Institution: University of Salford

Unit of Assessment: B13 Electrical and Electronic Engineering, Metallurgy and Materials

Title of case study: The behaviour of hydrogen in materials

1. Summary of the impact

This case study focuses on the use of hydrogen in a range of applications, developing the following techniques:

- Automated and precise measurement of the magnitude and kinetics of gas/vapour absorption in materials at controlled pressure and temperature;
- Methods for analysing structural changes during cycling of hydrogen storage materials, in particular *in situ* neutron diffraction;
- Methods for the regeneration of a palladium catalyst used in the production of hydrogen peroxide;
- Understanding the behaviour of hydrogen isotopes in palladium in relation to hydrogen isotope separation for fusion applications;
- A surface coating technique that stops hydrogen permeation through metals;
- Exploring the use of hydrogen storage for use with hydrogen/fuel cell cars using isotherm analysis, ab initio simulations and neutron scattering techniques;

Demonstrating impact in the commercial application of the techniques in the energy, environment and chemical industries; resulting in commercially viable processes and products, generating economic benefit.

2. Underpinning research

The key researchers and positions they held at the institution at the time of the research are as follows: Professor Keith Ross, Professor of Physics (from 1991), Professor Ian Morrison, Professor of Physics (from 1995), Dr Dan Bull, Lecturer in Physics (from 2003), and Dr Richard Pilkington, Senior Lecturer in Physics (from 2009), School of Computing, Science & Engineering.

Context: Materials characterisation and modelling researchers have been active in the area of gas sorption in solid media for over 30 years. Research focused recently on lightweight hydrogen stores, adopting a combination of experimental techniques (sorption measurements and neutron scattering) with theoretical 'ab initio' modelling to allow insight into the properties of hydrogen storage materials. The gravimetric technique for measuring gas-solid interactions, the Intelligent Gravimetric Analyser (IGA) method, an instrument that is now used internationally for assessing the gas storage performance of solids, was developed by Prof. Ross and Dr Benham in 1989 at the University of Birmingham and the IPR was transferred to HIDEN Isochema in 1991. Dr Benham moved to the company to exploit the IPR (now MD of the IsoChema subsidiary, in charge of marketing the IGA and related products), leading to a series of collaborative research projects with Ross et al at the University of Salford where research has focused on the use of gravimetric studies of the thermodynamics/ kinetics of the hydrogen absorption/ desorption process and the parallel use of a number of neutron scattering techniques. The impact of this case study is underpinned by the following research:

- **1998-2003:** Ross et al were the first to demonstrate that the Intelligent Gravimetric Analyzer (IGA) could be used to measure the diffusion of hydrogen in metals – specifically palladium-silver alloys foils **[1]**. Subsequent work on cycling metal hydrogen systems using IGA led to the development of in situ cycling experiments in neutron diffractometers **[2]**, a technique that has been widely adopted in practice.
- Surface coating techniques for reduction of H/D/T permeation through structural metals were first developed in connection with the design of the Next European Torus. The critical research concerned the sputtering of alumina on MANET **[3]** using a novel unbalanced magnetron sputtering technique developed at Salford **[4]**. These techniques for reducing H/D/T permeation reduced this quantity by ~4 orders of magnitude over a wide range of temperatures.
- Ab-initio calculations of the potential energy surface seen by hydrogen in palladium single crystals has yielded values for the energies of (non-harmonic) excited quantum states of

the proton and deuteron, and these results have been confirmed by inelastic neutron scattering measurements **[5]**. This work provides a 'first principles' approach to the calculation of the chemical potential of H and D in palladium, allowing a prediction of the H/D and D/T separation factors, important for isotope separation in fusion energy development.

- **2004:** Neutron inelastic scattering from hydrogen compounds adsorbed by catalysts on carbon substrates has proved a powerful way of identifying molecules on surfaces in low concentrations. This work is described in a research undertaken with Dr Peter Albers, of Degussa AQura **[6]** and demonstrates applications in a range of industrial processes.
- **2005-2008:** The HYTRAIN (Hydrogen storage research training network) project had the primary aim of training researchers in the area of hydrogen storage in solid media **[14]**.
- **2006-2010:** The NESSHy (Novel efficient solid storage for Hydrogen) EC Framework project demonstrated the use of combinatorial thin film technique in the Mg-Ni-Ti system. The research identified a favourable composition for hydrogen storage applications. Using Pd as a model system, the research found that thin films reproduce the thermodynamic parameters of bulk in desorption and a range of applications for hydrogenography **[15]**.
- **2010-onwards:** Collaborations on practical methods for hydrogen storage with industrial partners involved car manufacturers eg., Daimler Chrysler, materials manufacturers such as Johnson-Matthey and other major companies in the Hydrogen-Fuel Cell field.
- **2010-onwards**. Small Angle Neutron Scattering studies of porosity in activated carbons for use as hydrogen absorbers led to collaboration with Chemviron Carbon Ltd., focused on the use of small angle neutron scattering with contrast matching and variable adsorbate partial pressures in the study of porosity in activated carbons **[7]**. The development of the SANS/contrast matching technique was then applied to studies of neutron irradiation damage of reactor graphite, important in extending the lifetime of AGR reactors **[8]**.

3. References to the research

Key Outputs

1. E.Serra, M.Kemali, A. Perujo and D.K.Ross "*Hydrogen and deuterium in Pd-25%Ag: permeation, diffusion, solubility and surface reactions*" Met. Mat. Trans. A29 (1998) 1023-1028. DOI
2. P.A. Georgiev, J.Liu, D.K.Ross, "*An in situ neutron time of flight diffraction study of LaMM(NiCoAlMn) battery electrode materials and their deuterides for x=0 and x=0.2"*. J. Alloys and Compounds 349 (2003) 325-333. DOI
3. E.Serra, P.J.Kelly, D.K.Ross, R.D.Arnell, "*Alumina sputtered on MANET as an effective deuterium permeation barrier*". J Nucl Matter. 257(1998) 194-198. URL
4. P.J.Kelly and R.D.Arnell. "*Magnetron sputtering: a review of recent developments and applications"* Vacuum 56 (2000) 159-172. DOI
5. M. Kemali, J.E. Totolici, D.K.Ross and I.Morrison. *"Inelastic neutron scattering measurements and ab initio calculations of hydrogen in single crystal palladium*," Phys Rev. Lettrs. 84 (2000) 1531. DOI
6. P.W. Albers, J.G.E. Krautner, D.K.Ross, R.G. Heidenreich,K. Kohler and S.F.Parker, *"Identification of surface states on finely divided supported palladium catalysts by means of inelastic neutron scattering."* Langmuir 20 (2004) 8254-8260. URL
7. Z. Mileeva, D.K. Ross, D. Wilkinson, S.M. King, T.A. Ryan and H. Sharrock*. "The use of small angle neutron scattering with contrast matching and variable adsorbate partial pressures in the study of porosity in activated carbons"*, Carbon 50 (2012) 5062-5075. DOI **(REF 2)**
8. Mileeva, Z & Ross, K & King, S 2013, *'A study of the porosity of nuclear graphite using Small-Angle Neutron Scattering*.', Carbon. DOI **(REF 2)**

Key grants

9. **2011:** Meet the Scientist - Energy Materials, EPSRC, £20,289.00, Principal Investigator: I Morrison (75%). Co-Investigator: D Bull (25%).
10. **2009**: The Dynamics of nanomaterials and light metal deuterides studied by means of

coherent inelastic neutron scattering measurements and model simulations, EPSRC, £380,523.00. Principal Investigator: K Ross (80%). Co-Investigators: D Roach (10%), I Morrison (10%).

11. **2009**: Conversion of Existing Natural Gas Delivery Pipelines to Accommodate Hydrogen Gas by Pulsed Laser Deposition of Alumina Coatings In-Situ, Joule Centre (University of Manchester), £41,501.00. Principal Investigator: R Pilkington (80%). Co-Investigators: K Ross (10%), J Cowpe (10%).
12. **2007:** Nano-Structured Hybrid Hydrogen Storage Materials for Small Scale Energy Supply Technologies, Joule Centre (University of Manchester), £341,256.00. Investigators: K Ross (50%), I Shabalin (50%).
13. **2007:** Participation in the IEA Hydrogen Implementing Agreement - Extension II, AEA Technology plc, £8,010.00. Investigator: K Ross (100%).
14. **2006:** HySIC - Enhancing International Cooperation in running FP6 Hydrogen Solid Storage Activities EC (Framework), £26,130.00. Investigator: K Ross (100%).
15. **2005:** Marie Curie - HYTRAIN (Hydrogen storage research training network) EC (Framework), £176,063.00. Investigator: K Ross (100%).
16. **2006:** NESSHY (Novel efficient solid storage for Hydrogen) EC (Framework), £311,588.00. Investigators: K Ross (50%), I Morrison (50%).

4. Details of the impact

The original Intelligent Gravimetric Analyzer (IGA) is manufactured by HIDEN Isochema, a world leader in the design and manufacture of gas and vapor sorption instrumentation for research, development and production applications in surface chemistry and materials science. The IGA instrumentation suite has achieved a leading position worldwide in this field with a turnover exceeding £3Mpa. Ross et al's continuing collaboration with HIDEN Isochema has made a major contribution to the present commercial significance of the technique in a range of sectors:

- **Context:** The IGA series is now widely recognised as the most accurate analytical tool available for the characterisation of a range of different hydrogen storage materials and Ross et al have developed three IGA instruments in their lab with different characteristics which have been used to develop new applications. 5 Salford Ph.Ds have also continued their research as scientific developers at HIDEN.
- Carbon Capture and Storage (CCS), Volatile Organic Compound (VOC) removal, coal research, clean energy technology and the interaction of water with natural materials are all examples of the application of sorption instrumentation. Both the IGA and IGAsorp series are used widely in environmental vapor sorption research and in the pharmaceutical industry, while the IGA and IMI series offer higher pressure gas sorption capability for applications that require the determination of the uptake of gases such carbon dioxide and methane at elevated pressures (Carbon Storage and Capture). Research on the absorption of deuterated toluene in carbons **[7]** and more recently in reactor graphites **[8]** using contrast matching establishes which pores are open to the liquid and energy researchers using IGA technology include those in the oil and gas industry, and those developing membranes for fuel cell applications.
- **2008-onwards:** Ross et al used the IGA to measure the diffusion of hydrogen in metals, specifically, in palladium silver alloys foils, where knowledge of the behaviour of hydrogen isotopes is essential for hydrogen isotope separation in fusion applications.
- Cycling metal hydrogen systems using IGA led to the development of in situ cycling experiments on neutron diffractometers which has been widely adopted in practice, demonstrating the capacity to change the hydrogen content in situ by changing hydrogen pressures and temperatures. A derivative of the IGA instrument was installed on neutron scattering equipment at ISIS, Rutherford Appleton Laboratories for this purpose.
- Neutron inelastic scattering from hydrogen compounds adsorbed by catalysts on carbon substrates has proved a powerful way of identifying molecules on surfaces in low concentrations, demonstrating applications in a range of industrial processes in collaboration with Dr Peter Albers, of Degussa AQura **[b].** This work on the development of

commercial catalyst systems leading to the good carbonaceous catalyst support for fuel cell applications was important. Additionally, the method was deployed in the development of processes for regeneration of the catalyst used in the production of hydrogen peroxide. **2005-2009:** The HYTRAIN (Hydrogen storage research training network) project had the primary aim of training researchers in the area of hydrogen storage in solid media with 12 researchers trained and most now employed in research and development in the hydrogen/ renewable energy field.

- **2006-2010:** The NESSHy (Novel efficient solid storage for Hydrogen) EC Framework project tackled a wide range of possible materials for hydrogen storage. Morrison was responsible for ab initio modelling and Ross was responsible for characterisation. The project, which included the materials produced being tested by Daimler Chrysler, demonstrated the use of combinatorial thin film technique in the Mg-Ni-Ti system. The research identified a favourable composition for hydrogen storage applications.
- **2007-2010:** Small Angle Neutron Scattering studies of porosity in activated carbons for use as hydrogen absorbers led to collaboration with Chemviron Carbon Ltd focused on the use of small angle neutron scattering with contrast matching and variable adsorbate partial pressures in the study of porosity in activated carbons: *"The project involved successful industry-academia collaboration with partners Chemviron Carbon, and has led to over £1.1m follow on funding to develop this and related technology."* **[c]** Joule Centre, September 2010 http://www.isis.stfc.ac.uk/science/getting-the-hole-picture-porosity-in-activated-carbons12584.html
- **2010-present**: SANS measurements on reactor graphites have yielded important measurements of fractal porosity highly relevant to improved understanding of AGR graphite lifetime. http://www.isis.stfc.ac.uk/science/energy/isis-research-into-nuclear-graphite-could-keep-the-uks-lights-on14466.html
- **2011:** Our work on hydrogen storage and the development of demonstration equipment for this purpose has led to a considerable amount of outreach activity to schools. Additionally, funding of £30,000 was awarded to work in partnership with the Museum of Science and Industry, local schools and Manchester Science Festival, of which the University is a sponsor, to engage young people, their families and carers with science and making research accessible to non-experts. **[9]**

5. Sources to corroborate the impact

a) *Letter from Managing Director at Hiden Isochema Limited relating to IGA developments in collaboration with Salford.*
b) *Letter from Director, Electron Microscopy and Surface Spectroscopy at AQura relating to important commercial measurements using neutron scattering.*
c) *Joule Centre: http://www.joulecentre.org/index.php?option=com_content&view=article&id=402:new-research-updates-&catid=26:joule-news&Itemid=66*