REPORT DOCUMENTATION PAGE	*Form Approved* *OMB NO. 0704-0188*

Public reporting burden for this collection of information is estimated to average 1 hour per response, including the time for reviewing instructions, searching existing data sources, gathering and maintaining the data needed, and completing and reviewing the collection of information. Send comment regarding this burden estimates or any other aspect of this collection of information, including suggestions for reducing this burden, to Washington Headquarters Services, Directorate for information Operations and Reports, 1215 Jefferson Davis Highway, Suite 1204, Arlington, VA 22202-4302, and to the Office of Management and Budget, Paperwork Reduction Project (0704-0188), Washington, DC 20503.

1. AGENCY USE ONLY *(Leave blank)*	2. REPORT DATE	3. REPORT TYPE AND DATES COVERED Reprint

4. TITLE AND SUBTITLE

TITLE ON REPRINT

5. FUNDING NUMBERS

DAAG55-97-1-0357

6. AUTHOR(S)

AUTHOR(S) ON REPRINT

7. PERFORMING ORGANIZATION NAMES(S) AND ADDRESS(ES)

Portland State University

8. PERFORMING ORGANIZATION REPORT NUMBER

9. SPONSORING / MONITORING AGENCY NAME(S) AND ADDRESS(ES)

U.S. Army Research Office
P.O. Box 12211
Research Triangle Park, NC 27709-2211

10. SPONSORING / MONITORING AGENCY REPORT NUMBER

ARO 37386.5-MS

11. SUPPLEMENTARY NOTES

The views, opinions and/or findings contained in this report are those of the author(s) and should not be construed as an official Department of the Army position, policy or decision, unless so designated by other documentation.

12a. DISTRIBUTION / AVAILABILITY STATEMENT

Approved for public release; distribution unlimited.

12 b. DISTRIBUTION CODE

13. ABSTRACT *(Maximum 200 words)*

ABSTRACT ON REPRINT

20010517 019

14. SUBJECT TERMS			15. NUMBER IF PAGES
			16. PRICE CODE
17. SECURITY CLASSIFICATION OR REPORT UNCLASSIFIED	18. SECURITY CLASSIFICATION OF THIS PAGE UNCLASSIFIED	19. SECURITY CLASSIFICATION OF ABSTRACT UNCLASSIFIED	20. LIMITATION OF ABSTRACT UL

NSN 7540-01-280-5500

Standard Form 298 (Rev. 2-89)
Prescribed by ANSI Std. 239-18
298-102

Conference Proceedings Vol. 70
"ICCF8"
F. Scaramuzzi (Ed.)
SIF, Bologna, 2000

HEAT PRODUCED DURING THE ELECTROLYSIS OF D_2O WITH TITANIUM CATHODES

J. Warner and J. Dash
Physics Dept., Portland State University, P.O. Box 751, Portland, OR 97207

Abstract. Cold rolling 20% appears to increase both the amounts of excess heat and reproducibility obtained by electrolysis of acidified D_2O with titanium cathodes. Unexpected elements such as chromium and iron were detected on the surfaces of cathodes after electrolysis. The presence of chromium was confirmed by neutron activation analysis.

Experimental Methods and Results. Experiments have been performed using titanium cathodes with various amounts of deformation by cold rolling, which increases the amount of lattice disorder and stress in the cathodes.

The first calorimetric system employed is referred to as the "8-cell" system. Each cell is comprised of a small double-walled beaker with a temperature-transducer in the dead airspace between the cell walls. The inner chamber holds the catalyst, electrolyte and electrodes. Each cell is sealed to minimize gas losses. Seven of the eight cells were wired in series so the same, constant current passed through each cell. One of the seven cells is a control cell with platinum anode and cathode and electrolyte containing sulfuric acid and light water in the ratio one mole H_2SO_4 to 99 moles H_2O. The eighth cell, which was empty, was used to monitor ambient temperature. The remaining six experimental cells consisted of three pairs of cells, with the cells in each pair as identical as possible. The three pairs differed from each other in one parameter such as cathode size (from 0.12 to 0.34 cm^2) or degree of deformation. The experimental cells all contained Pt anodes, Ti cathodes (foils, triangular in shape) and an electrolyte composed of the ratio one mole H_2SO_4 to 99 moles D_2O. All of the data is stored in a computer for later analysis. To analyze the experiment, the following equation is used [1]:

$$\frac{dH_e}{dt}(Excess) = \frac{\Delta T_e}{\Delta T_c}\left(V_c I - \frac{dH_c}{dt}(esc)\right) + \frac{dH_e}{dt}(esc) - V_e I - \frac{dH_{TiO_2}}{dt} - \left[\frac{dH_{TiD_2}}{dt} - \frac{dH}{dt}(esc)\right] \quad (1),$$

where subscript c refers to the control cell, subscript e refers to the experimental cell, dH_e/dt (Excess) is the enthalpy released by cold fusion (or other unknown processes), ΔT is the temperature difference between the cell and its surroundings, VI is the power input into the cell, dH/dt (esc) is the recombination enthalpy lost by each cell due to escape of gases from the cell, dH_{TiO_2}/dt is the enthalpy due to the formation of titanium dioxide which results from erosion of the cathode during electrolysis, and [dH_{TiD_2}/dt - dH/dt (esc)] is the enthalpy loss due to the large difference between the enthalpy of formation of TiD_2 and the enthalpy of recombination of D_2O. Lost recombination enthalpy is determined from the weight lost by each cell during each experiment.

The other calorimeter employed is a Seebeck envelope calorimeter (SEC) from Thermonetics Corp., which allows for scaled up experiments (cathode areas from 2.81-4.29 cm^2). The cathode foils are shaped to maximize the uniformity of the electrical current density to make the erosion more uniform, thus giving the cathode a longer life. The SEC used here measures 18 cm by 18 cm by 18 cm in the inner cavity. Heat flows from the cell through air in the calorimeter and through the Seebeck envelope to an aluminum jacket incorporating constant temperature water-cooling coils.

The millivolt output signal, which is related to the heat release via an accurate calibration process, is fed to a computer for storage[2]. If no temperature difference between the cavity and the water jacket exists, no heat flux is measured and no signal is generated. If the cavity temperature is greater than the water jacket temperature, a positive signal is generated. The SEC was calibrated using two different methods: (1) a control cell with Pt anode and cathode in a light water/ sulfuric acid electrolyte (three data points) and a cell with a resistor immersed in water (16 data points). The SEC gives a linear input vs. output relationship over the range of interest:

$$\text{Power Output (Watts)} = 0.216\ \text{W/mV} \times \text{SEC output (mV)} + 0.029\ \text{W} \qquad (2),$$

with a coefficient of determination R^2 of 0.9996. The 0.029 W intercept at zero SEC output compensates for thermal leakage along wires fed through a 0.6 cm inner diameter tube inserted into the inner cavity of the SEC. These wires include the power leads to the cell, the leads to measure cell voltage, and the thermocouples used to monitor temperature on the outside of the cell.

According to the suppliers, the titanium used in this study (99.99 % Ti, metals basis) was hot worked from the ingot stage to about 5 mm thickness. It was then cold rolled to 0.5 mm thickness (about 90% reduction in thickness). It is sold in the cold rolled condition. The Ti was obtained from two vendors: Alfa Aesar which reported impurities of 3 ppm Fe, 2 ppm K, 2 ppm Mn, 1 ppm Cr and 20 other elements ≤ 1 ppm. This was the Ti used in the 8-Cell "as received" condition. The remainder of the data in fig. 1 was obtained using Ti supplied by Aldrich, which reported that the only impurities detected were 30 ppm Ca and 8 ppm Al. The experimental results are shown in fig. 1, in which the excess power output (W) is a function of percentage reduction in thickness by cold rolling of the titanium cathodes prior to electrolysis. The error values shown in fig. 1 vary from one experiment to another but the largest error values encountered are those reported. As a conservative estimate, only those data points above 100 mW will be reported as excess heat.

With the titanium cathodes in the as received condition, 3 of 8 experimental cells (38%) showed excess heat. The current densities at the cathode for the 8-cell experiments were 0.6 to 3.3 A/cm^2 with voltages from 1.8 to 6.0 V. The SEC cathode current densities ranged from 0.3 to 0.7 A/cm^2 with voltages between 4.3 to 6.0 V. There was no correlation between current density and excess heat. When the as received Ti was cold rolled to 20% reduction in thickness, 6 of 8 cells (75%) produced excess heat. Increasing the amount of cold rolling to 40% gave excess heat for 2 of 2 experimental cells, but the magnitude of the excess heat was not as great as that observed for three of the cells in which the Ti had been cold rolled 20%. At 50% reduction in thickness, 2 of 6 cells gave excess heat, and the magnitude was less than that observed at lower amounts of deformation. There were 7 experimental cells in which the titanium was cold rolled to 65% or greater reduction in thickness. None of these cells produced excess heat.

A possible reason for the results in fig.1 is that cold rolling increases the degree of disorder of the material, which increases the absorption of deuterium and hydrogen, and this enhances the excess heat effect. De Ninno et al [3] concluded that a grain size of about 50 μm gives the maximum concentration of hydrogen in Pd. Both smaller and larger grain sizes reduced the concentration of hydrogen. Further support comes from Kamiya et al[4].

Their studies found that the H/Pd absorption ratio was maximum (0.924) at 30% cold working and decreased to 0.842 at 90% cold work. Shock loading, another process which increases crystalline disorder, has been found to increase the photocatalytic activity of TiO_2 powder by a factor of two to three[5]. The optimum shock pressure was found to be 16 GPa. Photocatalytic activity decreased at higher shock pressures, but it was still much higher than observed for the unshocked powder.

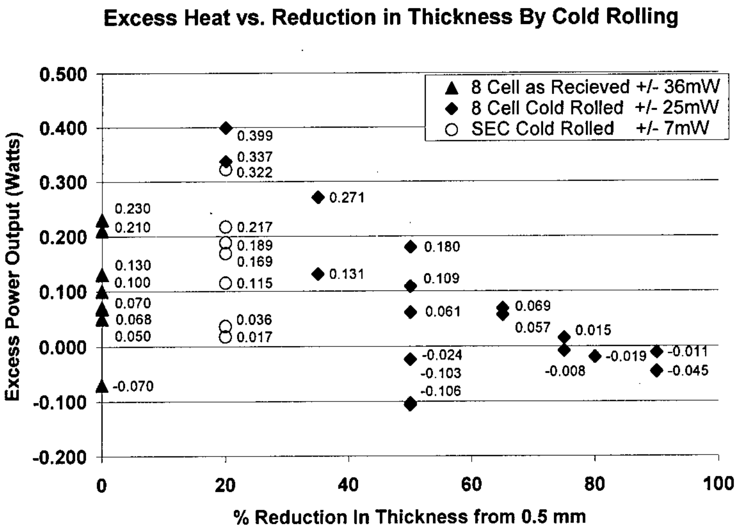


Figure 1. Excess heat as a function of reduction in thickness by cold rolling of the as received titanium.

A further example of excess heat can be found in fig. 2. Here, cell 2 of experiment 2 during the Summer of 1999, in which the titanium cathode was cold rolled to a reduction of 20% in thickness (from 0.5 mm to 0.4 mm), had almost the same power input as the control cell (fig. 2, left). There is however, a 6°C higher temperature in the experimental cell than in the control cell, for a period of 400 minutes (fig. 2, right). One would not expect this kind of behavior from two cells that are identical except for the substitution of a Pt cathode and light water in the control cell.

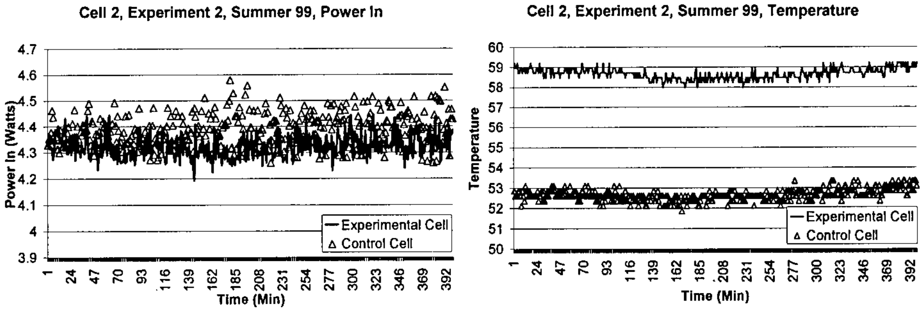


Figure 2. Comparison of power input and temperature of experimental cell 2 and the control cell for experiment 2, summer 1999.

A comparison of enthalpy output of a cell and the enthalpy released due to the formation of titanium deuteride can also be made. SEC cathode 3 (0.3194 g) was electrolyzed for 186 hours, and using the enthalpy of formation of TiD_2 (94KJ/mol) one calculates an enthalpy change of 627 joules. In addition, the cathodes were found to erode during electrolysis at the rate of about 0.3 nm per second. The precipitate was analyzed by x-ray diffraction and found to be to TiO_2. The enthalpy of formation of TiO_2 (913KJ/mol) can be used to calculate an enthalpy change of 2,302 joules. The total enthalpy change due to these chemical reactions is 2,929 joules, far less than the actual excess enthalpy output of 179,000 joules, which was calculated using equation 1.

Scanning electron microscopy (SEM), energy dispersive spectrometry (EDS), and neutron activation analysis (NAA) have been employed in the analysis of cathodes. It should be noted that EDS analyzes the surface to a depth of about 1µm, whereas NAA is a bulk analysis technique. Figure 3 shows one of the localized regions analyzed during a post experiment analysis of SEC cathode 1 using SEM and EDS. Pre-characterization of this cathode shows a flat, featureless topography with 100% titanium, whereas the post-characterization showed localized regions of changes in topography and composition. Figures 4, 5, 6, and 7 show the EDS data that corresponds to this region. Figure 4 shows that the area S14 is composed of 100% titanium while fig. 5 (S15) has a trace amount of Fe, 99% Ti and 1% Cr. Figure 6 shows < 1% S, < 1% Fe, 89% Ti and 10% Cr and fig. 7 shows about 9% Al, <1% S, 2% Fe, 79% Ti and 9% Cr.

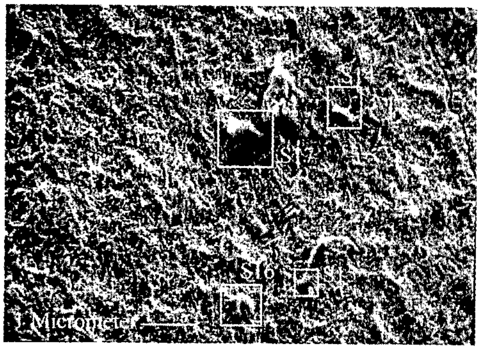


Figure 3. Region of SEC 1 titanium cathode after electrolysis. The squares locate regions where EDS spectra were obtained.

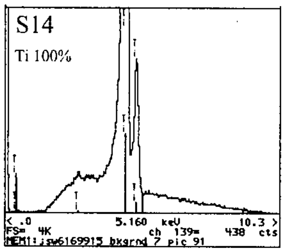


Figure 4. EDS spectrum from region S14 in fig. 3. Ti is the only element detected.

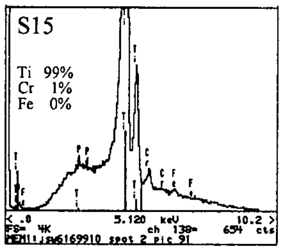


Figure 5. EDS of area S15.

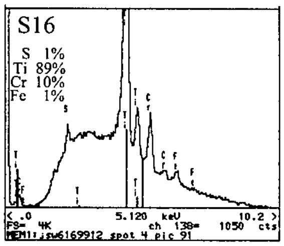


Figure 6. EDS of area S16.

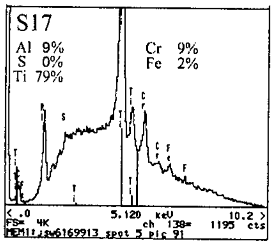


Figure 7. EDS of area S17.

These results are typical and have been found on about half of the experimental cathodes that have yielded excess heat. It should be pointed out that thorough SEM and EDS analysis of these electrodes is very tedious and time consuming. It is likely that further efforts would result in the discovery of unexpected elements on all of the electrodes that produced excess heat. The presence of Cr in an excess heat-producing titanium cathode has been confirmed by NAA analysis performed at the Reed College Nuclear Reactor facility in Portland, OR. Chromium (28 +/- 12 ppm) was found in an excess heat-producing cathode, which weighed about 5 mg, and in about 800 mg of the electrolyte from the same cell after electrolysis (0.5 +/- 0.1 ppm). This shows that most of the chromium is in the electrolyte, suggesting that it was formed by a surface reaction and was transported to the electrolyte by erosion of the titanium cathode. Using NAA analysis, no chromium was found in either the titanium cathode (cut from same batch) or in the electrolyte (drawn from same mixture) of an identical cell electrolyzed in series, which did not produce excess heat.

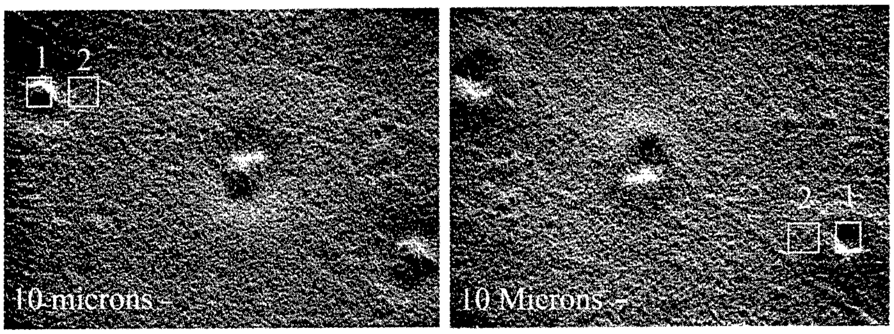
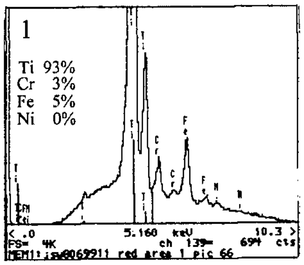


Figure 8. Changes in topography on a Ti cathode. The three mound-like features in the left photo appear to be valleys when the photo is inverted (right photo).



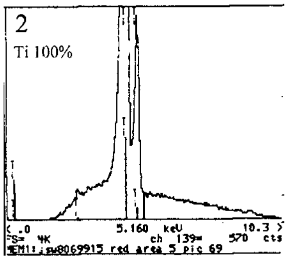


Figure 9. EDS of area 1 in fig.8.

Figure 10. EDS of area 2 in fig. 9.

Figure 8 shows three similar formations, which were found on a cathode that did not yield a reasonable steady state period. Due to this it is unknown if this cell produced excess heat or not. It was determined from a SEM photo that these were not present before the experiment. One can see from the EDS spectra in figs. 9 and 10 that area 2 shows 100% Ti while area 1 shows 93% Ti, 3% Cr, 5% Fe and a trace of Ni. Depending on the orientation of this picture, the features may look like hills or valleys.
With the aid of a light microscope it was determined that these features are valleys (about 4 μm deep) with rims. It may be possible for transmutation to occur without producing

significant levels of excess heat. Previous studies showed that unexpected elements were associated with certain topographical features which were found on Pd cathodes after electrolysis [6-8].

One possible explanation for the appearance of these new elements after an experiment is that these elements are impurities, which are being deposited during electrolysis. If this were the situation, then one would expect that Pt from the anode, which is the most abundant impurity and which can be deposited at a lower potential than either H or D, would appear on the Ti cathode. This is seldom observed. Secondly, it is found that the cathodes erode at a rate of about 0.3 nm per second. Over a 166-hour period, SEC cathode 6 lost 43% of its original thickness. It would be difficult to deposit material onto a cathode that erodes at the rate of about one atomic layer per second. Another possible explanation for the appearance of new elements is that impurities diffuse from the bulk of the material to the surface during electrolysis. Using the Boltzmann equation, a conservative calculation for room temperature diffusion showed that the average length of travel over a 166 hour period to be of the order of 10^{-12} mm. A travel length of 10^{-1} mm would be needed to diffuse from the bulk to the surface. Electromigration could enhance diffusion, but this should produce much more uniform distributions of diffusing elements, not the localized concentration levels ~10^4 times the bulk concentration adjacent to regions where no Cr or Fe is detected. Another factor which makes electromigration an unlikely explanation for the observations is that Ca, the most abundant impurity (30 ppm) in the Ti cathodes used to obtain figs. 4,5,6,7,9 and 10 is not present in any of those spectra. It should be noted that the melting point of Ca is about ½ the melting temperature of Cr and Fe, so Ca should diffuse much more rapidly than Cr or Fe.

Discussion of Results. A 20% reduction in thickness, which is in addition to cold rolling performed by the manufacturer, gave the best heat and reproducibility results, with 6 of 8 cells showing excess heat. The mechanical treatment of the cathode by cold rolling appears to be an important variable in the excess heat effect. The SEC experiments used much larger Ti cathodes than the 8- cell experiments, but the rate of excess heat production was about the same for both. The reason for this result is not known. Unexpected elements such as chromium have been found in about half of the excess heat producing cells. The NAA data cited above suggests that a nuclear reaction occurred, which converted Ti to Cr. The Cr content obtained could account for about 10^{15} events, which could release a few thousand joules of excess heat, far less than that observed. Therefore, other nuclear reactions may also have occurred in order to account for the observed excess heat (~ 10^5 joules).

We realize that absolute proof of transmutation requires extraordinary evidence. We have been gathering evidence for about a decade, and it all seems to fit the conclusion that transmutation occurs, both on Pd [6-8] and on Ti cathodes. Reference 8 includes documentation of time-dependent changes in morphology and microcomposition of a Pd cathode which occurred long after electrolysis was completed. In addition, analyses obtained by secondary ion mass spectroscopy have shown that changes in isotopic abundance occur on the surfaces of Pd cathodes after electrolysis [7, 9].

Also, analyses performed after electrolysis by inductively coupled plasma mass spectroscopy showed that changes in isotopic abundance occurred in both a Ti cathode and in the electrolyte[10].

We will continue our efforts to obtain irrefutable evidence. In the meantime, we can only conclude that our results suggest that transmutation is highly probable.

References

[1] WARNER J.: M.S. Thesis, Portland State University, 1998.

[2] BUSH B. AND LAGOWSKI J.: Proc. ICCF-7 (ENECO, Salt Lake City) 1998, pp. 38-42.

[3] DE NINNO A., ANTISARI M., GIANGIORDANO C.: ibid, pp. 103-107.

[4] KAMIYA N., SAKAI Y., WATANABE Y., YAMAZAKI O., MOTOHIRA N., OTA K., AND MORI K.: Proc. ICCF-6 (New Energy and Industrial Technology Development Organization and the Institute of Applied Energy, Japan) 1996, pp. 203-207.

[5] LIU J., YU Y., LI Y., HE H., TAN H., AND XU K.: Chem. Abs., 131, (1999) 1303.

[6] DASH J., NOBLE G., AND DIMAN D.: Trans. Fusion Tech., 26, (1994) 299 - 306.

[7] DASH J., Progress in New Hydrogen Energy, M. Okamoto, ed., (New Energy and Industrial Technology, Tokyo, 1997) pp. 477- 481.

[8] DASH J., KOPECEK R., AND MIGUET S., Proc. 32nd Intersociety Energy Conversion Engineering Conf., vol. 2, (1997) pp. 1350 -1355.

[9] SILVER D., Ph.D Dissertation, Portland State University, 1998.

[10] KLOPFENSTEIN M., AND DASH J., Proc.ICCF - 7 (ENECO, Salt Lake City) 1998, pp. 98 - 102.

Acknowledgments. We are indebted to the referee for valuable suggestions. Neutron activation analysis was performed by S. Frantz and C. Melhus, Reed Reactor Facility, Portland, OR. This research was supported by a gift from the New York Community Trust and by the U.S. Army Research Office under grant number DAAG 55-97-1-0357.