Institution: University of Oxford

Unit of Assessment: 8 Chemistry

Title of case study: UOA08-06: The first method of calibration-free pH measurement

1. Summary of the impact

Richard Compton's group at the University of Oxford has developed the world's first calibration-free pH meter, representing the first major advance in pH measurement for 80 years. In 2008, the technology was licensed to Senova Systems Inc, who subsequently produced a prototype hand-held calibration-free pH meter. In September 2012 the device won the Frost & Sullivan 2012 North American New Product Innovation Award, and in March 2013 it won Best New Product award at Pittcon 2013, the world's largest annual conference and expo for laboratory science. Following successful field trials with end-users in diverse sectors, Senova is now developing a commercial product. Senova has already secured $ 9.7M to commercialise the technology, with additional ongoing venture capital investments. [Text removed for publication].

2. Underpinning research

The electrochemical measurement of pH is a ubiquitous and routine tool used in industries ranging from pharmaceuticals to brewing. The standard apparatus for measuring pH has not changed significantly since it was developed by Beckman in the 1930s, and consists of a glass electrode connected to an electronic meter that measures and displays the pH reading. The electrodes are expensive and fragile, pH measurements are easily corrupted, and for precise work the meter needs calibration before every single measurement. Over the past eight decades, vast amounts of time (and therefore money) have been spent on pH meter calibration in both academia and industry. Incorrect calibration and other errors can also lead to huge costs for companies in terms of wasted supplies and products. These factors underline the pressing need for a pH meter that does not require calibration.

In 2001, Professor Richard Compton (Department of Chemistry, 1985 – present) and his research group at the University of Oxford sought to establish if it was possible to derivatise carbon nanotubes coated on an electrode surface in a way that made them reproducibly and predictably pH responsive. If his team could identify a molecule whose electrochemical properties varied consistently with pH, Compton believed it would be possible to create a new breed of pH sensors. Compton's team demonstrated that anthraquinone-derivatised carbon (AQcarbon) nanotube surfaces were in fact pH sensitive, accepting protons as pH conditions changed and hence exhibiting changing electrochemical properties. His team developed a simple pH probe based upon the covalent derivatisation of carbon particles with anthraquinone, and found that its amperometric response provided a Nernstian, linear response over the pH range 1 – 14 and over a temperature range from 20 - 70°C [1, 2, 5].

The broad range of observed pH sensitivity using AQcarbon suggested that an effective, calibration-free pH sensor could be created. Compton and his team developed electrodes which were coated with carbon nanotubes functionalised with anthraquinone. Alongside, they also developed redox probes which were rigorously pH insensitive when similarly deployed. Then, by modifying electrodes with both pH sensitive and pH insensitive probes and measuring the potential difference between the two signals, it was possible to directly assess the pH of the solution in which the electrodes were immersed [3]. The research described in [1], [2] and [3] was conducted in collaboration with Schlumberger.

Compton and his team showed that the AQcarbon pH measurement technique has distinct advantages over existing glass electrodes. Firstly, the amperometric signal shows a linear relationship with the tiny currents used, which offers far higher sensitivity than the logarithmic voltage relationships exhibited by potentiometric glass electrodes. Secondly, it is unaffected by alkali errors which can corrupt the results provided by present techniques. Thirdly (and most importantly), because it is a potential difference that is measured, the need for an ultra-stable reference electrode is eliminated, in turn leading to calibration-free pH measurement. Combined with practical benefits – such as durability and speed – the newfound theoretical insights provided a promising springboard for the development of a new, revolutionary, 'disruptive' technology for pH sensing. For these reasons, the concept was patented in 2005 by Richard Compton and Isis Innovation Ltd., the technology transfer arm of the University of Oxford [4].

3. References to the research

Asterisked outputs denote best indicators of quality; University of Oxford authors are underlined.

1. * Anthraquinone-derivatised carbon powder: reagentless voltammetric pH electrodes. GG Wildgoose, M Pandurangappa, NS Lawrence, L Jiang, TGJ Jones and RG Compton. Talanta 60 (2003) 887-893. DOI: 10.1016/S0039-9140(03)00150-4
   Reports the methodology for derivatising carbon surfaces with anthraquinone moieties.

2. Derivatised carbon powder electrodes: reagentless pH sensors. HC Leventis, I Streeter, GG Wildgoose, NS Lawrence, L Jiang, TGJ Jones and RG Compton. Talanta 63 (2004) 1039–1051. DOI: 10.1016/j.talanta.2004.01.017

3. A sensitive reagentless pH probe with a ca 120 mV/pH unit response. I Streeter, HC Leventis, GG Wildgoose, M Pandurangappa, NS Lawrence, L Jiang, TGJ Jones and RG Compton. J Solid State Electrochem 8 (2004) 718-721. DOI: 10.1007/s10008-004-0536-7

4. * Patent WO 2005085825 A1. Electrochemical sensors. SP McCormack and RG Compton, Assignee: Isis Innovation Ltd, UK. https://www.google.com/patents/WO2005085825A1
   The patent describes the principle of calibration-free measurement and identifies chemical systems for use in pH meters using such an approach.

5. *Investigating the reactive sites and the anomalously large changes in surface pK_a values of chemically modified carbon nanotubes of different morphologies. AT Masheter, P Abiman, GG Wildgoose, E Wong, L Xiao, NV Rees, R Taylor, GA Attard, R Baron, A Crossley, JH Jones and RG Compton. J. Materials Chemistry 17 (2007) 2616-2626. DOI: 10.1039/b702492d
   This paper reports the 2e, $2H^+$ reduction of anthraquinone-modified carbon nanotubes across the full aqueous pH range up to 14.

4. Details of the impact

The calibration-free pH measurement system invented by the Compton group is a truly innovative technology which represents a landmark in the field of pH sensing. It has led directly to the commercial success of Senova Systems Inc, [text removed for publication].

In September 2008 Isis Innovation Ltd. exclusively licensed the patent for calibration-free pH sensing to San Francisco-based Senova Systems Inc [6]. The company was founded in 2007 with the sole aim of developing a commercial pH meter based on the Compton research; Professor Compton sits on Senova's advisory board. Based on the potential of the technology and the high value of the IP, Senova secured initial seed funding of $ 3M and raised a further $ 6.7M in Series B financing by January 2012 [7]. During the three years between licensing and finalising funding, the company developed a smart sensor platform capable of being produced on a commercial scale. In the first instance Senova designed a prototype hand-held pH sensor – the pHit Scanner – which offered a number of significant advantages over current standard glass electrodes: it requires no calibration, is temperature stable, does not suffer signal drift, can be stored dry with no need for electrolyte solution, can be sterilised, is physically robust and is inexpensive to mass produce. The scanner was previewed at Pittcon 2012, the world's largest annual conference and expo for laboratory science [8], and in September 2012 won the Frost & Sullivan 2012 North American New Product Innovation Award [9]. In March 2013, the pHit Scanner was recognized with the Pittcon Editors' Gold Award for the best new product at Pittcon 2013 [10].

Feedback from an early adoption programme (EAP) evaluating the hand-held meter has confirmed the effectiveness of the technology and enabled Senova to embark on the development of a larger-scale meter aimed at the high-tech market, which will be more profitable than the hand-held meter [11]. [Text removed for publication] [11]. Additional venture capital funding (from Phoenix Venture Partners and Harris & Harris Group Inc) for Senova is ongoing [12]; the continued investment underlines the potential the technology has to revolutionise this field, and the expectation that Senova's products will be a commercial success.

As a result of the collaborative research between Oxford University and Schlumberger described in Section 2, Schlumberger filed a similar patent at roughly the same time as [4]. This has led to a mutually beneficial situation in which each party has rights on each other's patent. [Text removed for publication].

[Text removed for publication] [13].

5. Sources to corroborate the impact

6. http://senovasystems.com/press-release/oxford-university-licenses-ph-sensor-technology-senova-systems
   August 2008 press release on the Senova website, confirming that the calibration-free pH meter is based on the Compton research and licensed to Senova.

7. http://senovasystems.com/press-release/senova-systems-closes-6-7m-series-financing
   January 2012 press release on the Senova website, confirming details of Series B investment in Senova.

8. http://senovasystems.com/press-release/phit-ph-meter-introduction
   January 2012 press release on the Senova website, confirming preview of the pHit Scanner at Pittcon 2012.

9. http://www.frost.com/prod/servlet/press-release.pag?docid=266584923
   Frost & Sullivan webpage confirming the New Product Innovation Award made to Senova for its pHit Scanner.

10. http://www.pittconshowpreview-digital.com/pittconshowpreview/post201303?pg=1#pg1
    Pittcon 2013 webpage corroborating the Editors' Gold Award made to Senova Systems for its pHit Scanner.

11. Statement from the President and CEO of Senova (held on file), corroborating details of field trials and feedback from customers on the pHit Scanner.

12. http://senovasystems.com/about-us/investors
    Senova webpage confirming Phoenix Venture Partners and Harris and Harris Group Inc as current venture capital investors in the company.

13. [Text removed for publication]