

Development and Experiments on a Flow Calorimetry System

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Abstract

Demonstration experiments of excess heat generation have been conducted using the Fuel Cell Type Electrolysis System at NHE Laboratory since January 1994. In April 1995, a mass flow calorimetry system (FCS) was developed at the NHE Laboratory. A new series of experiments, referred to as NHE-FCS, combines the Fuel Cell Type Electrolysis System with mass flow calorimetry. The system is comprised of fuel cell type electrolysis cells, power supplies, vacuum insulators, water coolant, temperature measurement equipment, and a personal computer which controls the power supplies and digital multimeters. A data acquisition occurs every 60 seconds. Total input power is typically 10W. As a result of careful modification of the components, a heat recovery efficiency of ~98% has been attained. It has been confirmed that an excess heat of 0.2W is measurable in calibration tests.

Excess heat has been observed in the "Fuel Cell Type Electrolysis System". Observations of 7-18% excess heat have been reproduced in 11 cases. However, the reproducibility issue still remains. NHE-FCS experiments have been performed used identical protocol. Excess heat has not been observed yet in spite of the fact that we have attempted to duplicate the electrode materials that produced excess heat. One reason may be that other experimental conditions have differed in detail in cases in which excess heat has been observed.

1. Introduction

In previous experiments using the "Fuel Cell Type Electrolysis System", excess heat is calculated by comparing the measured temperature of the electrode and the electrolyte with a calibration curve. The calibration curve is provided from the measured temperature of a Ni electrode and the electrolyte. Thus this method is not a direct calorimetric measurement. If the measurement points are somehow moved during cell assembly after the calibration, the accuracy of calibration would be lost. Therefore it is necessary to improve the measurements and confirm the measured excess heat by other methods.

A flow calorimetry system, such as which has been developed by Stanford Research Institute,

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provides a direct measurement capability. Thus, a flow calorimetry system for NHE was designed and developed to confirm the observed excess heat at NHE Laboratory.

2. Experimental

2-1 Measurement System.

Fig.1 shows the overall system of NHE-FCS. As a matter of fact, 2 experimental cells are able to be measured at the same time for one system. Water in bath A as coolant is kept at the same temperature of bath B (23°C const.), and send to bath B using a constant-flow-rate (0.7g/s) pump through a degasser. Coolant water is continuously purified by an ion exchange resin bed. To damp the flow rate fluctuation, an accumulator is inserted between the pump and electrolysis cell. The temperature of water is close to that of bath B as it flows through the tube section in bath B before entering in the cell. The flow rate of water after exchanging heat at the cell is measured by the flow meter as it returns to bath A.

The temperature of the coolant water at inlet and outlet are sensed by Pt thermal resistors. Input voltage and current of electrolysis and heater, output of flow meter and vacuum meter, and the resistance of Pt thermal resistors are measured by digital multimeters. The power supplies and multimeters are controlled by a personal computer (PC).

The data acquisition typically occurs every 60 seconds. Constant total input power is assured by regulating the power supplies every 10 seconds. The PC can output the data files to magneto optical (MO) disk while the measurement program is running, so it is possible to analyze the results of experiments later.

2-2 Electrolysis Cell.

At first, two kinds of cells that have the different position of the heat exchange tubes were designed and made at April 1995, they are called "Type A" and "Type B" respectively. The "Type A" cell was showed at figure 6 of our ICCF5 report⁵⁾. After that, they have modified to improve the variations of heat measurement. It is called "Type C". All experiments have been performed using "Type C" cells since January 1996.

Fig.2 shows the electrolysis cell "Type C" in the vacuum insulator for NHE-FCS. It is the fuel cell type electrolysis cell composed of a cathode, the gas diffusion electrode, electric heater, and the pressure vessel. The electric heater is made from coiled Ni-Cr wire and sealed PTFE tubes. This cell has the heat exchange tube in its side, bottom, and cover wall. The coolant water enters into and goes out the cell through the cover of the vacuum vessel. The temperatures of the inlet and outlet coolant water are measured in the tubes under the cover by Pt thermal resistors.

The ceramic hermetic seals are used for the connectors between the inside and outside of the pressure vessel, and at the cover of the vacuum vessel for electrolysis and heater input lines. Their voltages are sensed at the connectors.

To prevent the gas leakage, a metal O-ring is used for the pressure vessel's seal.

2-3 Protocol.

Experiments are performed in two steps.

The first step is to measure the cell's heat recovery, using a Pt cathode and an electric heater, in order to determine cell performance. The estimated heat recovery is used for the calculation of excess heat during electrolysis with a Pd cathode.

The second step is the Pd electrolysis experiment, carried out according to the following protocol:

1. The Pd electrode is prepared according to the appropriate protocol.
The cell components are cleaned and the cell is assembled and leak-checked.

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2. The electrolyte is added, cell volume is measured, D₂ gas is pressurized at 9 kgf/cm².
3. The cell is installed in bath B, and left until the pressure and temperature reach steady-state conditions.
4. The heater is turned on (kept at 10W const. typically).
5. Electrolysis begins after the pressure and temperature reach constant values.
6. Output heat is measured as the electrolysis current changes.

The current profile was initially the same as that of the reference conditions. Afterwards, open circuit, Hi-Lo current exchanging, and anodic treatment are tried.

2-4 Calculations.

The method of calculation of D/Pd is same as previously used for the "Fuel Cell Type Electrolysis System". However, the cell volume, PTFE fixers and the electrolyte volume are relatively larger than for previous cases. Thus, the volume of gas effluent from the PTFE fixers and electrolyte outgasing must be accounted for when calculating D/Pd. Likewise, the averaged temperature of the gas is estimated from the calibration experiments.

Excess heat, W_{ex} , is calculated with the following equation.

$$W_{ex} = m \times c_p \times \Delta T / \xi - W_i$$

where m is the flow rate, c_p is the specific heat of water, ΔT is the difference between inlet and outlet fluid temperature, ξ is the heat recovery efficiency as determined from calibration experiments, and W_i is the total input power.

In this equation, the recovery power is $m \times c_p \times \Delta T$. Changes in the flow rate influences the heat recovery, therefore the flow rate setting at the pump is not changed for other experiments.

3. Results and Discussion

3-1 Calibration.

In calibration experiments using a Pt cathode and electric heater input, the heat recovery of each cells is 0.983 ± 0.010 . Fig.3 shows the results of the calibration experiments using one of Type C cell. In this case, the heat recovery, ξ , was 0.977. The heat recovery is determined by averaging the last 60 minutes of all constant current terms during the total input power kept at 10W.

Another heater was assembled in this cell as the dummy excess heat generator, and supplies 0.2W for 2 hours (designated with *1 in Fig.3 and Fig.4). Fig.4 shows that the calorimeter is capable of observing such small values of thermal energy.

In addition, the figure shows that the calculated results of excess heat was almost $0 \pm 0.1W$ except during the periods when the test heater was on. The 3-sigma uncertainty for this cell was 0.09W with the input power regulated at 10W. The 3-sigma value for other cells was estimated at 0.09 to 0.16W. Accordingly, it can be concluded that NHE-FCS has enough sensitivity to detect excess heat of 0.2W at total 10W constant input condition.

3-2 Pd Electrolysis.

All experiments of Pd cathodes have been performed used identical protocol which showed excess heat in prior "Fuel Cell Type Electrolysis System" experiments. Fig.5 shows typical results at Pd electrolysis using NHE-FCS. The material and treatment of Pd cathode and experimental procedure were identical.

Total input power was kept at 10W with heater before starting Pd electrolysis. In the first of measurement, the changing of the results of excess heat is presumed that the recovering of heat is

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unsteady because of the complexity of the heat exchanging tubes. D/Pd reached a maximum of 0.82, but slightly decreased at high current density. Excess heat was almost $0 \pm 0.1\text{W}$ during all over the experiment. Therefore it was decided that excess heat was not observed in this experiment.

In some experiments, D/Pd reached a maximum of 0.84, and 0.89 in one experiment. In the results from all experiments in this series, excess heat has not been observed. This may be insufficient for excess heat generation. Past experience indicates that D/Pd in the range of 0.85-0.90 are necessary for excess heat generation.

3-3 Discussion.

One possible reason that net excess heat has not been observed is that the experimental conditions have necessarily differed in slight details from those of prior experiments. Specifically, on account of the cooling method, the temperature of the cathode is different in the "Fuel Cell Type Electrolysis System" than in the NHE-FCS. Fig.6 shows the electrolyte temperatures versus input power for several experimental systems. In the "Fuel Cell Type Electrolysis System", the temperature rises at $10^\circ\text{C}/\text{W}$ from 10°C . However, the NHE-FCS cathode is exactly 38°C when total input power is kept at 10W. It is presumed that the temperature influences the D/Pd.

4. Summary

A mass flow calorimetry system (NHE-FCS) has been developed to confirm the observed excess heat at "Fuel Cell Type Electrolysis System" experiments. The heat recovery of NHE-FCS cells has been measured at 0.983 ± 0.010 during calibration experiments with a Pt cathode and electrical heater. NHE-FCS is capable to detect excess heat of 0.2W at total 10W constant input condition.

All experiments using Pd cathode have been performed used identical protocol which showed excess heat at the "Fuel Cell Type Electrolysis System". Max D/Pd has been 0.84 in some experiments cells, and 0.89 in one experiment. Excess heat has not been observed at all experiments.

One possible reason is that D/Pd may be insufficient for excess heat generation, for the temperature is deferred by the cell designs and influences the D/Pd.

5. Acknowledgment

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6. References

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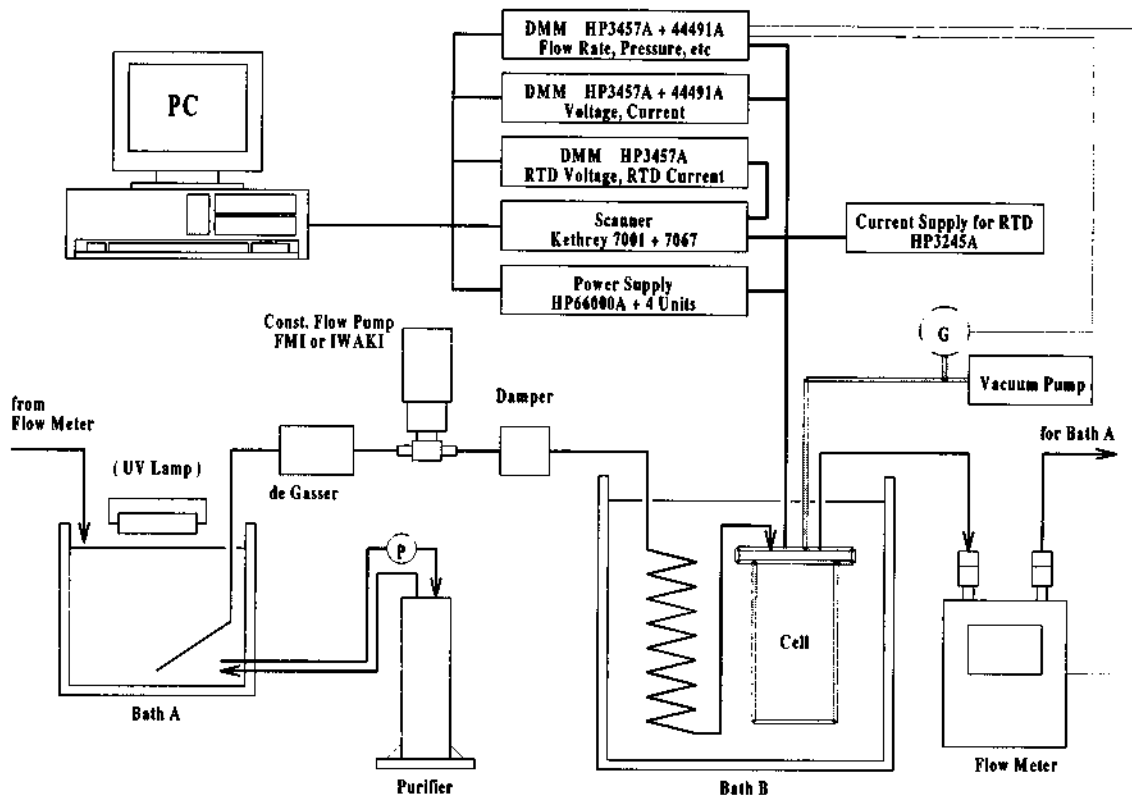


Fig. 1 The Overall System of NHE-FCS

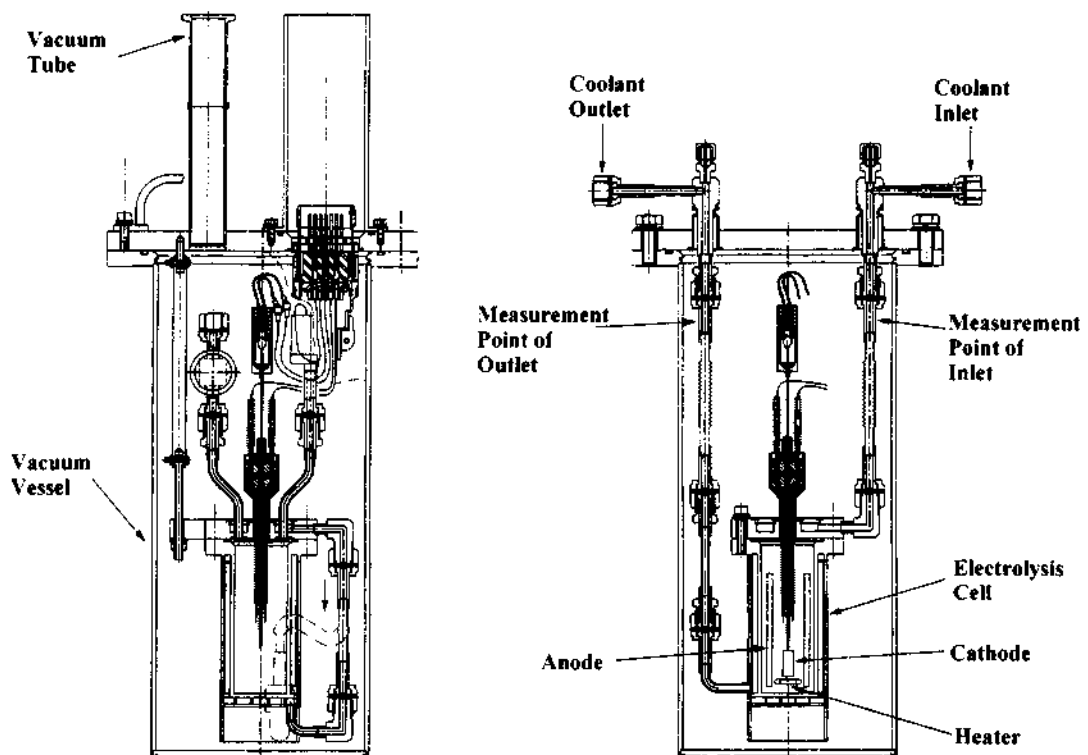


Fig. 2 The Cell Structure of Type C for NHE-FCS

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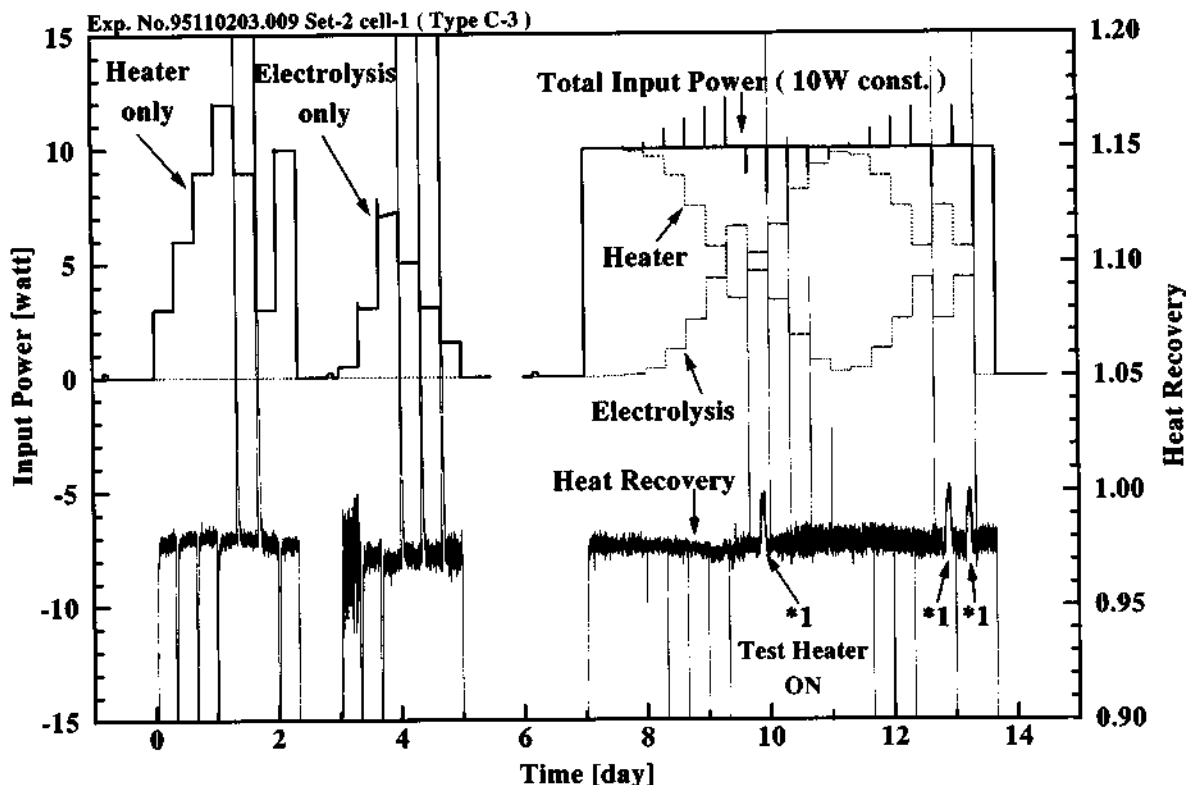


Fig. 3 Input Power, Heat Recovery v.s. Measurement Time
Pt(ϕ X 15), 1M LiOD, Inlet Fluid Temp 23deg.C

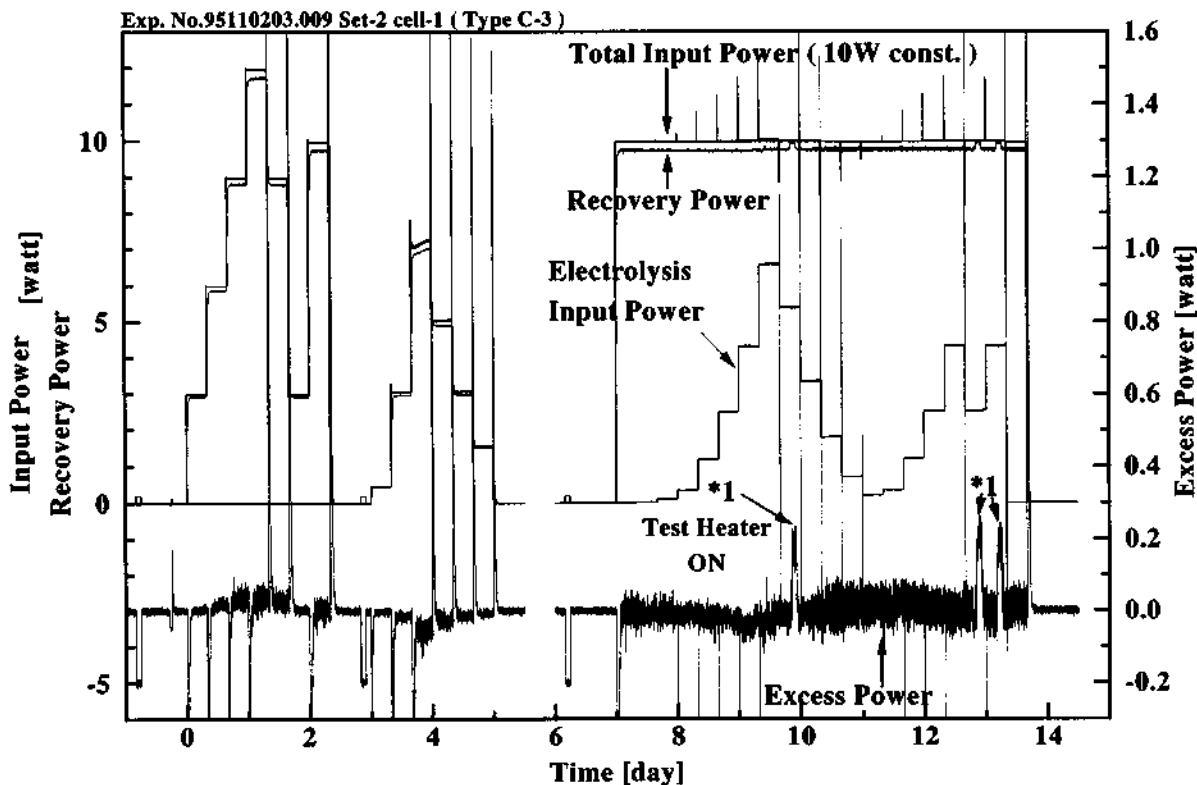


Fig. 4 Input Power, Recovery Power, Excess power v.s. Measurement Time
Pt(ϕ X 15), 1M LiOD, Inlet Fluid Temp 23deg.C

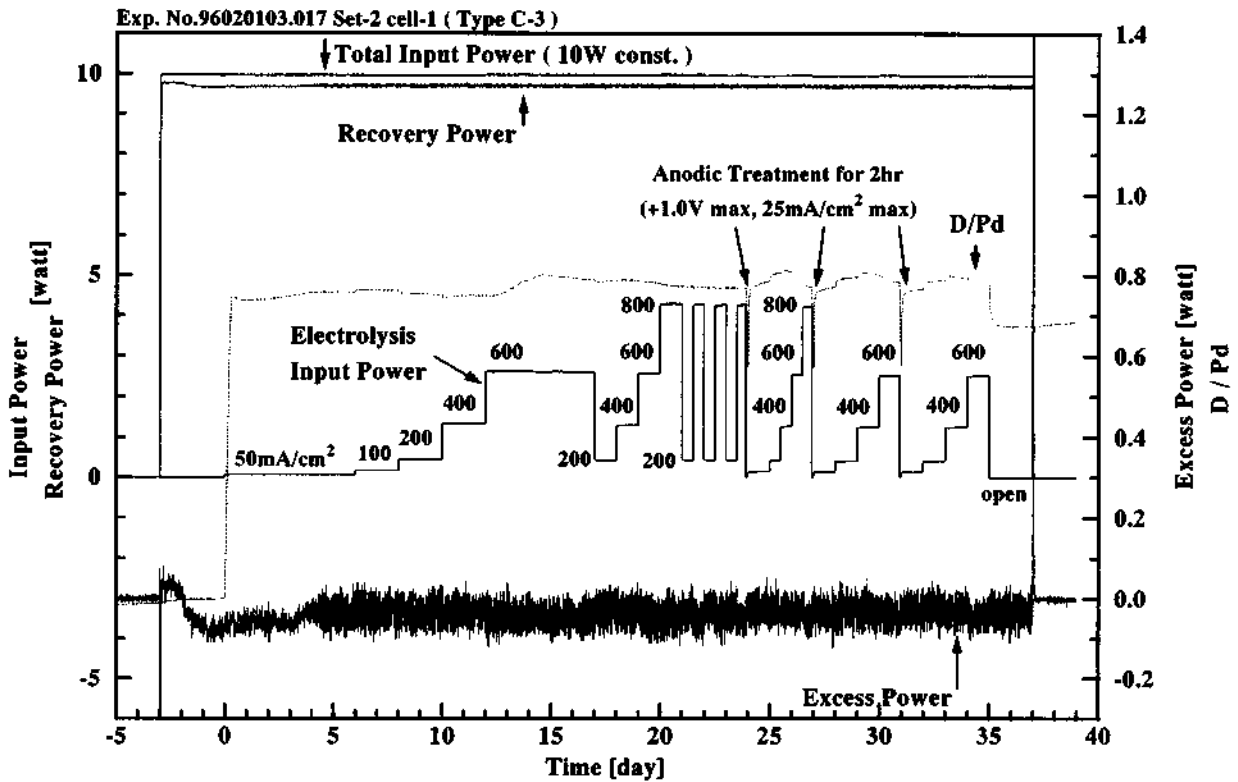


Fig. 5 Input Power, Recovery Power, Excess Power, D/Pd v.s. Electrolysis Time
 Pd(4N Hyojunzai φ4 X 15, 10min etching in Aqua regia, 1000deg.C 10hr annealed)
 1M LiOD, Inlet Fluid Temp. 23deg.C

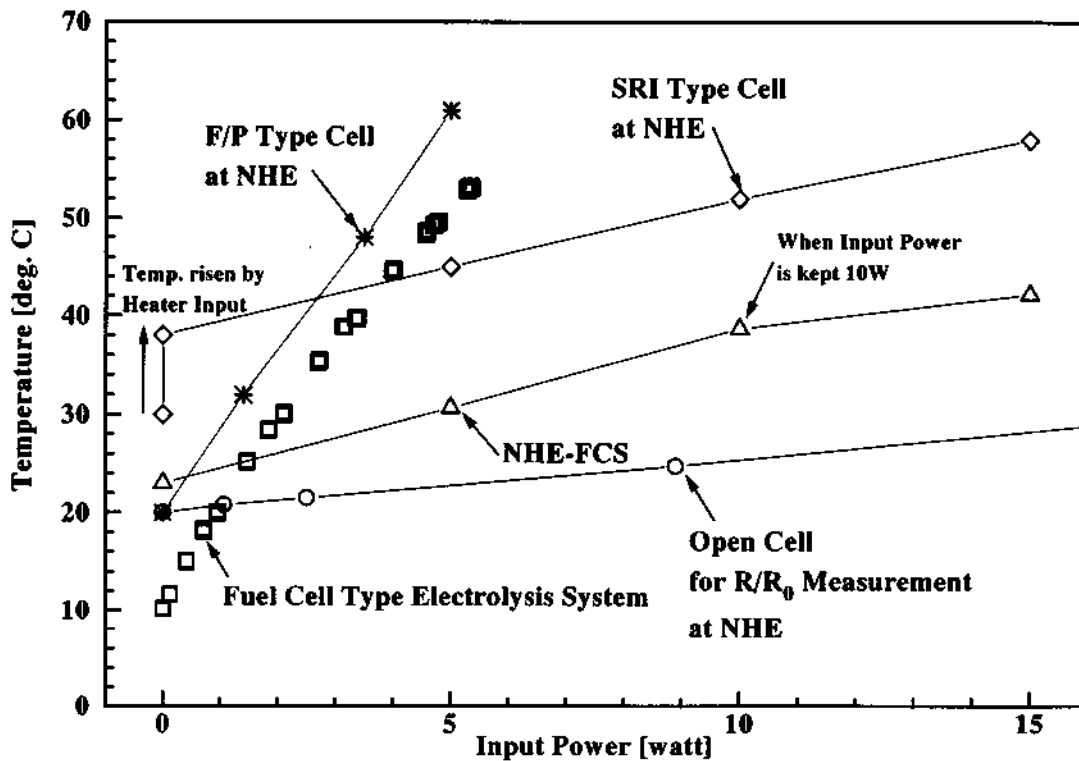


Fig. 6 Electrolyte Temp. of each System v.s. Input Power