

Obituary

Professor Martin Fleischmann, March 1927 – 3 August 2012.

Martin Fleischmann was one of the giants of 20th century electrochemistry. He was always stimulating and challenging, interesting, creative, iconoclastic and great fun.

Martin started his research career at Imperial College in 1947. He was supervised by Herrington; Bockris was the charismatic, hugely energetic personality driving the effort, and other students included Conway and Parsons who both became very influential figures in electrochemistry.¹ The Faraday Discussion of 1947 gives a flavour of the intense interest in electrode kinetics and mechanism that developed at this time with Bockris as one of the leading figures: arguably the cradle of modern electrochemistry.² Martin studied the diffusion of electrogenerated hydrogen through thin palladium foils.³ His first published work came after he had moved to Newcastle in 1951, to work with H R Thirsk. This first paper⁴ has many of the hallmarks of Martin's later work. First, there was the need to design and build a new instrument, in this case a fast and accurate potentiostat. (Such instruments did not exist then; it was a bold move to recognise that, as electrode potential was the important control variable, the design problem had to be tackled – controlled current experiments were much easier and were the norm at the time.) Then, there is a comprehensive set of careful experimental measurements; there is a carefully worked-out theoretical development – Martin was a consummate mathematician and liked nothing better than a good calculation – which was fitted to the experimental data to derive insight into the fundamentals of the electrode reaction mechanism. Finally, the paper is beautifully and clearly written. The series of papers on electrocrystallisation, electrochemically-induced solid-state transformations and the anodic deposition of insoluble phases^{5,6,7} are classics, and have defined the field ever since. Martin, with Alan Bewick, was a pioneer in the design of the fast potentiostats and pulse and ramp generators needed for accurate kinetic studies.⁸ Nowadays, when the potentiostat is a black box with a computer connection, it is easy to forget that it is a complex instrument whose behaviour in conjunction with the electrochemical cell to which it is connected has to be understood thoroughly if results are to be believable: it is very instructive to re-read these early papers. Spurred by the interests of Wynne-Jones in Newcastle, Martin had moved to the study of electro-organic reactions,^{9,10} and so potentiostats also had to have high output voltages. The potentiostat designs were commercialised first by Chemical Electronics and then by Hi-Tek. A Chemical Electronics instrument was in the lab in Auckland in the early 1970s. It was a beast and a formative and instructive experience in practical electrochemistry: a big blue box with 70V/1A output and 1 μ s rise time – much faster and more capable than most modern instruments: a Ferrari of potentiostats. The chart recorder had to be connected in a particular way, otherwise the capacitance across the cell was altered critically and the potentiostat turned into a high-powered radio station, eventually frying the output transistors, which then took some time to replace. This must have been a second generation instrument, with solid-state electronics. Laurence Peter recounts that

The output stage of the blue box potentiostat was driven by tuned pentodes⁸ to give the exceptional performance that is difficult to beat with transistors. They did indeed fry things if corrected incorrectly.

He recalls having a student in floods of tears in his office after she had blown the front off the potentiostat by putting a wire wound resistor across the terminals!

For electrosynthetic reactions to be practical, cells have to be designed that have sufficient throughput, so Martin naturally moved to the design of efficient electrochemical cells. His mathematical proficiency was a great advantage in the analysis and optimisation of the designs.^{11,12} When he moved to Southampton in 1967 he took with him a group of exceptionally talented people and soon attracted more. The whole gamut of electrochemistry was covered, from big electrochemical engineering projects to photoelectrochemistry and the first *in-situ* spectroelectrochemistry: uv-visible, infra-red and Raman, as well as early attempts at *in-situ* X-ray diffraction measurement. The spectroscopy projects were driven by the desire to drill down from the observed kinetics and understand the chemical nature of the intermediates present on the surface. Of course, these studies again needed advances in instrumentation and the lab was a hot-bed of experimentation around that. To visit Southampton Electrochemistry in the mid-1970s was a revelation: the place fizzed with energy. Graham Hills was a calming presence who led his own outstanding research and also took care of the administration, and Martin was free to be himself, churning out ideas by the bucket-load and then turning the ideas into great experiments. He was surrounded by creative people who sparked off one another and the lab – bigger than many entire Chemistry Departments at the time – was a mecca for anyone wanting to study at the frontiers of the subject.

Of Martin's great output from Southampton in the 1970s and 1980s, four particular strands stand out. The first is the discovery of the surface-enhanced Raman effect;¹³ the second is the development of microelectrodes;¹⁴ the third is the study of stochastic effects as a means to derive basic information about electrochemical reactions;¹⁵ and the fourth is the systematic development of concepts of electrochemical engineering. The first two of these, carried out contemporaneously with developments in the US, are recognised as amongst the most significant recent developments in electrochemistry. The atmosphere at Southampton at the time is captured in Jim McQuillan's recollection:¹⁶

I was a postdoctoral fellow at Southampton with Martin Fleischmann and Pat Hendra from June 1972. Physical chemistry at Southampton was a whole new world. Both Martin and Pat were innovative scientists, enjoyed competing with each other in scientific brainstorming, and were excited by the prospect of audacious experiments. I well remember those sessions when ideas were flying. One evening in August 1973 the extraordinary data from pyridine adsorbed to an electrochemically roughened silver electrode was obtained. The signals were much more

intense than expected from calculations and this aroused great excitement tempered with scepticism.

The SERS phenomenon is now understood as the outstanding example of a plasmon resonance effect¹⁷ and its discovery led to the field of plasmonics - a current hot topic in physical chemistry (e.g., single molecule spectroscopy) and in near field optics. Additionally, the original SERS paper gave Ron Shen the idea that led to sum frequency generation spectroscopy – the current pre-eminent vibrational spectroscopic technique for surfaces.¹⁸ Martin was rightly honoured for these discoveries by the award of the Palladium Medal of the Electrochemical Society and by election to the Fellowship of the Royal Society of London. Pat Hendra recalls that which for his friends and colleagues was the essence of the man:

Through the 70s and on until he left Southampton, Martin used me as an intellectual 'punch bag'. I well remember one morning (and there were many others) I was giving a tutorial to a small group of undergraduates. Suddenly, the door crashed open unseating my secretary whose desk was behind the door and in advanced the Great Man as I always called him- eyes slightly glazed, in a world of his own, with those oh so familiar words "I've had an idea". He was, of course, bearing a coffee cup in his left hand most of the contents of which was slopping into the saucer and whence onto the floor. Once he had slurped the contents of the saucer, he excitedly pushed the student at the board aside, rubbed off his efforts and started to explain and illustrate his latest wheeze. Several minutes later after repeated reassurances that I would find him after I had finished teaching, we managed to get him out of the door and sent him off to acquire another coffee and I returned to my students. No more tutorial – they were gob-smacked. "Who was THAT?" I explained that they had been privileged to see how genius worked.

In the 1970s, the headship of the Department of Chemistry circulated every two years between the full professors and Martin fulfilled this role in his own particular style. He was not a natural administrator. Derek Pletcher describes how his office was always covered with stacks of reports/correspondence, etc. If your interest dropped below a certain level you were wise to sneak in and return it to the top of the pile. His secretary, Kate, had a system where piles were regularly moved to a box in a cupboard and then destroyed if Martin had not noticed in two years! Derek also commented that he used to tease Martin by saying, "The only thing that you do efficiently is to book your skiing holidays." Despite these shortcomings, Martin was an effective leader with a great talent for inspiring novel research activity. Eventually, however, the stress got to him. He described how he used to get home in the evening and would then have to walk around the garden for an hour, breaking wind, he was so wound up. Hence, he took early retirement in 1983. He then arranged to split his time between Southampton, Utah and Harwell, enjoying the different collaborations. I had asked Martin on a staircase during a scientific meeting whether he'd like to think about applying stochastic modelling to the problem of pitting corrosion. It piqued his interest and led to a wonderful and career-defining time for me.¹⁹

One day he asked for a confidential meeting with senior

physicists at Harwell and described in outline some experiments he was directing in Utah, involving electrochemical loading of deuterium into palladium, where there seemed to be some excess heat being produced that did not apparently have any explanation other than a nuclear reaction. There was obviously scepticism, but he was supplied with a neutron safety monitor, and, at his request, preparations were made to do careful and sensitive measurements looking for any excess neutron emission from his system. About a week later, Martin suddenly asked for these experiments to be started immediately: the cells were set running but no neutrons appeared. Experimentation was driven by a sense of urgency and safety considerations were perhaps not as prominent at first as they should have been – there was subsequently a reminder of the dangers of stoichiometric mixtures of hydrogen and oxygen in the presence of palladium when a cell exploded inside the neutron counter. Then late one night there was a telephone call from Martin: he could not keep the lid on any longer and he had become convinced that the effect that he had hypothesised was real. The next day the press conference at Utah happened and things went crazy. Martin came to Harwell about a week after that and presented his results. First, there were the heat measurements: clearly these had to be repeated to seek confirmation; then there were results from the neutron monitor: clearly these were marginal and within the limits of noise for that device; finally there was the gamma-ray spectrum. There was an expert in the room who said simply, "That is not a gamma-ray peak." There was a silence. It was not that the peak was at the wrong energy – something that caused a great fuss later – but that the peak was too narrow. It might have been an instrument artefact at the limit of the measurement range. Was this the result that had convinced Martin: a sloppy measurement by someone else using an instrument that was outside Martin's normal domain of expertise? We will never know, but it is a trap we can all fall into. By then it was too late and the world was buying. All of the results in the original paper turned out to be of insufficient accuracy to support the claims that had been made. Although the results from the simple calorimeters of the original design could be interpreted to indicate some excess heat, measurements in instruments without the major error sources in the simple design showed nothing unexpected.²⁰ The idea, though, continues to attract serious and very careful measurement. The thermal measurements have been hugely refined.²¹ The magnitude of the claimed effects has become much smaller as the calorimetric methods have been improved. However, the idea continues to intrigue and has not died out, although it seems that irreproducibility still plagues the study, despite some fairly detailed specifications of the conditions required to achieve the effect.²² It seems that trace impurities in the electrolyte, such as silicate leached from the glass cells, may be of importance: intriguingly a reminder of some of the key considerations in the subject in 1947¹ that continue to jump up and bite the unwary,²³ and represent another connection to the beginning of Martin's scientific career.

Beyond the controversy, we hold memories of a wonderful warm, kind and engaging personality, full of insight and of energy, enthusiasm and quirky humour. As Laurence Peter recalls:

Martin was a real European intellectual with broad interests in the arts (and wine) as well as science. I first met

him in 1966 – needless to say I was absolutely captivated by Martin – the accent, the dynamic personality. That is what turned me into an electrochemist.

Martin was a formative influence on a whole generation of electrochemists, who will all remember those wonderful ideas sessions, a kind gesture (“I’ve taken a house at Villars: come skiing!”) and the love of a good wine and a good joke. Martin taught that science is great FUN. He is much missed.

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