CALORIMETRIC MEASUREMENTS DURING Pd-Ni THIN FILM–CATHODES ELECTROLYSIS IN Li_2SO_4/H_2O SOLUTION

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A sensitive open-type calorimeter was used to measure excess heat production during electrolysis in Li_2SO_4/H_2O solution with Pt-anode and Pd-Ni thin film cathodes 9000 Å thick, sputtered on Al_2O_3 substrate. In order to estimate the actual performance and possible measurement errors during electrolysis in the calorimeter used, including heat convection, bubbling and possible H_2+O_2 recombination, smooth Pt sheets were used as cathodes in special reference runs. It is shown that the Alumina/ Pd-Ni sample that survived during electrolysis achieved excess heat production of 20-25 % of the input power (equivalent to 300 ± 30 mW).

1. INTRODUCTION

For the last decade there were numerous reports concerning heat generation in the electrochemical cells with Pd or Ni cathodes. It was claimed that the bulk Pd cathodes may generate some excess heat in heavy water based alkaline electrolyte [1,2], both in open cell and in closed- type cells with a recombiner. In order to generate excess heat with a Pd cathode a certain parameter regime is required, including a very high current densities and over-potentials, high loading ratio (x=D/Pd) and high deuterium diffusivity, as well as especial treatment of the cathode-samples (annealing, etching, etc.) [3]. The same irreproducibility of heat generation was found for electrolysis of massive Ni-cathodes in the H_2O based electrolytes [4,5]. Heat production in the Ni-H system has been studied much less than in Pd-D. In that case possible heat generation has been attributed to formation of Ni-hydride β-phase under special loading conditions. At the same time it is well known that high loading for Ni samples is more difficult to obtain than that for Pd [6]. Thus, the irreproducibility of heat production in the Ni-H system with massive cathodes is generally regarded to be as poor as that of the Pd-D system. It should be noted that irreproducibility and the relatively low level of heat production in Pd or Ni-cathodes during electrochemical loading has prompted alternative trivial explanations of the observed thermal effects, e.g. gas H_2+O_2 recombination and/or changes in the faradic efficiency of open-cell electrolysis upon the cathodic polarization of Pd [7].

In this connection, the more perspective way to obtain reproducible heat generation in the metal-hydrogen electrochemical systems is, in our opinion, utilization of thin-metal film cathodes on dielectric substrates [8]. The advantages of the thin-film cathodes include: (i) a very short time is required to achieve as high hydrogen loading due to small metal thickness; (ii) an effective hydrogen reflection at the Pd-dielectric interface from the dielectric side, increasing the effective concentration of hydrogen in metal; (iii) relatively low current density can be used to provide the necessary condition for heat generation [3]; (iiii) a large input power density W_{in} is applied to the metal –hydrogen system (at film thickness of 2000 A, typically $W_{in} \sim 10^3$-10^4 W/cm^3, while for 1 mm thick Pd wire at least 3 orders of magnitude less even at much higher current density), which allow increase in the H-diffusion amplitude in Pd lattice.

In the present paper, a sensitive open-type calorimeter is used to demonstrate that Pd-Ni thin film cathodes sputtered on a Alumina dielectric substrate during electrolysis in 1M Li_2SO_4/H_2O with a Pt-wire anode reproducibly generates heat at the level of 20-25 % of the input power during long time runs. We show that the generated heat cannot be explained by conventional chemical mechanisms, including H_2+O_2 recombination.

2. EXPERIMENTAL TECHNIQUE

In order to detect possible heat evolution during electrolysis runs in the present work, a high sensitivity open-type calorimeter has been employed. This calorimeter consists of a large constant temperature water bath (30 l of water) in which four double-wall glass cells are immersed. During the experiments the bath temperature was strictly stabilized with Circulating Bath device and precisely fixed at the point of 28.0 ± 0.05 °C. Each cell was covered by a rubber cap and provided with two thermistors, magnetic stirrer (to exclude thermal gradients which can essentially distort the actual temperature in the cell due to convection) and plastic cathode-holder, to maintain the cathode inside the electrolyte (**Fig.1**). All thermistors were calibrated with a sensitive mercury thermometer. The error of this calibration was 0.1 °C. The temperature difference $\Delta T = T_x - T_0$ between the thermistors inside the cells (T_x) and the bath temperature (T_0) was monitored evry five minutes.

Calibration of cells in the range of 0.05 – 5.0 W input power was carried out using a standard R=70 ohm resistor. The calorimeter's time constant (time for stabilization of the temperature after a change in input power) is ~ 4 hrs. The average resistor-calibration error < 25 mW. Measurements show a high sensitivity of 200 ± 25 mW/°C or 5.0 °C per 1 W of input electric energy .

To account the actual ohmic heating of the electrolyte due to electrolysis (potential drop due to electrical resistance of electrolyte, cathode, anode and electric circuit) the water dissociation potential (WDP) is subtracted from the electrolysis voltage. The minimal WDP value for oxygen acid salts electrolyte [9] can be estimated as:

$$U_0 = U_{th} + \eta_0. \tag{1}$$

Here U_{th} = 1.48 V is the thermal neutral dissociation potential and η_0-is the sum of cathode and anode over-potentials (for a Ni(cathode)-Pt(anode) pair: η_0 = 0.58 V; for a Pt-Pt pair: η_0 = 0.53 V and so on). Direct experimental measurements of WDP (using volt-ampere characteristics in the cell measured between cathode and anode) performed for these electrode pairs in our electrochemical cells show a good agreement (within the 5 % of theoretical value) of U_0 values from formula (1).

In the present work, a double-layer Pd/Ni thin film sputtered on ceramic Al_2O_3 substrate was used as a cathode [10]. The flat substrate samples with area S=12.5 cm^2 were cut from ceramic plate of 1 mm thick and roughness of 8-10 kÅ. After chemical and ultrasonic cleaning of substrate plates, magnetron sputtering of 8000 Å Pd was carried out (sputtering rate ~ 0.41 Å/s). On the top of the Pd film the 1000 Å thick Ni film was sputtered with the same rate. The samples were then annealed in high-vacuum (p=10^{-7} tor) at t = 800 °C for 4 min using low heating and cooling rates

3. EXPERIMENTAL RESULTS

3.1 OPTIMIZATION OF EXPERIMENTAL ARRANGEMENT

To check actual performance during Foreground electrolysis runs (with Alumina/Pd-Ni samples), including heat convection, bubbling, electrode's geometry, and positioning, as well as H_2+O_2 recombination. Smooth Pt sheets were used as cathodes in Reference runs, since Pt does not produce excess heat in the light water electrolysis [3]. To closely replicate the runs the cathode Pt sheets were attached to the surface of a standard Alumina substrate. The reference experiments used three different Pt-wire anode types fixed at different distances from cathode Pt-sheets: (I) long-straight wire parallel in front of the center of the cathode surface (cathode-anode distance 10 mm); (II) loop-like wire coil parallel in front of the cathode surface and separated by 25 mm distance from the cathode; (III) hook-like coil 25mm above the cathode surface. Reference runs were performed in 3 cells containing the same cathodes and anodes (I-III) with the input power ranging from 0.1- 3.0 W. The performance of this runs at various current (50 – 600 mA) is defined by the calorimeter "heat recovery" value R as follows:

$$R = P_{th}/I(U-U_0) \tag{2}$$

where, P_{th} is the thermal power measured in calorimeter by thermistors; I and U are the electrolysis current and voltage, respectively; U_0 = 2.01 V is an effective water dissociation potential for Pt/Pt pair defined in Eq. (1). If the cell with Pt electrodes is calibrated correctly and it does not produce any excess heat, so R ≈ 100 %. That is, the thermal power generated is solely due to ohmic/Joule heating of the electrolyte by

applied current and voltage. If R > 100% for Pt/Pt electrodes indicates that there is H_2+O_2 recombination. If R<100 %, an incorrect calibration or increase of WDP (U_0) due to an anomalous increase in the cell inner resistance is suggested.

The results of experiments in cells I-III with the same Pt-cathodes and different Pt-anode configurations, described above are presented in **Table 1** (averaged by 50-600 mA current heat recovery values R). As seen, the R value closest to 100 % was in Cell II with a loop-like anode. Heat recovery R in cells I and III are larger than 100 %, suggesting that H_2+O_2 recombination is not negligible. For anode (I) in cell 1 the recombination contribution would be about 16 %, while for anode (III) in cell 3 it is about 10 %. In contrast to these "bad anode geometries" (cells I and III), cell II shows that recombination contribution is ≤ 3.0 %. Increasing the cathode-anode distance by 25 mm in cell I, leads to a decrease in R from 116 to 108 %. Thus, it is shown that the best arrangement of anode is consistent with (II).

In the other reference experiments with Pt-Pt electrodes possible changes in electrolyte concentration were estimated. Electrolysis runs carried out in electrolytes with different molarities show a quite constant R at Li_2SO_4/H_2O concentrations within 0.8-1.2 M (**Table 1**). Such large changes could only associated with evaporation of 20 % volume of the cell. Therefore, changes in the electrolyte concentration during the cell operation do not significantly affect the heat recovery R.

Note that substitution of thermal-neutral dissociation potential U=1.48 V (without accounting of electrodes over-voltages) in formula (2) for cell I-III leads to a drastic decrease R below 80 %. This fact indicates the non-negligibility of the electrodes over-potentials, at least, on calorimetry measurements at current densities $j \geq 10$ mA/cm^2.

3.2 ALUMINA/PD-NI CATHODE RESULTS

Experiments on detection of heat generation for Alumina/Pd-Ni cathodes (Foreground runs) were carried out at constant electrolysis current ranging from I =100-600 mA (j = 8.5 - 50.0 mA/cm^2) corresponding to a cell voltage U 3.5-5.5 V. To calculate Joule heating of the electrolyte P* the effective WDP value U_0 = 2.06 V is used in formula (2). This U_0 corresponds to a Ni(cathode)/Pt(anode) electrode pair WDP (1000 Å Ni film used on the top of the Pd layer).

Typical kinetics of the heat measurement (P_{th} vs. elapsed time t) are presented in **Fig.2** As seen after t > 2 hrs, the thermal yield P_{th} exceeds Joule heating P*. The maximal heat recovery R of 135 % occurs at electrolysis current I=100 mA (j = 8.0 mA/cm^2), while the corresponding absolute value of excess heat production is W_{ex} = 60 $\pm$ 28 mW. Increasing the current density to 48 mA/cm^2 leads to decrease in heat recovery R from 135 to 115 %. In typical cases the excesses heat evolution from the cathode at I = 200 mA continues for ~ 15 days. The decrease in R during a long Foreground run is accompanied by an increase in cell voltage. The last process indicates an increase in the cell inner resistance due to defects and micro-cracks generation in Pd/Ni cathode. The cathode samples survive, i.e. they do not detach the Alumina substrate during these long runs. Thermistor calibration runs repeated immediately after this Foreground run show that calorimeter parameters, (including ΔT vs. W_{in}) did not change during the time of operation with Alumina/Pd-Ni sample (15 days). This gives a proof of stability of the calorimetry system and indicates that our measurements of excess heat production were actually correct.

3.3 ERROR ANALYSIS IN THE HEAT MEASUREMENTS

The main errors of open-type calorimetry are associated with calorimeter accuracy as well as with gas recombination. As discussed in sec. 3.1 the recombination limit for the cell II-type configuration could not exceed 3.0 % of the input power. Other possible sources of errors would be referenced to uncertainty of calorimeter, such as thermistors accuracy, oscillation of bath and ambient temperatures, appearance of thermal gradients and the change in the electrolyte volume due to evaporation. Results for the calorimetric accuracy with respect to the precision of excess heat measurement are summarized in **Table 2**. The total average error of heat measurement, in accordance with error propagation, does not exceed $<\sigma_t>$ = $\pm$ 30 mW. In an actual experimental performance at low input power (W_{in} < 1.0 W) this error is $<\sigma_l>$ = $\pm$ 20 mW, while at high input power range (W_{in} > 1.0 W) it is twice larger: $<\sigma_h>$ = $\pm$ 40 mW.

Comparison of the calorimetry errors with excess power gains obtained in Foreground runs with Aumina/Pd-Ni cathode shows that observed amounts of excess heat generated during electrolysis are well above the error limit determined by both the calorimetry accuracy and possible recombination.

4. SUMMARY AND CONCLUSIONS

Measurements of excess heat production were carried out during electrolysis in 1M Li_2SO_4/H_2O solution with Pt-anode and Pd-Ni thin film cathodes (9000 Å thick) sputtered on the dielectric substrate (Alumina). In order to estimate the actual performance during electrolytic runs in the open-type calorimeter used, including heat convection, bubbling and possible H_2+O_2 recombination, smooth Pt sheets were used as cathodes. It was found that in the "good geometry" (with a loop-shape wire Pt-anode separated by 25 mm distance from cathode) a maximal contribution of H_2+O_2 recombination in the heat production does not exceed 3.0 %

No excess heat was measured if the metallic coating of cathode-sample was fractured and/or detached from the substrate, adding confidence in the calorimetric calibration. The best adhesion of Pd/Ni coating having a good film quality was achieved with Alumina (with maximal roughness of about 10 kÅ) as a substrate. This required a special procedure of high-vacuum annealing at t = 800 ºC. Then the Alumina/Pd-Ni sample survived 2 weeks electrolysis and produce an excess heat power reaching 20-25 % of the input power, equivalent to 300 ± 30 mW.

Comparison of calorimetry errors with excess power obtained in Foreground runs with the Aumina/Pd-Ni cathode as well as the theoretical analysis of oxygen reduction in the electrolytic cell shows that the excess heat measured during electrolysis is well above the error limit determined by both the calorimetry accuracy and by a possible gas recombination.

ACKNOWLEDGEMENTS

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Table 1
Parameters of electrolysis and "heat recovery" R for Pt-Pt reference runs in cells I-III

Cell # / parameter	M (Li_2SO_4/H_2O)	x, mm	R, %
I	1.0	10.0	116.0 ± 6.2
I	1.0	25.0	108.0 ± 7.1
II	1.0	25.0	102.5 ± 5.0
II	0.8	25.0	101.5 ± 6.0
III	1.0	25.0	110 ± 5.5
III	1.2	25.0	110 ± 6.5

Here, M- is a molarity of electrolyte; x-is the distance between the cathode and anode; R- is the heat recovery of the cell, averaged by applied current (ranging from 50-600 mA) and defined by formula (2).

Table 2
Sources of errors with respect to accuracy of calorimetry measurements

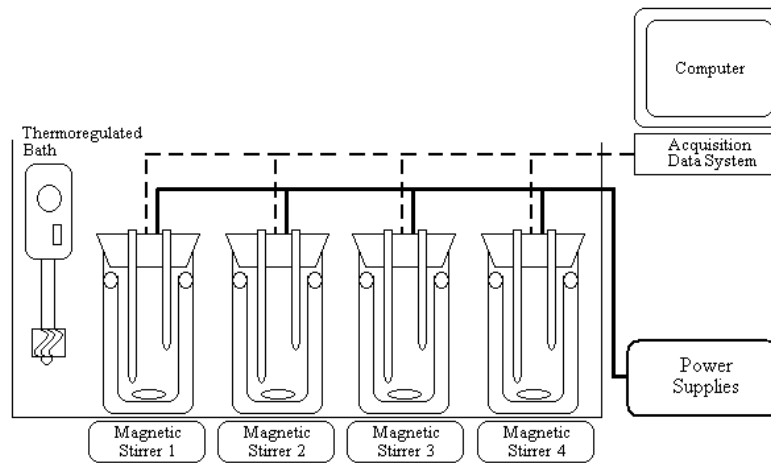| Error source	Accuracy/Precision	Error value, mW
Thermistors	0.1°C /0.02 °C	± 5.0
Bath Temperature	0.05 °C	±13.0
Thermal Gradients	0.02 ° C	±5.0
Ambient temperature	0.02 °C/°C	± 20.0
Electrolyte evaporation	< 5.0 ml	< 3.0 %
Total Error $\langle\sigma_t\rangle$	-	± 30.0

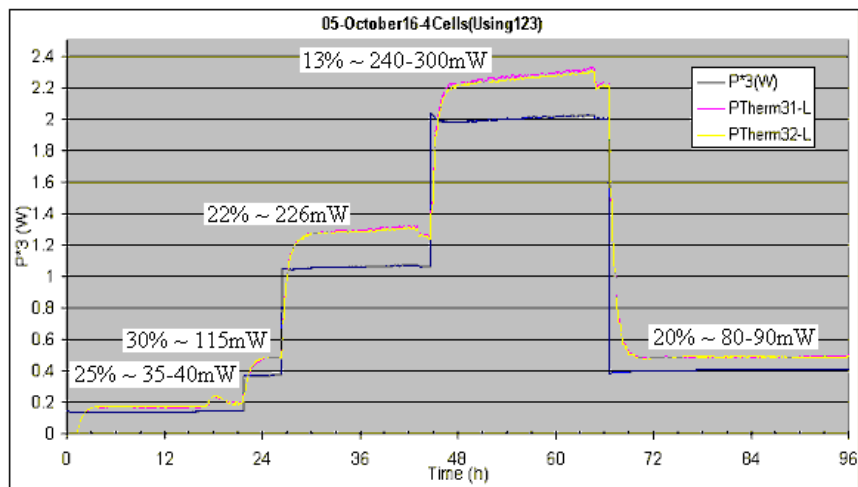Figure 1. Schematic representation of the calorimetric bank.

Figure 2. Typical case of moderate excess heat from an Alumina/Pd-Ni cathode.