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METHODS OF GENERATING EXCESS HEAT WITH THE PONS AND FLEISCHMANN EFFECT: RIGOROUS AND COST EFFECTIVE CALORIMETRY, NUCLEAR PRODUCTS ANALYSIS OF THE CATHODE AND HELIUM ANALYSIS.

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Abstract:

The results from a growing number of laboratories suggest that the Pons and Fleischmann effect (the production of "excess heat" during the electrolysis of D2O at palladium electrodes) is real. More over data from these laboratories indicate that excess heat events are accompanied by ^{4}He production. Excess heat generation appears to depend on a number of factors: the quality — nature — of the cathode, chemical species present in the D2O / LiOD electrolyte, the conditions surrounding the electrolysis process — current density, potential, time, and the previous history of the cathode. Methods for obtaining useful cathodes will be described.

Calorimetric problems have dominated the excess heat measurements. There is little standardization of methods employed by different laboratories and the performance characteristics of the various methods are obscure. We have settled upon high performance Calvet calorimetry as a cost effective, but highly reliable method for measuring excess heat. A 3 X 3 X 9cm device provides a dynamic range from milliwatts to hundreds of watts (depending on water bath capacity). Conceptually, the high performance Calvet calorimeter is a box with each of the six walls being a thermal flux transducer. Thus, the series sum voltage of the thermal flux transducers represents all the heat flow that occurs during an experiment. Thermal homogeneity (the isoperibolic assumption) is unimportant as long as the water bath temperature is stable. With multiplexed computer data acquisition high performance Calvet calorimetry (AKA SeebeckxM; Thermonetics, San Diego) is very labor efficient. The Calvet devices can be made in any size or shape, and they combine the fastest time response and largest dynamic range with the most fundamental method of calorimetry known.

We entered the field with concurrent heat versus helium analyses. Subsequent quantitative helium analyses showed that the excess heat appeared to be generated by the D + D → ^{4}He + 23.82MeV (heat) reaction pathway. The helium was found in the electrolysis off-gas indicating a surface reaction. As the electrolysis proceeds a non-conductive film of oxyhydroxides builds up on the cathode surface. This film acts as a temperature sensitive activity step up transformer; in the Pons and Fleischmann type isoperibolic calorimeter excess heat causes the cell temperature to rise which decreases the degree of hydration (hence decreases deuteron mobility) so fewer deuterons carry the current and their activity increases which increases the excess heat... in a cycle that goes to thermal run-away and boil down. In highly active cathodes one should expect multiple nuclear reaction pathways, hence the nuclear products analysis of the cathode will shed light on the reaction mechanism. Secondary ion mass spec, is a non-ideal method due to ion fractionation of the light isotopes, and sensitivity is dependent on the ionizability of the elements. Neutron activation analysis is sensitive to a few elements, but renders the sample radioactive. Prompt gamma activation analysis using a cryogenic neutron beam is ideal because of reasonable sensitivity, analyzes the entire sample and doesn't render it excessively radioactive.

Introduction:

Many laboratories have reported generating excess heat during deuterium oxide electrolysis at palladium cathodes, many of these reports being extremely convincing. The major difficulty with the topic of excess heat generation is not reproducibility, but rather control. The ability to control the circumstances of the electrolysis so that the excess heat can be "turned on, and turned up or down" has eluded us as yet. Generally, generating excess heat remains unpredictable.

Discussion, Cathode preparation:

Perhaps 50% of our experiments generate excess heat, depending on the quality of the palladium metal. Begin with palladium as a rod of 3mm or larger diameter (we commonly use a 2cm X 3mm cathode). Cut the rod with a common plumbers' tubing cutter, so that the rolling blade overworks the metal at both ends of the cathode. Chuck the cathode in a Dremel moto-tool and round both ends of the cathode to a hemispherical configuration using coarse sandpaper, and sand the cylindrical body to remove perhaps 0.001 inch of the surface. Polish the cathode using longitudinal strokes (with the Dremel not rotating) before switching to the next finer grit of sandpaper, as this levels the cathode surface. By polishing with successively finer grits of sandpaper (from ~240 to 400 to 600 to 1200 grits) one removes the surface layer of smeared (amorphous) palladium which results from the swaging and drawing operations used to fabricate the rod. We are careful to wear rubber gloves during the polishing operation to avoid contaminating the surface with skin oil. The final step is to polish the cathode with cerric oxide (lens polish) on a wet lens tissue, until a mirror finish is achieved. The purpose of the successively finer grits is to thin the smeared surface layer of metal without adding more to its depth.

The purpose of deliberately overworking the hemispherical ends of the cathode with the tubing cutter is to render the damage layer so thick at the cathode ends, that one won't polish through it. The purpose of removing the damage layer from the cylindrical sides of the cathode is to enhance its ability to absorb deuterium. By deliberately damaging the surface of the hemispherical ends of the cathode one hopes to prevent the egress of deuterium where the electrolysis current density is lowest; further, by cutting the ends to hemispherical configuration instead of leaving the ends flat, one increases the current density at the middle of the hemispherical end to ~90% that of the cylindrical side, instead of the ~50% current density for the middle of a flat end (also one avoids a bubble clinging to the bottom end of the cathode by cutting the end hemispherical, bubble cling will reduce the current density to *0%* under the bubble).

Once the cathode is polished a lead is carefully spot welded to one end. We use 1/32" stainless steel welding rod as the lead, because it is cheap, corrosion resistant, and available. Once the lead is spotwelded to the cathode, we anneal the cathode under argon at 850° C for 3 hours. If the palladium comes out specular (like a mirror) there is a very good chance of getting excess heat. We attach our voltage measurement wire as close to the calorimetric envelope as possible using 96% Sn 4% Ag solder with acid flux (wash off the flux with sodium bicarbonate in H_2O after soldering).

The uncontrolled variable in cathode preparation is the quality of the metal itself. Unless one has the resources to fabricate palladium from the sponge to a billet to the cathode; off the shelf rods must suffice. Simply be prepared to try several different suppliers until you find a workable material. After the electrolysis, the palladium can be carefully polished down one side and the metal examined under a microscope. If a profusion of pores are found in the polished surface, the metal isn't as good as it could be due to the presence of dissolved palladium oxide.

Because the palladium is deformed and stressed on loading with deuterium during the electrolysis, control of the electrolysis current is important. Loading at around 1 mA/cm^2 current density is sufficiently gentle that the cathode should not crack, after a day or so at 1 mA/cm^2 the current can be increased to 10 mA/cm^2, and from there to higher current densities. Excess heat will commonly be observed in the 10-30 mA/cm^2 range, after the initial exotherm caused by the formation of deuterium pallide. The electrolyte solution used is typically 0.3M LiOD with 200ppm worth of aluminum deliberately dissolved in it (along with the adventitious silicates and borates leached out of glass that the D2O comes in contact with).

Most methods of calorimetry used to date are not adequate to observe excess heat when the current densities are so small. It is the need to poise the calorimeter (typically, an isoperibolic calorimeter) by inputting large electrolysis heating that results in the myth that current densities over $100mA/cm^2$ are necessary to induce excess heat. The reason we are able to obtain such a high percentage of successful excess heat generating experiments (~50%) is because our calorimetry allows us to operate in the low current range.

Calorimetry:

A remedy to the limitations imposed by isoperibolic calorimetry was effected by developing high performance Calvet calorimetry. The chief attribute of high performance Calvet calorimetry is that it measures essentially all the heat flow in such a manner that temperature homogeneity is irrelevant, thus one escapes the isoperibolic requirement for thermal homogeneity. The device is. in effect a box wherein each of the six walls of the box are thermal flux transducers. Thus, the heat flows out of the box from the electrolysis cell to the thermostatic water bath by passing through a contiguous envelope of thermal flux transducers. If, by some means, all the heat flowed through the bottom thermal flux transducer the response of the device would be the same as if an equal fraction of the same amount of heat flowed through each of the six thermal flux transducers; because the electrical response of the thermal flux transducers are linear. (Note: recombination of D_2 and O_2 to from D_2O is routinely checked by measuring gas evolution rate; recombination is not the source of excess heat.)

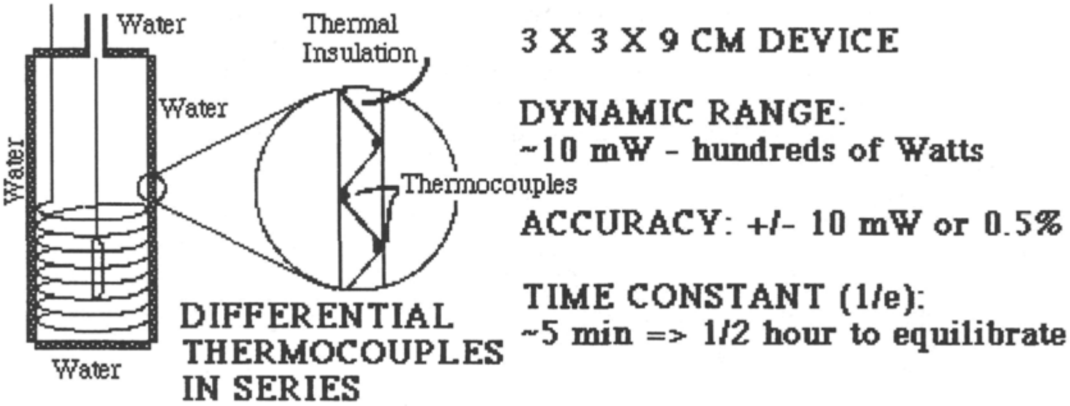

Figure 1: Schematic of high performance Calvet calorimeter. The device consists of a contiguous thermal flux transducer envelope. The thermal flux transducers sense thermal flux as the sum of the voltages set up across differential mode thermocouples, as shown. The thermocouples are placed across a thermally insulative layer so that heat flowing through the thermal flux transducer creates a difference in the emf's (voltage) of the inside and outside thermocouples of each differential pair. There are over a hundred differential thermocouple pairs per square inch of the Seebeck™ thermal flux transducers, so that the series sum voltage of all the differential mode thermocouples in the contiguous thermal flux transducer envelope give a very good linear representation of all the thermal flux; as a single voltage.

High performance Calvet calorimetry effects an integrating thermal flux transducer envelope calorimeter, its' fundamental advantage over isoperibolic calorimetry is that there is no need to worry with temperature measurement accuracy because the Calvet method measures the sum total of the thermal flux as a single voltage. This makes the method particularly amenable to computer data acquisition. High performance Calvet calorimeters are marketed under the trade name "Seebeck" by **Thermonetics Corp.,** (Reachable at **(619) 453-5483**), Box 9112, San Diego, CA 92169. A major difficulty in calorimetry which must operate for thousands of hours at a time is corrosion, particularly with regard to the environment associated with an electrolytic cell. Recent testing has shown that our anti-corrosion technology is effective. The ruggedized Thermonetics Seebeck calorimeter is very reliable. High performance Calvet calorimetry is the method of the future; it is extremely adaptable because they can be made in any reasonable size or shape, has an enormous dynamic range; and because it measures essentially all the thermal flux all the time it is the most fundamental and rigorous method known. Further, the response speed of Seebeck calorimeters is very fast because they are not heavily insulated like isoperibolic calorimeters. Versions of this technology are available which will operate at over 800°C (glowing red hot in a furnace!). **Warning: thermal flux calorimeters based on Peltier devices** (e.g. Melcor refrigichips) **will fail in the most insidious fashion possible ,** several man years have been wasted on Peltier devices between the Navy and ourselves.

We prefer to operate with the calorimeters submerged in a water bath, because this provides for reliable long term temperature stability. Further, because we are concerned with the helium produced by the excess heat generating reaction, we find it particularly useful to submerge the calorimeters in water, because helium is less soluble in water than in air and we can sparge the helium out of the water by bubbling liquid nitrogen boil-off gas through the enclosed water continuously to keep atmospheric contamination out. Circulator/controllers providing **+** 0.01 °C temperature stability are available for about $1,000, and provide years of dependable trouble free service. Submersion in the water bath largely circumvents the need for room temperature stabilization (a temperature stabilized room costs about $250K to install)**;** all that is necessary **is** that the room temperature fluctuate slowly so as to not "upset" the circulator/controller.

Helium analysis:

We entered this field by performing helium analysis as a nuclear products analysis.[1] Our first effort was qualitative: 8 times during the generation of excess heat, helium was detectable in the electrolysis off-gas; 6 times when no excess heat was being generated, no helium was detectable in the electrolysis off-gas. This qualitative finding showed that the Pons and Fleischmann effect is a nuclear process occurring at the surface of the cathode.

Subsequent quantitative helium versus energy analysis performed by ourselves,[2] and Dr. M. H. Miles working independently indicated that the excess heat and helium was produced via the D + D→ ^{4}He + 23.82 MeV(heat) reaction pathway. The conversion factor: 1 Watt = 6.24 X 10^{12}MeV/s was used and the data was normalized for 2 dimensional plotting by removing the influence of sample volume and electrolysis current. The data with error bars is our data, taken from a rigorously helium leak tight system; the data without error bars is Dr. Miles data.[3] Notice how the data points congregate around the theoretical 24MeV/^{4}-He line in Figure 2; this indicates that the excess heat is generated by the D + D → ^{4}He + 23.82MeV(heat) reaction pathway:[2]

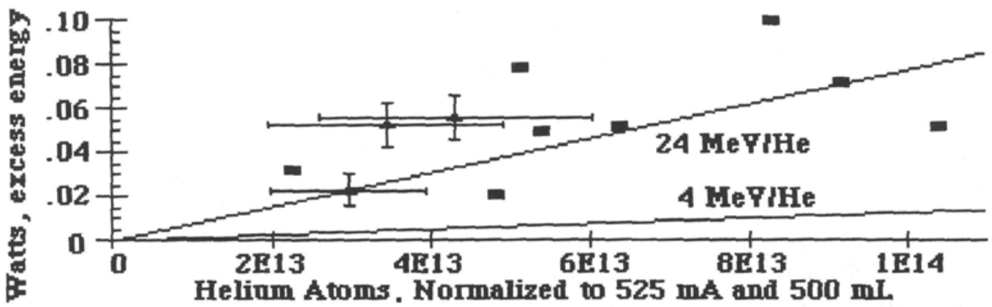

Figure 2: Heat versus helium data plotted at constant sample volume and electrolysis current to render the plot 2-dimensional. 1 Watt = 6.24 X 10^{12}MeV/s.

Contemporary helium analyses have focused on the helium and neon isotope ratios to identify atmospheric contamination, should it occur. Helium analysis of Pd cathode materials supplied by Pons and Fleischmann showed no helium-4 compared to virgin control "G": G= 1.295 X 10^9 ^{4}He/mg, A= 1.22 X 10^9 ^{4}He/mg, B= 1.44 X 10^9 ^{4}He/mg, D= 1.19X 10^9 ^{4}He/mg. The finding of no helium in the cathode material is expected;[4] because the Pons and Fleischmann effect is induced at the surface of the cathode, the helium leaves with the electrolysis off-gas.[1] The only reason people persist in analyzing the cathodes for helium is that sampling is trivial, one merely cuts off a piece of metal and melts it in the mass spec, analysis system.

The hard part of the helium analysis is completely removing D2 from the electrolysis off-gas. This is conveniently accomplished, by oxidizing the D2 to D2O using copper oxide heated to 450ºC, the D_2O being trapped at liquid nitrogen temperature:

Once the D2 is removed there is virtually no gas left in the system, so the ^{3}He:^{4}He:Ne analysis proceeds easily. All metal sampling and shipping flasks are used with Cajon VCR fittings to preclude diffusion as a vector of atmospheric contamination. The sample flasks are baked out at ~100°C under vacuum (~10μ) and flushed repeatedly with liquid nitrogen boil-off gas to preclude contamination by helium adsorbed in the surface of the metal (i.e. virtual leakage is precluded). Air contains 5.22 ppm (parts per million) ^{4}He; our system background is routinely below 100 ppt (parts per trillion) ^{4}He.

Theoretically: suppose the excess heat generating reaction of the Pons and Fleischmann effect is predominantly $D + D \rightarrow {}^4He + 23.82$ MeV(heat); one would expect the $H + D \rightarrow {}^3He + 5.395$ MeV(heat) reaction owing to the 0.5% proton impurity in the D_2O. Hence because the nuclear reactions are due to electromagnetic interaction (personal communication Prof. Peter Hagelstein/MIT) the nuclear reaction matrix elements cancel to a coefficient of 5, [the coefficient would be 4.7 if the nuclear reactions were due to weak force interaction], (personal communication Dr. Tom Ward/DoE). At the cathode surface, the reactants (D + D and D + H) are driven to react via the electrolysis current and they deliver their energy into the cathode via coherence effects (e.g. see Smirnov, et. al.[5]). By whatever mechanism, the reactants ascend the activation barrier and react to form products, or reverse to reform reactants (via the principal of microscopic reversibility). The relative rates of the nuclear reactions thus depends on how exothermic they are, because the more exothermic a reaction is the faster it will react. Thus, we should be able to calculate the ^{3}He:^{4}He isotope ratio expected from theory, knowing the approximate proton impurity (0.5% =0.005, or less), the exothermic release (5.395 MeV and 23.82 MeV) and the fact that the reactions are electromagnetic interactions so that both of their reaction coefficients are 5. Calculating as suggested by Dr. Tom Ward:

$$^{3}\mathrm{He}/^{4}\mathrm{He} = 0.005 \times (5.395\ \mathrm{MeV})5 / (23.82\ \mathrm{MeV})^{5} = 2.98 \times 10^{-6} \qquad (1)$$

Hard-won experimental results for ^{3}He:^{4}He analysis of excess heat from an NHE palladium cathode shows that the ^{3}He does not scale as it would for tritium decay; the ^{22}Ne:^{4}He isotope ratio indicates that the helium is not of atmospheric origin. Preliminary data follows:

Sample	Electrolysis mA	^{4}He/^{22}Ne (air=3.26)	^{4}He/~30mL (atoms)	^{3}He:^{4}He (2.98E-6 predicted (1))
12/04/97, l:20am	29.3	16.754	5.9E11	2.14E-6
12/16/97, l:30am	9.8	6.056	2.0E12	2.41E-6
12/23/97, ll:35am	10.2	7.397	4.1E10	3.17E-6

Hence, the data is again consistent with the D + D → ^{4}He + 23.82 MeV (heat) reaction as being the origin of the excess generated by the Pons and Fleischmann effect.

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5) G. V. Smirnov, et. al. Phys. Rev. Lett. (1996), Vol. 77, no. 15, p. 3232.