LETTER TO THE EDITOR

Thermoelectric heat pumping and the 'cold fusion' effect

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Abstract. This letter contains a brief description of an experiment to examine the importance of the process of thermoelectric heat pumping in the investigations of the cold fusion effect. The magnitude of the Peltier effect is measured for H- and D-loaded Pt/Pd junctions. The process of electromigration of impurities in the platinum and palladium is discussed together with its role in the formation of semiconducting junctions in the system.

The furore that accompanied the announcement of 'cold fusion' by Fleishmann and Pons (FP) [1] has long since died away; however, there is still interest in accounting for what they actually observed. Although comparatively little work is at present being done to understand this effect, some countries, noticeably Japan, have significant financial involvement in research in this area. If newspapers [2] are to be believed, the two original investigators are heavily involved and have made claims of even greater heat output in their present experiments than reported in their first paper on the subject. Following an earlier investigation by Keesing *et al* [3] in which, amongst other things, thermoelectric effects were studied, the process of thermoelectric heat pumping has been studied further. Our interest in these effects has been stimulated by the following observations. Firstly, the quantity of heat observed by FP was linearly related to the (electrolysis) current as would be expected if the Peltier effect were responsible for the excess energy rather than nuclear fusion. Secondly, the quantity of heat appearing in their experiments was about 0.4 W A^{-1}, which is that to be expected from a commercially available semiconducting Peltier junction. Thirdly, an intriguing fact of their investigation were the inordinately long charging periods required before the effect could be observed. At the charging currents used one would expect the H or D to reach an equilibrium concentration in the Pd lattice in a period of tens of hours whereas the times required were several weeks or months and depended markedly upon the actual specimen. We will return to this important point later.

It has been known since the 1920s that the thermoelectric coefficient of palladium changes sign and increases by a factor of about four upon charging with hydrogen (see Heimberg [4] and Reithjen [5]). We were therefore interested to repeat these early observations and extend them to deuterium to see whether the effect was markedly larger. As we were only interested in the magnitude of the thermoelectric coefficient upon charging with H or D no attempt was made to make an accurate estimate of their densities in the palladium lattice. Thus our observations are confined to the measurement of the temperature difference between two Pd/Pt junctions caused by the passage of a direct current in the 'forward' and 'reverse' directions, as a function of electrolytic charging time.

A 1 mm diameter, 20 mm long sample of palladium of 99.95% purity, fused to platinum wire supports and surrounded by a Pt wire cage was immersed in a 0.1 M solution of LiOH

and the differential temperature between the two Pd/Pt junctions measured with two glass-encapsulated thermocouples. The thermocouples were positioned in the electrolyte 1.5 mm directly above the junctions. The Peltier heat was measured by passing a direct current of 2 A through the Pt–Pd–Pt sample and the differential temperature change measured as a function of time. As the Peltier effect is reversible, the differential temperature was expected to change sign upon reversal of the 2 A 'Peltier' current.

The palladium was charged with hydrogen by making it a few volts negative with respect to the Pt cage and passing an electrolysis current of 80 mA through it. During the early stages of charging little if any hydrogen evolved at the palladium, however considerable amounts were observed to evolve at the Pt supports. As the H/Pd ratio approached approximately 0.6, (estimated from the product of the electrolysis current and time), hydrogen gas started to appear at the palladium and the charging rate decreased very considerably. The first stage of hydrogen absorption took approximately 40 minutes, however the electrolysis was allowed to continue for many hours, before measurements of the Peltier effect took place. For a detailed account of the charging of palladium with hydrogen and deuterium see, for example, Flannagan and Oates [5]. The experiment consisted in monitoring the temperature difference between the pair of Pt/Pd junctions for 60 s and then passing the 2 A Peltier current until the differential temperature stabilized at its new value, which occurred after about 20 s. The Peltier current was reversed for the same period of time and then switched off. Figure 1 shows the differential temperature between the pair of Pt/Pd junctions for (a) charged palladium, (b) uncharged palladium (c) the Peltier driving current, all as functions of time. During these measurements an electrolysis current of 100 mA was present. In case (a) the current caused hydrogen to evolve at the palladium thus keeping it charged, and in case (b) the electrolysis current was reversed to insure that the palladium remained uncharged. To discharge the hydrogen from the palladium lattice a reverse electrolysis current was passed for approximately 48 hours. The palladium was judged to be effectively free of hydrogen when the Peltier test produced a negative differential temperature which ceased to change with discharging time. The differential temperature was found to be a function of electrolysis current, decreasing as the current increased. The cause of this was traced to forced convective cooling due to gas bubbles rising from the specimen. The results have been corrected for this effect and are quoted at zero electrolysis current. It will be noticed from figure 1 that the sign of the differential temperature changes and its magnitude increases by a factor of about four upon the palladium charging with hydrogen. The differential Peltier coefficient for the Pt/Pd junction is known to be -1.37 mW A^{-1} at room temperature (Cussack and Kendall [7]) and thus the value for a hydrogen-loaded Pt/Pd junction is measured to be $+5.7$ mW A^{-1}.

After discharging the palladium sample by reverse electrolysis it was placed in a 0.1 M solution of LiOD and recharged with deuterium at an electrolysis current of 20 mA. During this period the differential temperature was measured every ten minutes over a period of 2.5 h and then three further measurements were made some four hours later. The results are shown in figure 2. At a forward electrolysis current of 20 mA the palladium was expected to charge to a D/Pd ratio of 0.6 in about 8500 s, and it can be seen that the differential temperature has essentially reached its maximum value by this time. The Peltier coefficient has again changed sign upon charging and the ratio of the minimum negative value to the maximum positive value is once more about a factor four. Thus within the accuracy of this experiment there is no significant difference between the induced Peltier coefficient for H- or D-loaded palladium. It is clear that the direct thermoelectric effects of deuterium on the palladium lattice are far too small to account for the results observed by FP.

A detailed understanding of thermoelectric heat transport in even the simplest of metals
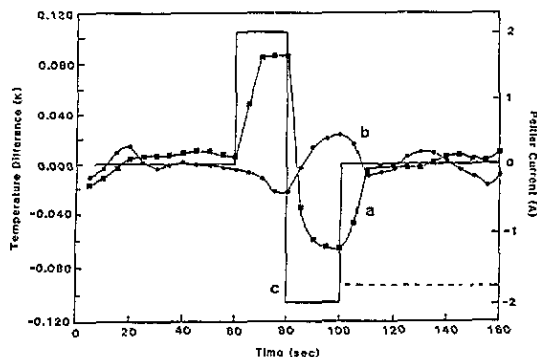
Figure 1. The differential temperature between the two Pt/Pd junctions as a function of time for a Peltier driving current of ±2 A. Curve (a) is for pure palladium, curve (b) for H-loaded palladium and curve (c) the Peltier current.
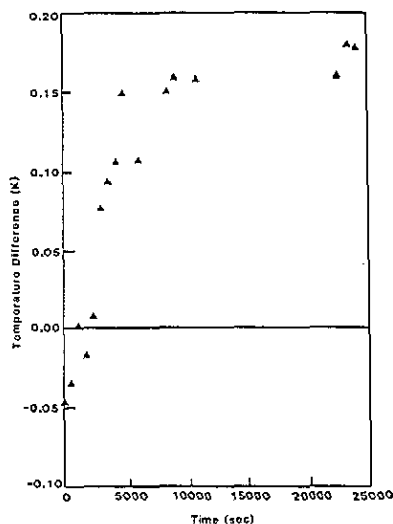
Figure 2. The differential temperature between the two Pt/Pd junctions during the charging of the palladium with deuterium.

is complicated. The basic principles are now well established but their application to individual cases proves difficult. Informative discussions of this subject appear in many texts, amongst which are Dugdale [8] and Chambers [9]. Heat transport involves an understanding of the roles played by the conduction electrons and holes and their interaction with the lattice through phonon scattering. Whether the heat is carried in the direction of the current carriers or its reverse depends upon subtle details of the band structure and the way in which the current carriers are scattered by the phonons. In hydrogen- or deuterium-loaded palladium the role of the H/D ions as direct transporters of heat and their possible effect upon the shape of the Fermi surface must also be taken into account. To complicate the matter still further it is possible that there are significant proton–phonon drag processes at work which could amplify the heat transport. At the present time no accurate theoretical estimate of heat transport in this system is possible. On the other hand simple estimates of the heat carried by the electrons together with the expected current of protons or deuterons leads one to believe that the maximum heat transport cannot exceed a value of a few mA A^{-1} at room temperature. This is two orders of magnitude less than that which FP claim to observe.

Heat transport of this magnitude can only realistically be attained if the Pd/Pt or the Pd/electrolyte junction becomes semiconducting. A process by which this could occur is that of 'electromigration'. Electromigration involves momentum transfer from the charge carriers (electrons, holes etc) to the atoms of the lattice which then migrate in the direction of motion of the charges. These effects have been studied for many years and have recently been reviewed by Ho and Kwok [10]. In the experiment of Fleishmann and Pons, a sample of palladium wire was fused to a platinum wire support and the Pd immersed in a 0.1 M solution of LiOD. The electrolytic charging of the Pd caused a continuous flow of electrons

through the platinum into the Pt/Pd junction and down the palladium sample out into the electrolyte. The action of this continuous electron flow, which FP stated must be maintained for week and months, could have caused impurities from the platinum and palladium to migrate into the Pt/Pd or Pd/electrolyte junction regions. Once there, these monolayer quantities may undergo a chemical reaction to form a semiconducting layer. An example of this process involves nickel, a common impurity in platinum. A sample of 99.95%-pure Pt was found to contain 20 ppm of nickel. If this migrated into the junction region it would react with deuterium to form NiD which is a semiconductor with a band gap of 2.0 or 3.8 eV (see [11]). There are many other trace impurities present in platinum and palladium and it only requires electromigration of the appropriate ones to occur in monolayer quantities at the various junctions for a semiconducting diode layer to occur. It must be noted, however, that significant electromigration normally occurs at current densities of the order of 10^4 A mm^{-2}, and those to be found in these experiments are normally less than 1 A mm^{-2}. The effect of the presence of the very mobile ions H^+ or D^+ at high densities, on electromigration, is uncertain, however it may enhance the process significantly so that sufficient migration of impurities can occur in the protracted charging times of these experiments for semiconducting layers to form. If the process of H/D stimulated electromigration of impurities were responsible for the production of monolayer semiconducting junctions this would explain two important facts: firstly, excess heat appears after protracted periods of time which depend upon the sample under investigation, as would be expected if the process were controlled by impurities; and secondly this process may only occur in the presence of deuterons, for D^+ is considerably more mobile in palladium than is H^+.

Experiments to test these conjectures are presently under way.

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