. However, the excess heat is not clear quantitatively, especially in related to the reaction conditions.

In this paper, we have measured the heat balance using Pd rods or Pd coated Ni(Pd/Ni) rods and balls in light water electrolysis to investigate the reproducibility of excess heat generation and establish the conditions of reproducibility using Patterson type power cell [5]-[8].

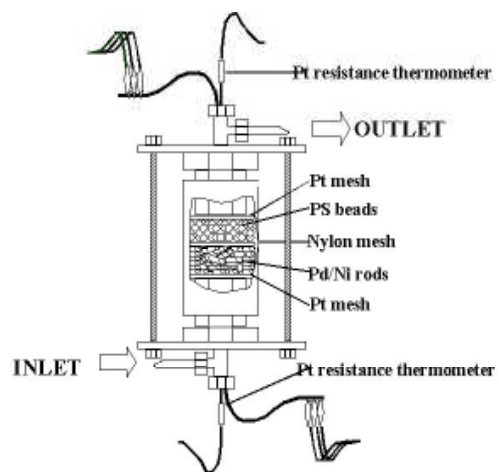


Fig. 1 Electrolysis cell.

2. EXPERIMENTAL

Figure 1 shows the cylindrical electrolysis cell made of acrylic resin. The inner and outer diameter are 3cm, 5cm and the height is 10cm. The distance between the anode and the cathode is about 2mm. Pt mesh (3cm ϕ , 55mesh) and Pd coated Ni (Pd/Ni) rods (1mm ϕ \times 2mm, 500 pieces) were used for the cathode, Pt mesh (3cm ϕ , 55mesh) was used for the anode in most experiments. In some cases, Pd rods, Pd coated Ni (Pd/Ni) balls (1mm ϕ , 1000 pieces), Pd sputtered Ni (Pd/Ni) rods and Pd sputtered Ni (Pd/Ni) balls (1mm ϕ , 1000pieces) were also used. The most Pd/Ni samples were prepared by chemical plating method. The plating bath consists of palladium chloride (0.01 mol dm⁻¹), ethylenediamine (0.08 mol dm⁻¹), thiodiglycolic acid (30 mg dm⁻¹) and sodium phosphate (0.02 mol dm⁻¹). After adjusting the plating bath to pH 7, Ni rods (1000 pieces) or Ni balls (2000 pieces) were dipped in the bath (300 ml) for 3 hours with stirring.

In some cases, Pd/Ni samples were prepared by sputtering. The Ni rods and balls were cleaned in acetone and then in 2N HNO₃. The Pd layer was deposited on the substrate under Ar atmosphere (5.0*10⁻¹ Pa), after evacuation to 10⁻⁴ Pa. The purity of Pd was 99.9%. The Ni rods and balls were set in a spherical and mesh basket. The sputtering was performed on power of 100W for 10 min, rotating the basket with 3 rpm. The Cu leading wire was covered with heat shrinkable tube. The leading wire and Pt mesh were connected by a sputter welding. 1M Li₂SO₄-H₂O solution was circulated in this system passing through a reservoir. The temperature of electrolyte in the reservoir was kept at 298K. The plastic beads were put on the upper part of the cathode to prevent the cathode from floating under circulation of electrolyte and generation of gas by electrolysis. The electrolysis was conducted mostly at 1A, in some cases, 0.5-2A and 0.8A. The flow rate of electrolyte was fixed at 45 ml min⁻¹. The gas generated during electrolysis was collected in the reservoir. The rate of gas generation was measured using a soap membrane flow meter and used to correct heat balance. The temperature difference of electrolyte was measured by a Pt resistance thermometer placed at the cell inlet and outlet. The data was recorded every three minutes in a personal computer through a data logger. For several hours before electrolysis, we measured temperature difference dT_{OW} between the cell inlet and outlet circulating electrolyte to correct for data of heat balance. The heat balance was calculated by the following equations.

$$W_{IN} = I \cdot V \quad (1)$$

$$W_{OUT} = FR(dT-dT_{OW})C_p d + H \quad (2)$$

$$HB = W_{OUT}/W_{IN} \quad (3)$$

, where W_{IN} (W) and W_{OUT} (W) are the input power and the output power, FR is the flow rate of electrolyte (ml s⁻¹), dT_{OW} (K) is the temperature difference between the cell inlet and outlet before the electrolysis, dT (K) is temperature difference between cell inlet and outlet, C_p is the heat capacity of electrolyte (298K) estimated 0.91(J K⁻¹ g⁻¹) and d is the density of electrolyte estimated 1.087 (g cm⁻³). HB is the heat balance obtained from the ratio of W_{OUT} to W_{IN} .

In measurement of the heat capacity, we used a DSC. The bottom of the silver vessel was polished by emery paper (#1500) to improve heat conduction between the holder and the vessel. This measurement was conducted between 273K (0oC) and 323K (50oC) with a heating rate of 1K min⁻¹. Figure 2 shows a DSC change with temperature, where Y_s is the difference of DSC between the empty and the sample vessels and Y_r is the difference of DSC between the empty and the standard sample containing ultra pure water. On the basis of these data, we obtain the heat capacity of 1M Li₂SO₄-H₂O at 293K using the following equation,

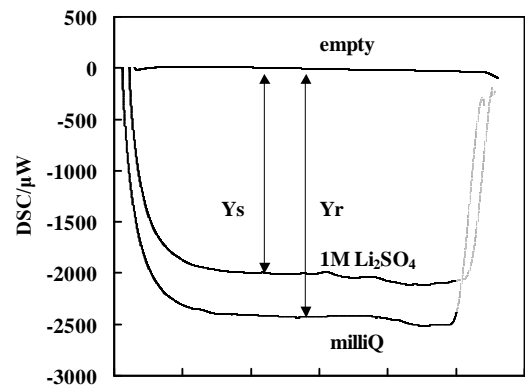


Fig. 2 Heat capacity measurement of 1M Li₂SO₄ light water solution by DSC.

$$C_{ps} = C_{pr} \cdot (m_r \cdot Y_s) / (Y_r \cdot m_s) \quad (4)$$

where C_{ps} is the heat capacity of the sample (1M Li_2SO_4 aqueous), C_{pr} is the heat capacity of the standard sample (ultra pure water), m_s and m_r are the weight of a sample and a standard sample, respectively. From this calculation, the heat capacity of $0.91 \text{ J K}^{-1} \text{ g}^{-1}$ was obtained for 1M Li_2SO_4 aqueous solution at 293K.

This experimental system is open to atmosphere and generated gases (H_2 , O_2) are released outside of the system. Since the gases generated by electrolysis of water, the enthalpy change of 286 kJ mol^{-1} should be considered. If only the first term in equation (2) is considered, the input energy would not be recovered completely, because the effect of gas generation can not be ignored. Therefore we measured the flow rate of gas that released outside of system during electrolysis, so that we could obtain heat balance correctly by compensating the amount of energy for the decomposition of water in the second term $H(W)$ of equation (2). The term, $H(W)$ is given below,

$$H = 2324 \text{ Pair FR}'/T \quad (5)$$

where Pair (atm) is the atmospheric pressure, $\text{FR}'(\text{ml s}^{-1})$ is the flow rate of evolved gas, T (K) is the temperature of the reservoir.

3. RESULTS AND DISCUSSION

Table 1 shows the heat balance using Pd coated Ni rods for cathode in 1M Li_2SO_4 aqueous solution. The averaged heat balance more than 1 was observed in most runs. Especially, No.1, 3, 5, 7, 23, 24 showed the large excess heat (more than 10%).

No.8 whose run time was for 54.75h at 1A, showed small excess heat, i.e. less than 10%. The run time is 54.75h. Figure3 shows the change of cell voltage with time. The cell voltage was about 10V at the

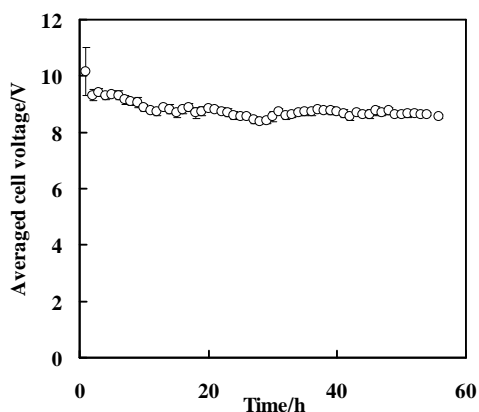


Fig. 3 Averaged cell voltage during electrolysis in 1M $\text{Li}_2\text{SO}_4\text{-H}_2\text{O}$ solution using Pd/Ni rod cathode.

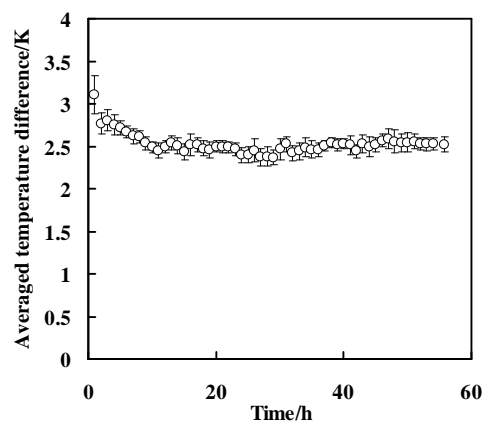


Fig. 4 Averaged temperature difference during electrolysis using Pd/Ni rods cathode.

beginning of electrolysis and decreased gradually to 8.4V. After 10 hours the voltage was kept constant. Figure 4 shows the trend of temperature difference between the cell inlet and outlet. The temperature difference was about 3.11K at the beginning of electrolysis and decreased gradually to about 2.5K at 10 hours. The temperature difference became constant after 10 hours. Behavior of the temperature change was almost corresponding to the change of cell voltage. The averaged flow rate of electrolyte was $43.09 \pm 0.14 \text{ ml min}^{-1}$ and the averaged rate of gas evolution was $11.37 \pm 0.46 \text{ ml min}^{-1}$. The averaged current efficiency was $94 \pm$

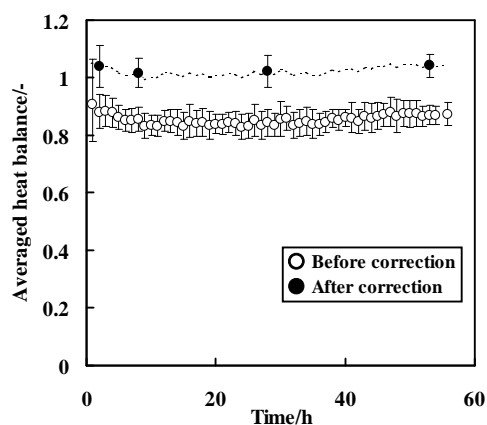


Fig. 5 Averaged heat balance during electrolysis in 1M $\text{Li}_2\text{SO}_4\text{-H}_2\text{O}$ solution using Pd/Ni rods cathode.

0.9%. The current efficiency was obtained by the rate of gas evolution and from these result, 94% of evolved gas was found releasing to outside of the system and 6% was recombined.

The heat balance was calculated from equation (3), after substituting these result to equation (2). Figure 5 shows the heat balance. The heat balance was a little high value at the beginning of electrolysis, but the heat balance was about 1.01 after 10 hours. It is difficult to evaluate this value as the excess heat generation because this excess heat is within the standard deviation.

Figure 6 shows the example of trend of the cell voltage under large excess heat of more than 10% (No.7). The cell voltage was about 9.2V at the beginning of electrolysis, and decreased gradually to 7.5V at 1A range (0-50h) and decreased from 10.5V to 9V in 2A range (50-70.05h). At 0.5A range (70.05-94.1h) and 1A range (94.1-123.3h), the cell voltage was kept almost constant, i.e. 4.8V, 6.2V, respectively.

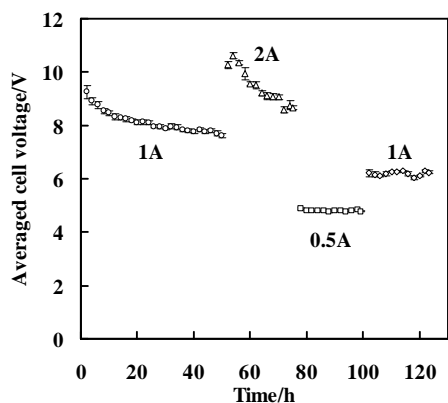


Fig. 6 Averaged cell voltage during electrolysis using Pd/Ni rods cathode.

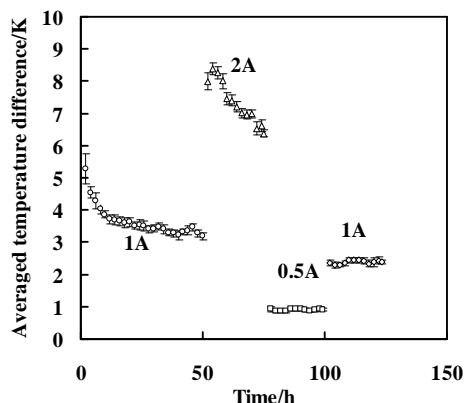


Fig. 7 Averaged temperature difference during electrolysis using Pd/Ni rods cathode.

Figure 7 shows the trend of temperature difference between the cell inlet and outlet. The temperature difference decreased from 5.3K to 3.3K at 1A range (0-50h), decreased from 8.7K to 6.6K at 2A range (50-70.05h). At 0.5A range (70.05-94.1h) and 1A range (94.1-123.3h), the temperature difference was kept almost constant, i.e. 0.9K, 2.39K, respectively. The flow rate of electrolyte was 42.93 ± 0.07 ml min⁻¹. The rate of gas evolution under electrolysis was 11.07 ± 0.68 ml min⁻¹ at 1A range (0-50A), 21.04 ± 0.97 ml min⁻¹ at 2A range (50-70.05h), 5.52 ± 0.29 ml min⁻¹ at 0.5A range (70.05-94.1h), 11.17 ± 0.38 ml min⁻¹ at 1A range (94.1-123.3h). The current efficiency was 91.2% (1A), 86.8% (2A), 91.1% (0.5A), 92.0% (1A), respectively. The term of correction H(W) was 1.43 ± 0.09 W at 1A range (0-50h), 2.73 ± 0.13 W at 2A range (50-70.05h), 0.72 ± 0.04 W at 0.5A range (70.05-94.1h), 1.45 ± 0.05 W at 1A range (94.1-123.3h).

From the above data, the heat balance was obtained to be 1.50 ± 0.08 at 1A range, 1.29 ± 0.05 at 2A range, 1.41 ± 0.10 at 0.5A range, 1.37 ± 0.07 at 1A range, respectively. Figure 8 shows the trend of averaged heat balance. We got the excess heat even without the correction of the current efficiency. The maximum of the averaged heat balance in these experiments was 1.84 and the minimum was 1.25. The maximum of the excess heat in these experiments was 7.8W (input 9.3W, output 17.1W) and the integrated excess heat generation was 1.5MJ. If this heat is generated in Pd layer on Ni rods, the energy density would

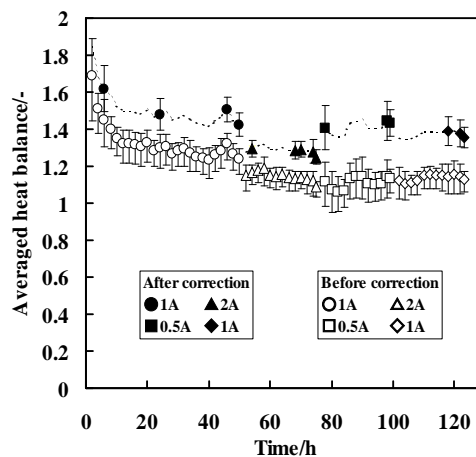


Fig. 8 Averaged heat balance for 2 hours during electrolysis in 1M Li₂SO₄ light water solution using Pd/Ni rods cathode.

be 1985W cm⁻³ Pd and in the case of Pd/Ni rods, the energy density would be 9.9W cm⁻³ Pd/Ni.

4.CONCLUSION

In this study, we observed the excess heat using Pd/Ni or Pd rods in 6 runs. However, in most of other runs, only the small excess or no excess was shown. We cannot say clearly the excess heat with the 5% excess, since the error limit of our system was 8-10%. In order to confirm the excess heat we have to elucidate the reason why these differences are between large excess and no excess.

5.REFERENCES

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Table.1 Heat balance of electrolysis in 1M Li₂SO₄-H₂O using Pd rods, Pd/Ni rods and Pd/Ni balls for cathode.

No	Time(h)	Cathode	Cell Voltage(V)	HB _{AVE}	Corrected HB _{AVE}
1	24.25	Pd	8.8-10.7	1.30±0.07	1.45±0.08
2	75.75	Pd	13.2-15.4	0.93±0.05	1.03±0.06
3	239.9	Pd/Ni	6.3-11.3	1.33±0.08	1.52±0.09
4	30	Pd	10.5-12.2	0.93±0.03	1.06±0.04
5	72.6	Pd/Ni	6.3-11.4	1.14±0.09	1.34±0.10
6	126.9	Pd	9.8-11.8	0.91±0.03	1.05±0.04
7 ^(a)	50	Pd/Ni	7.5-9.9	1.32±0.09	1.50±0.08
	20.05		8.3-10.9	1.11±0.09	1.41±0.10
	24.05		4.7-4.9	1.14±0.06	1.29±0.05
	29.2		5.9-6.4	1.14±0.07	1.37±0.07
8	55.75	Pd/Ni	8.1-11.8	0.85±0.05	1.02±0.06
9	25.6	Pd/Ni	10.9-12.0	0.95±0.04	1.03±0.05
10	81.5	Pd/Ni	10.0-12.3	0.88±0.04	1.03±0.06
11	20.3	Pd/Ni	12.7-16.0	0.83±0.06	0.93±0.07
12	43.35	Pd/Ni	14.9-20.5	0.95±0.05	1.04±0.06
13	76.5	Pd/Ni	9.3-12.0	0.90±0.07	1.03±0.08
14	77.2	Pd/Ni	9.4-10.9	0.88±0.06	1.03±0.06
15	74.65	Pd/Ni	9.1-10.9	0.89±0.05	1.05±0.06
16 ^(b)	73.3	Pd/Ni	7.3-8.5	0.86±0.06	1.05±0.08
17 ^(b)	52.2	Pd/Ni	6.4-7.1	0.84±0.05	1.06±0.06
18 ^(f)	54.1	Pd/Ni	7.2-8.3	0.86±0.04	1.05±0.06
19 ^(e)	73.4	Pd/Ni	7.87-9.52	0.86±0.06	1.01±0.08
20 ^(d)	75.7	Pd/Ni	6.88-9.05	0.76±0.07	0.96±0.08
21 ^(d)	71.5	Pd/Ni	5.78-9.27	0.73±0.04	0.98±0.05
22 ^(d)	49.35	Pd/Ni	5.95-8.96	0.75±0.06	0.99±0.06
23 ^(c)	122.7	Pd/Ni	5.79-8.77	1.08±0.08	1.31±0.09
	47.1		6.56-7.15	0.90±0.06	1.10±0.08
24 ^(e)	12	Pd/Ni	8.15-10.56	1.33±0.10	1.50±0.11
25 ^(f)	75.7	Pd/Ni	6.9-9.1	0.76±0.07	0.96±0.08
26 ^(f)	71.5	Pd/Ni	5.8-9.3	0.73±0.06	0.98±0.05
27 ^(f)	49.4	Pd/Ni	6.0-9.0	0.75±0.06	0.99±0.06
28	66.1	Pd/Ni	8.9-10.4	0.87±0.05	1.02±0.04

- (a) Cell current is 0.5-2.0A. In the other experiment, cell current is 1A
- (b) Cell current is 0.8A.
- (c) Cell current is 1-2A
- (d) Cathode is Pd/Ni balls by sputtering
- (e) Cathode is Pd/Ni balls by chemical plating
- (f) Cathode is Pd/Ni balls by sputtering