UKSAF Winter Meeting 2010

Energy and the Environment
- the applications of surface analysis -

Wednesday 13 January 2010

Host: University of Bristol

Venue: At-Bristol, Anchor Road, Harbourside, Bristol, BS1 5DB

09.30 - 10.00 Registration

10.00 - 10.10 Welcome & introduction
University of Bristol and
Dr Dave Sykes, UKSAF Chairman

10.10 – 10.40 Dr Neil Fox, Department of Physics, University of Bristol
Lithiated Nanoparticle Diamond and its Application to Energy Conversion

10.40 – 11.10 Dr Andreas Thissen, SPECS GmbH, Berlin
Characterisation of Solar Cells and Batteries

11.10 – 11.40 Dr Richard Smith, Johnson Matthey Technology Centre
Comparison of Supported Catalyst Particle Size Determination by Low Energy Ion Scattering (LEIS) and Transmission Electron Microscopy (TEM)

11.40 – 12.00 Coffee Break

(continued overleaf)

12.00 – 12.30 Professor Jamie Lead, School of Geography Earth & Environmental Sciences, University of Birmingham

Manufactured Nanoparticles in the Environment

12.30 – 13.00 Dr Tom Scott, Interface Analysis Centre, University of Bristol

TiO_2: Cleaning the Energy Industry Legacy

13.00 - 14.00 Lunch

14.00 – 14.30 Dr Philip Davies, School of Chemistry, Cardiff University

Oxidation of Chlorine-Containing Compounds over Fly Ash Surfaces

14.30 – 15.00 Dr Graham Smith, Shell Global Solutions (UK)

X-rays, Electrons and Crude Oil

15.00 – 15.30 Dr Andrew Walker, Shimadzu Research Laboratory Ltd.

Instrumental Developments for High Spatial Resolution AES

15.30 – 16.00 Tea and Close of Meeting

Lithiated Nanoparticle Diamond and its Application to Energy Conversion

Neil Fox

Department of Physics, University of Bristol, Bristol, BS8 1TL

Diamond is a desirable electronic material for concentrated solar energy devices because it exhibits stable electrical properties at elevated temperatures. For the thermionic converter application it is advantageous to use n-type semiconducting material as the active component in these devices. However, it is very expensive to produce thin layers or wafers of diamond commercially by chemical vapour deposition. Also it is only technically possible to produce semiconducting diamond wafers that are p-type, which precludes the use of diamond in high temperature pn junction devices.

A candidate dopant for n-type conductivity in diamond is lithium because it can potentially form a shallow donor level below the conduction band minimum. Numerous unsuccessful approaches, including ion implantation, thermal indiffusion and in-situ doping during CVD growth, have all been attempted to incorporate lithium atoms into sites in the diamond lattice to activate n-type electrical conductivity.

For the past five years, the in-diffusion of lithium into single crystal diamond nanoparticles has been studied at Bristol. Recently, it has been found to yield a material that exhibits a very low threshold for thermionic emission facilitating operation at temperatures much lower than commercially available materials. This observation offers the prospect of applications for diamond in future thermionic devices.

Characterisation of Solar Cells and Batteries

Andreas Thissen

SPECS GmbH, Voltastrasse 5, 13355 Berlin, Germany

Electronic devices have revolutionized everyday life in industrial countries over the last decades. Especially devices for energy conversion and storage like thin film solar cells and lithium ion batteries are of importance for the future. Recently two main tasks for research and development are dominant: miniaturization for sophisticated applications targetting at the nanoscale, and designing low cost large-scale devices.

In both fields the device performance is strongly determined by materials quality, composition, combination and last but not least by processes at materials interfaces. Nanostructures, minimization of material consumption and the need to improve device efficiencies consequently leads to the widespread focussing on thin film preparation. For thin film devices surface and interface analysis like photoelectron spectroscopy and surface (spectro-)microscopies are an important tools for material and device characterization.

Classical well-defined model experiments already reveal important insights using highly integrated vacuum systems for analysis and preparation. But analysis of materials and devices under near ambient conditions and even in situ during operation is an inevitable future development to improve the significance of data for development and quality management. In this respect the application of techniques like High Pressure XPS, XPS from liquids, hard x-ray PES (HAXPS), SPM and LEEM on solar cell and lithium ion battery materials is the challenging tasks for manufacturing companies of surface analytical equipment.

Comparison of Supported Catalyst Particle Size Determination by Low Energy Ion Scattering (LEIS) and Transmission Electron Microscopy (TEM)

Richard A. P. Smith

Johnson Matthey Technology Centre, Sonning Common, Reading, RG4 9NH

Richard Smith (1), Dogan Özkaya (1), Hidde Brongersma (2,3), Thomas Grehl (2), Rik ter Veen (3)

1 - Johnson Matthey Technology Centre, Sonning Common, Reading, UK

2 - ION-TOF GmbH, Münster, Germany

3 - Tascon GmbH, Münster, Germany

Improved control of metal deposition gives more efficient material use in catalysis. This is of particular importance for precious metals, common in automotive emission control and fuel cell applications. When the particle sizes of interest for many supported catalysts are in a single-digit nanometre range and hence difficult to study by many characterisation techniques, improving the accuracy and scope of particle size determination for supported metal catalysts is vital for technological improvement.

TEM is a particularly useful characterisation tool and is one of a limited number of techniques that can be applied in this particle size range. There are, however, inherent difficulties of Z-contrast and that areas studied and so overall statistics are limited, although it is possible to extract accurate and detailed information about local environments.

LEIS signals are related to the exposed surface area of an element. Smaller particle sizes lead to higher surface area to volume ratios and therefore larger signals of scattered ions so small particles yield good information when studied by LEIS. A large-area (1 mm scale) technique, LEIS provides averaged and statistically representative information. LEIS also works as easily on supports with heavy elements (zirconia, ceria) as light elements (carbon, alumina).

When both LEIS and TEM are used, comparison and contrast of results should lead to improved understanding of particle size distributions. We here show results of such a comparative study on platinum-on-carbon fuel cell materials showing good agreement with carbon monoxide chemisorption measurements and TEM results.

Manufactured Nanoparticles in the Environment

Jamie Lead

School of Geography Earth & Environmental Sciences, University of Birmingham, B15 2TT

Manufactured nanoparticles (NPs) are defined as being between 1 and 100 nm in size and are a major product of the nanotechnology industry, with silver NPs used in many consumer products as an antimicrobial, cerium oxide in diesel to improve fuel efficiency, oxides of zinc and titanium in cosmetics and suntan lotion etc.. Given the wide use, environmental discharge and exposure is already occurring. Given that toxicity for many NP types in vitro and in vivo has been established, there is a potentially large but poorly characterised risk to environmental and ecological health from NPs. Much ecotoxicology has sought to understand NP toxicity, while issues of fate and transport are less thoroughly examined. It is widely acknowledged that it is essential to quantify NP physico-chemical properties in order to understand their possible environmental and ecotoxicological effects.

Given the background detailed above, this talk will focus on three areas: 1) the interactions of natural nanoparticles and NPs; 2) the characterisation of nanoparticles for ecotoxicology and environmental studies; 3) the importance of a multi-method analytical approach for complex samples. The talk will focus on silver and cerium oxide and freshwater processes and organisms.

TiO_2: Cleaning the Energy Industry Legacy

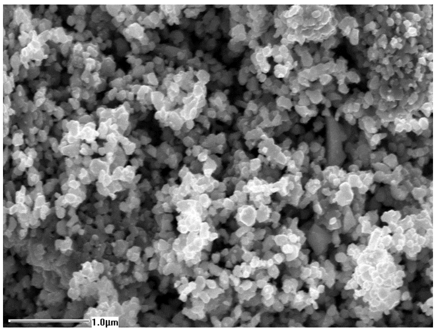
Thomas Scott

Interface Analysis Centre, University of Bristol, Bristol, BS8 1TS

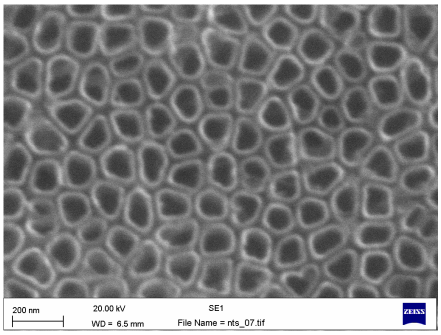
Titanium dioxide (TiO_2) is currently used in a wide range of applications from solar cells, to sun cream and even the white lines at the Wimbledon Tennis. The material exhibits many favourable properties which make it ideal as a potential material for environmental remediation of pollution arising from the energy industry: good transparency, high electron mobility, wide band-gap, strong room-temperature luminescence, etc.

TiO_2 is amongst a number of candidate nanoscale materials for environmental remediation studies at the Interface Analysis Centre in Bristol. This presentation will survey the use of nanoscale TiO_2 materials for (i) the removal of pollutant waste gases from the atmosphere arising from the burning of fossil fuels, and

(ii) the removal and chemical reduction of uranium from water, relating to effluents produced by the nuclear energy industry.



Nanoparticles of TiO_2



Nanotubes of TiO_2 on a Ti substrate.

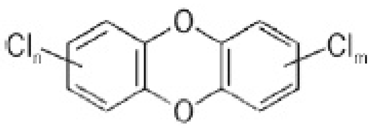
Acknowledgements: Financial support from EPSRC is gratefully acknowledged, as are the vital contributions from group members Marco Bonato, Chris Jones and Geoff Allen.

Oxidation of Chlorine-Containing Compounds over Fly Ash Surfaces

Philip R. Davies

School of Chemistry, Cardiff University, Cardiff, CF10 3AT

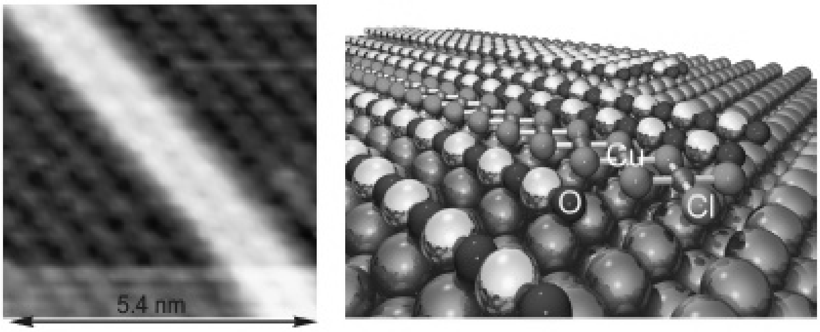
It is a common criticism that surface science experiments conducted under ultra high vacuum and at low temperatures are too far removed from real conditions to make a useful contribution to the understanding of reaction mechanisms. In this talk we will present another example where we believe surface science has shed new light, or at least raised new questions, about a “real world” reaction. The talk will discuss the reactions of chlorine containing molecules at copper surfaces and address the mechanism of polychlorinated dibenzo-p-dioxins (PCDD), and polychlorinated dibenzo-furans (PCDF) (referred to collectively as PCDD/F's).



A Dioxin

PCDD/F's are long lived toxic pollutants of the environment whose principle sources are anthropogenic – primarily combustion. A major formation pathway involves carbon based “fly ash” particles which contain nano-particles of transition metals. A strong correlation between copper content and PCDDF formation has been established [1] and it is thought that the copper particles catalyse the chlorination of phenol and/or benzene precursors. However, despite extensive work in this area, many aspects of reaction remain unclear and in particular, the nature of the copper state that is most catalytically active remains controversial.

Using XPS and STM to study a malonyl dichloride and HCl at a Cu(110) surface we have shown that there is a complex interaction between copper, chlorine and oxygen and we suggest a mechanism involving a surprising transient state [2].



$$Cu(110){:}\ 2HCl + Cu\text{-}O(a) \rightarrow CuCl_2(a) + H_2O$$

References
[1] B. R. Stanmore, Comb. Flame, 2004, **136**, 398-427.
[2] A.F. Carley, P.R. Davies, K.R. Harikumar and R.V. Jones, PCCP 2009, **11**, 10899-10907

X-Rays, Electrons and Crude Oil

Graham C. Smith

Shell Global Solutions UK, Shell Technology Centre Thornton, PO Box 1, Chester, CH1 3SH

Jeroen van der Veer, CEO of Royal Dutch Shell 2004 – 2009 has stated [1] that the energy industry faces three hard truths, namely

- Demand for energy is growing,
- Supplies of “easy oil” will struggle to keep up with demand,
- We live in a CO_2 – constrained world.

As a consequence Shell spent $1,266 million on research and development in 2008, to help meet the world’s growing demand for energy in a responsible way [2]. R&D is focussed on improving the ability to find, develop, recover and process greater volumes of oil and gas; on improving the efficiency of conversion of raw materials into products; and on reducing the environmental impact of operations and products, especially the reduction of greenhouse gas emissions.

As a consequence of the first two hard truths, we are now faced with the extraction and processing of increasingly heavy and viscous difficult crude oils. These oils have ever-higher asphaltene concentrations, which severely affect their flow properties and hence their ability to be processed. Although much work has been published on the structure and properties of asphaltenes in the open scientific literature, they are still the subject of considerable uncertainty and debate.

This talk will summarise the current open-literature knowledge on asphaltene structure and properties, and illustrate how X-ray scattering techniques and electron spectroscopies such as XPS can be applied to such difficult materials.

[1] e.g. State of the Industry speech at 14th Asia Oil and Gas Conference, Kuala Lumpur, 8th June 2009.
[2] Peter Sharpe, Shell Executive Vice President, Wells, 20th August 2009.

Instrumental Developments for High Spatial Resolution AES

Andrew Walker

Shimadzu Research Laboratory Ltd , Trafford Wharf Road, Manchester, M17 1GP

Shimadzu overseas developments have a major and independent research facility (SRL) based in Manchester. For a number of years, a surface analysis group have developed systems to facilitate the identification of nanometre structures. We present two such developments, a parallel energy analyser based upon a hyperbolic electrostatic field and a very high spatial resolution all electrostatic electron optical column designed for analytical applications.

The hyperbolic field analyser (HFA) is just one of many parallel analyser systems that have been investigated theoretically and experimentally at SRL. This energy analyser exhibits a relative energy resolution ?E/E of 0.5% and is extremely compact. Progress on the design, particularly of its detection system, has lead to significant improvements in its gain linearity and to the signal to noise ratio. This enables the analyser to perform a full spectrum acquisition in times as short as one second. As a consequence this analyser is on trial by the semiconductor inspection industry where high throughput of defect identification is necessary.

High spatial resolution electron optical columns have been developed at SRL using both magnetic and electrostatic lenses and components. The all electrostatic UHV compatible column we describe, is designed for analytical applications with high probe currents the order of 1nA -200nA. The design of the final objective lens is conical enabling a 50° line of sight to a field free (magnetic and electrostatic) analysis position at 10mm working distance. At this analysis position the SEM spatial resolution is 3nm.

Recently we have combined these two separate developments upon a test rig and have performed some very preliminary high spatial resolution Auger studies. Using the signal derived from the Gold 68eV peak area we claim a spatial resolution of ~4nm. The beam energy of the probe was 10keV and its working distance was 10mm.