

J. Electroanal. Chem., 306 (1991) 279–285
Elsevier Sequoia S.A., Lausanne

Preliminary note

Calorimetric observation of heat production during electrolysis of 0.1 M LiOD + D₂O solution

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(Received 27 February 1991; in revised form 8 April 1991)

INTRODUCTION

Excess heat production during the electrolysis of a solution of 0.1 M LiOD in D₂O with a palladium cathode and a platinum anode has been reported by Fleischmann et al. [1]. After their report, many research groups around the world have tried to observe excess heat production and other evidence for the phenomenon so far called "cold fusion". Reviews on this phenomenon have been written [2,3]. While most research groups have not observed any excess heat production [4–7] or any evidence of a fusion reaction during D₂O electrolysis [8–13], several research groups have claimed sporadic observation of excess heat [1,14–19] or evidence of reaction products believed to result from a fusion reaction [20–24]. This indicates that the reaction mechanism for the production of excess heat seems to depend strongly on the experimental conditions. There are many different experimental factors; environmental conditions; such as temperature, cell geometry, pressure, etc., methods of electrode preparation, electrode materials, electrochemical system parameters, and the duration of electrolysis. In this study, we have examined the phenomenon of excess heat generation during the D₂O electrolysis in relation to electrode materials and the method of electrode preparation.

EXPERIMENTAL

Measurement of the heat burst during the electrolysis of 0.1 M LiOD + D₂O solution was performed with heat-conduction type calorimeters shown in Fig. 1 and fabricated in our laboratory. Thermocouples (Chromel Alumel) were connected in series in order to yield a large emf signal due to the temperature differences between an outside wall (hot junction) of an electrolytic cell located in an aluminum block, and a water bath (cold junction) maintained at a constant temperature of 25 °C. For

this study, four calorimeters were fabricated. Two of them have 80 junctions (CAL-1); the others 288 junctions (CAL-2).

An electrolytic cell which has the same geometrical shape as the Fleischmann-Pons type cell shown in Fig. 1 was located inside a cylindrical cavity in a calorimeter made of a cylindrical aluminum block. As a counter electrode, Pt wire (1 mm dia.) was wound helically and fixed inside the pyrex glass cell in order to maintain axial symmetry with a Pd working electrode positioned at the center of the cell. After the insertion of a cell, the upper part of the calorimeter was sealed with an aluminum cover and silicon rubber adhesives, leaving an outlet for the gas discharge and the connecting wires for the power supply into the system. In several cases, we also used perfectly sealed calorimeters with Pt catalysts supported in activated carbon placed inside the cell, in order to provide recombination of D_2 and O_2 . The constant current was passed through a cell with a power supply (PAR 173, HP DC Power Supply 30 V). The emf changes from the thermo-junctions were monitored with a multichannel digital recorder (GH DPR-500) or a multichannel strip chart recorder (Pantos, U-228).

The palladium wires as cathodes were obtained from two different sources. One group of palladium wires (0.5 mm and 1.0 mm dia.) were prepared by the hot

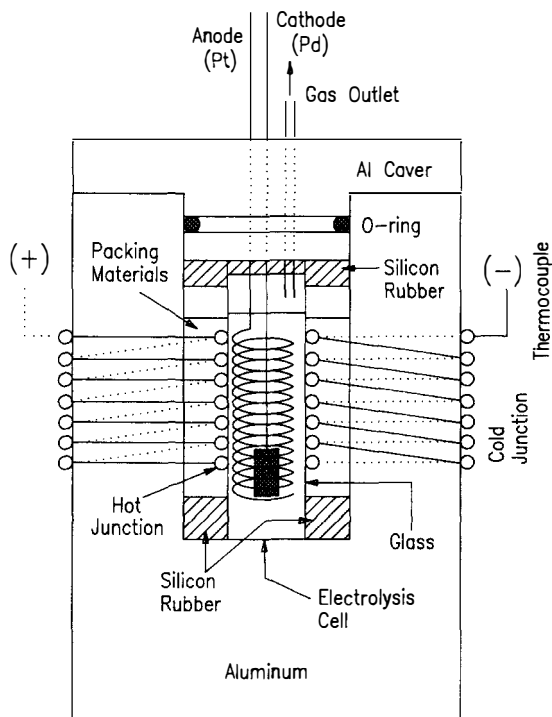


Fig. 1. A schematic diagram of a built-in heat-conduction type calorimeter.

extrusion of a palladium ingot (purity 99.9%) obtained from Lucky Metals Ltd., Korea (LM). Another group of wires was obtained from CERAC (purity 99.9%), USA (CM). Some wires were used as received; most were pretreated by annealing at 800 °C in vacuum or in D₂ gas for 20–24 h; in some experiments fresh D₂ gas was added several times. The wires were cut into 1 cm lengths and spot-welded to the copper wires (1 mm dia.) used for the connection to the power supply. The exposed part of the copper wires was shielded with teflon to avoid contact with the gas and the electrolyte.

RESULTS AND DISCUSSION

Prior to the measurement of excess heat during the electrolysis, calibration of a calorimeter was performed with a heat filament made of electrical resistance wire (1.5 ω , Nichrome wire) located in the electrolysis cell with 0.1 M LiOD + D₂O solution, by applying variable currents. The result of a calibration experiment is shown in Fig. 2. From the calibration plot of Fig. 2, the values of the emf changes monitored from thermo-junctions in the calorimeter were converted to the corresponding amount of heat. In this study the total amount of heat output during the electrolysis time was not considered, while the observation of heat produced as a burst or peak pattern was the aim. For the above purposes, the built-in calorimeters used in this study performed well, and they showed fast responses to changes in the heat output.

The Joule heat produced by the resistance of electrolytes furnishes a base line featured in Fig. 3; its theoretical value is $(E-1.54)I$. These theoretical amounts of Joule heat were in good agreement with those measured with the calorimeters ($\pm 2\%$). Figure 3 shows the presence of two events of heat burst, between 103 and 104 h and between 138 and 140 h after the electrolysis was started. This result was

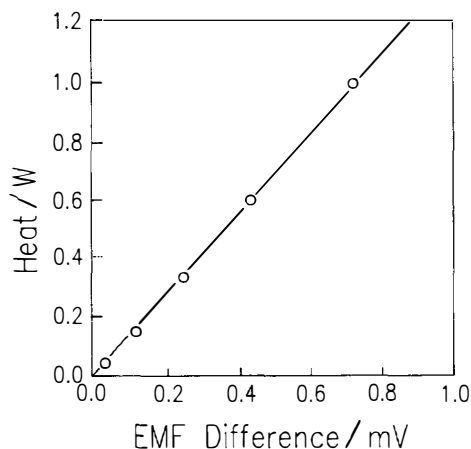


Fig. 2. A calibration plot for the measurement of heat output from a calorimeter (CAL-1).

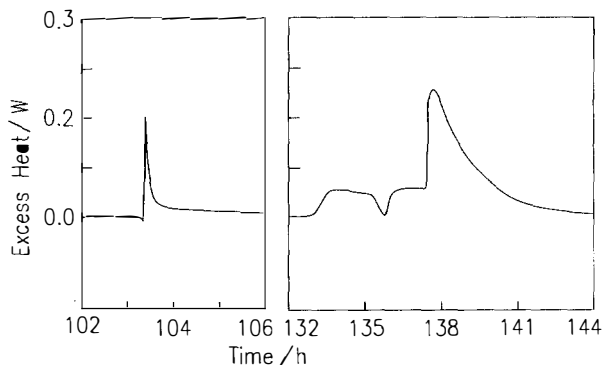


Fig. 3. The heat curves to show two heat burst events during the electrolysis of 0.1 M LiOD in D₂O (calorimeter: CAL-1, electrode: 0.5 mm dia., 1 cm long palladium wire (LM), as received, current density: 700 mA/cm²).

obtained only once out of five separate experimental runs, in which all experimental procedures and conditions were identical. The maximum values of the heat peaks correspond to about 0.24 W excess heat (128 W/cm³ Pd). This value is relatively higher than results reported by the other investigators [1,14–19]; however, the production rate of excess heat $[(W_{in} - W_{out})/W_{in}]$ is calculated to be 22%, which shows good agreement with the other investigators' reports [18,19]. In this series of experiments the surrounding bath temperature was maintained at 25°C, using a constant temperature bath circulator. Water was circulated into the Dewar inside which the calorimeter is positioned and the base line showed a stability of ± 0.02 W.

The calorimetric system was changed to a closed system in order to avoid any sudden failures in the above circulation system. A calorimeter (CAL-1) with 80 thermo-junctions was positioned and immersed in 70 l of water which was contained in a large Dewar. The overall system was sealed, leaving a gas outlet and power connections. This system gave a poorer stability of the base line (± 0.05 W, which may cause inaccurate quantitative values, but the sporadic heat bursts could be observed qualitatively because of the slow movement of the base line. This slow movement of the base line is considered to be a result of the natural heat convection occurring inside the Dewar. The unusual movements of the heat curve during the electrolysis were observed only once out of four separate experimental runs. Palladium wires (LM) were used as cathodes after annealing at 800°C in vacuum. Another series of experiments was performed with a pair of calorimeters (CAL-2) which have 288 thermo-junctions in the same environmental conditions. The movement of the base line with CAL-2 became more unstable than with CAL-1 because of its increased sensitivity; it showed a stability of ± 0.1 W. In order to overcome this instability problem, a pair of calorimeters consisting of one with an electrolysis cell with a 0.1 M LiOH + H₂O solution and one with a cell with a 0.1 M LiOD + D₂O solution, was used in order to detect possible heat burst curves. Two heat curves obtained from the above two different calorimeters are shown in Fig. 4.

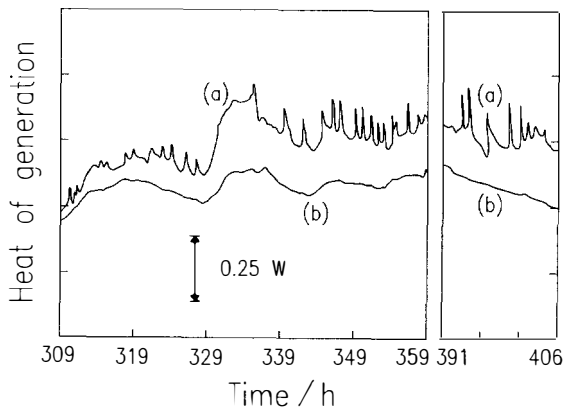


Fig. 4. Comparison of heat curves obtained from two different electrolysis cells: (a) in 0.1 M LiOD in D_2O ; (b) in 0.1 M LiOH in H_2O . Calorimeter: CAL-2, electrode: 1 mm dia., 1 cm long palladium wire (CM), annealed in vacuum at $800^\circ C$ for 24 h and charged with D_2 gas several times, current density: 500 mA/cm^2 .

It is clear that many peaks were occurring only when the electrolysis was performed in LiOD + D_2O solution. The highest peak shows an amount of heat of about 0.2 W. This result was obtained from only one experiment out of four separate identical experimental runs.

The above calorimetric system was changed once again, to a constant temperature bath system, in order to maintain constant environmental thermal conditions. Calorimeters were located inside a constant temperature bath ($\pm 0.01^\circ C$, SCR equipped) which is filled with distilled water and maintained at $25^\circ C$. Then the upper part of the bath was covered with styrene sheets, except the gas outlet and power connection part. Sometimes platinum catalyst pellets (on activated carbon supports) were attached inside the cell for the complete recombination of gases produced during the electrolysis and the gas outlet was closed. This system showed a good stability of base line (Joule-heat curve) with $\pm 0.01 \text{ W}$. As shown in Fig. 5, the amount of maximum heat peaks is in the range of 0.16 W to 0.24 W ($20.4\text{--}33.1 \text{ W/cm}^3 \text{ Pd}$). Any events of heat burst were independent of the duration of the electrolysis. The heat burst curve in Fig. 5b was obtained after a palladium wire (CM) having produced a heat burst was reapplied after etching in 0.1 M sulfuric acid for 4 h. It is noticeable that a heat burst occurs even at a low current density as compared to other experiments. In this case the maximum production rate $[(W_{in} - W_{out})/W_{in}]$ is about 75% of excess heat, whereas the other results usually yield about 10–25% of excess heat. This result is in agreement with the other results [15–19], but the excess heat above the break-even point corresponding to the results observed by Fleishmann et al. [1,14] cannot be observed in this study. The above results were obtained from three runs out of twelve separate experiments.

It is observed clearly that heat burst phenomena occur sporadically during the electrolysis of D_2O with a probability of about 24%, that is to say, six events out of

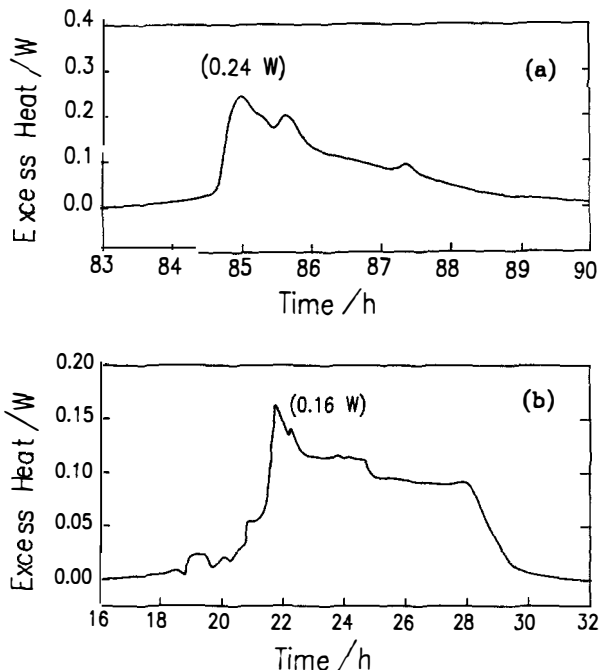


Fig. 5. A heat burst curve occurred during the electrolysis of 0.1 M LiOD+D₂O solution. (a) Calorimeter: CAL-1, electrode: 1 mm dia., 1 cm long palladium wire (CM), pretreated as in Fig. 4, current density: 700 mA/cm². (b) Calorimeter: CAL-1, electrode: the same electrode used in (a) and applied after etching in 0.5 M H₂SO₄ solution for 4 h, current density: 100 mA/cm².

twenty-five experimental runs; one event out of five runs for as-received Pd electrodes and five events out of twenty runs for annealed Pd electrodes. Kainthla et al. [25] suggested eight possible explanations for the heat production during the electrolysis of D₂O including the recombination of D₂ and O₂. They insisted that heat as much as 3 W/cm³ Pd can be produced if the eight possible events happen all together. The cause of as much heat as 25–128 W/cm³ Pd, observed in this study, cannot be explained with the above eight possible explanations, although certain evidence that a fusion reaction causes the excess heat cannot be obtained in this study. In order to verify this, it will be necessary to increase the reproducibility of the excess heat production and then to perform calorimetric measurements with simultaneous observation of radiation.

CONCLUSION

The production of heat during the electrolysis of D₂O has been examined. A heat-conduction type calorimetric system for the detection of heat bursts was designed and fabricated. Five events of excess heat burst were observed in 22 separate experiments. The maximum amounts of excess heat measured from the

heat burst curves were 0.16 W to 0.26 W (25–128 W/cm³ Pd). Heat production occurred sporadically and seems to be independent of the electrolysis time. Pretreatment by annealing the palladium electrode tends to increase the reproducibility of heat product slightly.

ACKNOWLEDGEMENTS

This study was performed with financial support from the Ministry of Science and Technology of Korea. The authors are thankful to Dr. Chang-Koo Yun for the help to start this project and all the workers in electrochemistry laboratory for their encouragement and help during this study.

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