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DEVELOPMENTS IN ELECTROCHEMISTRY

Science Inspired by Martin Fleischmann
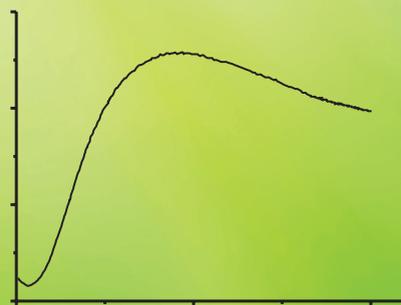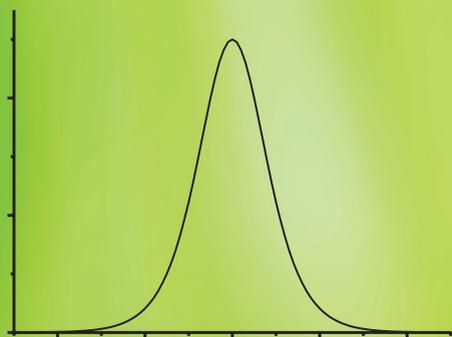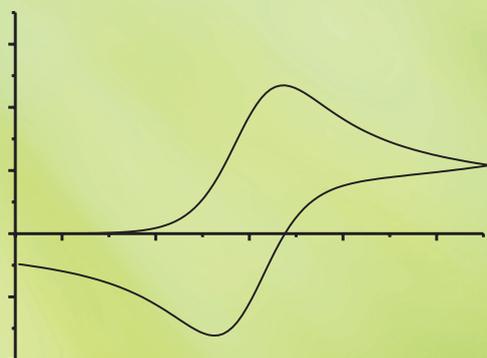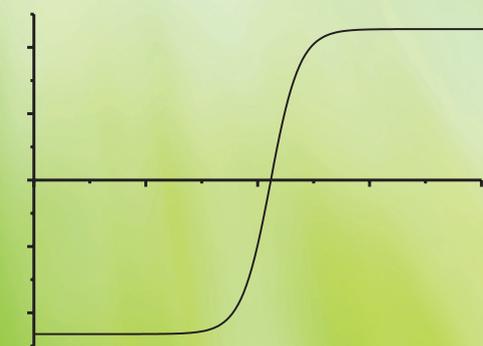
Editors: **Derek Pletcher** • **Zhong-Qun Tian** • **David E. Williams**

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Martin Fleischmann[1] – The Scientist and the Person
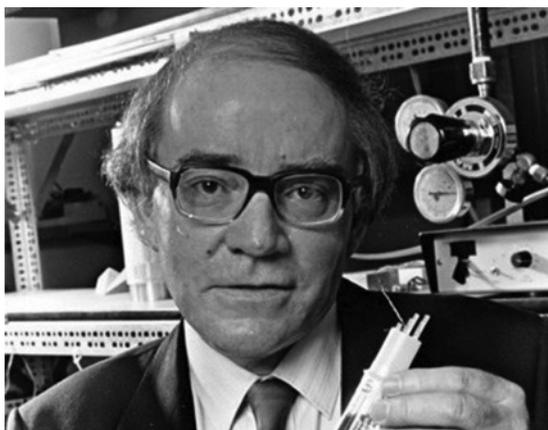
A group of electrochemists whose lives were enhanced by their contacts with Martin Fleischmann have joined together to produce this book; it is intended to celebrate the legacy that he has left to modern electrochemistry. Martin was an outstanding scientist with a great vision that allowed him to initiate a number of fields of activity. His detailed grasp

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[1]Figure reproduced from http://en.wikipedia.org/wiki/File:Fleischmann-cf.jpg

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of chemistry, physics and mathematics provided a background for a continuous flow of new approaches and experiments. Martin was essentially "an ideas man." Indeed, often his ideas were ahead of the ability of equipment to carry out the experiments, and it was only a few years later that the ideas came to fruition and it became possible to obtain high-quality experimental data. As can be seen by the authorship of the following chapters, this ability to be ahead of "the state-of-the-art," combined with inspirational leadership, made him a reliable stepping stone to successful careers for many of his coworkers. His enthusiasm for science, combined with a very warm personality and a lifetime's interest in the arts, skiing, food and wine, led him to have a large group of friends, ex-students and other coworkers, throughout the world. Stories about Martin abound, and a few of these are set out below. Indeed, the affection with which Martin is held can be seen in all the following chapters. All authors have, however, been asked to concentrate on the developments from the work of Fleischmann that are important now, and hence to produce a book that is relevant to "Electrochemistry in 2014." This would surely have been the wish of Martin Fleischmann.

Martin Fleischmann FRS was born in Karlsbad, Czechoslovakia in March 1927 to a wealthy, German-speaking family. His father was a well-known lawyer and his mother the daughter of a senior Austrian civil servant whose family traced its roots back to the thirteenth century in Prague. In Martin's own words, he was born into a castle with a fantastic collection of paintings. All this was to change dramatically, however. His parents were vocal opponents of the Nazi regime and, inevitably, they were forced to flee their home and leave behind all their possessions. They arrived in England after a lengthy and dangerous journey by taxi and train through Germany and Holland with a total of £1.30 in their purse! Following a period living in a "chicken hut," and the death of his father resulting from injuries received during a period of imprisonment by the Nazis, the family circumstances began to improve. Support from a refugee committee led to the lease of a cottage in Rustington (Sussex), where his mother was to start a business making dolls (that was to continue for more than 30 years, http://www.oldcottagedolls.co.uk) and Martin went back to education at Worthing High School for Boys. During the war he served in the Czech Air Force Training Unit. Martin was both an Undergraduate and Postgraduate in the Department of Chemistry at Imperial College London. During these student days he courted – and married – Sheila, who was to be his wife and support for 62 years. Together, they brought up three children, Nicholas, Vanessa and Charlotte, and Martin was always a devoted and stimulating father. He died on August 3rd, 2012 at the age of 85 after an extended illness.

His introduction to electrochemistry was as a PhD student with Professor Herrington at Imperial College. His own project concerned the diffusion of electrogenerated hydrogen through thin palladium foils! Importantly to his later career, he became part of a larger group that included John Bockris, Brian Conway and Roger Parsons, all to become leading figures in the world of electrochemistry. These contacts led to a stimulating environment for discussion and catalyzed broad interests in electrochemistry. After graduation in 1951, Martin went to the University of Newcastle where he was to interact with Lord Wynne-Jones, Reg Thirsk, Alan Bewick, Ron Armstrong and Frank Goodridge, amongst others. He was quickly promoted to a Readership before, in 1967, being appointed to the Faraday Chair of Chemistry at the University of Southampton where, with the support of Graham Hills, he was to establish a large Electrochemistry Group that soon had a worldwide reputation and still flourishes today. Key colleagues included Alan Bewick . . .

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Cold Fusion After A Quarter-Century: The Pd/D System

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On March 23rd 1989, Fleischmann, Pons and Hawkins [1] publicly reported the results of an anomalous heat effect resulting from the intensive, electrochemical insertion of deuterium into palladium cathodes occurring over an extended period of time. This was already a well-studied system, and the SRI team, having worked on Pd/D_2O for more than a decade, was better positioned than most to judge this claim experimentally. If anomalous large heat production was indeed present in palladium cathodes loaded electrolytically with D, then the only possibility was that this occurred in the very high loading regime with the atomic loading ratio D/Pd greater than about 0.8, where the system had been infrequently and poorly studied. In the space available, the aim of this chapter is to focus on two details of Martin Fleischmann's final project: (i) the multithreshold materials constraints that prevented easy reproducibility of the Fleischmann–Pons heat effect (FPHE); and (ii) the brilliant, but largely not understood, implementation of the Fleischmann–Pons calorimeter, designed to take advantage of positive thermal feedback.

Some readers of this book will consider that this chapter on cold fusion represents Martin Fleischmann's greatest scientific failure; however, the authors believe that this may instead be one of the greatest contributions that Martin Fleischmann, along with Stanley Pons, made to science [1, 2]. Unfortunately, early attacks on this field were vigorous, even resorting to personal and unscientific criticisms [3–5], and progress in this field has been slow because of the consequential lack of funding and the difficult problem

of reproducibility of the experimental results. Furthermore, the publication of research results on cold fusion soon became blocked by the editors of many scientific journals, and this discouraged academic entry into the field. The apparent irreproducibility is likely a materials problem, because results seem to depend on the palladium source and the metallurgical methods that were used in its preparation. Nevertheless, many research groups in various countries have now reported excess enthalpy effects for the Pd/D system [3–5]. The main nuclear reaction product that correlates with the excess enthalpy was found to be helium-4 [6–9]. Smaller amounts of other nuclear reaction products include tritium [10–12], neutrons [13, 14], radiation [3, 7, 15], and elemental transmutations [3–5]. There have been eighteen international conferences on cold fusion (ICCF) beginning in 1990 with alternating locations in the US or Canada, Europe and Asia.

Those of us who worked with Martin Fleischmann likely remember him for different aspects of his multifaceted personality and extreme scientific diversity. For the authors of this chapter, his major accomplishment was the discovery of anomalous heat effects in the electrochemical palladium deuterium system (Pd/D). Few would have had the vision to see such a possibility, the courage to pursue it, and the skill to test it. These anomalous effects were and are consistent in magnitude with excess enthalpy production by nuclear reactions. These are several orders of magnitude larger than can be explained by chemical reactions or lattice storage energy.

Initially called cold fusion,[1] this usage generated both confusion and hostility, and was in any case premature.[2] This field of endeavour, unveiled by Martin Fleischmann and Stanley Pons [1, 2], has broadened substantially in 25 years of research and is now known by several acronyms. The general classification of this field is Condensed Matter Nuclear Science (CMNS), and an electronic journal of that name is often used to publish papers in this field. This CMNS name highlights the observation, first suggested by Julian Schwinger [16], that nuclear reactions take place differently in a metal lattice than in free space. This chapter will be confined mostly to a discussion of the FPHE, a term which signifies anomalous excess heat production from electrochemical and gas-phase experiments in the Pd/D system. An attempt will be made in this chapter to demonstrate the consensus of the CMNS community that the FPHE is both anomalous and real, is nuclear in origin, has associated products that are quantitatively and temporally associated with the anomalous enthalpy, and results in products unique to nuclear reactions. As expected by Schwinger, the product distributions are not those of hot fusion and give rise to the possibility of practical energy production. Several dozen theoretical approaches are being actively developed, but none offers a clear and complete explanation for all observations. Martin Fleischmann often stated that a major reason for his study of the Pd/D system was to find experimental results that could only be explained by quantum electrodynamics (QED) and not by quantum mechanics. This led to his close relationship with Giuliano Preparata, who proposed an early theory for the FPHE that was based on QED [17] and correctly predicted helium-4 as the main fusion product [17].

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[1] The term "cold fusion" was originally adopted to describe muon-catalyzed fusion.

[2] The original 1989 manuscript title contained a question mark "—cold fusion?". The word "fusion" was an unfortunate choice because high-energy and particle physicists reserve this historic term for well-known reactions that are not the same as those observed in the Pd/D system.

13.1   The Reproducibility Issue

While the lack of reproducibility in Pd/D experiments certainly makes the advancement of this science much more difficult, it does not mean that the FPHE is due to experimental errors. For example, the semiconductor field encountered a similar problem that persisted until the role of impurities was properly understood and the harmful impurities eliminated. Perhaps impurities in the palladium also play a critical role. The summary of the US Navy Laboratory (NAWCWD) at China Lake [18] shows that the FPHE was observed in 17 out of 28 experiments using palladium material from Johnson-Matthey. Also, palladium-boron (Pd-B) produced by the Naval Research Laboratory (NRL) gave excess enthalpy in seven out of eight experiments [18]; in contrast, palladium from other sources produced excess heat in only two of 24 experiments. Experiments at SRI also showed that the success rate varied greatly with the source of the palladium, with the most successful early set of experiments being performed with the most impure material [19].

Fleischmann and Pons had good success in the production of excess enthalpy using Johnson-Matthey palladium up until about the time of their 1989 announcement. However, at about this time Johnson-Matthey made a major change in their method of producing palladium, and this newer material was very poor for obtaining the FPHE. In private conversations, as well as in a later publication [20], Martin Fleischmann revealed that the good (or type A) Johnson-Matthey palladium was made under a cracked ammonia atmosphere [20]. The melting of the palladium under this $H_2 + N_2$ atmosphere likely resulted in H_2 reacting with any oxygen impurity in the palladium and removing it as H_2O vapor. However, this cracked ammonia atmosphere was no longer used when Johnson-Matthey changed their method of manufacturing palladium. The high success rate at China Lake for the NRL Pd-B material can also be explained by an oxygen removal mechanism. During arc-melting of the Pd-B material under argon, any oxygen in the palladium would react with the boron present to form B_2O_3, and this lower-density product would rise to the surface and skim off the top of the molten palladium.[3]

13.2   Palladium–Deuterium Loading

Directly related to the reproducibility issue is the requirement of high loading of the palladium with deuterium during electrolysis in heavy water. McKubre and others have shown that no excess power was produced with Pd wire cathodes until the D/Pd atomic ratio reached 0.85, or higher. Furthermore, the excess power production increases rapidly to large values above this 0.85 threshold. This effect of the D/Pd loading ratio on excess power production was reported simultaneously and independently by McKubre [21] and by Kunimatsu [22] at a conference in Japan in 1992. For bulk pure palladium wire cathodes, such as those used by Fleischmann and most early replicators, the problem is compounded by the multithreshold nature of the FPHE. Not only does initiation of the effect require D/Pd loadings rarely achieved before 1989, but these loadings must also be maintained

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[3] Assuming that the palladium metal is a critical factor for the anomalous FPHE, it is not possible to make two palladium cathodes with exactly the same atomic arrangements, impurity levels, etc. Therefore, two "identical experiments" cannot be carried out.

for hundreds of hours in the presence of threshold current densities of 100 mA cm^{-2} or larger, well beyond the current density of maximum loading.[4] Very few bulk Pd samples are capable of sustaining high loading, because of the mechanical damage caused by mismatched lattice expansion and the formation of internal voids filled at equilibrium with D$_2$ at high gas pressure. Electrochemical damage of the interface and the build-up of surface impurities also tend to reduce the maximum loading achievable by a particular sample with time. Of equal importance, surface damage and poor interface conditioning and control, reduces the flux of deuterium through the interface. The magnitude (but not direction) of this flux is now known to be proportional to the magnitude of the excess heat effect as expressed in the following empirical equation [23].

$$P_X = M(x - x°)^2 \, (i - i°) \, |i_D| \quad \text{at } t > t° \tag{13.1}$$

where P_X is the excess power, $x = $ D/Pd, $x° \sim 0.875$, i is the electrochemical current density for the cathode, i_D is the absorption deuteron flux through the surface expressed as current density (2–20 mA cm^{-2}), and $t° > 20$ times the deuterium diffusional time constant in the cathode [23].

The failure to meet one or more of these threshold conditions provides an easy explanation for important early failures to reproduce the FPHE. Large significance was attached to early null heat results reported by a small number of groups at prestigious institutions. In light of the discussion above, it is useful to see whether these experiments – as well as other early experiments – were operated in a relevant regime. Perhaps the most cited early result reporting no anomalous effects was that of Lewis *et al.* [24] from Caltech, in which they stated that "D/Pd stoichiometries of 0.77, 0.79, and 0.80 obtained from these measurements were taken to be representative of the D/Pd stoichiometry for the charged cathodes used in this work." Also widely cited is the early null result of Albagli *et al.* [25] from MIT, who suggested that "... average loading ratios were found to be 0.75 ± 0.05 and 0.78 ± 0.05 for the D and H loaded cathodes, respectively." The Caltech and MIT reports of no excess heat effects are noted in Figure 13.1 in a histogram illustrating a number of early SRI and ENEA (Frascati) experiments producing positive excess power results as a function of maximum loading achieved.[5]

Even lower loading results were estimated by Fleming *et al.* [26] at Bell Labs in another report of no excess heat. In this case, the authors stated that "... the degree of deuterium incorporation was comparable to that for the open cells for the same time duration. The amount incorporated in longer electrolysis experiments was typically PdD$_x$ ($0.45 < x < 0.75$)." From what is known today (and as clearly shown in Figure 13.1), *none* of the cells in *any* of these cited studies would be expected to evidence any excess heat. In addition to insufficient loading, commonly the duration of the experiments were too short, the current density stimuli were too low and/or the deuterium flux was not measured. None of the criteria of Equation 13.1 was shown to be met, and at least two demonstrably were not met. In hindsight, it is evident that the authors were victims of "unknown unknowns", and

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[4] The current density of maximum loading for D into Pd cathodes is between 15 and 25 mA cm^{-2} in 0.1–1.0 M LiOD solutions typically used in these experiments.

[5] Fleischmann and Pons were well aware of the significance of loading and the need to measure it, and they did so by means of the cathode overvoltage. Since it is now clear that the FPHE occurs at or near the cathode surface, this measurement is possibly more relevant than the average loading inferred from bulk resistivity measurements, but requires experienced interpretation.
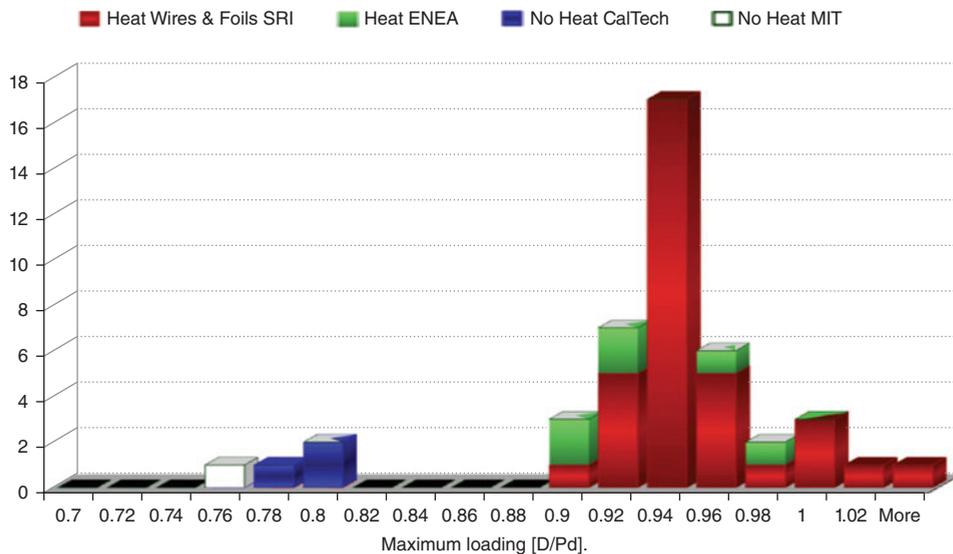
Figure 13.1   *Histogram illustrating the number of early experiments at SRI and ENEA, showing measurable excess power as a function of maximum cathode loading. Also illustrated are points for the MIT calorimetric experimental result, with a stated loading of 0.75 ± 0.05 (Ref. [25]); and for the Caltech null experimental result, with loading measurements quoted at 0.77, 0.78, and 0.80.*

perhaps "undue haste" – but this is understandable in the circumstances of 1989. What is important is that these experiments are recognized for what they are, not what they are not. They are important members of the experimental database that teaches us under what conditions one encounters the FPHE. They are not any part of a proof of nonexistence; absence of evidence is not evidence of absence.[6]

13.3   Electrochemical Calorimetry

There was never a significant problem with the isoperibolic Dewar calorimetric cell used by Fleischmann and Pons (F–P), but possible errors were often proposed by critics as an explanation for their excess enthalpy measurements [24, 25]. However, improvements were made over time that increased the accuracy of the calorimetry and reduced the error to only ± 0.1 mW [27]. It should be noted that significant calorimetry problems have been identified for several important groups that failed to find excess enthalpy production [28–30].

The Fleischmann–Pons studies of the Pd/D system required very accurate measurements over long time periods for the cell voltage (E), the cell current (I), the cell temperature (T), and the bath temperature (T_b). The limiting accuracy for the calorimetry is . . .

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[6] The NAWCWD group at China Lake (formerly NWC) reported no excess heat effects for various experiments until September of 1989, and they were listed with the unsuccessful Caltech, MIT, and other groups in the November, 1989 DOE ERAB Panel Report.