Applied Surface Science Division
Room 13 - Session AS+BI+MI-MoM

Practical Surface Analysis: Getting the Most Out of Your Analysis using Complementary Techniques

Moderators: Mark Engelhard, EMSL, Environmental Molecular Sciences Laboratory, Michaeleen Pacholski, The Dow Chemical Company

8:20am **AS+BI+MI-MoM-1 Obtaining Complete Characterisation of Core-shell Nanoparticle Structure and Composition *via* the use of Complementary Techniques***, **David Cant**, C Minelli,* National Physical Laboratory, UK*; K Sparnacci,* Università degli Studi del Piemonte Orientale, Italy*; W Unger,* Bundesanstalt für Materialforschung und -prüfung (BAM), Germany*; A Hermanns,* Bundesanstalt für Materialforschung und -prüfung (BAM)*; W Werner, H Kalbe,* TU Wien, Austria*; R Garcia-Diez, C Gollwitzer, M Krumrey,* Physikalisch-Technische Bundesanstalt, Germany*; A Shard,* National Physical Laboratory, UK

Core-shell nanoparticles are commonly used in a variety of applications, including medicine, catalysis, optoelectronics, and others. Accurate identification of core-shell nanoparticle structure and morphology is an important challenge to overcome before such nanoparticles can be effectively utilised. This is not necessarily a trivial obstacle, as no single characterisation technique can accurately identify every possible peculiarity of structure or composition that may exist.

For example, characterisation methods that observe bulk properties, such as differential centrifugal sedimentation (DCS), thermogravimetric analysis (TGA), or techniques based on observation of Brownian motion such as dynamic light scattering (DLS) may be unable to distinguish particles with a standard core-shell morphology from those with the same core and shell masses, but with an uneven shell, or where the core and shell have merged to form a homogenous particle.

Similarly, surface sensitive techniques which analyse a population of particles, such as x-ray photoelectron spectroscopy (XPS) or small angle x-ray scattering (SAXS), may be able to provide information on shell thicknesses in standard core-shell particles and distinguish them from particles with an uneven shell or a homogenous particle, but may have difficulty distinguishing homogeneity from an uneven shell or off-centred core.

Techniques that allow observation of individual particles, such as electron microscopy, may be able to clearly show the structure, but are rarely able to provide any in-depth quantification of the composition. As such it is necessary to use a careful selection of appropriate techniques to fully characterise any given nanoparticle system. To illustrate these issues, two polymeric core-shell nanoparticle systems have been characterised, both consisting of a Hyflon® core coated in varying thicknesses of either PMMA or polystyrene. These systems are nominally very similar, but differ notably in structure. The results from several different characterisation techniques (XPS, SAXS, DCS, TGA, DLS, and SEM.) were compared in order to demonstrate the difference in information provided by each and obtain a full understanding of both types of nanoparticle.

9:00am **AS+BI+MI-MoM-3 Correlative Microscopy based on Secondary Ion Mass Spectrometry for High-Resolution High-Sensitivity Nano-Analytics***, **Tom Wirtz**, J Audinot, D Dowsett, S Eswara,* Luxembourg Institute of Science and Technology (LIST), Luxembourg **INVITED**

Development of innovative characterization tools is of paramount importance to advance the frontiers of science and technology in nearly all areas of research. In order to overcome the limitations of individual techniques, correlative microscopy has been recognized as a powerful approach to obtain complementary information about the investigated materials. High-resolution imaging techniques such as Transmission Electron Microscopy (TEM) or Helium Ion Microscopy (HIM) offer excellent spatial resolution. However, the analytical techniques associated with TEM such as Energy Dispersive X-ray spectroscopy (EDX) or Electron Energy-Loss Spectroscopy (EELS) are inadequate for the analysis of (i) isotopes, (ii) trace concentrations (< 0.1 at. % or < 1000 ppm) and (iii) light elements (H, Li, B). Likewise, for the case of HIM, until recently there was no direct possibility to perform elemental mapping because sub-30 keV He^+ or Ne^+ ion irradiation do not excite X-ray emission. Secondary Ion Mass Spectrometry (SIMS), on the other hand, is an extremely powerful technique for analysing surfaces owing in particular to its excellent sensitivity (detection limits down to the ppb are possible, so that SIMS can be used to detect both major and trace elements), high dynamic range (a same signal can be followed over several orders of magnitude), high mass resolution and ability to differentiate between isotopes.

In order to combine the high spatial resolution of TEM and HIM with the analytical sensitivity of SIMS, we developed integrated TEM-SIMS [1,2] and HIM-SIMS [2-4] instruments. The main advantage of this in-situ correlative approach is its capability to analyse the same area of interest of any sample without need of transferring the sample from one instrument to another one, which would result in a number of artefacts ranging from surface contamination to issues with localizing exactly the same ROIs. Moreover, the integrated approach allows fast and multiple interlacing between the different imaging and analysis modes.

In this talk, we will first introduce the TEM-SIMS and HIM-SIMS instruments and discuss their performance characteristics. We will then present a number of examples taken from various fields of materials science and life science to show the powerful correlative microscopy possibilities enabled by these new in-situ methods.

[1] L. Yedra et al., Sci. Rep. 6, 28705, 2016

[2] T. Wirtz et al., Nanotechnology 26 (2015) 434001

[3] T. Wirtz et al., Helium Ion Microscopy, ed. G. Hlawacek, A. Gölzhäuser, Springer, 2017

[4] P. Gratia et al, J. Am. Chem. Soc. 138 (49) 15821–15824, 2016

9:40am **AS+BI+MI-MoM-5 New Insights on Layered Polymer Systems, Polymer Networks and Polymerization in Defined Geometries by Combining Surface Analysis with Depth Profiling using ToF-SIMS and XPS as Analytical Tools***, **Sven Steinmüller**,* Institute for Applied Materials, Karlsruhe Institute of Technology, Germany*; A Llevot,* Institute of Organic Chemistry, Karlsruhe Institute of Technology, Germany*; D Moock,* Institute for Applied Materials, Karlsruhe Institute of Technology, Germany*; B Bitterer,* Institute of Organic Chemistry, Karlsruhe Institute of Technology, Germany*; F Cavalli,* Institute for Biological Interfaces, Karlsruhe Institute of Technology, Germany*; S Hurrle,* Institute for Chemical Technology and Polymer Chemistry, Karlsruhe Institute of Technology, Germany*; M Bruns,* Institute for Applied Materials, Karlsruhe Institute of Technology, Germany

Surface analytical characterization of polymers is still a tough topic if precise information are favored. Especially for characterization of stepwise layered systems and for studying reaction rates and composition of network formation or to confirm polymerization within defined geometries a lot of techniques are not sensitive enough to fulfill the desired degree of precision and resolution. Within the recently installed Cooperate Research Center "SFB 1176" at KIT (Molecular Structuring of Soft Matter), a high degree of precision is necessary to qualitatively and quantitatively confirm the defined structures achieved during the polymer syntheses. Here a new surface analysis approach combining X-ray Photoelectron Spectroscopy (XPS) and Time of Flight Secondary Ion Mass Spectrometry (ToF-SIMS) including Ar cluster ion sputter depth profiling for three dimensional systems is utilized to prove every reaction step of polymer syntheses and to evidence three-dimensional structures at high lateral resolution. By using different marker molecules as well as specific molecule ion fragments, the combination of these two methods enables to obtain the precise characterization and evaluation of the different polymeric systems.

We present our results on the implementation of new methods for precise surface analysis of polymers. Starting with the investigation of molecular layered systems prepared via electrografting of surfaces followed by successive thiol-yne or thiol-ene reactions, we show controlled functionalization on silicon as well as on highly oriented pyrrolytic graphit substrates. Finally the developed strategy will be transferred to real graphite electrodes. This is an important step to design and tailor the properties of artificial solid electrolyte interfaces (SEI) for lithium ion batteries.

From the characterization of these two dimensional systems (according to the surface analytical tasks), we follow up with polymer systems with three dimensional analysis questions. We present analytical results of network formation using the *Para*-fluoro-thiol reaction and strategies for the confirmation of polymer position after polymerization within defined geometries. Surface analytical recipes to confirm synthesis routes were established. The analytical results of the three dimensional chemical picture are taken to further optimize the synthesis routes and network properties.

We kindly acknowledge the SFB 1176, funded by the German Research Council (DFG), in the context of projects B2, C1, C4 and Z1 for funding. The K-Alpha+ instrument was financially supported by the Federal Ministry of

Economics and Technology on the basis of a decision by the German Bundestag.

10:00am **AS+BI+MI-MoM-6 Combining Monoatomic- and Cluster Ion Sputtering in ToF-SIMS and XPS Depth Profiling of Organic-inorganic Multilayer Structures***, **Eric Langer**, J Barnes, O Renault, T Maindron,* CEA-Leti, France*; L Houssiau,* University of Namur, Belgium

Organic electronics have risen to great importance in the world of consumer electronics. Especially organic light emitting diode (OLED) displays have brought new possibilities to the market. However, organic materials are more susceptible to electrical dysfunctions than conventionally used inorganic materials. This leads to a shortened lifetime for those materials. Environmental impacts like humidity or ultraviolet irradiation can create chemical reactions that lead to dark spots and device failures. Additionally, the flow of current through the device can further promote device degradation and can even induce migration and diffusion of dopants and small molecules. Precise chemical depth profiling is therefore essential to identify sources of failure and improve the device lifetime of organic electronics. Surface analysis techniques such as time-of-flight secondary ion mass spectrometry (ToF-SIMS) and x-ray photoelectron spectroscopy (XPS) are efficient tools to characterize the chemical composition in depth. With the recent introduction of gas cluster ion beam (GCIB) sources, it is possible to sputter through organic materials without inducing a significant amount of damage to the sample [1]. Typically, argon clusters (1000 – 5000 atoms per cluster) with low energy per atom ratios (1 – 5 eV/atom) are used for gentle sputtering. However, these low energies are not sufficient to break the atomic bonds in inorganic materials. This poses a major problem in the characterization of hybrid inorganic-organic devices.

In this work, we present an approach to overcome the difficulties in depth profiling of inorganic-organic interfaces. Green OLED devices are characterized by ToF-SIMS depth profiling using GCIB as well as monoatomic sources for sputtering. This allows for precise tracking of characteristic chemical species in both the inorganic and the organic parts of the multilayer structures. Additionally, XPS depth profiling is used to measure the sputter induced damage during analysis [2]. We show, that by optimizing the sputter parameters, the sputter induced damage can be minimized and precise and reliable chemical information of hybrid inorganic-organic devices can be gained by combining ToF-SIMS and XPS analysis.

This work was carried out on the Platform for Nanocharacterization (PFNC) at the CEA Grenoble.

[1] Ninomiya, S ; Ichiki, K ; Yamada, H ; Nakata, Y ; Seki, T ; Aoki, T ; Matsuo, J Rapid Comm. Mass Spec. **23** 20 (2009) 3264.

[2] Miyayama, T ; Sanada, N ; Bryan, SR ; Hammond, JS ; Suzuki, M ; Surf. Interface Anal. **42** 9 (2010) 1453

10:40am **AS+BI+MI-MoM-8 Ultra High Surface Sensitivity – Elemental Analysis of the Outer Layer***, **Thomas Grehl**, P Brüner, H Brongersma,* ION-TOF GmbH, Germany

In materials science and applications, the outer surface plays a vital role for a range of properties and in general for the interaction of a solid with its surroundings. The chemical properties of the surface govern macroscopic properties like wettability/contact angle, but also the chemical interactions as in catalysis, corrosion or thin film growth. The outer surface and its understanding is crucial for catalysis, fuel cells, thin film formation, nanoparticles and a wide range of other processes.

The analysis of the outer surface is frequently hampered by the fact that the origin of the signal is not completely limited to the first atomic layer, but bulk and surface signals are mixed. This issue is avoided in the case of Low Energy Ion Scattering (LEIS). The elemental composition of the outer atomic layer is determined quantitatively and separately from deeper layers. We will demonstrate a number of cases where this is essential to draw the relevant conclusions and reveal surface properties that would not be detected by other surface analytical techniques.

Nevertheless, the combination of complementary techniques is always required to address complex problems. We will demonstrate how the combination of LEIS with other established analytical techniques is beneficial for a comprehensive analysis.

One of these cases is the interaction of Ar cluster ions with a solid sample: it is well known that the sputtering yield of massive argon clusters is some orders of magnitude larger for organic than for inorganic materials. Therefore, Ar cluster beams have been discussed as a means of removing atmospheric adsorbents from surfaces prior to analysis. Using thin film samples, we have evaluated this approach applying LEIS in order to detect the removal of the organic material and the influence on the underlying inorganic surface. Despite the low sputtering yield for the inorganic material, a complete removal of the organic material will lead to a significant modification of the inorganic surface even when the actual erosion is limited.

Other examples from nanoparticles, catalysis and thin films will support the importance of outer layer surface analysis for materials research and other applications.

11:00am **AS+BI+MI-MoM-9 Towards Predictive Understanding of Li-S Battery Materials through Multimodal Analysis***, **Vijayakumar Murugesan**, K Han, M Nandasiri, V Shutthanandan,* Pacific Northwest National Laboratory*; S Thevuthasan,* Pacific Northwest National Laboratory, Qatar*; K Mueller,* Pacific Northwest National Laboratory

Comprehensive understanding about the interfacial reactions between electrode and electrolyte is the major knowledge gap which inhibit the development of the lithium sulfur (Li-S) batteries. Despite numerous studies, the interfacial reaction mechanism such as SEI layer evolution and polysulfides dissolution process is still unclear. Hence, it is critical to develop a multi-modal approach that can provide unprecedented chemical imaging of complex interfaces in wide lateral (ranging from subatomic to micron) and temporal scales (few ns to seconds). Herein, we report an *in-situ* X-ray photoelectron spectroscopy (XPS), X-ray absorption spectroscopy (XAS) and nuclear magnetic resonance (NMR) combined with ab initio molecular dynamics (AIMD) computational modelling to gain fundamental understanding about the complex interfacial interactions in Li-S batteries. A multi-modal approach involving AIMD modelling and in situ XPS and NMR characterization uniquely reveals the chemical identity and distribution of active participants of interfacial reactions as well as the -battery capacity fading mechanism.

11:20am **AS+BI+MI-MoM-10 Combined use of Back Side SIMS and FIB Sample Preparation***, **Mikhail Klimov**,* University of Central Florida

When profiling multilayered samples or even a homogeneous samples with rough surface SIMS depth resolution can suffer a rapid deterioration, particularly when polycrystalline metal layers are concerned. The back side SIMS was traditionally used to alleviate a loss of depth resolution during front side depth profiling. The traditional back side SIMS sample preparation involves painstaking polishing or/and ion milling, that requires considerable skills to produce a high quality finish surface that is parallel to front surface and terminated not too far from the interface of interest. Also, because the traditionally prepared sample is relatively large, the precise site specificity is, in general, unattainable.

I offer a relatively expedient FIB sample preparation (~2hrs.) for back side SIMS analysis at precise location and at exact distance from the front surface. The FIB sample extracted from the bulk has a typical lateral dimensions of 10 µ by 10 µ or less. In order to analyze such a small area, even smaller ion beam is required with diameter of 1µ or less to provide good depth resolution and high sensitivity. Also, it's very much desirable that the ion beam was Oxygen or Cesium to achieve a secondary ion yield enhancement, particularly important for small area analysis. In my case, micron and sub- micron beam of O_2^+ ions was produced by RF Plasma source by Oregon Physics that replaced, for the first time, Duoplasmatron on ADEPT1010 Dynamic SIMS System by Physical Electronics.

The FIB sample preparation procedure is discussed in detail and the first back side SIMS results compared to the front side depth profiles.

11:40am **AS+BI+MI-MoM-11 Phase Quantification of Mixed TiO_2 Powders by X-ray Photoemission Valence Band Analysis and Raman Spectroscopy***, **Paul Mack**, T Nunney,* Thermo Fisher Scientific, UK*; R Palgrave,* University College London, United Kingdom of Great Britain and Northern Ireland

Titanium dioxide is one of the most studied materials in surface science. It has applications in heterogeneous catalysis, dye-sensitised solar cells, bone implants and self-cleaning windows. Many polymorphs of TiO_2 are known to exist but only two occur naturally in abundance: rutile and anatase. Rutile is the more thermodynamically stable form but anatase is more energetically favourable when forming nanoparticles at atmospheric temperature and pressure. The anatase polymorph has been recognised as more photoactive than rutile, although recent research indicates that the greatest photovoltaic efficiencies are achieved in devices that contain a mixture of anatase and rutile. The degree of mixing between two polymorphs influences other material properties, such as catalytic activity. This raises the question: how can one determine the polymorph ratio in a sample that contains a mixture of anatase and rutile?

Quantitative phase analysis of anatase-rutile mixtures by two experimental methods is presented in this work. Spectra of pure reference anatase and rutile were acquired X-ray Photoelectron Spectroscopy (XPS) and Raman spectroscopy. These spectral shapes were then used to fit similar data from mixed phase samples. XPS and Raman spectroscopy give information from different depth regions in a sample. The surface sensitive character of XPS yields a surface phase fraction of anatase and rutile. Mixed phase samples were prepared from high and low surface area anatase and rutile powders. In this work, the surface phase fraction of anatase was found to be linearly correlated with photocatalytic activity of the mixed phase samples, even for samples with very different anatase and rutile surface areas.

Author Index

Bold page numbers indicate presenter