

EVIDENCE FOR LITHIUM-6 DEPLETION IN Pd EXPOSED TO GASEOUS DEUTERIUM AND HYDROGEN

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ABSTRACT

Some 17 separate samples of palladium, 14 of small diameter particulates and 3 wires, were analyzed by Time of Flight Secondary Ion Mass Spectrometry (TOF SIMS). All had been exposed to gaseous deuterium or hydrogen for long periods (months). The TOF SIMS analyses followed a long effort of neutron activation analysis (NAA) on a significant subset of the total, having been initiated to resolve the question of zinc isotopic abundance ratios not susceptible to NAA. While the zinc isotopes were found to be within reasonable uncertainty limits of terrestrial zinc, impurity lithium showed Li-7/Li-6 ratios much higher than the 12.48 value for terrestrial lithium. This observation led to the consideration of hypotheses involving lithium as an active agent in production of excess heat and helium observed in experiments by the investigators providing the samples. The only obvious reason to suspect Li-6 as more susceptible to nuclear reactions with protons or deuterons than Li-7 is that its reaction with deuterium has the highest positive Q of 22.36 MeV. These results will be discussed in terms of a possible explanation of the paucity of neutrons and tritium in numerous cold fusion experiments since 1989.

1, INTRODUCTION

Since the 1990 paper by Fleischmann, Pons, Anderson, Jun Li, and Hawkins (P&F) (1) the question of what possible nuclear reaction(s) could be the source of the observed excess heat have been difficult to answer definitely. One approach to answer this question is represented in this paper, which describes analytical results on palladium from successful and unsuccessful heat production experiments as well as the virgin material, where possible. The changes between virgin material or material giving negative results and those with positive signals have been sought using three different methods of analysis: 1) prompt gamma neutron activation analysis (PGNAA); neutron activation analysis (NAA); and time of flight secondary ion mass spectrometry (TOF SIMS). (2-4). Results from only the last of these three methods are reported here.

Herein is proposed a hypothesis to explain the results from exposure of palladium surfaces to gaseous hydrogen and deuterium. The hypothesis can be stated simply thus: Is it possible that one or both of the two lithium isotopes have been one member of a set of nuclear reactions with deuterium or protium producing the observed excess heat and the episodic low levels of tritium, neutrons, He-4, and He-3? The measurements of lithium 6 and 7 will first be presented in tables 1 and 2. Then the plausibility of the hypothesis will be discussed. Finally, conclusions and suggestions for research to test further the hypothesis will be given.

2, MEASUREMENT RESULTS

Tables 1 and 2 present the results of the TOF SIMS study on 17 palladium samples. The samples need to be considered in subgroups. First the Pd-A, Pd-B, Pd-C and Pd-D are grouped together because all came from Professor Arata and Dr. Zhang of Osaka University via R. George. Pd-D was the unused or virgin material, and the other three were powdered Pd from inside the hollow cathodes that produced varying amounts of excess heat (10's of megajoules). In this case, only Pd-B stands out with an anomalous Li-7/Li-6 ratio well outside the limits of error. However, Pd-C shows the ratio almost two sigma above that of the virgin material. Pd-A is under one sigma positive.

The next group to be considered together is that of SRI-H2O and SRI-D2O. These samples are from two experiments at SRI attempting to measure excess heat to replicate results reported by Arata and Zhang (5). There is no information relative to which batch of palladium powder these materials represent, but the fact that the SRI-D2O produced 64 + or -6 megajoules of excess heat (8), while the SRI-H2O sample

produced $-1 +$ or -6 megajoules. allows us a more robust baseline to use for comparison. Unfortunately, the SRI-H₂O sample had much less total lithium and hence much greater uncertainty in the ratio Li-7/Li-6. Table 2 shows, however, that the ratio of the Li-7/Li-6 ratios in the two samples encompass the range from 0.838 to 1.066. Hence it leaves open the possibility that our hypothesis is still alive.

The third group of powdered samples, Arata S-8, S-5, S-2, and S-1 show very little departure from Pd-D, which was arbitrarily assumed to be the virgin baseline. Since there is no information on the history of these samples as yet from Arata, the measurements cannot be correlated with production of excess heat or helium. It should be noted that all but S-2 show a slight positive behavior relative to terrestrial lithium.

The fourth group is that of three wire samples exposed in China for about 6 months to gaseous hydrogen.(6) Sample Li Tsinghua E is the most interesting of the three, giving a Li-7/Li-6 ratio almost twice the terrestrial value. The unexposed sample B in this series gives the expected terrestrial value. The sample D is not significantly above the terrestrial value of the unexposed one. A more complete description of the treatment of these samples should give some hints as to what correlations and conclusions to draw from these three measurements.

The fifth set of samples are of a different character from the above metallic materials. Samples SC-1, SC-2, SC-19, and SC-20 are all commercially available catalysts, first studied by Case.(7) They consist of 99.5 % coconut charcoal and 0.5% palladium, the latter as small particles produced by chemically reducing to the metal, palladium chloride complex negative ions adsorbed from an aqueous solution onto the charcoal. These samples were exposed to deuterium gas at 2 to 4 atmospheres pressure in stainless steel cylindrical vessels of 50 cc volume at about 180 degrees C over a period of about one month. (8) The SC-1 material is original unexposed catalyst serving as a baseline for SC-2. SC-20 serves as a baseline for SC-19 since under the same conditions it produced no observable increase of He-4 in the gaseous deuterium. Unfortunately, the levels of palladium particles relative to background charcoal varied such that the uncertainty in lithium results was increased in the low total counts obtained in the particular case of SC-2. In spite of this problem, the helium-producing catalysts have, in the one pair, SC-19/SC-20 a positive value of their Li-7/Li-6 ratios almost 2 sigma above 1.0. The large uncertainty in the SC-2/SC-1 ratio of Li-7/Li-6 ratios encompass the value range from 0.832 to 1.274, again leaving our hypothesis still breathing. It appears that the lithium impurity is mostly associated with the palladium as opposed to the charcoal background, since the lithium observed is roughly proportional to the Pd-108 counts. Table 3 gives the Li-7/Pd-108 and Li-7/Na-23 ratios for each of the four samples. The Na-23 impurity is closely associated with the carbon (coconut charcoal) substrate, since coconut shells are a natural product grown in salt-containing water.

3, DISCUSSION

The somewhat surprising fact is the widespread presence of tramp impurity lithium in all palladium samples so far analyzed. The scarcity of tritium and neutrons in cells producing excess heat leads one to consider other reactions than D+D as possible nuclear reaction sources of the heat.

The two samples Pd-B and Li Tsinghua Sample E, were observed early in this investigation, and being so much above terrestrial Li-7/Li-6 ratios, gave a high expectation for the success of this hypothesis. However it is not entirely original with this paper. Thompson of Johnson-Matthey Company showed a similar result at ICCF-1 in March, 1990, indicating Li-7/Li-6 ratios of 24, 19.9 and 20.3 for three separate measurements by TOF SIMS in the surface layer of 2 solid palladium cathodes producing excess heat in early P&F cells (9). However, he was not able to check the same ratios in the original electrolyte.

Since lithium impurity is widely present, it follows that its presence is probably still highly variable. It is tempting to consider this variability as one of several causes of successful appearance of excess heat being related to particular batches of palladium samples.(10) Against this hypothesis is the fact that almost all the electrolytes used in electrochemical cells seeking excess heat were lithium deuterioxide. However, the long delay time of about 300 hours prior to the appearance of excess heat, led to suggestions that lithium had to diffuse into the Pd cathode from the electrolyte a certain distance or perhaps into favored positions in grain boundaries to initiate the production of nuclear reactions and subsequent heat. Thus perhaps all lithium was not created equal but had to be in a certain location within the solid or its surface layers.

The preferred location is probably at the surface of the material or at least at a grain boundary if in the interior of the solid. The experimental evidence provided by Storms (11) at ICCF-8 wherein excess heat

was observed in cells with **platinum** cathodes after long use and not with clean platinum suggests the action is in a surface layer that must be built up over a long time. In turn this suggests a diffusion process of assumed active agents (such as lithium) to a preferred location within the first few layers of atoms near the surface. Another possibility is the need to build up a new metallic layer on the cathode from metals dissolved from the anode – either the anode primary material or some of the anode impurities.

Pursuit of trace element causes of the excess heat at first led to considering boron, another element almost universally present in Pd. (2,3). It was found in the metal and also in electrolytes contained in pyrex-walled cells, a glass from which caustic electrolytes readily leach boric oxide into the liquid phase. Search for B-10 depletions in cathode material producing excess heat was partially successful. Also, the addition of boric acid to electrolytes in the SRI effort appeared to be a significant help to the appearance of episodes of excess heat.(10) Its diffusion into the solid palladium also dramatically changed the dependence of cathode electrical resistance upon its average D/Pd ratio. Thus to add boric acid made it difficult to maintain a continuous measure of the loading, that at that time was felt to be an all-important variable in the appearance of excess heat. The down side of the boron hypothesis was the possibility of chemical leaching of cathode boron by the electrolyte.

One might ask why anything but DD fusion should be considered in hypotheses about these phenomena, since the coulomb barrier is already so daunting an obstacle at atomic number 1. One answer is obviously that since the D-D reaction is 40 orders of magnitude above expectations from standard principles of nuclear physics, only a few more orders of magnitude are needed to reach atomic numbers 3 (lithium), 4 (beryllium), and 5 (boron). These three elements have several reactions of positive Q (exothermic with zero input energy) with deuterons AND protons that result in helium-4, and also tritium, neutrons, and helium-3.

From the measurements of Rolison, et.al.,(12), the Li-7/Li-6 ratio is quite variable among commercially available lithium salts and the metal, (ranging from 31 to 11.6) stocked at the Naval Research Laboratory in 1989-90. It is for that reason that we have attempted to use a virgin material or a material subject to the same conditions as the baseline for comparison where possible. Still, this variability could be the source of all these results due to the random nature of the processes by which impurities entered the palladium. The primary reason for the variability is thought to be from extensive extraction of Li-6 for use in nuclear weapons, followed by return of the depleted lithium to the industrial sector. However, the gas-exposed samples studied here are at least not subject to the possibility of dilution by in-diffusion from an electrolyte having a non-terrestrial value of Li-7/Li-6.

4, CONCLUSIONS

These results suggest the possibility that lithium isotopes may be involved in the nuclear reactions assumed responsible for the large excess heats observed originally by P&F and subsequently by a significant number of credible investigators. As observable in Table 4, the variety of possible reactions able to produce heat without tritium or neutrons between deuterons and either Li-6 or Li-7 is impressive. For the small output of tritium or neutrons observed episodically (13), lithium reactions can be postulated to deliver. The reaction with the largest Q value (22.36 MeV/reaction) is $\text{Li-6} + \text{D} \rightarrow 2 \text{He-4}$. If one postulates that the higher Q reactions are heavily favored over those of lower Q, then the relative depletion of Li-6 would be a logical result.

If one further assumes that reactions resulting in 2 charged particles are favored over pure capture of the proton or deuteron with only gamma ray de-excitation following capture, then the next highest Q reaction is $\text{Li-7} + \text{p} \rightarrow 2 \text{He-4}$ (17.24 MeV/reaction). Although a smaller Q, it would predict the viability of excess heat results from ordinary light hydrogen, which has occasionally been reported. The relative lack of light hydrogen measurements may be due to the relative lack of intensive study of this system based upon low expectation of success. The low expectation may have resulted from most investigators belief that the D+D reaction was the only one likely in this system. Also note that He-4 is the predominant product with these two highest Q reactions.

These results do not necessarily favor use of lithium alloys of palladium or platinum but rather judicious addition of lithium in surface layers sufficient for significant reaction targets but not so large as to destroy the surface catalysis apparently characteristic of these metal surfaces.

If lithium can react with deuterium or protium, why not other light elements such as beryllium and boron? The success of Miles (14) in obtaining excess heat with Pd-B alloys may speak to boron being a significant reactant. Both isotopes of boron give positive Q reactions with D and p, for example B-10 + D → 3 He-4 (+17.81 MeV/reaction) and B-11 + D → Be-9 + He-4 (+ 8.02 MeV/reaction). Here protons are possible reactants with the B-11 + p → 3 He-4 (+8.58 MeV/reaction). Beryllium is a possible reactant with the Be-9 + D → T + 2 He-4 (+ 4.59 MeV/ reaction). Also, Be-9 + D → He-4 + Li-7 (7.15 MeV/reaction) and Be-9 + p → He-4 + Li-6 (2.13 MeV/reaction) are possible heat producers. Note that the tritium and neutron producing reactions have generally lower Q values which may speak to their scarcity among the reaction products.

It will require an intensive effort to sort out which, if any, of these light element impurities are significant reactants in producing excess heat. In spite of their higher coulombic barriers compared to D + D, they relieve us from insisting on observing neutrons and tritium commensurate with the excess heat. Lithium, beryllium and boron are ALL present in palladium at PPM levels. A controlled experiment with known impurity amounts added to high purity palladium (and platinum) would help resolve the merits of this hypothesis.

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TABLE 1 Li-7 to Li-6 Ratios in Pd Exposed to Gaseous D2& H2 From TOF-SIMS

SAMPLE DESIGNATION	Li-7/Li-6 Ratio (1 sigma)	Active/Virgin Ratio (1 Sigma)
Pd-D Arata (Virgin)	13.6 (1.0)	*****
Pd-A Arata (Active)	14.5 (0.3)	1.066 (0.082)
Pd-B Arata (Active)	22.0 (1.4)	1.618 (0.159)
Pd-C Arata (Active)	16.2 (0.1)	1.191 (0.088)
SRI-H2O Arata (Virgin?)	14.5 (1.7)	*****
SRI D2O Arata (Active)	13.8 (0.1)	0.952 (0.114)
Arata S-8 (Active?)	14.6 (3.4)	1.074 (0.268)
Arata S-5 (Active?)	13.5 (1.8)	0.993 (0.151)
Arata S-2 (Active?)	12.3 (0.8)	0.904 (0.090)
Arata S-1 (Active?)	13.1 (0.5)	0.963 (0.081)
Tsinghua -E (Active)	23.3 (1.8)	1.806 (0.181)
Tsinghua -D (Active)	13.1 (1.1)	1.016 (0.107)
Tsinghua -B (Virgin)	12.9 (0.8)	*****
SC-1 Catalyst (Virgin)	16.7 (1.4)	*****
SC-2 Catalyst (Active)	17.5 (3.3)	1.053 (0.221)
SC-20 Catalyst (Virgin?)	10.2 (0.8)	*****
SC-19 Catalyst (Active)	12.6 (0.7)	1.232 (0.120)
Terrestrial Lithium	12.48	

TABLE 2 Ratio of Li-7 to Pd-108 and Li-7 to Na-23 in each of the 4 samples of Pd from TOF SIMS where Na-23 is considered to be impurity primarily associated with the carbon substrate

Sample Description	Li-7/Pd-108	Li-7/Na-23
SC-1	0.34	0.006
SC-2	0.56	0.00056
SC-19	0.92	0.006
SC-20	1.68	0.0018

TABLE 3 Positive Q Reactions of Lithium Isotopes with Protons and Deuterons

$\text{Li-6} + \text{D} \rightarrow 2 \text{He-4}$	$Q = +22.36 \text{ MeV}$
$\text{Li-6} + \text{D} \rightarrow \text{Li-7} + \text{p}$	$Q = +5.03 \text{ MeV}$
$\text{Li-6} + \text{D} \rightarrow \text{T} + \text{He-4} + \text{p}$	$Q = +2.56 \text{ MeV}$
$\text{Li-6} + \text{D} \rightarrow \text{He-3} + \text{He-4} + \text{n}$	$Q = +1.67 \text{ MeV}$
$\text{Li-6} + \text{p} \rightarrow \text{He-4} + \text{He-3}$	$Q = +4.02 \text{ MeV}$
$\text{Li-7} + \text{D} \rightarrow 2 \text{He-4} + \text{n}$	$Q = +15.02 \text{ MeV}$
$\text{Li-7} + \text{p} \rightarrow 2 \text{He-4}$	$Q = +17.24 \text{ MeV}$